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C. H. BREERWOOD ET AL

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MANUFACTURE OF CEMENT

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FIG. 1.

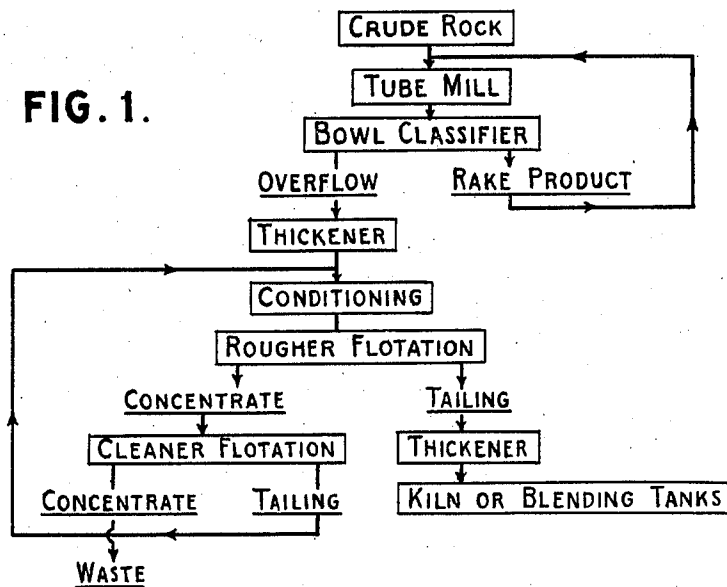
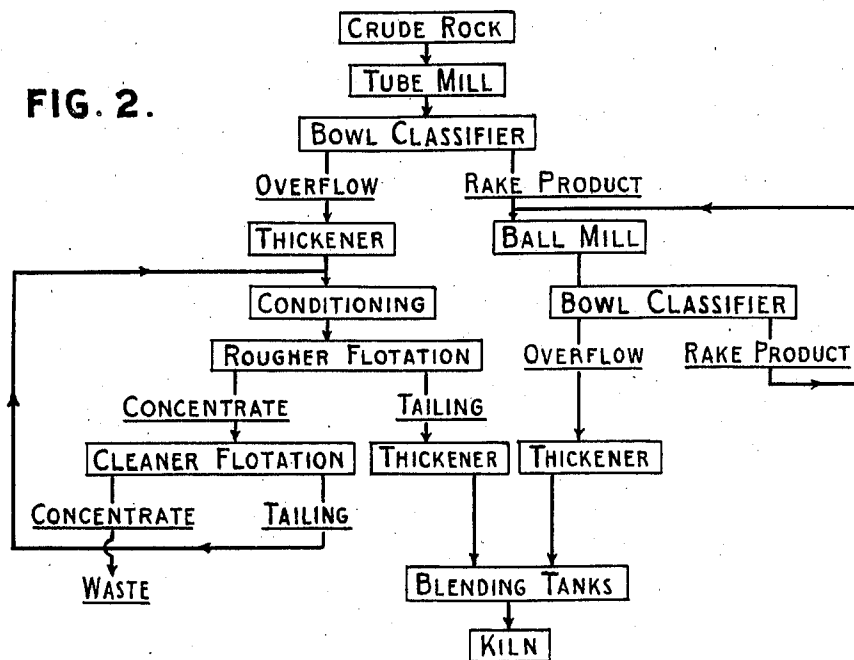


FIG. 2.



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MANUFACTURE OF CEMENT

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18 Claims. (Cl. 209—167)

This invention relates to the froth flotation treatment of cement raw materials and more particularly to the reduction of the proportions of siliceous minerals, especially silicates of alumina, in argillaceous limestones, marls and chalks, whereby the beneficiated materials may be used as the ultimate mixtures, or major proportions of raw material mixtures, to produce modern cements of predetermined compound compositions. It has especially to do with the utilization of froth flotation in a subtractive operation or operations, in which a reagent, of a class to be described more fully hereinafter, having in solution the long-chain group in the positive ion, is employed to concentrate the siliceous minerals, and in most cases to effect a differential flotation thereof.

It is among the purposes of the invention, and particularly in view of the low commercial value of Portland cement, to beneficiate inferior raw materials in a process involving a minimum of equipment, a minimum of processing steps, and especially with a minimum consumption of a reagent of an unusual class, as the reagents of this class are inherently considerably more expensive than the fatty acids, or reagents based upon fatty acids, used heretofore in the treatment of such materials in processes in which the oxide mineral, calcite, is concentrated in the flotation froth.

In contrast to the earlier processes, the concentrates of the present method are the waste or by-product minerals, and the flotation tailings are the useful minerals. Depending upon the natural composition of the available material, the tailings may constitute the ultimate raw material mixture, properly corrected as to the proportions and ratios of the four essential constituents, or will form the major proportion of a mixture to be completely corrected by the addition of a quantity of another material, as when the natural material is deficient in an essential constituent to a degree that its recovery by flotation would involve an unnecessary and uneconomical waste of useful minerals, or when the material is above composition in its proportion of calcite, but excessive in a siliceous mineral and must be beneficiated whereby it may be used as a component of a mixture in which a siliceous material, such as a clay or a shale is the other.

The inferior natural raw materials contemplated herein are of almost infinite variety by reference both to mineralogical and physical composition, i. e., degree of recrystallization. As Portland cements are produced by combining

oxides of silicon, iron, aluminum and calcium, the mineral sources of these oxides are of little practical effect in the clinkering reactions provided mixture and contact is complete, but the natural mineral constituents have a very decided bearing upon the processing steps that may be adopted to eliminate excessive quantities of one or more minerals, i. e., quantities that will result in a mixture, or mixture component, corrected chemically within desirable or permissible limits.

The principal mineral constituents, of the materials with which this invention is concerned, are calcite; silica in crystalline and crypto-crystalline forms, usually quartz, flint and/or chalcedony; alumina, which always occurs in practical quantities in the form of silicates of alumina, principally the various micas, but also as kaolin, kaolinite, the feldspar minerals, etc.; iron as oxides, the hydroxide, limonite and/or pyrite. Magnesia, an undesirable adulterant, is usually present principally as dolomite, but also as magnesian aluminous silicates, e. g., phlogopite mica, and/or brucite. Carbon, in a form commonly called "graphitic" is frequently present and although it has no apparent effect upon the clinkering reactions, it is highly undesirable in a flotation pulp and adversely effects flotation concentration, as will be described more fully hereinafter. A wide variety of other minerals in minor quantities are usually present, but the proportions involved are usually too small to warrant consideration.

Throughout the specification and claims the terms "silica", "silicate" and "siliceous" are specifically limited to and are to be construed in accordance with the following definitions. "Silica" refers to crystalline and crypto-crystalline silicon dioxide (SiO_2) only. "Silicate" refers to any mineral salt of silicic acids, particularly compounds containing alumina, magnesia or both. "Siliceous" is generic and refers to either or both silica and silicate minerals as defined above.

Natural crystallization of these mineral constituents, with the possible exception of the carbonaceous matter, occurs throughout extreme ranges, from large visible crystals down to materials of such incomplete or fine crystallization that grinding must be carried out to an extreme degree of fineness to release the physical bonds, or at least to free a sufficient proportion of the mineral or minerals occurring in excess, that the necessary elimination can be accomplished. An example of the latter will be found hereinafter, in which the extreme fineness of the crystalliza-

tion required grinding of the material to a slime, from which the principal concentrations of the silicates of alumina were accomplished in the particle size fractions below 20 microns.

Each of the materials described above may be benefited by the present method, and although an ancillary step or steps may be desirable or required to produce satisfactory results under specific conditions, to be described hereinafter, the essential steps of the method are substantially identical under all conditions. Ordinarily, the objectives of the process are to reduce the proportions of the alumina in the natural material, frequently to reduce the alumina together with magnesia and especially magnesian silicates, and in rare cases to eliminate in part at least, crystalline silica, especially fine sand grains from marls and so-called "sand limestones".

With a few exceptions, the limestones, marls and chalks, available for cement manufacture, contain alumina in too great abundance for use in producing cements capable of satisfying the requirements of present specifications of the Federal and several State Governments, for cements of low-heat of hydration, particularly specifications which fix a maximum limit for the proportion of tri-calcium aluminate at or near 5%. In many cases, and particularly in the materials available in the eastern cement producing districts, the natural proportions of alumina are too high to permit the production of cement of moderate heat of hydration, even when correctives are added to the materials. In some cases, and by compromise with theoretically desirable mixtures, the specification requirements can be met by additions of iron oxide, to combine with a part of the alumina, and particularly where the calcite content of the material is high enough to permit further correction of the ultimate composition by additions of high grade silica, such as sandstone, where such correctives are available. Additions of iron oxides are not satisfactory or complete solutions of the problem, not only because of their effect on the color of the concrete but principally because of the reduction of the silica ratio. Further, it is now generally believed that substantial proportions of tetra-calcium aluminoferrite decrease the resistance of concrete to attack by sulphates in marine and ground waters. One present specification limits the sum of tetra-calcium aluminoferrite and tri-calcium aluminate in the finished cement to 10% and another specification sets a limit at 12%, and it will be evident that few natural materials can be utilized, by additions of iron oxides, to produce compositions within these low limits. It should also be borne in mind that tetra-calcium aluminoferrite has little if any hydraulic value, and regardless of the beneficial effects of iron as a flux or catalyst in burning, this compound is an adulterant.

Magnesia, at least in quantities above a maximum limit, as established by various specifications, is an undesirable constituent of a cement raw material mixture. Only a negligible proportion reacts in burning in the range of Portland cement clinker, and although if the liquid phase of the clinker is solidified before complete crystallization takes place, a part of the magnesia is suspended in solid solution in the "glass", the remainder is present in the clinker as periclase. This compound is a principal contributor to delayed expansion and ultimate disintegration of concrete.

In general, the practice of the invention com-

prises the flotation concentration of a minimum of the total weight of the raw materials, and when the composition of the materials permits, the flotation cell feed, relative to the total quantity of materials, is also limited to or near the minimum proportion that will permit ultimate correction of the total or final mixture. The minerals concentrated, and thereby eliminated, are the excessive quantities of the siliceous minerals, usually the silicates, whereby all but a minor quantity of the principal constituent of the ultimate mixture, namely calcite, is deposited as a flotation tailing, together with the useful quantities of the siliceous minerals and iron compounds, essential as constituents of the ultimate composition desired for burning.

One of the most important steps of the present method is the preliminary reduction of the natural materials by grinding. This step is not comparable either to customary cement raw material grinding, as the recovered mineral particles may have to be further reduced to make them suitable for burning, or to normal grinding as a preliminary to flotation separation by other processes and for the recovery of other minerals. In normal preliminary grinding prior to froth flotation concentration, the objective is to reduce the mineral bonds to a degree that a maximum recovery of high grade concentrate can be obtained. In the present method, however, the minerals are preferably reduced only to a degree that will permit the necessary elimination by flotation, for chemical and economical reasons, and especially when the materials are fine grained. At such a degree of grinding, it will be evident that a substantial proportion of the particles in the flotation tailings are unbroken, i. e., they are comprised of two or more distinct minerals, and it will be understood that a minimum proportion of the total mineral weight has been subtracted from the flotation pulp as a concentrate.

The chemical purposes of this procedure have primarily to do with the conditions under which the clinkering reactions take place. Only a relatively small proportion of the materials enter a liquid phase in the course of burning, and it is accordingly essential, in addition to the necessary fineness, that the minerals from which the four essential oxides are derived be thoroughly mixed and in intimate contact, for uniformity and completeness of the reactions. Provided the mineral particles are sufficiently fine, the proportion of unbroken or composite mineral particles, above described, are especially desirable as the mineral bonds assure contact of different constituents. Accordingly, further reduction is chemically undesirable, and it also will be realized that by subtracting a minimum of the total weight that the natural blend and contact of the original materials, and which has been improved by the mixing effect of grinding, has been disturbed only to a degree that will enable chemical correction of the composition.

As grinding is one of the most expensive operations in the manufacture of cement, it will be evident that substantially complete grinding of fine grained materials is economically impractical, and even in cases where the crystallization is relatively coarse, it will be obvious that mineral eliminations should be made without wasting power by unnecessarily reducing the quantity to be discarded.

The proportion of the total lime-bearing material to be treated by froth flotation depends upon both its mineralogical and chemical com-

position, especially the deviation from the desired composition, and the size ranges of natural crystallization. It is desirable, for purposes of economy, to limit the quantity of flotation cell feed to the proportion of the total quantity which will permit correction of the mixture, when the flotation tailings and the remainder or the untreated part are mixed in proper proportions. Any such division is preferably made on a basis of particle size, rather than a mere division of the ground materials, to improve the results of the flotation operations and to economize in equipment and reagents. Thus, if the crystals are relatively coarse, and a sufficient proportion of the siliceous matter or mineral is free in the coarser fractions resulting from a limited degree of grinding, the next step is to classify the ground materials to segregate a chemically permissible maximum of the finer particle size fractions, and to subtract the siliceous matter only from the coarser fractions by flotation. This also enables the chemist to discard the undesirable proportions of a mineral or minerals without waste of grinding power, and to utilize the fine particles of all constituents, which are especially suitable for burning.

When the constituent minerals are dispersed in a wide range of sizes, such that after moderate grinding, bond breakage in the coarser fractions is too incomplete to permit effective separations, the ground materials are preferably classified into "slimes", intermediate and coarse fractions. The intermediate size fractions are treated by froth flotation and their tailings combined with quantities of the slimes and coarse fractions, the latter usually being first re-ground.

Usually, the material to be eliminated in part is micaceous, and although natural crystallization may be relatively coarse, the ease with which mica is reduced by grinding, as compared with the harder minerals, tends to concentrate a greater proportion of mica in the finer particle size fractions. Even in such cases, the proportion of the flotation cell feed may be limited by preliminary classification, but the finer fractions are subjected to flotation, and their tailings utilized in combination with the untreated coarse fractions. It is to be understood that although the term "coarse" has been used to describe these materials, the ground materials are largely slimes, as the term is used in the art of flotation, or the proportion of slimes is far too great to make it practical to discard them, and the improvement in composition of the coarser fractions ordinarily is not complete and recombination with the flotation tailings is necessary to make the ultimate correction.

However, the more common materials available, especially in the eastern cement producing districts, and which may be beneficiated for use in the production of cement of the types described, require flotation treatment preferably of the entire supply. These materials are argillaceous limestones in which re-crystallization is so incomplete that extremely fine grinding must be resorted to to free a sufficient proportion of the micaceous matter, particularly sericite, to make it possible to effect the desired corrections. The average materials are excessive in alumina and silica and deficient in calcite. This, together with the wide distribution of the constituent minerals throughout extreme ranges of particle size makes it necessary to grind the total quantity to such fineness that the resulting materials are "slimes". The actual or prin-

cipal flotation separations are made in the particle size fractions below 20 microns, in the first three examples to be given hereinafter, and as at this degree of fineness, hydraulic classification is unnecessary, preferably the entire supply of ground materials are subjected to flotation. However, the process is economical and competitive because only a minor part of the total weight is collected in the flotation concentrates, in contrast to the large calcite weight recovery in the concentrates of fatty acid flotation operations. The flotation tailings contain large proportions of unbroken rock particles, which for reasons previously discussed, are especially desirable to promote uniform and complete reactions in burning.

The flotation step of the process is carried out in the presence of a reagent, the surface active portion of which is a positive ion such as those of the class discovered by Lenher and described in his Patent No. 2,132,902, for a "Flotation process". The reagents found to be effective are those which in solution give a positively charged ion containing an aliphatic hydrocarbon group of at least 8 carbon atoms, preferably quaternary ammonium compounds containing a hydrocarbon group of from 12 to 18 carbon atoms wherein the aforesaid constituents in solution give a positively charged ion, preferably the negative ion in solution being a halogen.

Of the foregoing class, two have been found to be especially satisfactory for the present purposes, and in the order of preference are, first, dodecyl amine hydrochloride, hereinafter referred to for brevity as "C-1", and second, a mixture of hydrochlorides of the higher primary aliphatic amines in which the alkyl groups correspond in carbon content and composition to the fatty acids occurring naturally in coconut oil, hereinafter referred to for brevity as "C-2".

We have discovered, and it is an important feature of the practice of the invention, that although these reagents have capacity to collect or concentrate acidic minerals, and all of the principal constituent minerals in pulps of the class described, including the oxide mineral, calcite, that they may be employed to effect a plurality of differential concentrations, when the operations are controlled, as will be illustrated by the examples to be described hereinafter.

We have succeeded in effecting differential concentrations in the following order, first, the aluminum and magnesian micas, second, the feldspar minerals, and third, crystalline silica, particularly quartz, without concentrating a substantial proportion of the free calcite grains in the froth. The practical significance of this discovery will be understood if it is remembered that the more common materials are excessive in alumina, and usually excessive in silica, and when present in substantial proportions magnesia is an undesirable adulterant. Thus, a very limited concentration of the total weight of the common materials effects the desired reduction of alumina, and as it occurs as a silicate, the total silica is necessarily reduced, in the flotation tailings. Particularly when magnesian mica is present, this concentration effects desirable reductions in alumina, silica and magnesia, retaining in the tailings the calcite and the usually desirable crystalline silica. Iron oxides tend to concentrate but as the collecting power of these reagents is relatively low with respect to the oxides of iron, as well as calcite, froth cleaning by flotation, without the addition of collecting

reagents, is effective in increasing the recovery in the flotation tailings. The unbroken rock particles are not as amenable to concentration, in the presence of these reagents, as the crystalline silica and can accordingly be retained in the tailings.

The differential separations are effected by conditioning the pulp with very limited quantities of the collecting reagent, and in light stage "oiling" circuits in which the total quantity is introduced in small increments. It will be understood that the term "oiled" is used to identify the flotation cell circuit, as the reagents are not "oils". Especially in the treatment of fine pulps, the reagent is preferably diluted in a substantial volume of water to obtain accuracy in the control of each quantity introduced, and to effect rapid and complete dispersion in the relatively enormous volume of the pulp. Failure to control the quantities and dispersion of the reagent results in partial over-oiling and consequent partial heavy flocculation in which useful minerals are included. Expressed in another way, the concentrates are of low grade, unnecessary weight losses of the desirable minerals occur, the desired composition correction may not be completed, and the consumption of reagent makes the operation uneconomical.

Further, lower weight losses of the finer particles of the useful minerals are usually obtained if the air volumes entering the pulp through the flotation cells are reduced below normal. The purpose in controlling the air volume is primarily to take advantage of the peculiar settling characteristics of mica particles. The shapes of the mica particles give them a much slower settling rate in water, the rate being about equal to particles of other minerals of half their diameter. Accordingly, although the surface effect of the collecting reagent upon the micaceous particles may be incomplete, the partial coating together with their low settling rates makes it possible to concentrate the mica with a negligible quantity of reagent.

The use of very small quantities of these reagents under careful control in introducing and dispersing them in the pulp, as above described, results in the formation of siliceous concentrates of only a minor proportion of the total weight of the flotation cell feed. These are important features of the invention, because under equivalent conditions, the consumption of these expensive reagents in an "inverted concentration" is about one-fourth, and usually less, the consumption of fatty acids, or the fatty acid component of a reagent, required to concentrate the calcite in the known processes, in which the concentrates represent a major proportion of the weight of the feed. Accordingly, these features make the present method economically competitive with the older processes, despite the fact that the positive ion reagents cost several times as much as the fatty acids, per pound. Calcite pulps, of the class contemplated herein, are slightly alkaline, the normal alkalinity usually being within the range pH 7.4 to 7.8, and as the reagents specifically described are effective in alkaline pulps below about pH 8.5, no reagents need be employed to modify the natural alkalinity.

Further, the action of these reagents is not adversely affected by the use of depressing and dispersing agents, at least those of the types to be referred to hereinafter, when necessary to meet specific conditions. The limited quantities

used permit the accurate control of froth volumes, at each stage, essential for the best results in light stage oiling circuits, by suitable additions of common frothing agents, such as cresylic acid, but preferably a frothing agent comprising a mixture of branched and straight chain aliphatic monohydric alcohols boiling between about 152° C. and about 162° C. obtainable along with methanol by the catalytic hydrogenization of carbon oxides, hereinafter referred to for brevity as "F-1".

The practice of the invention can best be explained by reference to examples, which will serve as guides for the treatment of other inferior cement raw materials. The material selected for the three following examples is especially suitable for purposes of illustration, as it is especially difficult to beneficiate, and was generally believed to be not amenable to froth flotation concentration. The principal difficulties have to do with the extremely fine state of natural crystallization and the wide distribution or dispersion of colloidal or near colloidal "graphitic" carbon.

The material is typical of the finer grained argillaceous limestones of the Lehigh Valley cement producing district of Pennsylvania. It is classifiable geologically as Jacksonburg limestone of the Ordovician Age, and is intermediate in composition between limestone and shale, the color and general appearance more nearly resembling slate, but calcite is the most abundant mineral. The other principal minerals are quartz; mica, mostly of the sericite variety, dolomite, and iron, principally as the hydroxide, limonite. Petrographic examinations of thin sections of the rock reveal distinct layers of fine calcite grains alternating with thin layers of fine scaly and fibrous sericite. There are occasional elongate lenses and elongated isolated grains of quartz. The quartz is widely distributed, usually as fine grains of a few microns or tens of microns in diameter. The carbonaceous matter is dispersed throughout the rock in intimate contact with the various other constituents, and constitutes about one half of one percent of the total mineral weight.

Petrographic examination of this rock, after grinding to 98% minus the 325 mesh sieve, reveals that even in the particle size fractions below 20 microns, mineral bond breakage is incomplete, and that the coarser fractions are largely unbroken rock particles, i. e., the individual particles are composites of calcite, quartz and/or sericite. There is, however, a somewhat increased proportion of the mica in the finer fractions, in the form of free particles, and it is from the fractions below 20 microns that the principal concentrations are made. Carbonaceous inclusions and coatings of the calcite grains are frequent, and abundant on the quartz particles.

As will be seen from the analyses of the flotation cell feed in the first two tables appearing hereinafter, the rock is unsuitable for cement manufacture without substantial correction. The total silica and the alumina are too high and the proportions of calcite and pure silica (quartz) are too low. The concentration and elimination of a part of the mica will effect the correction of both the silica and alumina, and increase the proportion of the calcite and quartz in the flotation tailings. This will be understood when it is realized that the weight ratio of silica to alumina in sericite mica is approximately 1.2:1.

The presence of carbonaceous matter even in

proportions below 0.5%, inhibits successful concentration of the siliceous constituents of such materials. It has "natural floatability" and tends to flocculate and thereby concentrate a substantial proportion of the fine calcite and quartz grains, as well as other fine minerals, thereby contaminating the flotation concentrates, and involving substantial weight losses of the especially desirable fine calcite and quartz. Further, it has the effect of adsorbing or otherwise consuming relatively large quantities of the positive ion reagents, the quantity so consumed making the practice of the invention, at the present cost of these reagents, economically impractical. The carbonaceous matter should therefore either be substantially completely removed, as illustrated hereinafter in the first example, or depressed and rendered substantially harmless, as illustrated in the third example.

For the two following flotation operations the rock, after normal preliminary reduction, was ground in a tube mill in closed circuit with a bowl classifier, the rake sands being returned to the mill. The overflow used as the flotation cell feed had the following average physical analysis:

	Per cent
Plus 325 mesh plus 44 microns.....	1.50
Minus 43 microns plus 28 microns.....	7.85
Minus 28 microns plus 22 microns.....	6.75
Minus 22 microns plus 15 microns.....	10.20
Minus 15 microns plus 10 microns.....	14.50
Minus 10 microns.....	59.20

The objective of the first three examples was to derive a raw material mixture solely from this inferior material, i. e., without the addition of correctives, having a higher ratio of silica to total iron and alumina than could be obtained by additions of high grade limestone, and suitable to produce a general purpose Portland cement of high quality, allowance being made for coal ash correction in burning.

First example

The first example is intended to illustrate general principles in the application of the invention. It was a batch flotation operation carried out in an 18" Fagergren flotation machine, this cell being large enough to produce results equivalent to practical commercial operations. It illustrates one of the preliminary alternative steps that may be employed to make it possible to effect a satisfactory concentration of siliceous minerals in the presence of carbonaceous matter. In this example, the carbonaceous matter was first removed by froth flotation.

The general conditions of the pulp were: dilution 20% dry solids; temperature 72° F., and alkalinity normal at pH 7.8.

The carbonaceous matter was concentrated solely by alternate conditioning and flotation in the presence of a frothing agent, F-1 identified above, introduced in small increments until a total of 0.25 pound per ton of dry solids had been added, the total flotation time being 7 minutes. At the end of this time substantially all of the carbon had been eliminated.

As shown by the foregoing physical analysis, this pulp is a slime, and as colloidal and near-colloidal particles of the constituent minerals are abundant, natural flocculation is pronounced. As the floccules are aggregates of the various minerals, the natural flocculation must be substantially reduced, to make effective separations possible. This may be accomplished by condi-

tioning the pulp in the presence of a dispersing agent. Some of the common dispersing agents are ineffective, and others appear to promote flocculation, probably because of the wide variety of minerals present in the pulp, but the lignin sulphonates, more fully described and claimed in Breerwood application Serial No. 163,303, filed September 10, 1937, are satisfactory.

The next step was therefore to disperse the natural flocculation, by conditioning the pulp for 3 minutes with 1.0 lb. of calcium lignin sulphonate.

This was followed by rougher concentration of the micaceous matter in alternate steps of conditioning and flotation, in the presence of dodecyl amine hydrochloride, C-1, as the collecting reagent. This collecting reagent was added as a 3% solution, to obtain rapid and complete dispersion, in successive increments until 0.22 lb. had been introduced.

The rougher concentrates were then cleaned by froth flotation, without additional reagents, to deposit as tailings the uncoated and/or incompletely surface-coated quartz, calcite, iron minerals and unbroken rock particles, the cleaner flotation concentrates being the micaceous matter to be discarded as waste.

The principal flotation results were as follows:

Product	Per cent weight	Analyses as percent				SiO ₂ ratio
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃	
Feed.....	100.0	16.24	1.88	6.48	69.60	1.94
Carbon.....	6.1	18.72	4.38	9.56	55.46	-----
Cleaner conc.....	10.0	33.28	2.35	17.59	35.69	-----
Cleaner tails.....	9.7	19.20	2.00	7.76	65.28	-----
Rougher tails.....	74.2	13.30	1.55	4.09	77.47	2.39
Combined tails.....	83.9	13.98	1.60	4.52	76.2	2.28

It will be seen from the foregoing table that the final micaceous concentrates, produced by the collecting reagent, constituted only 10% of the total weight of the feed. The carbon concentrates involve a weight loss, but this was negligible and it will be seen that the alumina content was increased about 3% above that of the feed.

The fine quartz, essential in the final mixture, was recovered principally in the rougher tailings, in which quartz constituted about two-thirds of the total silica, having been accomplished by using only a limited quantity of the collecting reagent. The content of calcite was increased in the rougher tailings beyond the proportion desired for burning, and as the cleaner tailings were of lower grade and about one-half of the total silica was quartz, the rougher and cleaner tailings were combined, thereby effecting the desired ultimate composition correction, and providing a total weight recovery of 83.9%.

It is especially to be noted that the addition of enough high grade limestone to increase the proportion of calcite from 69.6 to 76.2%, would not materially modify the unsatisfactory low silica ratio, but by the reduction of the proportion of micaceous matter, the silica ratio of the combined rougher and cleaner tailings was 2.28.

For a better understanding of the complete practice of the invention, reference is made to the accompanying drawing in which:

Fig. 1 is a flow diagram, showing the preferred method of treating the limestone described specifically in connection with the previous example, and materials substantially equivalent thereto, and

Fig. 2 is a slightly modified flow diagram, of advantage where the constituent or constituents occurring in excessive proportions are free in sufficient abundance in the finer fractions to make it practical to submit these fractions only to froth flotation.

Second example

In the preferred procedure, illustrated in Fig. 1, the operations are continuous, and the second example corresponds to this flow of materials in pilot plant operation on a practical scale, in which the ultimate mixture was burned and ground to Portland cement, to demonstrate the practical advantages of the invention.

The crude rock, crushed to tube mill feed sizes, was ground in closed circuit with a Dorr bowl classifier, the rake product being returned to the mill for further reduction. This grinding circuit was adopted to make it economically practical to reduce the classifier overflow to the extreme fineness previously shown.

The average overflow included 340 pounds of dry solids an hour. The overflow was thickened in a Dorr thickener within a range from 18.5 to 19% dry solids for flotation feed. This pulp was then conditioned in a 24" Fagergren flotation machine, with the air supply permanently cut off, in the presence of a carbon depressing agent, this step being an alternative to the carbon concentration step described in the first example, and which has the advantage of making the carbonaceous matter harmless to the subsequent flotation concentrations, although it is retained in the pulp, and the weight losses set forth in the previous table are avoided, as will be seen in the analyses to be given hereinafter. The carbon depressing agent used was calcium lignin sulphate, more fully described and claimed in Breerwood Patent No. 2,130,574, the quantity used being 2.10 pounds per ton of feed, this quantity being greater than necessary to depress the graphitic carbon, to employ the excess to disperse natural flocculation during the subsequent flotation operations, as more fully described and claimed in the co-pending application of Breerwood Serial No. 163,303, filed September 10, 1937. In addition to this agent, 0.25 pound of frothing agent F-1, and 0.44 pound of commercial No. 3 fuel oil per ton were added to the pulp during the conditioning period in this cell.

The conditioned pulp, continuously discharged, was then subjected to rougher concentration in a series of five 18" Fagergren flotation machines, in which the air volumes induced were restricted for reasons previously described. The collecting reagent employed was positive ion reagent C-2, identified specifically above. It was introduced in 5% solution in water to effect rapid and complete dispersion in cold water for the pulp and was added in stages to the flotation machine used as the conditioner and to each of the five rougher cells. The total quantity required to complete rougher concentration was 0.46 pound per ton.

The concentrates were cleaned by froth flotation, without additions of reagent in three 18" Fagergren cells, the tailings of which were returned in continuous closed circuit, as middlings, to the conditioning cell. The cleaner concentrates included the proportion of mica to be eliminated, and were, accordingly, the waste products of the process.

The rougher tailings were correct in composition, for the production of a modern cement for

general purposes, and were thickened to normal cement slurry density in a Dorr thickener and burned in an oil fired kiln.

The principal analyses are given below, and it is especially significant that these results were obtained at average pulp temperatures of 55° F.

	Per-cent weight	Analyses as percent					Silica ratio
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃	MgCO ₃	
Cell feed	100	15.30	1.84	5.59	71.26	4.47	2.06
Conc----	12	27.64	3.19	13.40	43.35	5.29	1.67
Tails----	88	13.60	1.60	4.40	75.13	4.37	2.27

It will be seen from the analyses given above that the total weight loss has been improved, due principally to the effect of calcium lignin sulphate in depressing the carbonaceous matter, and dispersing natural flocculation. The composition and silica ratio of the tailings are satisfactory for the production of high quality general purpose cement. It is to be noted that, although there is little if any magnesian mica in this material, the magnesia was not concentrated in the tailings, and that the final proportion is even less than in the feed. As a slight modification of this procedure, the middlings may be re-ground, to release more of the mica and again subjected to flotation in the rougher circuit.

Third example

By reference to Fig. 2, it will be seen that it is of advantage to submit to flotation less than the entire supply of materials to economize in reagent consumption and flotation cell equipment. The extreme degree of fineness, to which the material of the foregoing examples must be reduced, does not make the treatment of a limited proportion substantially more economical than flotation of the entire supply in the manner described in the second example. However, this parallel but partially alternative method will be described specifically in its application to the same material for the sake of brevity.

The grinding circuit was arranged so that the classifier over-flow equalled 77% of the total ground materials, the fineness being substantially identical to the physical analysis given above, namely with 98% minus 325 mesh. The classifier overflow was the flotation cell feed. The rake sands from the classifier were the remaining 23% of the original weight of material. These sands were not subjected to flotation, but as the fineness was minus 50 mesh with 15% minus 325 mesh, they were reduced to suitable cement slurry fineness by separate closed circuit grinding, thickened and finally mixed with the flotation tailings to be described hereinafter.

The tendency of the mica to become concentrated in the finer fractions, as previously described, caused an increase in the silica ratio of the coarser fraction, i. e., the rake sands, to 2.2, although the proportions of calcite and total silica did not change materially from those of the original material, being approximately off-set by increased concentration of quartz in the coarser fractions.

The finer fractions were subjected to conditioning for carbon depression, dispersion of flocculation, and froth flotation, with the same reagents, as described in the second example. The total reagent consumption was decreased, approximately proportionally to the relative weights of the materials treated. The flotation results were

slightly less effective in view of the greater proportion of mica in the feed, and the use of the same proportion of collecting reagent. The recombination of the flotation tailings and the ground rake sands resulted in a raw material mixture, corrected as to the proportion of calcite and with a satisfactory but somewhat low silica ratio of 2.02.

It is to be understood that the methods of the second and third examples are continuous, and that the objective was to produce a useful composition from an available inferior material without additions of correctives obtained from another source. However, it is to be understood that the grades of the tailings can be modified by changing the quantities of the collecting reagent whereby final correction can be completed, or a modified type of cement may be ultimately produced, by additions of quantities of available correctives. It is also to be realized that the proportion of the total material treated, as in the third example, directly affects the final composition, and that latter may also be modified by varying the proportions re-combined, and further by additions of correctives.

Fourth example

This example is not illustrated in the drawing, as the procedure closely parallels that previously described, and will be clearly understood from the following description.

The purpose of the example is to explain a more economical procedure that may be adopted when the mineralogical and physical nature of the material permits elimination of the finest fractions from the flotation cell feed. The presence of colloids, particles having colloidal behavior and those of extremely slow settling rates in water, seriously complicates the difficulties in making effective separations by flotation. These difficulties, in pulps of the types contemplated herein, may be attributed to colloidal coating of mineral grains, pronounced tendency of these fine minerals to flocculate naturally, and the liability of particles of slow settling rates to become trapped in the froth, even though they may not be substantially surface-coated by the collecting reagent.

The flotation of the relatively coarser fractions sharply reduces the consumption of collecting reagent, although the reduction does not appear to be directly proportional to the reduction in specific surface. Likewise, the reduction in flotation time provides for economy in flotation cell equipment.

It is accordingly a purpose to separate from the ground materials the maximum proportions, in increasing order of particle sizes, that may be recombined with the flotation tailings, derived from the coarser fractions without affecting the chemical composition desired for burning.

The material of this example was metamorphosed limestone, referred to as the Conestoga formation, but probably of the Jacksonburg formation. Its chemical composition is generally equivalent to the materials previously described, but only a trace of carbonaceous matter is present, too little to affect froth flotation. A principal mineralogical difference is that a substantial proportion of the magnesia is combined as phlogopite mica, although the most abundant silicate is sericite mica. Natural crystallization is much coarser, the broken rock presenting mica shist on the bedding-plane surfaces, in overlapping flakes along the planes. The edges reveal rela-

tively coarse calcite and quartz crystals between the planes, but the crystals are too fine for identification except by petrographic examination.

A sample of this material, the composition of which will be given hereinafter, was ground to a fineness of 88% minus the 200 mesh sieve, with 72% minus the 325 mesh sieve, at which degree of fineness a sufficient proportion of free mica was present in the coarser fractions to permit the desired correction.

The ground material was diluted to 15.7% dry solids and dispersed with 2.5 lbs. of calcium lignin sulphonate per tons of solids, to reduce natural flocculation, whereby effective classification could be made to separate the finer slimes. The quantity of this agent required to complete dispersion can usually be materially reduced by adding it to the pulp with about 1 lb. of soda ash per ton of solids, as described more fully in the co-pending application of Breerwood Serial No. 163,303, filed September 10, 1937.

After dispersion, the pulp was hydraulically classified to separate the finer slimes from the coarser fractions, hereinafter called "sands", the particle size separation having been made at 20 microns. The results of classification were as follows:

	Percent weight	Analyses as percent			
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃
Feed.....	100.0	15.12	1.98	5.78	70.99
Slimes.....	38.0	11.30	1.68	5.95	74.50
Sand.....	62.0	17.48	2.16	5.66	68.26

It will be seen that the proportion of quartz increased in the sands.

The sands were subjected to flotation to effect the necessary reduction, particularly in alumina and also in total silica, whereby the flotation tailings in direct recombination with the untreated fines would provide a satisfactory mixture, with the addition of a very small quantity of high grade silica, with allowance for coal ash correction.

The pulp was then diluted to 20% dry solids and subjected to froth flotation in the presence of 0.05 lb. of positive ion reagent C-2 in dilute aqueous solution and 0.027 lb. of frothing agent F-1 per ton of flotation feed only. Rougher flotation was completed in 3 minutes. The pulp temperature was 70° F. and alkalinity was normal at pH 7.6.

The results of flotation were as follows:

No.	Product	Percent weight	Analyses as percent			
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃
	Flotation feed.....	100.0	17.48	2.16	5.66	68.26
1.....	Rougher conc.....	16.5	53.00	2.79	19.58	12.72
2.....	Rougher tails.....	81.5	11.71	2.10	3.02	78.75
3.....	Tails+slimes.....	89.77	11.54	1.93	4.25	76.8

It is especially to be noted that about 56% of the alumina available in the flotation feed was concentrated in only 16% of the weight of the feed. The combination of the untreated slimes with the rougher tailings provided a total weight recovery of nearly 90% of the original materials and it will be evident that the addition of one or two percent of high grade silica would effect

the ultimate correction more economically than to make more complicated separations. It will also be understood that these results may further be modified by making the original classification at other particle size ranges, by subjecting the concentrates to flotation cleaning and the slimes to froth flotation. It will be recalled that economy in positive ion reagent consumption is a primary object of the invention, and it will be seen that by treating a limited proportion of the total available materials, as described above, the consumption of this reagent with relation to the original supply was only 0.031 lb. per ton.

We claim:

1. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials containing at least two of the constituents essential to an ultimate cement raw material mixture and including an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having selective collecting capacity for the constituents of the naturally occurring raw materials including said siliceous mineral, sufficient to collect the excess proportion of said siliceous mineral, but insufficient in amount to collect all of the normally floatable portion of said siliceous constituent, to concentrate a minimum of the weight of said material in the froth, whereby the excess of said siliceous mineral is carried off in the froth.

2. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials containing at least two of the constituents essential to an ultimate cement raw material mixture and including an amount of at least one silicate mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said silicate mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having selective collecting capacity for the constituents of the naturally occurring raw materials including siliceous minerals, sufficient to collect the excess proportion of said silicate mineral, but insufficient in amount to collect all of the normally floatable portion of said constituents, to concentrate a minimum of the weight of said material in the froth, whereby the excess of said silicate mineral is carried off in the froth.

3. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials containing at least two of the constituents essential to an ultimate cement raw material mixture and including an amount of at least one silicate mineral in excess of that desired in the ultimate mixture and a proportion of silica desired for said mixture, to reduce the percentage of said silicate mineral and increase the percentage of silica; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface active portion of which is a positive ion having selective collecting capacity for the constituents of the naturally occurring raw materials including silicates and silica, sufficient to collect the excess proportion of said silicate mineral, but

insufficient in amount to collect a substantial proportion of silica, to concentrate a minimum of the weight of said material in the froth, whereby the excess of the silicate mineral is carried off in the froth, and the proportion of silicate mineral in the tailings is reduced and the proportion of silica therein is increased.

4. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials containing at least two of the constituents essential to an ultimate cement raw material mixture and including an amount of micaceous matter in excess and a proportion of silica desired for said mixture, to reduce the percentage of said micaceous matter and increase the percentage of silica; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having selective collecting capacity for the constituents of the naturally occurring raw materials including micaceous matter and silica, sufficient to collect the excess proportion of the micaceous matter, but insufficient in amount to collect a substantial proportion of the silica, to concentrate a minimum of the weight of said material in the froth, whereby the excess of micaceous matter is carried off in the froth and the proportion of micaceous matter in the tailings is reduced and the proportion of silica therein is increased.

5. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of micaceous matter in excess of that desired in the ultimate mixture and a proportion of silica desired for said mixture, to reduce the percentage of micaceous matter and increase the percentage of silica; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of micaceous material, but insufficient to collect all of the normally floatable portion of said constituents, and insufficient to collect a substantial proportion of the silica and calcite, to concentrate a minimum of the weight of said material in the froth, whereby the excess of micaceous matter is carried off in the froth and the proportion of micaceous matter in the tailings is reduced and the proportions of silica and calcite therein are increased.

6. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, where-

by the excess of siliceous mineral is carried off in the froth and the proportion of the siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

7. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises classifying a ground supply of the material to separate a part comprising the finer fractions from a part comprising the coarser fractions, subjecting a pulp of one of the separated parts to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of said pulp in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of the siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

8. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral by subtracting the excess from a fraction of the materials comprising the coarser particles and recombining the remainder of the fraction with a fraction comprising the finer particle sizes; the improvement which comprises classifying a ground supply of the material to separate a part comprising the finer fractions from a part comprising the coarser fractions, subjecting a pulp of the coarse part to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of said pulp in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

9. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral by subtracting the excess from a fraction of the materials comprising the coarser particles; the improvement which comprises classifying a ground supply of the material to separate a part comprising at least the finest slimes from a part comprising the coarser particles, subjecting a pulp of the coarser part to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity

for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the solids of the pulp in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of siliceous mineral in the tailing is reduced and the proportion of calcite therein is increased.

10. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral by subtracting the excess from a fraction of the materials comprising the coarser particles; the improvement which comprises classifying a ground supply of the material to separate a part comprising at least the finest slimes from a part comprising the coarser particles, subjecting a pulp of the coarser part to rougher froth flotation in the presence of an amount of a reagent, the surface active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient to collect all of the normally floatable portion of said siliceous constituent and insufficient to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the pulp in the froth, subjecting the rougher concentrates to froth flotation to clean the concentrates of useful quantities of minerals, whereby the excess of said siliceous mineral is carried off in the cleaned froth.

11. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises conditioning a pulp of the ground raw material containing an abundance of fine slimes in the presence of a dispersing agent to reduce natural flocculation, classifying the conditioned pulp to separate a quantity comprising at least the finest slimes, subjecting the remainder of the pulp to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

12. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises con-

ditioning a pulp of the ground raw material containing an abundance of fine slimes in the presence of a dispersing agent to reduce natural flocculation, subjecting the conditioned pulp to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

13. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises conditioning a pulp of the ground raw material containing an abundance of fine slimes in the presence of a dispersing agent to reduce natural flocculation, subjecting the conditioned pulp to froth flotation in a light stage oiling circuit in the presence of amounts of a reagent, added in increments to the pulp in said circuit, the surface-active portion of the reagent being a positive ion having differential selective collecting capacity for siliceous minerals and calcite, the total amount of the reagent being sufficient to collect the excess of siliceous mineral, each amount so added being insufficient to concentrate a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

14. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, the surface-active portion of which is a positive ion containing an aliphatic hydrocarbon group of at least eight carbon atoms, said ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of the siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

15. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate

mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a reagent, of a class quaternary ammonium compounds containing a hydrocarbon group of from twelve to eighteen carbon atoms, wherein the constituents in solution give a positively charged ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion in the tailings is reduced and the proportion of calcite therein is increased.

16. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of reagent, of a class quaternary ammonium compounds containing a hydrocarbon group of from twelve to eighteen carbon atoms, wherein the constituents in solution give a positively charged ion having differential selective collecting capacity for siliceous minerals and calcite of the naturally occurring raw materials, the negative ion in solution being a halogen, sufficient to collect the excess of siliceous mineral, but insufficient to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion in the tailings is reduced and the proportion of calcite therein is increased.

17. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of dodecyl amine hydrochloride sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous mineral is carried off in the froth and the proportion of the siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

18. In the method of beneficiating, for the preparation of an ultimate cement raw material mixture, inferior cement raw materials of the class argillaceous limestones, marls and chalks, which contain an amount of at least one siliceous mineral in excess of that desired in the ultimate mixture, to reduce the percentage of said siliceous mineral; the improvement which comprises subjecting a pulp of the ground material to froth flotation in the presence of an amount of a mixture of hydrochlorides of the higher primary aliphatic amines in which the alkyl groups cor-

respond in carbon content and composition to the fatty acids occurring naturally in coconut oil, sufficient to collect the excess of siliceous mineral, but insufficient in amount to collect a substantial proportion of the calcite, to concentrate a minimum of the weight of the material in the froth, whereby the excess of siliceous

mineral is carried off in the froth and the proportion of the siliceous mineral in the tailings is reduced and the proportion of calcite therein is increased.

CHARLES H. BREERWOOD. 5
JOHN C. WILLIAMS.