

UNITED STATES PATENT OFFICE

2,040,187

PROCESS FOR SEPARATING SOLIDS BY
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MacDonald, La Jolla, Calif.No Drawing. Application May 11, 1934,
Serial No. 725,098

10 Claims. (Cl. 209—167)

This invention relates to a process for separating solids by flotation, and especially for the separation or concentration of ores, and more particularly ores such as carbonates, sulfates, and oxides, to which flotation processes heretofore known have not been satisfactorily applicable for the production of concentrates of sufficient purity, with a commercially satisfactory recovery.

In the art of flotation as generally practiced, some reagent or group of reagents is usually employed which is called the collector reagent, and it is generally found that the mineral or minerals which have been collected in the froth by the flotation process have reacted with this particular reagent. With some types of minerals and collector reagents, this reaction appears to be only one of physical adsorption, as in the case of a sulfid and an oil considered to be chemically inert. More often in modern practice, however, a collector reagent is employed which is capable of forming a very slightly soluble compound with some intrinsic component or surface ion of the mineral desired to be floated. Thus a soluble xanthate, such as sodium ethyl xanthate, is employed as the collector reagent for metallic sulfids; such a xanthate has the property of forming very slightly soluble metallic xanthates, probably by direct chemical reactance with some of the surface ions of the metal or metals in the sulfids to be floated. Collector reagents of this type have the further characteristic of being of a dual nature; part of their molecule is polar (and water-wettable) while another part is non-polar (and non-water-wettable). Thus, in the case of sodium xanthate, the sodium end is polar and the xanthate end is non-polar, and similarly, after precipitation, as the metallic xanthate, the metallic end of the molecule is polar while the xanthate end remains non-polar. These are heteropolar reagents. The property of non-wettability, in the exposed part of the molecule, is essential to a solid substance or its coating, for it to be amenable to collection in a flotation froth.

It is also well-known that oleic acid and certain other fatty acids or derivatives thereof are effective collector agents for the concentration of many minerals by means of the flotation process. Oleic acid belongs to the unsaturated fatty acid group. The commercial difficulty impeding the use of fatty acids, their soaps, or other derivatives for this purpose, has been the impracticability of maintaining sufficient selectivity as between the several minerals in the ore being

treated, for generally there is more than one mineral in the ore which is responsive to soap as a collector agent, so that the separation between several such minerals is often difficult if not impossible.

The fatty acids, fatty acid soaps, and other fatty acid derivatives, which will be hereinafter referred to, in general, as "fatty acid collector agents", are collector reagents of the required type. First, they are heteropolar compounds. Secondly, they form heteropolar compounds of relatively slight solubility with metallic elements (excepting only with the alkali metals, which compounds are soluble). Thus oleic acid is a particularly effective collector agent in the flotation of calcium and barium minerals, and it is well-known that calcium and barium oleates are of slight solubility. Calcium and barium minerals are not satisfactorily floatable by means of xanthates, because calcium and barium xanthates are quite soluble. The term "metallic element" is used herein in its broad sense, as including also those elements sometimes referred to as "sub-metallic," and in fact, any element capable of forming a soap.

Though barite (barium sulfate) is readily floatable by means of oleic acid, for instance, this mineral frequently occurs in nature associated with limestone and clay, which latter minerals are also responsive to flotation by means of fatty acid collector agents, so that limestone and clay congregate in the froth along with the barite, thus producing a concentrate of insufficient purity.

Barite may be considered to be responsive to oleic acid because barium oleate is relatively insoluble; the barium ions available on the surface of the barite mineral grains react with fatty acid to form in this case relatively insoluble barium oleate. Furthermore, this reaction proceeds directly at the surface of the barite mineral grains, and the barium oleate being formed directly at the surface and within the exposed molecular lattice adheres thereto, with the result that the barite mineral acquires a surface which to all intents and purposes consists of barium oleate. Such a surface, being not water-wettable, causes the mineral grains coated with it to tend to gather in the froth in an ordinary flotation operation. Thus a commercially useful concentration may be brought about by skimming or otherwise removing the froth as formed.

Many other minerals respond to a fatty acid collector agent in the same way and may be so floated. Indeed, any mineral in whose surface

can occur ions which react with fatty acid collector agents to form relatively insoluble, non-wettable compounds, or which tends to adsorb fatty acid collector agents, responds to flotation by means of such fatty acid collector agents. Among such minerals may be mentioned as examples those of manganese, iron, aluminum, tin, magnesium, copper, lead, zinc, calcium, barium, etc., and in fact any mineral containing an element capable of forming compounds of slight solubility, with fatty acids or their derivatives. Such minerals are hereinafter called "soap-forming" minerals, and compounds formed by reaction with, or adsorption by, such minerals of fatty acid collector agents are called "soaps".

Pure silica does not respond in the same way, because silicon does not form a soap stable in water, though it may happen in practice that silica may absorb or combine with soap-forming cations, such as barium or calcium ion, (probably by direct chemical action) whereupon these adsorbed or combined ions may form soaps in the way above-described, if a soluble soap or fatty acid or fatty acid derivative be introduced into the flotation pulp, and the silicates may therefore be caused to float through the indirect agency of its adsorbed or combined soap forming ions. When desired, however, such adsorptions by silica can largely be prevented by ordinary and well-known means (usually by the introduction of a soluble silicate to increase the concentration of silicate ion), so that the flotation of silica may be prevented without hindering the flotation of the soap-forming minerals. Minerals consisting of the silicates of the soap-forming elements are only reluctantly floatable by means of soaps because of the very slight solubility of those silicates, so that heretofore in practice it has been found possible to reject some silicates also when desired.

As among the minerals which contain soap-forming constituents, however, no entirely satisfactory method has heretofore been disclosed to permit the separation of one from another by means of a fatty acid collector agent, and it is this which is the purpose of the present invention.

The fatty acids and their derivatives vary among themselves in the solubility of the compounds which they form with a given metallic element. Thus barium oleate is less soluble than barium laurate. Also, the several metallic elements differ among themselves in the solubilities of the compounds which they form with a given fatty acid or fatty acid derivative. Thus barium oleate is less soluble than copper oleate. We believe that in general the floatability of any soap-forming mineral is proportional to the degree of insolubility of the soap coating which can be precipitated upon its surface. That mineral will float first and most abundantly whose soap coating is least soluble, and that mineral will float last and least abundantly whose soap coating is most soluble, other conditions being the same.

However, these differences in solubility are usually insufficient in magnitude to allow satisfactory flotation separation of one soap-forming mineral from another by any present-known choice of collector agents.

The principal object of this invention, therefore, is to provide a new and advantageous process for the separation of solids or minerals from one another by soap flotation.

A particular object of the invention is to provide a new means for selectively or differentially depressing or inhibiting the soap flotation of differ-

ent mineral constituents of an ore, or other mineral mixture.

A further object of the invention is to obtain a differential depressing action on the floatability, by soap flotation, of different minerals by adding to the pulp containing such minerals a novel type of reagent capable of selectively modifying or influencing the soap coating on particles of different minerals, in such a way as to materially lessen the flotation of one or more of the minerals present, while permitting one or more other minerals to be floated to a relatively high degree.

Another object of the invention is to provide for controlling the selective separation, by soap flotation, of different minerals by coating the surfaces of the particles of one or more of said minerals with a metallic salt or salts capable of forming a soap or soaps of different solubility than the soap or soaps formed by the metallic constituents of the particles so coated, so that the floatability or non-floatability of the various mineral constituents is determined in accordance with the floatability or non-floatability of the surface coating substance, and to thus obtain a selective flotation effect which is different from that exhibited by the mineral particles without such surface coatings. This feature of our invention, for example, makes it possible to effect a satisfactory separation of two or more minerals, which, in themselves are not susceptible to ready separation by previously known methods of soap flotation.

A further object of the invention is to obtain a novel selective action by the combined use of surface coatings of metallic salts on one or more of the mineral constituents present, and a selective depressing agent, whereby the flotation of the reactive constituents is influenced not only by the presence of the surface coating substance or substances, but also by the differential depressing action of the depressing agent on the respective coated or uncoated mineral particles.

We have discovered that certain partially or incompletely molecularly hydrated phosphates admirably serve the purpose of creating maximum differentials of solubility as among the fatty acid compounds of the several soap-forming minerals. We particularly prefer a relatively soluble metaphosphate, such as sodium metaphosphate. A phosphate of the second degree of hydration, such as a pyrophosphate, is effective to a considerable degree but is not nearly as effective as a metaphosphate, while phosphates of the third degree of hydration, such as the orthophosphates, are only slightly effective for the purpose.

The meaning of the expression "incompletely molecularly hydrated phosphates" will be made clear by considering the three forms of phosphoric acid, namely, metaphosphoric acid, pyrophosphoric acid, and orthophosphoric acid. The chemical formulae for these three phosphoric acids are ordinarily written as follows:

Metaphosphoric acid.....	HPO ₃
Pyrophosphoric acid.....	H ₂ P ₂ O ₇
Orthophosphoric acid.....	H ₃ PO ₄

The difference in their degree of molecular hydration may be more clearly brought out by writing their formulae as compounds of phosphorus pentoxide and water, thus:

Metaphosphoric acid.....	P ₂ O ₅ .H ₂ O
Pyrophosphoric acid.....	P ₂ O ₅ .2H ₂ O
Orthophosphoric acid.....	P ₂ O ₅ .3H ₂ O

Orthophosphoric acid contains three replaceable hydrogen atoms, and accordingly can form three classes of salts, depending upon whether one, two or all three of the hydrogen atoms are displaced. Thus we may have:

Monobasic sodium orthophosphate..... NaH_2PO_4
 Dibasic sodium orthophosphate..... Na_2HPO_4
 Tribasic sodium orthophosphate..... Na_3PO_4

We have found that each of the phosphoric acids, in the form of its sodium salt, or other convenient relatively soluble salt, has an effect upon the soap flotation of any mineral which is floatable by means of a soap, fatty acid, or fatty acid derivative. This is well illustrated by the following series of laboratory flotation tests, in which pure limestone (calcium carbonate) was exclusively the flotation feed.

Eight individual tests were conducted, each using 500 grams of pure limestone as the "ore". The feed in each case was ground four minutes in a laboratory rod mill, in the presence of 1000 cubic centimeters of water and 0.20 gram of oleic acid. At the conclusion of the grinding operation, the mineral was all minus 65 mesh in size, with about 50% of it minus 200 mesh in size. The ore pulp was then transferred to a laboratory flotation machine of an ordinary, mechanically aerated type, diluted with water to 5000 cubic centimeters total volume, and the flotation operation was begun after the addition of 0.09 gram steam-distilled pine oil as a frothing agent, and also after the addition of some one of the individual modifying agents being tested, as enumerated below for the respective tests. In every case, the froth was skimmed for exactly five minutes at a uniform rate. The total froth so skimmed off was filtered, dried and weighed, and the percentage recovery calculated from the then known weights of concentrate and feed. In this series of tests, the first was without any modifying agent, and the subsequent seven tests were respectively with 0.5 gram of the modifying agent noted in the table below. In this table, the name of the particular modifying salt is given, together with the percentage of feed recovery effected in the test in which that salt was used. It has been claimed by certain investigators that the valence of the cation is of some importance, and so as to prove or disprove this point, the orthophosphate of trivalent aluminum was used in one test, instead of the monovalent sodium. Also in one test, sodium metasilicate was used for comparative purposes. The results of these tests are next given, and are arranged in the descending order of per cent recovery, that is, in the increasing order of effectiveness of the respective salts in preventing the flotation of limestone.

Modifier reagent used	Per cent recovery
None.....	53.16
Aluminum orthophosphate.....	46.20
Sodium metasilicate.....	38.69
Tribasic sodium orthophosphate.....	36.00
Dibasic sodium orthophosphate.....	34.20
Monobasic sodium orthophosphate.....	29.94
Sodium pyrophosphate.....	16.26
Sodium metaphosphate.....	6.42

It is seen in the foregoing table that the orthophosphates, both of sodium and of aluminum, do tend to inhibit the flotation of calcium carbonate, but that sodium pyrophosphate is more effective than any of the orthophosphates, and sodium

metaphosphate is considerably more effective than sodium pyrophosphate. As among the phosphates, their increasing effectiveness is in the same order as their increasing alkali-neutralizing power. The foregoing series of tests has subsequently been repeated, using 1/200 gram equivalent of the modifier salt in the respective cases, instead of the fixed 0.5 gram, in order to correct for differences in molar weight. The same order of effectiveness was observed in the second series.

It will be apparent from the above discussion that sodium metaphosphate and sodium pyrophosphate are incompletely molecularly hydrated, and that these compounds have a more pronounced depressing effect in soap flotation than the ortho-phosphates, which are completely molecularly hydrated. Furthermore, the metaphosphate, which is the least hydrated molecularly, gives the best results. Therefore, we prefer to use an incompletely molecularly hydrated phosphate, and most preferably a metaphosphate.

We have found that, under suitable conditions of hydrogen ion concentration, temperature, dilutions, etc., sodium metaphosphate, brought into contact with a mineral coated with a slightly soluble soap, such as limestone coated with calcium oleate, will so modify the calcium oleate coating that flotation of the limestone is inhibited. If the metaphosphate be added first, the floatative oleate coating is prevented from forming. The phosphates mentioned have a similar effect upon the soap-flotation of other minerals, but with a given amount of the soluble phosphate added to a mixture of several soap-coated minerals, the modifying action is not equal in speed and degree upon all of them. Thus it is possible, by suitable adjustment of the concentration of the collector agent, the phosphate, and other constituents present, including the degree of hydrolysis, to create such a condition that the floatative soap coating upon one mineral is altered or otherwise nullified with a relatively high degree of speed and completeness, while the soap coating on other minerals is not affected to nearly the same degree. Under these conditions, the mineral whose coating has been altered is inhibited from floating, while other minerals are at the same time left in a floatable condition, so that a separation of ordinarily soap-floatable minerals is made possible by otherwise ordinary flotation procedure.

We have further found that sodium metaphosphate or sodium pyrophosphate has a strong inhibiting effect when used in connection with many other minerals which respond to a fatty acid or fatty acid derivative as the flotation collector reagent, and that the effect is not limited to calcium minerals. The effect varies widely in degree, however, comparing one mineral with another. Thus, if enough sodium metaphosphate be used, the flotation of such minerals as apatite, barite, witherite, fluorspar, chromite, bauxite, cassiterite, etc., can be completely inhibited and, up to the point of complete inhibition in any given case, the degree of inhibition is roughly proportional to the quantity of sodium metaphosphate used, amount of collector reagent and other conditions being the same.

We find that a given quantity of sodium metaphosphate does not have an equal inhibiting effect upon the flotation of all of the above-named minerals. In the example cited in the foregoing table, the use of 0.5 gram sodium metaphosphate

in the flotation of 500 grams of limestone in 5000 cubic centimeters of pulp volume was sufficient to reduce the recovery from 53.16% to 6.42%, but upon an equal quantity of witherite, for example, the reduction in recovery caused by 0.5 gram sodium metaphosphate is very much less. That is, a given quantity of sodium metaphosphate does not inhibit the flotation of a given quantity of barium mineral so readily as it inhibits the flotation of the same quantity of calcium mineral. Or again, the same quantity of sodium metaphosphate upon an iron mineral has a still different degree of inhibitory effect than upon the same quantity of either barium or calcium minerals.

In this way, we find that if a just-sufficient quantity of sodium metaphosphate be added to a flotation pulp containing a mixture of soap-floatable minerals, the difference in their natural response to the soapy collector reagent can be widened to such a degree that commercially satisfactory separations can be made.

In carrying out the flotation process according to our invention, using an incompletely hydrated phosphate as a selective depressing agent, the ore or mixture of minerals to be treated is ground, mixed with water to form a pulp, and the desired reagents added thereto. These reagents include a fatty acid collector agent, such as oleic acid, sodium oleate, or corn oil soap; and a depressing agent such as sodium metaphosphate or one of the other incompletely molecularly hydrated reagents herein mentioned. A froth stabilizing agent such as pine oil, kerosene or fuel oil, may be used if thought needed in any individual case. Also, if desired, a pH modifying agent, such as soda ash or sodium silicate, may be used, but we have found that in many cases a suitable pH value can be obtained by the use of sodium metaphosphate or other depressing agent of the type herein described, without the addition of any other pH modifier. The proportions of the several reagents used are subject to considerable variation, and may be determined by experiment for any particular case, but we have found that good results may be obtained, in certain cases, by using proportions of reagents by weight of ore as given in the following table, it being understood that these proportions are merely illustrative and that the invention is by no means limited thereto.

Reagent	Pounds per ton of solids
Fatty acid collector agent.....	0.10 to 1.50.
Depressing agent of the type herein described.....	0.05 to 1.0.
Other pH modifying agent.....	None to 2.0.
Frothing agent.....	None to 0.50.

After thorough mixing with the added reagents, the pulp is subjected to flotation in any suitable type of flotation apparatus, and the floated froth is separated therefrom in the usual manner, as by skimming or overflow, giving a concentrate which is relatively higher in one mineral, and relatively lower in another mineral, than the original feed.

We will now illustrate what has been said thus far, by giving the actual assay result of a series of laboratory flotation tests in which the ore consisted of a mixture of one part witherite (barium carbonate), three parts limestone (calcium carbonate), and six parts clean silica sand.

After thorough mixing, 1000 gram charges of the mixture were weighed out and individually

subjected to laboratory flotation tests. Each charge was separately ground and floated under conditions essentially identical in all cases excepting only the single difference that the amount of sodium metaphosphate used as varied from test to test.

In every case, a rougher concentrate was first made, using 0.2 gram of oleic acid, 0.03 gram steam-distilled pine oil, 1.0 gram soda ash, and the variable quantity of sodium metaphosphate. This rougher concentrate was then re-floated as a cleaning operation, without any further reagents except 0.02 gram pine oil as a frothing agent.

The final products were all dried, weighed, and assayed for barium and calcium, so that the grades of the final concentrates, as well as the percentages of recovery of the respective minerals, were determined. The results of this series are shown in the table next given:

Final cleaned concentrate

Lbs. NaPO ₃ per ton of ore	Weight grams	Assay, percent		Percent original feed recovered	
		BaCO ₃	CaCO ₃	BaCO ₃	CaCO ₃
None.....	261	34.00	57.00	96.16	37.59
0.20.....	120	54.54	36.97	81.14	16.67
0.40.....	82	63.92	23.88	57.83	6.83
0.50.....	57	64.93	18.77	40.17	3.75

The foregoing results are given as illustrative of the differential effect as the quantity of sodium metaphosphate is varied. Later tests, which included modifications of procedure to be described herein, have given still better separations with both higher grade concentrate and higher recovery of the barium mineral.

The most important feature of the foregoing table is that, as the amount of sodium metaphosphate increases from none to 0.5 lb. per ton of feed, the barium carbonate assay of the cleaner concentrate increases from 34.00% to 64.93%, while at the same time the calcium carbonate assay decreases from 57.00% to 18.77%. This specifically shows the differential effect of sodium metaphosphate in the flotation of mixed carbonates of calcium and barium. Within this range, the recovery of barium carbonate decreases from 96.16% to 40.17%, while the recovery of calcium carbonate decreases much more, from 37.59% to 3.75%.

We have applied a similar technique to a wide variety of ores, and have found in every case that sodium metaphosphate or other molecularly dehydrated phosphate has a greater or less effect upon the floatability of one mineral than upon the floatability of another. For instance, in the absence of sodium metaphosphate, limestone is more readily floatable than the mineral chromite, using oleic acid as the collector, but in the presence of sodium metaphosphate, the reverse is true.

As a further part of our present invention, we have discovered a method of strengthening the effect of the partially hydrated phosphates herein referred to, in creating differentials of floatability between minerals. We have stated our belief that those minerals are most floatable which form the least soluble compound with the given collector agent. We also believe that those minerals which form the least soluble compounds with the collector agent are also the least acted upon by the partially hydrated phosphates, and

vice versa. Now, of the metallic soaps, those of nickel and iron are among the most soluble (other than those of the alkali metals), while those of barium and lead are among the least soluble. Consequently, as between minerals like those of barium and lead on the one hand, and minerals like those of nickel and iron on the other, flotation separation with a soap collector is relatively easy, and may sometimes be accomplished even without the use of a selectivity modifier, with fairly satisfactory results. With a selectivity modifier like sodium metaphosphate, separation between these respective groups of minerals is particularly simple and satisfactory.

We find that it is often possible to cover the surface of a mineral with a compound say of barium or lead, or other element capable of forming a very slightly soluble soap, and thus facilitate its soap flotation. Likewise, it is often possible to cover the surface of a mineral with a compound of iron or nickel or other element capable of forming a relatively soluble soap, and thus impede its soap flotation. The same operation at the same time facilitates or impedes the effect of the selectivity modifier in a compatible direction with reference to floatability. That is, not only will a barium or lead compound coating improve the soap floatability of an iron mineral, for instance, but it will prevent the selectivity modifier from unduly impeding the floatability of an iron mineral. Conversely, not only will a nickel or iron compound coating impede the floatability of a calcium mineral, for instance, but the further impedance exerted by a selectivity modifier like sodium metaphosphate will be greater upon a nickel- or iron-coated calcium mineral than upon a calcium mineral not so coated.

In our use of the molecularly dehydrated phosphates as selectivity modifiers, we therefore prefer to cover the minerals we desire to float with a salt or compound of a soap-forming element whose soaps are of a low order of solubility. We also prefer to coat the minerals we desire to reject, with a salt or compound of a soap-forming element whose soaps are of a relatively higher order of solubility. It will be understood that coatings of the above types may be used either separately or in conjunction with one another, and it will also be understood that such coatings may not only be employed as a means of modifying the depressing action of an incompletely molecularly hydrated depressing agent added to the pulp, but may also be employed as a means of modifying the soap floatability of minerals, independently of the use of such a depressing agent. Our choice of the metallic salts to be used in the respective cases is not always established solely by considering the solubilities of the soaps which those metallic salts form, for we may advantageously choose one which is capable of being formed as a coating on the mineral we desire it to influence, by chemical reaction between the mineral which is to be coated and a compound of the metal which we desire to have present in the coating, that is, the metal of the metallic salt chosen may advantageously be one which forms with some component of the mineral a compound which is less soluble than the pre-existing surface of the mineral itself. Thus, for instance, we can coat calcium carbonate with solid lead carbonate by adding a relatively soluble lead salt, because lead carbonate is less soluble than calcium carbonate, and the added lead salt will therefore react with the calcium carbonate to form a coating of solid lead carbonate on the

surfaces of the calcium carbonate particles, but we cannot coat calcium carbonate with barium carbonate to any appreciable degree by using a relatively soluble barium salt, because barium carbonate is more soluble than calcium carbonate. Thus, though coatings of either lead or barium salts would increase the floatability of calcium carbonate, our choice between the two should be a lead salt as the salt to use in this particular case. On the other hand, if gypsum (calcium sulfate) were the mineral we were attempting to coat, a salt of barium would be our choice rather than lead, because barium sulfate is less soluble than lead sulfate and is also less soluble than calcium sulfate.

The proportion of metallic salt thus added for the purpose of modifying the surface of one or more of the constituent minerals may be varied between rather wide limits, and we have found, by way of illustration only, that good results may be obtained when the proportion thereof varies from none to 2.0 pounds per ton of solids in the pulp.

Considering calcium carbonate further, this is a widely occurring mineral of relatively little economic value, and the desire is usually to depress it in a flotation operation. An iron salt admirably meets the requirements of a coating material for this purpose, because not only are iron soaps quite soluble, but also iron carbonate is less soluble than calcium carbonate and hence calcium carbonate can readily be coated with iron carbonate.

The mineral chromite (ferrous chromite) will serve as a further illustration of our use of metallic salts supplementary to the use of our molecularly dehydrated phosphates. This is a mineral of high economic value, and one whose flotation is usually desired to be facilitated. However, since the cation of this mineral is iron, and since iron soaps are relatively soluble, the response of chromite to soap flotation is not entirely satisfactory. Chromite can be readily coated with lead chromite or chromate, however, by using a relatively soluble lead salt like lead nitrate, because lead chromite or chromate is less soluble than ferrous chromite or chromate. This coating facilitates the soap flotation of chromite, because lead soaps are less soluble than iron soaps.

As an illustration of our complete procedure in the use of metallic salts, as adjuncts of molecularly dehydrated phosphates in the selective soap flotation of minerals, we will now consider an ore composed essentially of the two minerals, chromite and limestone. We will say that we desire to float the chromite in the froth and reject the limestone in the tailing. Ordinarily, the order of floatability of these two minerals would be the opposite of that stated as desired, for the cation of limestone is calcium which in this case forms a slightly soluble soap, causing limestone to float in preference to chromite, whose iron cation forms the more soluble iron soap. However, these two minerals tend to react with each other in an aqueous medium, the iron from the chromite tending to coat and depress the limestone by forming iron carbonate upon it, so that when we use, say, sodium metaphosphate as the sole selectivity modifier, in this case, we tend to get depression of both minerals to an undesirable extent. We therefore prefer to coat the surfaces of both minerals in such a way that the effect of the metaphosphate is not contrary to our purpose. To do this, we may add to a pulp containing the above-mentioned ore, a soluble

lead (or barium) salt so as to coat the chromite with lead (or barium) chromite or chromate which increases its floatability and decreases its susceptibility to depression by metaphosphate, and at the same time we may add a soluble nickel (or iron) salt so as to coat the limestone with nickel (or iron) carbonate, which decreases its floatability and increases its susceptibility to depression by metaphosphate. For example, if salts of lead and nickel are added, the lead salt will react with the ferrous chromite to form on the surface of the latter a coating of less soluble lead chromite or chromate in solid form, while the nickel salt will react with the limestone to form on the surface of the latter a coating of less soluble nickel carbonate in solid form. Furthermore, the iron displaced by the lead or barium upon the chromite surface is thrown into solution whereupon it has further value in depressing the limestone. Also, although lead would tend to coat the calcium carbonate because lead carbonate is less soluble than calcium carbonate, and although this is undesirable because it would increase the floatability of the calcium carbonate, any lead carbonate coating which so forms is immediately displaced by a coating of nickel or iron carbonate because the latter are less soluble than lead carbonate. Besides, lead chromite or chromate is less soluble than lead carbonate, which also serves to attract the lead to the chromite and away from the limestone.

The net result, after these reactions have come to equilibrium, is that the calcium carbonate has become in effect a nickel or iron mineral (due to its coating of nickel or iron carbonate) which is readily depressed by sodium metaphosphate, and at the same time the chromite has become in effect a lead or barium mineral (due to its coating of lead or barium chromite or chromate) which is relatively immune to the depressing effect of sodium metaphosphate. As, furthermore, lead or barium minerals respond better than iron minerals to soap flotation, satisfactory selective soap flotation between chromite and limestone has been made possible, with the chromite appearing in the froth concentrate, and the limestone being rejected as tailing.

We next give the results of a series of eight laboratory flotation tests, upon an ore composed of a mixture of equal parts of limestone and impure chromite. The chromite was about 70 per cent pure, the impurities consisting of aluminum and magnesium silicates. All tests were made on 500 grams of feed, ground for five minutes in a laboratory rod mill and diluted with water to a total volume of 5,000 cubic centimeters. All used the same amounts of oleic acid as the sole collector and of pine oil as the frother. None used any other reagents except some one of the three selectivity modifiers mentioned (sodium metaphosphate, a lead salt, and an iron salt), or some combination, or all, of these. The temperature was the same in all cases, 55° F. A rougher concentrate was first made, using 0.25 gram oleic acid and 0.04 gram pine oil, with or without either or both the lead and the iron salt, but always without any metaphosphate; the rougher concentrate was then cleaned and re-cleaned using no additional oleic acid and 0.03 gram additional pine oil, with or without sodium metaphosphate, but always without any further addition of the lead or iron salt. That is to say, whenever the lead or iron salt was used, it was added prior to the rougher operation, and when-

ever sodium metaphosphate was used, it was added to the cleaner operation subsequent to the rougher operation. The following table gives the assay results of each of the eight individual tests composing this series:

Test No.	Grams selectivity modifier used			Final cleaner concentrate			
	Sodium metaphosphate	Lead nitrate	Ferrous sulfate	Assay, percent		Percent recovery	
				Chromite	Limestone	Chromite	Limestone
86	None.	None.	None.	37.82	62.18	51.00	58.60
85	None.	None.	2.0	54.85	45.15	42.62	24.50
95	None.	2.0	None.	51.05	48.95	94.00	74.30
96	Nons.	2.0	2.0	59.05	40.95	92.00	50.23
84	0.2	None.	None.	58.02	41.98	29.18	14.78
81	0.2	None.	2.0	76.90	23.10	69.43	14.48
90	0.2	2.0	None.	77.20	22.80	59.11	12.22
97	0.2	2.0	2.0	86.15	13.85	62.70	6.81

To illustrate the latitude which in some cases we have in our choice of metallic salts to use as modifiers, we will cite the results of another flotation test which exactly duplicated No. 97 above, except that two grams of barium chloride was used instead of lead nitrate to assist the flotation of the chromite, and that two grams of nickelous chloride was used instead of ferrous sulfate to impede the flotation of limestone. Sodium metaphosphate was used just as in No. 97. This test yielded a concentrate assaying 79.38 per cent chromite and 20.62 per cent limestone, containing 74.4 per cent of the original feed chromite and only 13.52 per cent of the original feed limestone.

Selective alteration of the surfaces of some of the minerals present, as compared to those of other minerals, by the use of a suitably chosen metallic salt, enables us to make useful flotation separations in a number of cases, even when the minerals to be separated contain in the natural state an element common to both. As an instance of this, we will now cite laboratory flotation results upon an ore consisting of equal parts of fluor spar (calcium fluoride) and limestone (calcium carbonate), with no other minerals present. In soap flotation, both these minerals float by virtue of the formation upon their surfaces of a calcium soap, and if sodium metaphosphate be the only selectivity modifier present, it will act about equally on both. However, we may alter the surface of the calcium carbonate by precipitating ferrous carbonate upon it. As has already been shown, this result may be attained merely by the addition of a soluble iron salt, such as ferrous sulfate. At the same time, the surface of calcium fluoride will not change in the presence of ferrous sulfate, because calcium fluoride is less soluble than either ferrous fluoride or calcium sulfate. After this change has been caused to occur, sodium metaphosphate becomes a particularly effective selectivity modifier, because we are now dealing with a calcium mineral (calcium fluoride) on the one hand, and in effect an iron mineral (iron carbonate coated calcium carbonate) on the other. In one laboratory flotation test, we used an ore consisting of 50 per cent fluor spar and 50 per cent limestone. Five hundred grams of this ore was ground in the presence of 2.0 grams ferrous sulfate and 1000 cubic centimeters of water. A flotation rougher concentrate was then made, using 0.3 gram oleic acid as the collector agent, without any pine oil or frothing agent other than the oleic acid. 0.2 gram sodium

metaphosphate was added to this rougher concentrate, which was then refloat, in one stage, to make a final cleaned concentrate. This final concentrate was weighed and assayed, from which data the results of the test were calculated, and were found to be as follows:

Per cent recovery in final concentrate

Assay of final concentrate		Referred to original ore	
CaF ₂	CaCO ₃	CaF ₂	CaCO ₃
84.40	15.60	86.22	15.54

The tailing thus obtained, when subjected to the well-known hydrochloric acid and stannous chloride test for tungsten, gave an entirely negative reaction, thus indicating practically a 100 per cent recovery of the tungsten in the rougher concentration. The middling gave a very faint reaction, while the cleaner concentrate gave an intense and immediate reaction. A second test was made on this same material, duplicating the conditions of the first test, except that 0.10 gram of sodium metaphosphate was used as a modifying agent in the cleaning operation. The final products obtained in this case were as follows:

Cleaner concentrate	87 grams
Middling	113 grams
Tailing	300 grams

In this case also, the cleaner concentrate contained practically all of the tungsten, and was therefore of higher grade than in the first test, since its weight was materially less than before.

Similar tests were also made on the concentration of scheelite from the mill tailing material above-mentioned. In the first test, we obtained a practically complete recovery of the scheelite with a ratio of concentration of 13.9 tons into one ton, using 1 pound of lead nitrate per ton, 2 pounds of soda ash per ton, and 0.35 pound of oleic acid per ton, but without any sodium metaphosphate. All reagents were added prior to the rougher concentration, which was followed by a cleaning operation without addition of any further reagents. In the second test, which duplicated the first except that sodium metaphosphate was used in the cleaning operation in the proportion of 0.40 pound per ton of original feed, we also obtained a practically complete recovery of the tungsten, but the ratio of concentration was increased to 31.2 tons into one ton. In both of these tests on the tailing material, we also used 2.0 pounds of sodium silicate per ton, in order to prevent activation of quartz by the lead nitrate.

Since iron salts are frequently of importance in our process, and may be either beneficial or detrimental, depending upon the minerals involved in a particular flotation operation, we do not overlook the fact that iron salts may be generated within the operation or within the equipment, as the result of contact between the ore pulp and iron equipment which may be used, such as grinding mills, grinding media, pumps, tanks, etc. Iron salts so generated have the same effect as though they were deliberately added. Therefore, if the presence of iron salts is detrimental to the operations in which the invention is to be utilized, suitable precautions should be taken to prevent formation thereof.

Our general process of modifying mineral surfaces by the use of metallic salts and then differentiating between those surfaces in flotation by means of a partially hydrated phosphate is also applicable to sulfid ores, for such minerals have a strong tendency, superficially to oxidize to sulfates. Indeed, such surface oxidation of sulfids is inevitable in the presence of water; for all commercial water contains dissolved oxygen which is a powerful oxidizing agent. Lead and zinc ores respond readily to soap flotation because lead and zinc soaps are of low solubility; sodium metaphosphate will, however, not only differentiate soap flotation as between lead and zinc minerals on the one hand, and gangue on the other, but also, we believe, will differentiate lead and zinc minerals from each other. Cop-

The foregoing results show an excellent separation of two calcium minerals from each other, with a high degree of selectivity and a satisfactory recovery of the preferred mineral. As far as we are aware, no flotation process heretofore disclosed has been able to make a separation between two different minerals of the same alkaline earth, unless one were a silicate. As another instance of the same kind of separation between two alkali-earths, barium carbonate (witherite) may be selectively separated from barium sulfate (barite) by superficially converting the barium carbonate to iron or nickel carbonate for instance, by the use of a suitable iron or nickel salt, then differentiating the soap flotation by the use of a molecularly dehydrated phosphate like sodium metaphosphate or pyrophosphate. As another example, we are able to make satisfactory separations in this general way, between calcium tungstate (scheelite) and calcium carbonate (limestone).

We have also successfully applied this invention, including the step of surface alteration by addition of a soluble salt, to the concentration of scheelite (calcium tungstate) from materials containing the same, including a placer material and a mill tailing resulting from previous operations. It was found that these materials were not readily amenable to soap flotation either when oleic acid alone was used as the collector agent, or when, in addition, the circuit was made alkaline with soda ash. The inability to obtain satisfactory separation in this manner may have been due to the fact that the surface of the scheelite was badly contaminated by iron salt. Since lead tungstate is less soluble than either calcium tungstate or ferric tungstate, we found that a soluble lead salt added to such an ore caused the contaminated scheelite to respond readily to soap flotation in an alkaline circuit, probably by coating or surfacing the scheelite grains with lead tungstate. The following results were obtained with the above-mentioned materials:

In one test, 500 grams of the placer scheelite material was ground to pass 65 mesh, in the presence of 1 gram of lead nitrate, 2 grams of soda ash and 1,000 grams of water. A rougher flotation concentrate was then made, using 0.35 gram of oleic acid as the only other reagent. A clean, heavily-laden froth quickly formed in this operation, carrying practically all of the scheelite. The rougher concentrate was refloat in a cleaning operation, using no further reagents. The final products obtained were as follows:

Cleaner concentrate	112 grams
Middling	86 grams
Tailing	300 grams

per and iron minerals respond less readily to soap flotation, because of the greater solubility of their soaps, which relatively poor response may either be accepted as an advantage in the separation of copper and iron minerals, for instance, from those of lead and zinc, or which may be changed by the addition of a salt of an element whose soap and whose sulfate are both of less solubility, such as salts of barium and lead.

It will be understood from what has been said in the foregoing that relative solubilities play a most important part in our procedure. Solubilities have natural values, but may be altered in various ways. In the first place, solubility is intimately related to temperature, so that in the case of some ores it may be necessary to adjust the operating temperature to that giving the desired equilibria between the several concentrations.

Secondly, relative concentrations in the same medium are a function of each other and of the acidity or the alkalinity, that is, the hydrogen ion concentration. It is to be understood that the addition of acids or alkalies, or in other ways adjusting relative concentrations in accordance with the well-known chemical law of molar concentration, comes within the scope of our present disclosure. No exact concentrations of general application can be given, because they will vary widely with ores of different compositions and as a function of the specific gravities of the minerals, and as a function of the fineness of grinding, upon which depends the amount of reacting mineral surface exposed.

We will now more completely define the phosphates and the fatty acids and fatty acid derivatives which we use in our process.

In regard to the phosphates, we have said that we use those which are not completely hydrated molecularly, and the meaning of that term has been explained. The pyrophosphates and the metaphosphates are prepared by heating suitable orthophosphates to the appropriate temperature, whereupon water is driven off, accompanied by a molecular re-arrangement of the phosphate radical. When these phosphates are then brought into contact with water they tend to rehydrate and recombine with water, reproducing hydrogen ion. The rehydration is a relatively slow reaction at ordinary flotation temperatures, allowing time for the flotation operation to be conducted during the time the reaction is in progress. We believe that the hydrogen ion reproduced during this reaction is sufficient to decompose the soap coating on soap coated minerals with which the metaphosphate may come in contact in the flotation operation, and at the same time the metallic or sub-metallic ion of the soap so liberated is re-precipitated as the very slightly soluble orthophosphate, as made possible by the rehydration of the meta- or pyrophosphate. Other compounds which may be molecularly dehydrated with accompanying molecular re-arrangement and which then rehydrate in the presence of water would also serve our purpose provided they and the compounds which they may form with other constituents of the flotation pulp with which they come in contact in a flotation operation are of a suitable order of solubility. The pyro- and metaphosphates, the pyro- and meta-arsenates, and pyro and meta-arsenites, may be cited as type examples of the other incompletely molecularly hy-

drated compounds which we may use as depressing agents.

In a table which we have given, it will be seen that tribasic sodium orthophosphate is not so effective a depressing agent for limestone as the dibasic or monobasic orthophosphates. In aqueous solution, the tribasic orthophosphate hydrolyzes to yield a slight alkalinity, whereas the dibasic and monobasic orthophosphates hydrolyze to yield a slight acidity. The pyro-phosphates and metaphosphates have an even greater alkalinizing power than the dibasic and monobasic orthophosphates, and yet after rehydration have an equal precipitating power, which we believe to be of significance in our finding them to be more effective than the orthophosphates as selectivity modifiers in soap flotation of minerals.

We have found that the mentioned phosphates make selective flotation possible when derivatives of the fatty acids other than the fatty acids themselves or their soaps are used in place of, or together with, the fatty acids or their soaps, as the collector agent. Among such derivatives may be mentioned amino-soaps and sulfonated or sulfated fatty alcohols. Thus, in one flotation test, we used a sulfonated fatty alcohol in place of oleic acid. In this test, no other collector agent was used. Using as the feed a mixture of 600 grams of silica sand, 300 grams of limestone, and 100 grams of witherite, we made 139 grams of concentrate, without any phosphate or any other reagent except pine oil as a frothing agent. In a subsequent test, upon identical feed, proceeding in the same manner throughout except that 0.2 gram sodium metaphosphate was present, only 50 grams of concentrate was produced. Thus the metaphosphate definitely reduced the floatability of minerals ordinarily floatable by means of a sulfonated alcohol.

In another test, using sodium lauryl sulfate as the sole fatty acid compound, and floating pure limestone, we made 360 grams of concentrate from 500 grams of feed, while in a subsequent test, identical with the first except for the addition of 0.1 gram sodium metaphosphate, the amount of concentrate made was only 180 grams or just half as much.

In another test, using sodium lauryl sulfate as the sole fatty acid compound, and floating pure witherite (barium carbonate), we made 346 grams of concentrate, while in a subsequent test, identical except for the addition of 0.2 gram sodium metaphosphate, the amount of concentrate produced was zero.

We have found that the dehydrated or partially dehydrated phosphates herein referred to, not only serve to selectively nullify the formation or effectiveness of soaps in flotation, but are also effective dispersing agents for use in flotation generally, regardless of the collecting agent used. This dispersion or deflocculation we believe to take place in the same general way as above described for the replacement of soap coatings. Flocculation is often caused by adsorbed hydroxyl ion, which is then neutralized by the hydrogen ion arising from the rehydration of the phosphate, thus allowing deflocculation to take place. The production of hydrogen ion, however, is evidently insufficient to materially attach the ore itself, as is shown by the evident sufficiency of the relatively minute quantities of sodium metaphosphate which we used in the numerous flotation tests which we have cited. It will be apparent, therefore, that such incompletely mo-

lecularly hydrated compounds may also be advantageously used as depressing agents in other types of flotation processes than soap flotation.

It is to be understood also that we do not pre-
 5 scribe the point in the sequence of operation at which the phosphate or other reagent is to be added. Depending upon various conditions, the phosphate may be used in the grinding operation, before or during the rougher flotation operation,
 10 or any subsequent cleaning, or middlings retreatment operation, or stepwise among any of these operations, or at any other point which is followed by a subsequent flotation operation. The equilibria of the several possible reactions are ultimately fixed by relative solubilities, so that the relative sequence of reagent additions is not always of prime importance.

While we have referred to the use of sodium salts of incompletely molecularly hydrated phosphoric or other acids, it will be understood that salts of other metals may also be used; for example, we may use potassium metaphosphate, and calcium metaphosphate may also be used in some cases provided the solubility thereof is greater
 25 than the solubility of the product or products which might be formed by reaction with other substances contained in the pulp.

It is to be understood also that where a metallic salt is used as a selectivity modifier, as well as a phosphate or other depressing agent, it is within the sense of our conception and description that these may be combined as a single reagent. As an example, ferrous metaphosphate might be used instead of sodium metaphosphate and ferrous sulfate.

We find it advantageous in many cases not to use any separate frothing agent such as pine oil. The collector agent itself, especially such a collector agent as oleic acid, forms in many cases a froth which is sufficiently stabilized by the mineral grains therein contained to permit being skimmed off or otherwise removed in the form of a concentrate. Such a frother as pine oil tends to entrain unwanted mineral grains, especially those of very fine or slimy sizes, thus carrying impurities into the froth. Using the collector agent itself as the frother not only has the advantage of greater specificity, but also avoids the cost of a separate frothing agent.

In the claims which follow, it is to be understood that wherever the expression "fatty acid collector agent" is used, the term comprehends any compound or derivative either of a saturated or an unsaturated fatty acid or the fatty acid itself. The term is also meant to include soaps, amino-soaps, or fatty acid compounds which have been reduced, as to the corresponding alcohols or otherwise modified in any way.

It is also to be understood that, in said claims, the term "mineral" as applied to a constituent of the pulp, may refer either to a mineral which is present in the pulp and whose surface is not coated with a salt of a different metal, or to a mineral constituent whose particles have been surface coated with a salt of some other metal, in the manner above described. In the latter case, the behaviour of said mineral, with respect to its ability to form an insoluble soap with the added fatty acid collector agent, is determined by the nature of the metallic element present in the said surface coating.

We claim:

1. The method of separating solids by froth
 75 flotation which comprises depositing, upon the

surface of two constituent minerals of a pulp, salts of two different metallic elements, capable of forming soaps whose solubilities differ from one another and also from the solubilities of the soaps formed by the constituent minerals on which the respective salts are deposited, and then
 5 subjecting the pulp containing said two minerals thus coated with said deposited salts to froth flotation in the presence of a fatty acid collector agent and a depressing agent selected from the group consisting of metaphosphates, metaphosphites, metarsenates and metarsenites, said depressing agent being present in such proportion as to exert a differential inhibiting effect upon the formation of insoluble soap coatings on the
 10 respective salt-coated minerals.

2. The method of separating solids by froth flotation which comprises depositing, upon the surface of two constituent minerals of a pulp, salts of two different metallic elements capable of forming soaps whose solubilities differ from one another and also from the solubilities of the soaps formed by the constituent minerals on which the respective salts are deposited, and then subjecting the pulp containing said two minerals thus coated with said deposited salts to froth flotation in the presence of a fatty acid collector agent and a metaphosphate, said metaphosphate being present in such proportion as to exert a differential inhibiting effect upon the formation of insoluble soap coatings on the respective salt-coated minerals.

3. In a froth flotation process, the steps which comprise: adding a fatty acid collector agent to a pulp containing two minerals capable of forming with such agent difficultly soluble soaps; also adding to said pulp a depressing agent selected from the group consisting of metaphosphates, metaphosphites, metarsenates, and metarsenites, in such proportion as to exert a differential inhibiting effect upon the formation of insoluble soap coatings upon the surfaces of said two minerals; agitating said pulp in the presence of said collector agent and depressing agent to obtain a differential soap coating of said two minerals, and then subjecting said pulp, containing said differentially coated minerals, to froth flotation.

4. In a froth flotation process, the steps which comprise: adding a fatty acid collector agent to a pulp containing two minerals capable of forming with such agent difficultly soluble soaps; also adding to said pulp sodium metaphosphate in such proportion as to exert a differential inhibiting effect upon the formation of insoluble soap coatings upon the surfaces of said two minerals; agitating said pulp in the presence of said collector agent and said sodium metaphosphate to obtain a differential soap coating of said two minerals; and then subjecting said pulp, containing said differentially coated minerals, to froth flotation.

5. In a froth flotation process, the steps which comprise: adding a fatty acid collector agent to a pulp containing two minerals capable of forming with such agent difficultly soluble soaps of different solubilities; also adding to said pulp a depressing agent selected from the group consisting of metaphosphates, metaphosphites, metarsenates, and metarsenites, in such proportion as to increase the difference between the solubilities of the soaps formed by said two minerals; agitating said pulp in the presence of said collector agent and depressing agent to cause the surfaces of said minerals to be differentially coated with
 75

the soaps formed thereby, in inverse relation to the modified solubilities of said soaps; and then subjecting said pulp, containing said differentially coated minerals, to froth flotation.

5 6. In a froth flotation process, the steps which comprise: adding a fatty acid collector agent to a pulp containing two minerals capable of forming with such agent difficultly soluble soaps of different solubilities; also adding to said pulp sodium 10 metaphosphate in such proportion as to increase the difference between the solubilities of the soaps formed by said two minerals; agitating said pulp in the presence of said collector agent and sodium metaphosphate to cause the surfaces of said 15 minerals to be differentially coated with the soaps formed thereby, in inverse relation to the modified solubilities of said soaps; and then subjecting said pulp, containing said differentially coated min-

erals, to froth flotation.
20 7. The method of separating solids by froth flotation which comprises precipitating, upon the surface of a constituent mineral of a pulp containing at least two minerals, a salt of a metallic element capable of forming a soap of different 25 solubility than the soap formed by said constituent mineral; adding to said pulp a fatty acid collector agent; also adding to said pulp a depressing agent selected from the group consisting of metaphosphates, metaphosphites, metarsenates and metarsenites, in such proportion as to exert a differential inhibiting effect upon the 30 formation of insoluble soap coatings on the surface of said constituent mineral coated with said deposited salt and on the surface of another mineral present in the pulp; agitating said pulp in the presence of said collector agent and said depressing agent to obtain a differential soap coating of said constituent mineral and said other mineral; and then subjecting said pulp containing 40 said differentially coated minerals, to froth flotation.

8. The method of separating solids by froth flotation which comprises precipitating, upon the 45 surface of a constituent mineral of a pulp containing at least two minerals, a salt of a metallic element capable of forming a soap of different solubility than the soap formed by said constituent mineral; adding to said pulp a fatty acid collector agent; also adding to said pulp 50 sodium metaphosphate in such proportion as to exert a differential inhibiting effect upon the

formation of insoluble soap coatings on the surface of said constituent mineral coated with said deposited salt and on the surface of another mineral present in the pulp; agitating said pulp 5 in the presence of said collector agent and said sodium metaphosphate to obtain a differential soap coating of said constituent mineral and said other mineral; and then subjecting said pulp, containing said differentially coated minerals, to 10 froth flotation.

9. The method of separating solids by froth flotation which comprises depositing, upon the surface of two constituent minerals of a pulp, salts of two different metallic elements capable of forming soaps whose respective solubilities 15 have a materially different relation to one another than the respective solubilities of the soaps normally formed by said constituent minerals themselves, whereby the normal relation between the soap flotation characteristics of said two 20 minerals is materially altered due to the coating thereof with said deposited salts, and then subjecting the pulp containing said two minerals thus coated with said deposited salts to froth 25 flotation in the presence of a fatty acid collector agent, to obtain a separation between said minerals in accordance with the relative solubilities of the soaps formed by said collector agent with the respective deposited salts.

10. The method of separating solids by froth 30 flotation which comprises depositing, upon the surface of two constituent minerals of a pulp whose cations normally form soaps of different solubilities, salts of two different metallic elements capable of forming soaps whose respective 35 solubilities differ materially from one another in the reverse order to the respective solubilities of the soaps normally formed by the cations of said constituent minerals, whereby the normal relation between the soap flotation characteristics of 40 said two minerals is reversed due to the coating thereof with said deposited salts, and then subjecting the pulp containing said two minerals thus coated with said deposited salts to froth 45 flotation in the presence of a fatty acid collector agent, to obtain a separation between said minerals in accordance with the relative solubilities of the soaps formed by said collector agent with the respective deposited salts.

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