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METHOD OF TREATING ORES

Theodore Earle, Pacific Palisades, Calif.

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This invention is a continuation in part and a development of my invention as disclosed in my application for Letters Patent of the United States, Serial Number 685,743, and has to do with the field of froth flotation separation and selective concentration of ores, minerals and other inorganic compounds, and more particularly with the preliminary preparation of materials to be later flotatively separated, and has as an object to provide a novel and improved technique giving effect to hitherto unknown discoveries wherethrough separations and concentrations heretofore considered impossible through flotation methods may be efficiently accomplished, and wherethrough finer separations, cleaner concentrates and higher recoveries may be more efficiently and more economically had in the generally known field of froth flotation separation.

Standard froth flotation methods at present commercially employed are highly successful when applied to materials characterized by strong adsorptive power in respect to the applied flotation reagents, in which class may be included most of the metals and metallic sulphides. However, such methods are at best but moderately efficient when applied to the flotation of the metallic oxides and quite inefficient when utilized in attempts to float the silicates and non-metallic oxides.

The hereinafter described improved method will efficiently float the silicates and non-metallic oxides, improve the recoveries now possible through flotation of the metallic oxides and even enhance the recoveries now had through flotation of the metals and sulphides. In the last cited case, both oxidized and unoxidized particles of the material sought to be floated do not always respond to conventional methods and are lost to the recovery, when, through application of the improved method, such particles can be made to float easily and readily.

In the field of the true metallic oxides such minerals as azurite ($2CuCO_3.Cu(OH)_2$), malachite ($CuCO_3Cu(OH)_2$), and wulfenite ($PbMnO_4$) are rather easily treated by standard flotation methods with rather low grade recoveries and concentrates, but when treated by the improved method herebelow described all of these minerals were efficiently floated with high recoveries. Among other oxide minerals successfully and inexpensively floated with the improved technique may be listed

Cuprite (Cu_2O)
Chrysocolla ($CuSiO_3.2H_2O$)
Zincite (ZnO)
Smithsonite ($ZnCO_3$)
Franklinite ($(Fe, Mn, Zn)O(FeMn)_2O_3$)
Anglesite ($PbSO_4$)
Lead molybdates
Lead vanadates
Hematite (Fe_2O_3)
Magnetite (Fe_3O_4)
Limonite ($2Fe_2O_3,3H_2O$)
Scheelite ($CaWO_4$)
Placer gold where the gold is found in grains of specular hematite.
Ferberite
The manganese oxide ores
Cassiterire (SnO_2)
Bauxite (aluminum oxide)
Chromite ($FeO.Cr_2O_3$)
Carnotite (Va and U oxide)
Brass from bronze filings
Brass from iron filings
Witherite from bauxite
Ochre

A few of the above metallic oxides are at present being treated by flotation with but indifferent success. For instance, a manganese oxide ore is being floated in Cuba through a very delicate process and with but a fair recovery. On the other hand, the improved method applied to a closely similar ore produced a 95% recovery and a concentrate showing 56% manganese.

Considering the true silicates and the metallic oxides it is found that many such can not be commercially separated or floated at all with conventional methods, and the others only inefficiently through the use of expensive reagents to activate the particle surfaces, while the improved method has been applied to the successful, efficient and inexpensive flotation of the following:

Silica sand and quartz of minus 16 mesh (SiO_2)
The feldspars in coarse and fine sizes (K, Ca or Na aluminum silicates)
Beryl ($Be_3Al_2(SiO_3)_6$)
The micas (K and Mg aluminum silicates)
Garnet (Ca, Mg, Fe or Mn aluminum silicates)
Cryolite (Na_3AlF_6)
Lepidolite (lithia aluminum silicate)
Crystalline limestone from amorphous limestone
Monazite (Ce, La, Di)PO_4)
Emery (Fe_2O_3 and Al_2O_3)
Kaolin (hydrous silicate of aluminum)
Clay (hydrous silicate of aluminum)
Vermiculite—either crude or roasted (ace mica).

Since the technique wherethrough the improved method is made effective is concerned with adsorptive characteristics of the material

to be floated and with niceties of water regulation, for both of which an adequately specific terminology is not available, certain terms and phrases to be employed in the elaboration of the improved method herebelow are herein specifically defined for limitation to that particular meaning readable therein throughout this exposition and the included claims.

Affinity as used herein means surface attraction and adhesion between a mineral particle and water, only; in other words, the adsorptive effect of the mineral as evidenced in respect to water, and not in respect to any other chemical reagent.

Affinitive capacity designates the amount of water or thickness of water film held to a mineral particle against removal therefrom by a particle of relatively lower affinitive power.

Affinity value is the measure of the affinitive capacity of a mineral particle.

Affinitive power is the measure of the effective affinity or affinitive force of a mineral particle.

Adsorption as used herein is limited to the surface attraction and adhesion between a mineral particle and a chemical reagent other than and distinguished from water.

Adsorptive power is used to designate the force with which chemical reagents are attracted to and held on the surface of a mineral particle; this force varies with the nature of the mineral particle and will vary for a given particle in respect to different reagents.

Adsorptive capacity refers to the amount of reagent or thickness of reagent film held to a mineral particle against removal therefrom by a particle of relatively lower adsorptive power.

Adsorptive effect denotes the practical result obtained in respect to concentration of reagent on and about a mineral particle through exercise of the adsorptive power of such particle.

Adsorptive differential designates the difference between adsorptive capacities of mineral particles in respect to the same reagent.

Flotatively modify is used to describe the action resulting in change in surface characteristics of a mineral particle through affinity or adsorption affecting the behavior of such particle in a flotation cell.

Flotatively increase describes such modifying action as results in or enhances the relative flotability of the particle so modified.

Flotatively prevent describes such modifying action as destroys or decreases the relative flotability of the particle so modified.

Free water refers to the moisture or water content of the ore or mineral other than the water of chemical combination of such ore or mineral and includes both adsorbed and absorbed water and interstitial water. Free water includes all water that can be drained, filtered or evaporated at temperatures below 212 degrees F. from an ore or mineral.

Variable-film water is herein limited to a designation of the amount of water adsorbed to the exterior surfaces of the ore and mineral particles and held to these surfaces by the affinity of the particles.

Dry for purposes of this exposition defines a condition of ore or mineral wherein all variable-film water has been eliminated. This condition can be obtained only through evaporation of the water at temperatures considerably above atmospheric and can be maintained only through maintenance of such temperatures in the ore or mineral, since the material when at lower temperatures will adsorb moisture from the atmosphere. A dry ore as here considered may have free water absorbed within the interior of the particles.

Moist defines an ore or mineral condition wherein the variable-film water content varies from just above the dry condition as a lower limit to an upper limit determined by that amount of water which will satisfy the affinitive needs of all the material particles. The total amount of water to satisfy these affinitive needs will vary with the degree of comminution and specific gravity of the material; the finer grinding requiring the larger amounts of water because of the larger surface areas to be covered. For material ground to pass 16 mesh and with few fines the upper limit of variable film water may be as low as ½ of 1% or it may approach 3%; if the material is ground to pass a 100 mesh screen the upper limit of variable film water will approach 8% by weight of the material. In no case will the affinitive needs of the material treated by this method be larger than 8% by weight. Material in a moist condition will not contain interstitial water but it may have water absorbed within the interiors of the various particles in addition to the variable film water. Under no conditions can the small amount of water required by the improved process be obtained by natural drainage alone. If natural drainage is used as a step in the dewatering it must be augmented by evaporation or other means. The improved method to be described deals entirely with materials in the moist condition.

Moisture, as herein used, has the same limitations of meanng as are above employed in respect to moist.

Wet refers to a condition of ore or mineral where there is sufficient free water to give an excess over that needed to satisfy the affinitive needs of the ore particles. An ore which has been allowed to drain naturally (without evaporation) over long periods of time is still in the wet condition.

Excessively wet defines that condition where the amount of free water in an ore or mineral is such as to substantially suspend the ore particles in the water when agitated. Except in the case of very fine comminution of the material, any mix containing over 25% by weight of water would be termed excessively wet.

Film as used herein refers to that quantity of liquid, either water or reagent, adsorptively held to the surfaces of ore or mineral particles. The film adsorbable to a given mineral particle will vary in thickness in accord with the adsorptive capacity of such mineral in respect to the specific liquid concerned and in any given instance will be the resultant of two variables, namely, the adsorptive or affinitive capacity of the mineral and the character of the liquid, assuming an adequate supply of the liquid.

Active reagent designates herein a reagent capable of flotative modification of a mineral surface. As examples under this heading may be grouped the fatty acids and their derivatives, soaps, xanthates, aeroflot, sodium sulphide, copper sulphate, water, cyanide, etc., etc.

Inactive reagent is employed herein to designate a reagent incapable of flotatively modifying mineral surfaces and employed to satisfy physical qualities of the mineral, such as absorption,

and to serve as solvents for the active reagents. Kerosene, crude oil and castor oil are examples of inactive reagents.

Insulate is herein used to denote the action of variable-film water adherent to a mineral particle in negativing, through partial or complete satisfaction of the affinitive capacity of such particle, the adsorptive power of such particle in respect to an applied reagent.

The improved method deals with the regulation of the free water in the material to be separated, and more particularly with regulation of the variable-film water of such material.

In standard flotation practice the reagents are added to, agitated with or ground with a thoroughly wet or excessively wet mixture wherein the presence of interstitial water insures that the affinitive capacity of each particle has been satisfied to permit thorough coating of each particle with its maximum thickness of water film. That is, in standard flotation only those minerals of high adsorptive power are able to adsorb sufficient of the flotation reagents to flotatively modify their surfaces through displacement of water film by reagent film. If the affinity of the particle for water is greater than its adsorptive power in respect to the reagents employed, it follows as a matter of course, that no concentration of reagents will serve to modify the particle for selective separation by flotation if the affinitive capacity of such particle has once been satisfied.

Water regulation, as hereinafter described, has several functions when employed with the other steps of the improved method. Since a reduction in the amount of variable-film water results in advantages of economy and separation, it might appear that entire elimination of the free water and treatment of the material in a dry condition would be ideal. This is not the case. Due to variations in composition of the materials, fineness of grinding, thoroughness of agitation, and the like, it is found practically inexpedient to determine the exact minute quantity of flotation reagents to be applied to a given dry material to float just the mineral desired, excess reagent bringing up undesired mineral and insufficient reagent failing to bring up the desired percentage of mineral sought.

In addition, it is expensive to thoroughly dry the material in the first instance and very difficult as well as expensive to maintain the dry condition of the material and prevent adsorption of water thereto from the atmosphere during conditioning and treatment. Consequently, the improved method does not contemplate entire elimination of the variable-film water and utilizes as a lower limit on the amount of variable-film water that amount which could be adsorbed to the material from the atmosphere, which lower limit may be but infrequently approached in actual practice.

The variable-film water thus ever present in the material to be treated is utilized for its inhibiting effect on the material particles of greatest affinity therefor to the end of insulating said particles from adsorption of reagents and permitting the use of sufficient quantity of reagents to flotatively modify all of the desired particles without danger of dirty concentrates.

In other words, the variable-film water acts to further lower the adsorptive power effect of the relatively lower adsorptive-powered particles and thus more definitely establishes the line of flotative separation between particles of the mix.

A further reason for leaving a certain amount of variable-film water in the material may be found in the fact that certain of the flotative reagents require a vehicle of solution and a fluid medium to facilitate spreading thereof throughout the material, both of which requirements can be met to a considerable degree and to advantage by the variable-film water inherent in the material.

In addition, instances occur when the variable-film water serves both of the foregoing functions and acts as an adsorptive inhibitor while simultaneously aiding as a solution vehicle and as a spreading agent.

The reasons for a moist condition of the material as utilized in the improved method may then be listed as follows:

1. Because it is impractical to determine the exact amount of reagents required for a given separation.
2. Because of the expense of drying material and maintaining the material in a dry condition.
3. Because moisture acts as an insulator to inhibit adsorption of reagents to material particles, thus permitting use of enough reagent to float all of the desired particles.
4. Because moisture permits of more definitely establishing of the line of flotative separation of a mix.
5. Because moisture acts as a vehicle of reagent solution and as a fluid medium to facilitate spreading of reagents throughout the material being treated.
6. Because moisture acts simultaneously as an adsorptive inhibitor, a solution vehicle and a spreading agent.
7. Because moist condition of the material permits use of less quantities of reagents due to enhanced action and effect of such reagents when in concentrated condition.

It has long been recognized that a tremendous difference exists in respect to affinity and adsorptive power for water and flotation reagents between the metals and sulphide minerals on the one hand and the silicates and the oxides on the other hand, but it has not previously been shown that sufficient differences in adsorptive powers of the silicates and oxides existed to permit of their selective separation within their own classifications as well as one from the other.

Through application of the improved technique taught herein, and especially through regulation and control of the variable-film water in a moist mixture, it can be practically demonstrated that each and every mineral has a distinct and definite affinity for water and a distinct and definite adsorptive power in respect to each of the various flotation reagents, which characteristics may be employed to effect froth flotation separation of the minerals, including even those of exceedingly lower adsorptive powers.

For a better understanding of the effects and results obtainable through regulation of variable-film water in an ore mix, it might be well to consider the affinitive capacity of a given mineral particle as representing the number of water layers of uniform thickness adherent to the surfaces of such particles from an excess supply of water and which will adhere to such particle when the excess water has been drained away. Thus, a mineral particle with an affinitive ca-

pacity of 1 would, in the presence of adequate water, surround itself with a water film of one layer thickness, while a mineral particle with an affinitive capacity of 10 would, in the presence of adequate water, surround itself with a water film of ten layers' thickness, or ten times as thick as the film carried by the particle of one-tenth affinitive capacity.

The thickness of water film represented by the affinitive capacity of the particle will be retained by such particle after draining away of excess water, and it is with variation in the thickness of such film that regulation of the variable-film water is concerned.

When any interstitial water is present in an ore mix the affinitive capacities of all of the mineral particles have been satisfied and all such particles carry water films of the maximum thickness permitted by their respective affinitive capacities, all particles of like affinitive capacity carrying water films of like thickness.

When the water in the mix is less than sufficient to satisfy the affinitive capacities of all of the particles, what water there is may be spread, by suitable agitation and time-conditioning, uniformly through the mix for film adherence to those particles of higher affinitive capacity, first, the water film thus formed about said particles of higher affinitive capacity being of like thickness on the particles of like capacity, even though much less in thickness, due to insufficient water, than the maximum film possible for the particular particle capacity, and such higher powered particles will continue to take up and uniformly hold the available water to the exclusion of the lower powered particles until the unsatisfied affinitive capacities of the higher powered particles are brought to approximately that of the lower powered particles.

It would appear from results experimentally obtained that the higher affinitive powered particles may in many instances abstract water film from lower affinitive powered particles until the affinitive capacities of such higher powered particles are completely satisfied, so that only such excess as may exist above the affinitive capacities of the higher powered particles is available for water-filming of the particles of lower affinitive capacities.

The regulation of variable-film water herein taught is concerned with regulation of the amount of variable-film water in the ore mix to that which will provide water film of the desired thickness for the purposes of a given separation on and about some or all of the particles of the mix, such regulation, naturally, being proportioned to the affinitive capacities of the particles in relation to the adsorptive capacities of such particles in respect to the reagents to be employed.

It should be obvious that no specific limits, in the form of weight percentages or otherwise, can be established for control of the variable-film water apart from the upper and lower limits previously stated, since many factors enter into the determination of the exact amount of variable-film water required for successful flotative separation of a particular ore mix, not the least of which factors is the degree of comminution to which the mix has been brought, it being apparent that it would require a much greater amount of water to film each particle of a 200 mesh grind than it would to film each particle of a 6 mesh grind of the same weight, film thickness being equal. Specific gravity of the various particles is also a factor.

Application of the improved technique to flotative separation of a given mineral involves consideration of two determinants, namely the water affinity of the materials to be separated and the relative adsorptive powers of such minerals in respect to the reagents to be employed. Where the mineral to be floated has great adsorptive power in respect to the reagents and is combined with a gangue of low adsorptive power, as is commonly the case with the metals and metal sulphide ores having a silicate gangue, the water affinity can be disregarded and conventional flotation methods employed, since the high-adsorptive-powered minerals are able to adsorb the reagents to a flotative concentration about their particles through even the maximum water film permitted by their affinity, while the low-adsorptive-powered gangue could not hold a flotative concentration of reagents in the presence of the higher powered particles, even without the inhibiting effect of the water film, unless a vast excess of reagents was available.

Even in the situation cited, however, nicety of separation and economy of reagents can be enhanced through control of the variable-film water to that amount readily filmable about the lower-adsorptive-powered particles only, thus supplying such particles with the desired inhibitor and freeing the higher-powered particles for effective flotative combination with a relatively minute amount of the reagents.

Where it is desired to flotatively separate one mineral of high adsorptive power from another of like character, the relative water affinity of the minerals is of great importance, since it is in many such cases impossible to gauge the reagents required in a wet mixture to that amount which will flotatively adsorb to those particles only of the slightly higher powered mineral. In such a case, regulation of the higher variable-film water to an amount less than will satisfy the water affinity of all of the particles results in maximum concentration of water on and about the particles of greater affinity with maximum insulation of such particles against adsorption of reagents thereto, while the particles of lesser affinity, possibly having lost water film to those of higher affinity, are enabled to exert a relatively much higher adsorptive power and effect a flotative concentration of reagents on their surfaces to the exclusion of the water-filmed particles from such concentration, when a small amount of reagents is employed.

The more closely the variable-film water is regulated to that amount combinable with only the particles of greater affinity, thus substantially freeing the particles of lesser affinity from water film, the more complete and perfect can be the flotative separation and the smaller can be the quantity of reagents required therefor.

When the separation desired is to be had between minerals of low adsorptive powers or high affinities, regulation of the variable-film water is of primary importance, since the presence of a thick water film on all of the particles will, in most such instances, inhibit flotation of any of the particles.

In treating such lower-adsorptive-powered minerals for flotative separation, it may be necessary to regulate the variable-film water to an amount less than will satisfy the affinity of the mineral having the relatively greater water affinity, thus freeing the particles of lesser affinity from water film so that no inhibiting effect is present as between reagents and such latter par-

ticles and the low adsorptive power of such particles may then act to effect flotative concentration of reagents on and about such particles while those particles of greater affinity are completely insulated by water film and can adsorb none of the reagents whatever.

With some minerals of low adsorptive powers, notably silicates, a dry condition of the mix treated with a quantity of reagents sufficient to satisfy the adsorptive capacities of the minerals present permits adsorption of reagents to all of the particles and a consequent non-selective flotation.

Hence it follows that both water film and reagent film are essential for the desired selective flotation separation, the first to act as an inhibitor in respect to flotation of certain particles and the second to be adsorbed to and effect flotation of the desired particles, and that regulation of the variable-film water coupled with a suitable proportioning of reagents is the prerequisite to flotative separation of minerals other than those of notably great adsorptive powers.

As indicative of the importance of regulation of the variable-film water in flotation separations, a mix of beryl and feldspar may be considered. Simply to better illustrate the point, the water affinity of the beryl is given a value of 20 and feldspar may be given an arbitrary affinity value of 25, the adsorptive power of the beryl for oleic acid a value of 10, and the adsorptive power of the feldspar for oleic acid a value of 5. With the variable-film water of the mix regulated to one tenth of one percent, the water affinity of the minerals is only partially satisfied but not sufficiently so as to destroy their adsorptive power values. Assuming that the water supplied by the small amounts of added variable-film water now has only a value of 3, it is seen that there still remains some available adsorptive power in each mineral and also an unsatisfied affinitive capacity; the available adsorptive power of the beryl having a value of 7 and that of the feldspar a value of 2. Now if oleic acid be added to the mix in an amount not quite sufficient to satisfy the adsorptive capacity of the beryl, such reagent will be adsorbed to the beryl and abstracted from the feldspar particles until the adsorptive differential of the beryl is satisfied to the extent permitted by the reagent supplied, and the beryl particles can be floated from the feldspar in a froth flotation cell. However, since both the beryl and the feldspar have greater affinity than adsorptive power, continued agitation of the particles in a body of water will result in replacement of reagent film by a water film and less of any flotative characteristic, with consequent sinking of all particles, though the adsorbed reagent will adhere to the beryl long enough to effect a froth separation of the beryl from the feldspar. Any excess of reagent in the above example beyond that required to satisfy the adsorptive differential of the beryl would be adsorbed to the feldspar, providing the latter did not have too thick a film of variable-film water, and result in dirty concentrates and poor separation. Treated dry with sufficient oleic acid to satisfy their respective adsorptive needs, the particles of both minerals of the above mix could be floated together. Going to the other extreme, there is the case of a mix of galena and feldspar. The galena might have an affinity of 1 and an adsorptive power of 100 and consequently could never have its film of reagent replaced by water film so long as any reagent was present, though excess reagent applied to such a mix when dry would result in flotation of some feldspar. The ideal treatment for such a mix would include regulation of the variable-film water to an amount sufficient to satisfy the affinity of the feldspar and prevent any adsorption of reagent thereto, in which even either large or small amounts of reagent would serve to efficiently float the galena alone.

Because of the varying adsorptive powers a given mineral may exhibit in respect to various reagents and because of the almost infinite mineral combinations wherein separations are desired, it is impossible to establish any one general rule as to regulation of the variable-film water as employed in the improved method. However, the minerals to be dealt with may be divided into two general classes according to the relation each shows between its water affinity and its adsorptive power in respect to flotation reagents in use at the time, such a grouping resulting in one class, Class I, containing the minerals having a water affinity generally greater than their respective adsorptive powers and which includes nearly all silicates, many of the oxides, some of the carbonates, hydrates and sulphides, and some other less common types of minerals, and a second class, Class II, containing the minerals having adsorptive powers generally greater than their respective water affinities and which includes the metallics, most sulphides, many organic minerals, some carbonates, some non-metallics, a few oxides and practically no silicates.

In respect to these classes it may be generally stated that flotation separations can not be made commercially with minerals of Class I when standard methods are employed and the variable-film water is of sufficient amount to permit any interstitial water in the mix, since in such case not only is the water affinity of the mineral satisfied, but an excess is represented by the interstitial water; and that flotation separations can be made with minerals of Class II when the variable-film water is of such quantity as to provide interstitial or more water. However, some minerals may be in Class I with respect to certain flotation reagents and in Class II with respect to other such reagents and the allocation of a specific mineral to either class may change during treatment due to surface modification by reagents, hence the character and requirements of a given combination to be separated will need to be studied to determine the specific treatment in respect to water regulation best suited to the situation. Again, speaking generally, the following guides may be established for regulation of variable-film water in making separations of minerals classified as above set forth:

A. For separation of one Class II mineral from all Class I minerals—No water regulation required, for such separations can be made with excess water and standard flotation methods—water regulation advantageous for economy of reagents and closer separations.

B. For separation in one concentrate of one Class II mineral and one Class I mineral from other Class I minerals—Regulation of variable-film water required and no interstitial water permitted, in order to float the Class I mineral.

C. For separation of one Class I mineral from another Class I mineral—Regulation of variable-film water required and no interstitial water permitted.

D. For separation of one Class II mineral from another Class II mineral—Possible with excessive water, interstitial water or with variable-film water only, in various specific instances. Generally, better and more delicate separations possible with regulation of variable-film water as in "C".

As indicative of the difficulty attendant upon any attempt to establish a rigid classification based on the flotative characteristics of minerals, sphalerite (ZnS) may be specifically considered. This mineral can not be floated by standard methods, nor even with the ore in a moist condition, when potassium ethyl xanthate is employed as the flotation reagent, hence is in Class I with respect to xanthate. However, when copper sulphate is added to the ore pulp prior to the xanthate, the sphalerite evidences a greater adsorptive power for the copper sulphate than affinity for water and consequently suffers an adsorptive surface modification by the copper sulphate resulting in a surface coating of the sphalerite particles with copper sulphide, which coating has such great adsorptive capacity for xanthate as to permit flotative concentration of such reagent on and about the coated sphalerite particles in the presence of excessive water, the coated particles now being in Class II insofar as xanthate is concerned. However, the uncoated sphalerite in a moist ore condition and after proper regulation of the variable-film water can be floated with oleic acid as a reagent, since, with the water film about the sphalerite particles reduced to proper thickness by variable-film water regulation, the relatively small adsorptive power of the mineral relative to oleic acid is not entirely negatived by water film and may act to flotative concentration of such reagent on and about the mineral particles.

As a concrete example of the flotation possibilities inherent in regulation of variable-film water, comparative tests were run on a coarse-grained (—20 mesh plus 60 mesh) silica glass sand. This material contained pure silica grains, impure and discolored silica grains and grains of foreign matter here designated as mineral grains, and was chosen for test purposes because all authorities agree that coarse silica can not be floated, let alone separated from the impure grains. The material was thoroughly washed and scrubbed and 200 gram samples were used in each of the following four tests:

Test I. Variable-film water present only that taken up by the material from the atmosphere, approximately $\frac{1}{10}$th of one percent by weight of material. 3 drops of oleic acid (0.75 lb. per ton) added to the sample and thoroughly mixed therewith. After one minute agitation in a froth flotation cell 137 grams (68.5%) of pure silica and mineral grains floated. The concentrate was of much better color than the tails.

Test II. Conditions the same as in Test I save that 5 drops of oleic acid (1.25 lbs. per ton) were employed. Flotation concentrate 187 grams (93.5%) and improvement in color more marked than in Test I.

Test III. Conditions the same as in Test II save that 1 c. c. of water (½ of 1%) was added to and mixed with the sand before the admixture of the oleic acid. Concentrate 6 grams composed entirely of the mineral grains having relatively high adsorptive powers. No silica floated due to the inhibiting effect of the variable-film water.

Test IV. Test III repeated with 20 drops (5 lbs. per ton) of oleic acid. Concentrate only 3 grams of mineral grains. Large excess of reagent tends to be immediately washed off the grains and coagulates them so that they sink and also forms a scum on the surface of the water in the cell so that poor froth or no froth at all can be secured with consequently lower recovery.

These tests conclusively show the advantages to be gained through regulation of the variable-film water and consequent variation in the thickness of water film adherent to ore and mineral particles, and thoroughly demonstrate the novelty of the improved method.

Treated dry with the proper amount of oleic acid, the entire sample could be floated and no separation had, hence the water limit range wherein the variable-film water regulation taught herein may be most effectively employed is from just above the dry condition to an amount just below that which would provide interstitial water in the material. Within such range, proper regulation of the variable-film water permits of selective flotation as between materials not previously considered flotable and between materials of closely similar adsorptive powers and capacities.

In addition to the possibilities of water regulation above discussed, it has been determined that small amounts of certain chemicals commonly employed as flotation reagents will spread to form extremely thin films over moist granular minerals, and this principle is applied in the improved method of treating ores and minerals to facilitate, modify and control the separation of the desired ores and minerals from the gangue or other material with which they may be associated. This treatment is applicable to a wide range of substances and it is believed that the reagent or reagents used on this more or less moist material has the effect, in some cases, of reacting chemically with certain constituents of the particles to form compounds that modify the behavior of the particles when subjected to froth flotation. In other cases, however, it is believed that the treatment modifies the adsorptive powers of the particles or of certain constituents thereof, and also has the effect of producing marked changes in the behavior of the particles in the froth flotation cell.

In a word, therefore, the invention relates broadly to variable-film water regulation of ores, minerals and inorganic compounds and subsequent treatment of the water regulated material with a reagent or reagents for modification and control of the material behavior when subjected to froth flotation, and more specifically to treatment of such water regulated material with relatively concentrated reagents in comparatively minute quantities prior to froth flotation.

The invention further consists in the new and novel features of operation and the new and original arrangements and combinations of steps in the process hereinafter described and more particularly set forth in the claims.

In carrying out the improved process or method, the ore, mineral or inorganic compound to be treated is ground or otherwise reduced to the fineness required by the particular type of material to be treated. If the material contains a metal such as iron, copper or zinc compounds in a fine state of subdivision throughout the ore or matrix,

then the material is ground to a fineness which may be determined by any well-known method to expose, if possible, all or part of the desired mineral on the surfaces of the respective particles. The degree of grinding can be determined by metallographical examination as well as by empirical or practical tests. In the case of non-metallic ores where it is desired to separate the different minerals or different purities of the same mineral, the ground particles may be appreciably coarser and still float and separate. No fixed range of fineness is required except that the material must be in condition readily to pass through the standard froth flotation cell and the exact amount or degree of fine grinding is usually ascertained by observation or simple test.

The ground material is first regulated as to variable-film water content to control the thickness of water film on and about the particles, or certain particles, of the mix in accord with the principles hereabove set forth and to best suit the character of the materials and the nature of the separation desired, whereafter it is mixed with a reagent or reagents in comparatively concentrated form. If the reagent employed is normally a solid, it must be put into solution or enough water must be present in the ore to effect the desired solution and aid in the spreading of the reagent. The reagents employed encompass a wide range, depending on the physical condition of the material to be treated and its metallographical and molecular structure. In certain cases, it may sometimes be desirable to add a small quantity of sulphuric or other acid prior to or simultaneously with the addition of the other reagent or reagents in order to remove any oxidized film from the surfaces of the desired particles, or otherwise to help in the later flotation thereof. Also, appropriate neutral diluents may be used to determine the viscosity and spreading ability of the reagents. While an addition of sulphuric acid has at times been found desirable to clean particle surfaces and permit better adherence of other reagents thereto, it may be found preferable in certain cases to employ an alkali to enhance the action of the reagents used for flotation. The addition of alkalies or acids follows the same well-known facts as are now applied to standard flotation practice for hydrogen-ion concentration or, as it is better known, pH control.

Some ores, such as the Florida phosphates, certain manganese oxides, carnotite, and other more or less sponge-like minerals, require not only the water regulation as herein described, but the addition of inactive reagents to fill up their pores before the addition and admixing of the collecting reagents. Such inactive reagents have no effect except that of lessening the cost and amount of the higher cost active reagents necessary for the final separation. When such ore is thus treated, the total amount of reagent used, both active and inactive, is much less than when the material is treated by present standard methods.

The well-known flotation reagents, including collectors, frothers, sulphidizers, and activators and depressants, and others such, for illustration, as the fatty acids and their derivatives, the xanthates, sodium sulphide, pine oil, and the like, have been found useful in treating a wide variety of minerals.

The greatest difference in flotative effect between the standard "wet" method and the improved process is most often noticed where the reagents used are those that are insoluble or only slightly soluble in water. The latter method is better because actual contact is obtained between mineral particle and reagent where they are mixed in the moist condition, for this assures the filming of the particle surface and its consequent flotation. Where the more water soluble reagents are used the advantage in using the improved method lies in the fact that they are in a more highly concentrated condition and, therefore, less reagent is needed and the action on the particle surface is much faster and more positive.

The reagents are used in very small quantities, such quantities being in the order of one one-hundredth of a pound per ton of treated material to 40 pounds per ton of such material, according to the nature of the material and the degree of fineness to which it is ground.

The material and the reagents should be thoroughly mixed although no elaborate apparatus is required for this purpose. The reagents seem to spread by contact and in a comparatively short time will permeate and cover a large mass of material. It has been found in certain cases that mixing may be accomplished to a satisfactory extent by adding the reagents in small amounts to the material as the latter is fed to one of various types of well-known mixing apparatus, it being necessary in many cases only to bring the particles for a brief period of time into contact with the reagent itself or with other particles to which the reagent has adhered.

Repeated tests have definitely proved that minute amounts of certain reagents can be made to spread, by agitation, and cover the surfaces of a large number of slightly moist ore particles of varying sizes from very fine to rather coarse. Different materials have different adsorptive powers for different reagents and, of any two minerals, one has a greater adsorptive power than the other for a certain reagent. The fact that different minerals have these different powers is most forcibly demonstrated when the ore is only slightly moist and contains less than one-fourth of one percent of variable-film water, by weight. While it is in this condition any reagent added and mixed with the particles is in an extremely concentrated condition as compared with standard froth flotation practice. These concentrated reagents are then able to cover the particles of moist ore with a film and are immeasurably better able to attach themselves directly to the surfaces of the particles by adsorption.

Then, by continued agitation and contact of the particles, this film of reagent surrounding or attached to certain parts of them is rubbed off those particles having the lower adsorptive powers for that certain reagent and adheres to, is adsorbed by and covers with a film those particles having the higher adsorptive powers.

The continued agitation gradually brings the various mineral particles into contact with each other and, on contacting, the film is transferred from the surface of one mineral to the surface of another. Contact of the particles is all that is needed to make this transfer of reagent film.

When the adsorptive, or other, needs of the strongest minerals have been satisfied, any extra reagent is taken up on the surfaces of the next strongest mineral particles and, when enough reagent is present to satisfy the adsorptive needs of all of the particles, all non-inhibited particles will float.

The following example will show how minerals of higher adsorptive powers for oleic acid and regulated to less than one-fourth of one percent of variable-film water can abstract the film of reagent from minerals of lower adsorptive powers and, therefore, be selectively floated:

First.—200 grams of −30 plus 100 mesh silica sand regulated to 1/10th of 1% variable-film water was mixed for 5 minutes in a glass bottle with 4 drops of oleic acid and 1 drop of terpineol (35 drops equal 1 c. c.)

Second.—25 grams of the above was put in a flotation cell. 24.5 grams floated.

Third.—To the 175 gram balance of the sand was added 200 grams of pink potash feldspar, −30 plus 100 mesh. The sand and feldspar were mixed for five minutes in the bottle. From this mix 25 grams was put in the flotation cell. 12 grams floated and this was 90% feldspar.

Fourth.—To the 350 gram balance of sand and feldspar was added 100 grams of light blue beryl. This had been crushed to −20 mesh. All were mixed in the bottle for 10 minutes. 25 grams were put in the flotation cell and 4.5 grams floated which was nearly pure beryl.

Fifth.—To 425 grams balance of sand, feldspar and beryl was added 100 grams of −30 mesh crystalline limestone. All were mixed for 10 minutes in the bottle and then the entire 525 gram sample put in the flotation cell. The concentrate was 94.5 grams of lime of 98% purity.

These tests show how the sand, which had the original film of reagents on the particles and would therefore float, then had this film abstracted from it and adsorbed by the feldspar; the mix of sand and feldspar lost to the beryl and this last lost to the limestone. No other reagents were added during the test and the film of reagents formed by the 4 drops of oleic acid had to be transferred from the surfaces of one mineral to the surfaces of the stronger as the latter was added and mixed with the others.

The length of time that the mixture stands prior to its introduction into the flotation cell has, in some cases, a very decided effect in the subsequent froth flotation. In the case of some very slightly moist silica sands containing pure and impure grains, if the mixture is allowed to stand for approximately five minutes and then introduced into the flotation cell, none of the grains will float. But if the mixture is allowed to stand for a period of two hours after passing through the mixing apparatus, the pure silica grains are immediately floated to the top of the cell and the impure grains do not float. Apparently, when the affinitive capacity of the grains is nearly satisfied, it takes a longer time of contact for the reagents to act on or replace the variable-film water to flotatively modify the grains sufficiently to float them.

The froth flotation cell may be of any standard and well-known make adapted to supply the requisite amounts of water and of air or other gas now required under ordinary operating conditions. No special form of cell appears to be necessary in order to practice the invention with improved results compared to present day methods. Other froth flotation reagents may be added to the cell either with the mix pretreated as above stated or separately. The same kind of reagents used in pretreating the mix or charge may be added to the cell or different reagents may be employed, if desired. The exact method of adding the flotation reagents which were not originally mixed with the moist ore is not essential to the operation of the process and forms no part of the instant invention.

Because of the fact that the particles of the ore to be floated have already been covered with a film of the reagent needed to modify the surfaces and either prevent their being wet by water or otherwise change the surface characteristics, these particles are much more quickly floated than if treated by standard flotation methods. This ease of separation and quickness of flotation will greatly reduce the number of froth flotation cells needed in the mill and thereby reduce not only the installation costs but the costs of operation in the flotation unit as well.

The following examples of the practical application of the improved method to certain minerals and ores illustrate the character of the reactions and the results that may be secured.

Example 1.—An ore containing chrysocolla ($CuSiO_3.2H_2O$) and malachite having a quartz gangue was crushed to pass a 20 mesh screen and was water-regulated to 2% by weight of variable-film water and then mixed with the following quantity of reagents per ton of ore: 0.5 lb. sodium oleate; 0.6 lb. of 15% aeroflot; 2.0 lbs. sodium sulphide. The mixture was put in a flotation cell and the following quantity of reagents per ton of ore added to the cell; 0.25 lb. potassium xanthate and 0.1 lb. terpineol. The concentrate was 3.6% by weight of the whole and assayed 23.03% copper. The tailings were 96.4% by weight of the whole and assayed 0.23% copper. The recovery was equal to 78.7% of the copper. When this same ore was treated by standard wet flotation methods, only 6% of the copper was recovered.

Example 2.—The ore treated was low grade chromium oxide with silica gangue. The ore was crushed to pass a 30 mesh screen and water-regulated to 3% by weight of variable-film water and then mixed with 0.2 lb. oleic acid and 0.3 lb. terpineol per ton of ore. No reagents were added to the flotation cell. The flotative concentrate was equal to 6.8% of the weight of the ore and assayed 47.31% Cr_2O_3. The tailings were equal to 93.2% of the weight of the ore and assayed 2.25% Cr_2O_3, giving a recovery equal to 59.1%. Treating the same ore with the same kinds and amounts of reagents by standard wet flotation methods produced only an 18% recovery of the Cr_2O_3 and a concentrate assaying 16% Cr_2O_3.

Example 3.—An ore containing oxidized chalcopyrite ($CuFeS_2$), bornite (Cu_2FeS_3) and various true oxides of copper with a quartz gangue was crushed to pass a 20 mesh screen and water-regulated to 3% of variable-film water. The ore was then mixed for five minutes with the following reagents in quantities per ton of ore as shown; 0.6 lb. of potassium xanthate, 2.4 lbs. of sodium sulphide, 0.4 lb. of 15% aeroflot. The mixture was put in a flotation cell with water alone and a concentrate consisting of bornite, copper oxides and a little chalcopyrite was removed. After the first concentrate was removed, the following reagents per ton of ore were added to the flotation cell; 0.2 lb. of potassium xanthate and 0.1 lb. of terpineol. The second concentrate was nearly all chalcopyrite with a little bornite. A total saving of 94.6% of the copper was made in the two concentrates which were nearly pure mineral. The first concentrate equalled 12.6% by

weight of the total concentrate. The second concentrate equalled 87.4% of the total concentrate. Treatment of the same mix by standard wet flotation methods using the same reagents recovered only 74% of the total copper, the oxidized sulphide particles and the true oxides not floating with the standard methods.

This example shows how certain of the oxidized and oxide grains of copper ore could be easily sulphidized when a concentrated solution of Na_2S was used and this material then floted by the xanthate. The second concentrate would have come up with the first if the full amount of xanthate had been added at once.

Example 4.—Beryl ore ($Be_3Al_2(SiO_3)6$) assaying approximately 20% beryl and with a gangue or matrix of feldspar and quartz was ground to pass a 20 mesh screen and water-regulated to substantially 1% of variable-film water. Oleic acid, approximately 0.25 lb. to the ton of ore and terpineol, approximately 0.1 lb. to the ton of ore were mixed therewith for about five minutes. The mixture was then fed to a standard flotation cell and the froth concentrate from such cell was practically pure beryl and contained over 95% of the beryl, leaving less than 5% of the beryl in the tails. With the same ore treated by standard wet flotation methods and the same reagents nothing floated.

Example 5.—Impure silica sand was passed through a 20 mesh screen, water-regulated to about $\frac{1}{10}$th of 1% variable-film water and mixed with 1.0 lb. of oleic acid and 0.2 lb. of terpineol per ton of sand. This mix was allowed to stand for two hours and was then put through a standard flotation cell with water alone. The pure sand floated in the froth from the cell equalled 98.8% by weight of the total sand and the impure rejected sand not floated comprised 1.2% of the total weight of the sand, the floated sand being practically all pure silica. Coarse silica sand can not be floated by standard wet flotation methods.

This last example shows how normally non-flotable silica can be floated if the variable-film water is kept low and also how two minerals, both having a higher affinity for water than adsorptive power for oleic acid must carry only a very thin film of variable-film water in order to effect a separation therebetween in the flotation cell.

As shown in the foregoing examples, the improved method may be successfully employed to treat a large number of desirable minerals readily floatable thereby, which minerals are floated with difficulty, or not at all, when standard wet flotation methods are employed.

As illustrated by the examples set forth, less reagent is required in practicing the improved method than is exacted in the present standard methods, which standard methods will not even float many of the materials flotable by the improved method. Furthermore, the improved method is definite and positive in its reactions, since the reagent is therein brought into direct and intimate contact with the particles in a concentrated form instead of being disseminated through a relatively large body of water where the contact of each individual particle with reagent is more or less a matter of chance.

A much wider range of reagents is permissible by use of the improved method, since the reagent is applied directly to the surface of the ore or mineral in a relatively concentrated form. Reagents of a different character which will not properly adhere to the ore or mineral in the presence of excess water or have any chemical effect in a dilute condition may be employed successfully when the ore is treated directly and by relatively concentrated reagents.

In general, no special drying operation is required in carrying out the improved method, although if such drying is required for any reason it will not interfere with exercise of the method unless the drying temperature employed on the mix of ore and reagent is carried above the vaporizing or boiling points of the reagents. Where water-regulation to very low amounts of variable-film water is required, it might be found best to dry the ore by application of heat to that percentage of retained variable-film water desired, or it might, in specific instances, prove better to entirely dry the ore and then add the desired percentage of water. Commercial expediency should of course control the degree of water-regulation within the limits of practical recovery desired, since, in certain instances, the cost of drying an ore for removal of a slight excess of water might easily be greater than the added recovery resulting from such refinement of water regulation. The ore can be ground while moist and thereafter the reagent can be mixed therewith, or, as will be obvious, the reagent can be mixed in the grinder with certain classes of ore, during the grinding operation.

It is to be understood that the terms ores and minerals, as used herein, are not restricted to these materials in their natural state or condition, but comprise the products of metallurgical operations and concentrates from previous flotation processes and likewise many non-metallic minerals.

In view of the many changes, additions, omissions and modifications possible, and indeed necessary, in the application of the improved method to specific separations by those skilled in the art, wherein no departure from the spirit and essence of the invention is involved, it is to be understood that the invention is limited solely by the scope of the appended claims, rather than by any details of the foregoing exposition.

I claim as my invention—

1. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes regulation of the moisture content of the material between an upper limit less in amount than will satisfy the affinitive capacities of all of the separated particles and a lower limit determined by the amount of moisture adsorbable to the material from the atmosphere, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents.

2. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes regulation of the moisture content of the material to a variable-film quantity less than will satisfy the affinitive capacities of all of the separated particles, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents.

3. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes regulation of the thickness of water film adherent to the material particles so that the maximum moisture content is less than will satisfy the affinitive capacities of all of the separated particles, and subsequent thorough admixture with such moisture-regulated material of relatively minute quantities of selective reagents.

4. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes effectively selective modification of the adsorptive capacities of the material particles through regulation of the moisture content of the material between an upper limit less in amount than will satisfy the affinitive capacities of all of the separated particles, and a lower limit determined by the amount of moisture adsorbable to the material from the atmosphere, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents.

5. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes effectively selective modification of the adsorptive capacities of the material particles through regulation of the moisture content of the material to a variable-film quantity less than will satisfy the affinitive capacities of all of the separated particles, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents.

6. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes effectively selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a total maximum amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents.

7. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes effectively selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a total maximum amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, and continued agitation of such admixture to effective concentration of the reagents on and about those particles of greater adsorptive capacities.

8. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes effectively selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a total maximum amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, and subsequent thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, and time-conditioning of such admixture while in the moist condition to effective concentration of the reagents on and about those particles of greater adsorptive capacities.

9. The method of selectively separating sands, comminuted ores and similar materials which comprises modification of the adsorptive capacities of the material particles through regulation of the moisture content of the material below a maximum less in amount than will satisfy the affinitive capacities of all of the separated particles, thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, and agitation of the resultant admixture in a froth flotation cell for separation of the desired particles.

10. The method of selectively separating sands, comminuted ores and similar materials which comprises selective modification of the adsorptive capacities of the material particles through regulation of the moisture content of the material to a variable-film quantity less than will satisfy the affinitive capacities of all of the separated particles of the material, thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, and agitation of the resulant admixture in a froth flotation cell for separation of the desired particles.

11. The method of selectively separating sands, comminuted ores and similar materials which comprises selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a maximum total amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, and agitation of the resultant admixture in a froth flotation cell for separation of the various particles.

12. The method of selectively separating sands, comminuted ores and similar materials which comprises selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a maximum total amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, continued agitation of such admixture while in the moist condition to effective concentration of the reagents on and about those particles of greater adsorptive capacities, and subsequent agitation of the resultant admixture in a froth flotation cell for separation of the various particles.

13. The method of selectively separating sands, comminuted ores and similar materials which comprises selective modification of the adsorptive capacities of the material particles through regulation of the thickness of water film adherent to the material particles within a maximum total amount of water film less than will satisfy the affinitive capacities of all of the separated particles of the material, thorough admixture with the moisture-regulated material of relatively minute quantities of selective reagents, time-conditioning of such admixture while in the moist condition to effective concentration of the reagents on and about those particles of greater adsorptive capacities, and subsequent agitation of the resultant admixture in a froth flotation cell for separation of the various particles.

14. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes the regulation of the variable-film water to that amount which prevents the adsorption of the selective reagents by certain only of the mineral particles but permits such adsorption by the other mineral particles, thorough admixture of the moist ore with the desired reagents, and subsequent separation of the particles in a froth flotation cell.

15. The method of preparing sands, commi-

nuted ores and similar materials for separation by froth flotation which includes the regulation of the variable-film water to that amount which prevents the adsorption of the selective reagents by certain only of the mineral particles but permits such adsorption by the other mineral particles, thorough admixture of the moist ore with the desired reagents, continuation of contact between the moist ore and reagents while still in the moist condition a predetermined length of time, and subsequent separation of the particles in a froth flotation cell.

16. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes mixing with the material that amount of combined water and selective reagents such as will limit the variable film water of the mixture to an amount less than will satisfy the affinitive capacities of all of the material particles, and subsequent separation of the particles in a froth flotation cell.

17. The method of preparing sands, comminuted ores and similar materials for separation by froth flotation which includes the regulation of the variable-film water to an amount less than will satisfy the affinitive capacity of the material, thorough admixture of the moist material with neutral reagents to satisfy absorptive needs of the material, thorough admixture of the conditioned material with collecting reagents, and subsequent separation of the material particles in a froth flotation cell.

THEODORE EARLE.