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(54) Title: SEPARATION OF CALCIUM-CONTAINING MATERIAL FROM ORE

(57) Abstract

A method for the separation of calcium-containing limestone ore containing particles of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and gangue, including magnesite ($MgCO_3$) and siliceous materials. The method comprises conditioning the limestone ore with at least one coupling agent selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms, or at least one coupling agent selected from the group consisting of aliphatic amines containing from about 8 to about 22 carbon atoms, and beta amines containing from about 7 to about 21 carbon atoms, to selectively coat the calcium-containing limestone or the gangue in the ore to the substantial exclusion of the other in combination with providing at least one fluorescent dye to said coupling agent; radiating the conditioned ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the coated particles from the non-coated particles and separating the fluorescing, coated particles from the non-fluorescing, non-coated particles.

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SEPARATION OF CALCIUM-CONTAINING MATERIAL FROM ORE

Background of the Invention

The present invention relates to a method for the separation of calcium-containing limestone from limestone ore. More particularly, it relates to a method for separating calcite ($CaCO_3$) from magnesite, iron-bearing rock (magnatite), chert, granite, and quartz and other silicates present in limestone ore, especially calcium carbonate from magnesite, quartz and/or other silicates. The method can also be utilized for separating and recovering magnesite. Magnesite is valuable as a precursor to pure magnesium oxide, the primary use being in refractories.

Limestone is a common mineral and appears in many different concentrations in different limestone-containing ores. Also present in these limestone ores are impurities such as chert, iron-bearing rock (magnatite), magnesite, granite, quartz and various other silicates. Such impurities are hereinafter collectively referred to as gangue. The limestone ore as mined must be upgraded to obtain the beneficial properties of the calcium-containing limestone and especially the calcite ($CaCO_3$) in the ore, to produce limestone of the desired quality for commercial uses such as in the glass and cattle feed industries. Further, the limestone for use in cement manufacture must also meet specifications, especially with respect to alkaline material.

It is the general practice to separate calcium-containing limestone from the gangue by methods that have distinguished between the physical properties of the calcium-containing limestone and gangue. Such methods include handsorting or optical sorting of the limestone ore. Handsorting is slow and tedious and is economically unattractive. Optical sorting is limited because of difficulty in the resolution of colors and the difficulty of distinguishing among the various shades of colors in limestone and gangue rock. Limestone ore may be upgraded with respect to alkaline material by selective mining; but with selective mining, much limestone is left unmined and thereby unusable. Flotation concentration has also been used to upgrade limestone, but flotation processing costs are relatively high and, as such, economically unattractive.

Summary of the Invention

In accordance with this invention there is disclosed a method for the separation of higher-grade limestone from lower-grade limestone and the gangue present in particulate limestone ore which comprises conditioning the particulate limestone ore with at least one coupling agent selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms, said coupling agent selectively coating the calcium-containing limestone in the limestone ore to the substantial exclusion of coating gangue in combination with providing at least one fluorescent dye to said coupling agent; radiating the conditioned particulate limestone ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the coated higher-grade limestone particles from the coated lower-grade limestone and the substantially non-coated gangue particles and separating the fluorescing coated higher-grade limestone particles from the coated lower-grade limestone and nonfluorescing gangue particles.

Further, in accordance with this invention, there is disclosed a method for the separation of higher-grade limestone from lower-grade limestone and/or the silicate-containing gangue present in particulate limestone ore comprising conditioning the particulate limestone ore with at least one coupling agent selected from the group consisting of aliphatic amines containing from about 8 to about 22 carbon atoms and beta amines containing from about 7 to about 21 carbon atoms, said coupling agent selectively coating the silicates in the gangue particles to the substantial exclusion of coating the calcium-containing limestone and magnesite particles, in combination with providing at least one fluorescent dye to said coupling agent; radiating the conditioned particulate limestone ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the coated silicate-containing particles and partially coated lower-grade limestone from the lesser coated higher-grade limestone particles and separating the fluorescing, coated silicates and lower-grade limestone particles from the higher-grade limestone particles.

Following separation of the silicate-containing gangue particles, the substantially nonfluorescing limestone ore particles containing substantially little siliceous material but containing non-calcium-containing gangue, such as magnesite, can be treated for separation of magnesite from the calcium-containing limestone such as calcite and dolomite. Additionally, magnesite can be separated from calcite and/or dolomite, which calcite and/or dolomite has not been pretreated for separation of siliceous matter. For example, a magnesite ore containing calcite and/or dolomite can be treated by the process herein for separation of magnesite from calcite and/or dolomite.

For separating the magnesite from the calcium-containing particles, such as calcite and dolomite, the particles are conditioned with a coupling agent which selectively coats the calcium-containing particles to the substantial exclusion of coating the magnesite. Such a coupling agent can be selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms. Such a coupling agent substantially coats the calcite and, to a lesser amount, the dolomite to the substantial exclusion of coating magnesite. A fluorescent dye, as described above, can be provided to said coupling agent. The particles are radiated with actinic radiation for inducing fluorescence of the fluorescent dye to a degree sufficient for distinguishing the coated and fluorescing dolomite and/or calcite in the particles from the substantially non-coated, non-fluorescing magnesite in the particles. The particles are separated as above because of the differential in fluorescence.

To provide the dye to the coupling agent coated particles to the substantial exclusion of the non-coated particles, the coupling agent is water insoluble when the fluorescent dye is water insoluble. However, a water soluble coupling agent and a water insoluble dye can be used to provide a dye-coupled to the coating on a selected particle. For example, a water soluble amine coupling agent can be coated on one substance (e.g., the silicates) in a mixture of particles, then applying an oil soluble dye such as fluoranthene in a nonreactive oil such as a paraffinic oil (e.g., S.A.E. 20 base lubricating oil without additives). The silicate particles are rendered hydrophobic or oleophilic by the amine coating, which attracts the water insoluble dye in the oil thereby coupling the dye to the coated particles.

Water soluble coupling agents and water soluble dyes can be used if a chemical bond is formed during conditioning having sufficient strength to avoid removal during the subsequent stages of the method such as a subsequent rinsing step. Also, nonreactive water soluble dyes and water soluble coupling agents can be used if not removed in the subsequent steps of the method. For example, a water soluble dye can be applied at a temperature which is higher than the temperature of the subsequent steps (e.g., a hot dye application and a cold rinse). Also exemplary, a water soluble amine can be used as a coupling agent, whereupon following conditioning of the particles with the amine a prepolymer forming agent, such as formaldehyde, is added forming a prepolymer with the amine which upon subsequent contact with acid and/or heat polymerizes forming a water insoluble coating.

To provide the dye to the particles which are selectively non-coated with the coupling agent to the substantial exclusion of the coated particles, a water insoluble coupling agent and a water soluble dye, or a water soluble coupling agent and a water insoluble dye can be used. For example, a water insoluble coupling agent such as oleic acid can be applied to one substance within a mixture of particles (e.g., the calcium-containing limestone), then the entire mixture can be exposed to an aqueous water soluble dye, such as rhodamine B, flavine FF, or uranine, whereby the water insoluble coupling agent renders the calcium-containing limestone particle hydrophobic wherein the dye does not adhere but wherein the dye does adhere to the hydrophilic non-coated particles. In such an application of the method of this invention, a relatively gentle stream of air can be used to remove small droplets of the water soluble dye from the hydrophobic particles, thus eliminating the need for a subsequent rinse step in the method. The rinse step can also be eliminated in the practice of the method of this invention, if the concentration of the coupling agent and the concentration of the dye is sufficiently low.

It is understood, of course, that the principles described herein can be used to separate a higher-grade limestone from a lower-grade limestone as the coated higher-grade limestone particles have a greater intensity of fluorescence than the lower-grade limestone particles. The higher-grade and lower-grade limestone particles can thereby be separated by adjusting the sorting apparatus to accept those particles exhibiting fluorescence above a certain minimum intensity level and rejecting those particles exhibiting no fluorescence and/or fluorescence below such minimum intensity level.

Detailed Description of the Invention

According to the present invention, there is provided a method for the separation of calcium-containing limestone from gangue present in limestone ore to recover calcium-containing limestone values therefrom. The term "limestone" is used hereinafter to refer to calcium-containing limestone, such as calcium carbonate calcite, dolomite and other calcium carbonate-containing or related minerals. The term "limestone ore" is used hereinafter to refer to a limestone-containing ore which can contain material other than calcium-containing limestone, e.g., magnesite, siliceous material, etc. as defined hereinabove collectively as "gangue." As used herein the phrase "separation of limestone from gangue" includes the separation of higher-grade limestone from lower-grade limestone as well as separation of limestone from gangue. By the terms "higher-grade limestone" and "lower-grade limestone" is meant a relative distinction in calcium carbonate content between two grades of limestone, i.e., between calcite and dolomite. Such a relative distinction can be variable depending upon the reasoning for distinguishing between limestone grades, such as grading the limestone in consonance with the numerous end uses of the limestone. The practice of the method of this invention comprises the selective coating of either the limestone or gangue, and more particularly, the $CaCO_3$ or silicates, present in limestone ore with a coupling agent or mixture of coupling agents, combining therewith a fluorescent dye, and radiating the limestone ore with electromagnetic radiation to induce the fluorescent dye on the conditioned, selectively coated particles to fluoresce. The fluorescent material is then separated from the substantially nonfluorescing material.

The method of the present invention is based upon the differences in surface properties of the various materials present in limestone ores to accept coupling agents and dyes attracted thereto or repulsed thereby. Due to these differences, there can be chosen a coupling agent or mixture of coupling agents that will effectively selectively coat only the limestone or the gangue. Surface properties are relatively more consistent than other properties such as color, reflectance, or conductivity. These other properties generally tend to be similar such that a fine degree of resolution is required to distinguish between the materials. Such a degree of resolution is difficult to obtain and the efficiency of separation based upon these properties, therefore, suffers. Separation of material based upon the surface properties is, therefore, more consistent than techniques based upon the above other properties.

To distinguish between the coupling agent coated material and the non-coated material, there is incorporated with the coupling agent a tagging agent such as a fluorescent dye or there is added a tagging agent, such as a fluorescent dye, that is repulsed by the coupling agent. The ore can then be radiated with electromagnetic radiation to induce the dye to fluoresce. The dye combined with the coupling agent coating some of the material fluoresces and the substantially non-coated material does not fluoresce to any substantial degree, or if the dye is repulsed by the coupling agent, the non-coupling-agent-coated particles exhibit fluorescence while the coupling agent coated particles do not fluoresce to any substantial degree. Thereby, the different materials can be separated.

Generally, fluorescence refers to the property of absorbing radiation at one particular wavelength and simultaneously reemitting light of a different wavelength so long as the stimulus is active. It is intended in the present method to use the term fluorescence to indicate that property of absorbing radiation at one particular wavelength and reemitting it at a different wavelength, whether or not visible, during exposure to an active stimulus or after exposure or during both these time periods. Thus, fluorescence is used generically herein to include fluorescence, phosphorescence, and envisions the emission of electromagnetic waves whether or not within the visible spectrum.

Electromagnetic radiation generally refers to the emission of energy waves of all the various wavelengths encompassed by the entire electromagnetic spectrum. It is intended in the present method to use the term electromagnetic radiation to indicate any and all stimuli that will excite and induce fluorescence of the fluorescent dye. Thus, electromagnetic radiation is used generically herein to include electromagnetic radiation and envisions other stimuli that will excite and induce fluorescence of the fluorescent dye.

In practicing the present method in regard to limestone ore, the ore is first subjected to a crushing step. In this crushing step, the ore is crushed to physically separate the limestone from the gangue present. Crushing increases the surface area of the particles and further provides a greater surface and reactive site for the coating of the particles by the coupling agent. The limestone ore is crushed to a particle size of from about 1/4 inch to about 8 inches. Particle sizes of less than 1/4 inch can be used in the practice of this invention; however, such sizes require greater amounts of coupling agent and are more difficult to separate. Paricle sizes of greater than 8 inches can be used in the practice of this invention, but generally entrain impurities such that separation efficiency decreases. It is preferred to use ore particles of from about 1/2 inch to about 3 inches. Following the crushing and sizing steps, the limestone ore particles can be deslimed to remove soluble impurities and surface fines on the particles.

The method of this invention is practiced in regard to limestone ore by conditioning the limestone ore following sizing with a coupling agent or mixture of coupling agents that selectively adheres to the limestone or the gangue present in the limestone ore. It is preferred to condition the limestone ore with a coupling agent or mixture of coupling agents that selectively coats the limestone in the ore. The coupling agents that are selective for limestone (i.e., the calcium-containing material) are more selective than the coupling agents for the gangue. Thus, the coupling agents selective for the gangue are less efficient to use in separating the limestone from the gangue than the coupling agents selective for limestone.

Coupling agents that are useful in the practice of this method to coat the calcium-containing material present in the limestone ore particles can be selected from saturated and unsaturated carboxylic acids including fatty acids which contain from about 5 to about 22 carbon atoms, or a mixture thereof. Carboxylic acids that can be used include palmitoleic acid, oleic acid, linoleic acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, tall oil fatty acids and the like. It is preferred to use at least one carboxylic acid containing from about 8 to about 18 carbon atoms. Carboxylic acids containing more than about 22 carbon atoms can be used, but generally tend to be less selective and thereby coat both limestone and gangue particles. Carboxylic acids of less than 5 carbon atoms generally do not possess the ability to coat any of the particles in any significant amount. In general, the preferred carboxylic acid enters a chemical reaction with the calcium present; for example, oleic acid reacts to form calcium oleate.

To coat the silicate-containing gangue present in limestone ore a coupling agent is selected from aliphatic amines, or a mixture thereof, containing from about 8 to about 22 carbon atoms and beta amines or mixture thereof containing from about 7 to about 21 carbon atoms. Aliphatic amines useful in the method of this invention include octyl amine, decyl amine, dodecyl amine, tetradecyl amine, hexadecyl amine, octadecyl amine, eicosanyl amine, docosanyl amine and the like. Beta amines can include commercially available beta amines such as ARMEEN L-7 through L-15 series, which are registered trademarked products of Armak Chemicals and are known to those skilled in the art. Generally, the amines containing more than about 22 carbon atoms are not as selective as the amines containing less than about 22 carbon atoms. Aliphatic amines of less than about 8 carbon atoms and beta amines of less than about 7 carbon atoms generally do not have the desired coating properties. It is preferred to use an aliphatic amine containing from about 10 to about 18 carbon atoms and a beta amine containing from about 7 to about 15 carbon atoms. Of the amines, the beta amines are more selective for silicates rather than calcium-containing material and, therefore, are preferred. A water soluble amine coupling agent selected from the water soluble salts of the above-identified aliphatic and beta amines can also be used.

A fluorescent dye is combined with the coupling agents used to condition the limestone ore. The fluorescent dye can be combined with the coupling agent either before or after the ore is conditioned. Fluorescent dyes known to those skilled in the art, and which are compatible with the coupling agents, can be used in the practice of the method of this invention. It is preferred to use a water insoluble fluorescent dye when a water insoluble coupling agent is used. Water soluble fluorescent dyes can dissolve into the water dispersant during the conditioning step and can, thereby, impart a fluorescing property to substantially all the particles if an aqueous layer coats their surface.

Fluorescent dyes that can be used include fluoranthene, fluorescent yellow G (a product of Morton Norwich Chemical Co.), rhodamine B, flavine FF, uranine and the like. The fluorescent dye can be used in any form such as a solution, suspension, emulsion, dispersion or alone. The fluorescent dye can be combined with the coupling agent prior to conditioning the ore by either mixing the fluorescent dye directly with the coupling agent or by mixing the fluorescent dye with a suitable diluent or solvent, such as an oil, then mixing with the coupling agent. If the fluorescent dye is combined with the coupling agent following the conditioning, it can be applied directly to the conditioned ore or it can be used in any of the above-mentioned convenient forms. The fluorescent dye has an affinity toward the coupling agent coating and will, therefore, be preferentially entrained in only the coated ore particles. Any dye that adheres to the non-coated particles generally is removed by an aqueous wash of the ore. It is preferred to combine the coupling agent and fluorescent dye prior to conditioning the ore. Such prior treatment uses less fluorescent dye, requires fewer steps, and is generally more efficient both economically and in separation results.

Following the crushing and sizing of the limestone ore, the ore is conditioned with the coupling agent. Conditioning of the ore with the coupling agent is accomplished by contacting the sized ore with the coupling agent. The coupling agent can be used in any suitable manner such as in solution, dispersion, or by itself. It is preferred to form a dispersion of the coupling agent in water. Many methods of contacting the ore with the aqueous dispersion are available and known to those skilled in the art. Such methods include the spraying of the aqueous dispersion onto the sized ore, the passing of the ore through a dispersion bath, and the like. It is preferred to spray the sized ore with the aqueous dispersion. Spraying techniques include, but are not limited to, spraying the dispersion onto the ore as the ore passes the spraying nozzle on a vibrating screen or belt, or spraying the ore as it passes through a ring or series of ring sprayers.

Following the spraying of the ore with the aqueous dispersion, the ore is rinsed with a suitable washing agent, such as water, to remove excess dispersion from the ore and any dispersion physically entrained in the ore particles. The coupling agent, combined with the fluorescent dye, selectively remains coated on the particles for which it has a preference due to the surface properties of the particles. The coated particles are capable of fluorescence when radiated with electromagnetic radiation. As the coupling agents are preferential, they selectively coat either the limestone or the gangue in the limestone ore. The ore particles not coated generally do not fluoresce to the same degree as the coated particles.

Following the conditioning of the limestone ore, the ore is exposed to electromagnetic radiation to induce the coating on the particles to fluoresce. The coated, fluorescing particles can be separated by any convenient means, such as by hand, by optical sorting device, and by apparatus as taught by Mathews' United States Patent No. 3,472,375, which is incorporated herein by reference. In such apparatus a free falling mixture of ore passes in front of a row of detectors. Each detector by proper attenuation is capable of distinguishing between non-fluorescence and fluorescence or in intensity of fluorescence. Each detector in turn controls one flowing fluid stream selectively directed transverse to the path of the falling particle, the fluid stream being permitted to impinge only on the properly emitting ore particles. The directed fluid stream deflects the ore particles into a divergent path by which they are separated from the undesired ore particles. Such an apparatus is capable of detecting and separating the coupling agent and dye-coated particles from the non-coated particles.

The invention is further illustrated by the following examples, which are not intended to be limiting.

Example I

A quantity of crushed limestone ore, consisting of 47.5 percent by weight limestone with an average particle size of about 3/4 inch and primarily containing limestone, chert, iron-bearing rock, granite, quartz, and various other silicates, was conditioned with a coupling agent of oleic acid combined with fluoranthene fluorescent dye. The oleic acid had been combined with fluoranthene by dissolving the fluoranthene in oil (e.g., S.A.E. 20 base lubricating oil without additives) and mixing it with oleic acid. An aqueous disperson of oleic acid combined with fluoranthene was made. This aqueous dispersion was sprayed onto the crushed and sized ore. The oleic acid coupling agent combined with fluoranthene selectively coated the limestone particles and was rejected by the gangue particles in the ore. The excess aqueous dispersion was washed from the ore with a water wash.

The coated limestone particles were separated from the non-coated gangue particles by the use of a Mathews' separator apparatus by passing free falling particles of the ore in front of an electromagnetic radiating source and sequentially, fluorescence detectors. The coated limestone particles fluoresced substantially to a greater degree than the gangue when radiated. Each detector had been attenuated to detect fluorescence of the coated particles and each controlled one flowing fluid stream selectively directed transverse to the path of the falling particles. The fluid stream impinged only on the fluorescing ore particles. The directed fluid streams deflected the fluorescing limestone particles on a divergent path from the free falling gangue particles.

The limestone particles separated contained 94.3 percent limestone and there was 93.7 percent recovery of the limestone present in the initial feed material.

Example II

The procedure of Example I was repeated in all essential details except that the limestone ore was crushed to a particle size of about 1.5 inches and the coupling agent used was caprylic acid combined with fluoranthene fluorescent dye. The caprylic acid selectively coated the limestone particles and was rejected by the gangue. The initial limestone ore contained 77.8 percent by weight limestone. The fluorescing limestone particles separated from the nonfluorescing gangue particles contained 99.5 percent limestone.

The limestone particles recovered by the method of this invention constituted 88.9 percent of the limestone present in the initial feed.

Example III

The procedure of Example I was repeated in all essential details. The initial limestone concentration in the ore was 45.1 percent by weight and the limestone concentration in the recovered fluorescing limestone particles was 95 percent. The total limestone recovered by the method of this invention was 87 percent of the limestone present in the initial feed.

Example IV

The procedure of Example I was repeated in all essential details except the initial limestone ore was crushed to a particle size of from 0.5 to 2.5 inches and the coupling agent used was ARMEEN L-9, a trademarked product of Armak Chemicals which is a beta amine containing 9 carbon atoms. The ARMEEN L-9 coupling agent was combined with fluoranthene fluorescent dye. The ARMEEN L-9 coupling agent selectively coated the siliceous gangue present in the limestone ore.

The initial limestone ore contained by weight 25.13 percent silicates, 0.93 percent Fe_2O_3, 35.65 percent CaO and 1.07 percent K_2O. The nonfluorescing limestone particles separated by the method of this invention contained 1.07 percent silicates, 0.23 percent Fe_2O_3, 53.12 percent CaO and 0.12 percent K_2O. The fluorescing gangue separated contained 42.99 percent silicates, 1.45 percent Fe_2O_3, 22.77 percent CaO and 1.79 percent K_2O.

ARMEEN L-11 and ARMEEN L-15 can also be used in the experiment of this Example IV, however, the ARMEEN L-9 has the greater selectivity for silicates versus calcium carbonate.

Example V

The procedure of Example I was repeated in all essential details except the initial limestone ore was crushed to a particle size of from 0.5 to 2.5 inches and the coupling agent used to condition the ore was tall oil fatty acid combined with fluoranthene dye. The tall oil fatty acid coupling agent selectively coated the limestone and thereby caused the limestone particles to fluoresce when exposed to electromagnetic radiation.

The initial limestone ore contained 5.04 percent silicates, 0.24 percent Fe_2O_3, 51.14 percent CaO and 0.16 percent K_2O by weight. The fluorescing limestone particles separated by the method of this invention contained 0.53 percent silicates, 0.13 percent Fe_2O_3, 53.58 percent CaO and 0.95 percent K_2O. The nonfluorescing gangue separated contained 10.39 percent silicates, 0.38 percent Fe_2O_3, 45.82 percent CaO and 0.28 percent K_2O.

Example VI

The procedure of Example V was repeated in all essential details.

The initial limestone ore contained 11.95 percent silicates, 0.6 percent Fe_2O_3, 46.6 percent CaO and 0.05 percent K_2O by weight. The fluorescing limestone particles separated by the method of this invention contained 5.65 percent silicates, 0.40 percent Fe_2O_3, 50.15 percent CaO and 0.93 percent K_2O. The nonfluorescing gangue separated contained 42.70 percent silicates, 1.53 percent Fe_2O_3, 29.52 percent CaO and 0.05 percent K_2O.

Example VII

The procedure of Example IV was repeated in all essential details.

The initial limestone ore contained 8.98 percent silicates, 0.34 percent Fe_2O_3, 47.52 percent CaO and 0.68 percent K_2O by weight. The nonfluorescing limestone particles separated from the gangue particles by the method of this invention contained 0.55 percent silicates, 0.10 percent Fe_2O_3, 53.73 percent CaO and 0.04 percent K_2O. The fluorescing gangue particles contained 24.18 percent silicates, 0.77 percent Fe_2O_3, 36.51 percent CaO and 1.8 percent K_2O.

Example VIII

The procedure of Example 4 is repeated in all essential details except decyl amine is selected as the coupling agent. The decyl amine coupling agent selectively coats the siliceous gangue present in the limestone ore. The fluorescing gangue particles are separated from the nonfluorescing limestone particles.

Example IX

The procedure of Example IV is repeated in all essential details except the coupling agent selected is n-dodecyl amine. The n-dodecyl amine coupling agent selectively coats the siliceous gangue present in the limestone ore.

The fluorescing gangue is separated from the nonfluorescing limestone particles.

The method of the present invention using the carboxylic acids as a coupling agent can also be used to separate calcite from magnesite and dolomite from magnesite. As used herein the phrase "separation of magnesite from calcite and/or dolomite" includes the separation of higher-grade magnesite from lower-grade magnesite as well as separation of magnesite and/or calcite and/or dolomite from gangue. By the terms "higher-grade magnesite" and "lower-grade magnesite" is meant a relative distinction in magnesium carbonate content between two grades of magnesite. Such a relative distinction can be variable depending upon the reason for distinguishing between magnesite grades such as grading the magnesite in consonance with the numerous end uses of the magnesite.

In practicing the present method in regard to an ore which contains magnesite and calcite and/or dolomite, the ore is first subjected to a crushing step. In this crushing step, the ore is crushed to physically separate the magnesite from the other material present. Crushing increases the surface area of the particles and further provides a greater surface and reactive site for the coating of the particles by the coupling agent. The ore is preferably crushed to a particle size of from about 1/4 inch to about 8 inches. Particle sizes of less than 1/4 inch can be used in the practice of this invention; however, such sizes require greater amounts of coupling agent and are more difficult to separate. Particle sizes of greater than 8 inches can be used in the practice of this invention, but generally entrain impurities such that separation efficiency decreases. It is preferred to use ore particles of from about 1/2 inch to about 3 inches. Following the crushing and sizing steps the ore particles can be deslimed to remove soluble impurities and surface fines on the particles.

The method is practiced in regard to magnesite ore by conditioning the ore following sizing with a coupling agent or mixture of ocupling agents that selectively adheres to the magnesite or the dolomite and/or calcite present in the ore. It is preferred to condition the ore with a coupling agent or mixture of coupling agents that selectively coats the calcite and/or dolomite in the ore.

Coupling agents that are useful in the practice of this method to coat the calcite and/or dolomite present in the magnesite ore particles can be selected from saturated and unsaturated carboxylic acids including fatty acids which contain from about 5 to about 22 carbon atoms, or a mixture thereof. Carboxylic acids that can be used include palmitoleic acid, oleic acid, linoleic acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, tall oil fatty acids and the like. It is preferred to use at least one carboxylic acid containing from about 8 to about 18 carbon atoms. Carboxylic acids containing more than about 22 carbon atoms can be used, but generally tend to be less selective and thereby coat both limestone and gangue particles. Carboxylic acids of less than 5 carbon atoms generally do not possess the ability to coat any of the particles. In general, the preferred carboxylic acid enters a chemical reaction with the calcium carbonate or calcium-magnesium carbonate; for example, oleic acid reacts to form calcium oleate.

A fluorescent dye is combined with the coupling agents used to condition the ore. The fluorescent dye can be combined with the coupling agent either before or after the ore is conditioned. Fluorescent dyes which are compatible with the coupling agents,and described above, can be used. In the practice of the method with regard to magnesite ore, the fluorescent dye is used as described above with regard to limestone ore.

Following the crushing and sizing of the magnesite ore, the ore is conditioned with the coupling agent. Conditioning of the ore with the coupling agent is accomplished by contacting the sized ore with the coupling agent. The coupling agent can be used in any suitable manner, such as in solution, dispersion, or by itself. It is preferred to form a dispersion of the coupling agent in water. Contacting methods include the spraying of the aqueous dispersion onto the sized ore, the passing of the ore through a dispersion bath and the like. It is preferred to spray the sized ore with the aqueous dispersion. Spraying techniques include, but are not limited to, spraying the dispersion onto the ore as the ore passes the spraying nozzle on a vibrating screen or belt, or spraying the ore as it passes through a ring or series of ring sprayers.

Following the spraying of the ore with the aqueous dispersion, the ore is rinsed with a suitable washing agent, such as water, to remove excess dispersion from the ore and any dispersion physically entrained in the ore. A fine spray of air can also be used for removing entrained dispersion. The coupling agent, combined with the fluorescent dye, selectively remains coated on the particles for which it has a preference due to the surface properties of the particles. The coated particles are capable of fluorescence when radiated with electromagnetic radiation.

Following the conditioning of the ore, if the adherent dye or pigment is fluorescent, the ore is exposed to electromagnetic radiation to induce the coating on the particles to fluoresce. The coated, fluorescing particles can be separated by any convenient means, such as by hand, by optical sorting device, and by apparatus as taught by Mathews' United States Patent No. 3,472,375.

This invention is further illustrated by the following examples, which are not intended to be limiting.

Example X

A synthetic sample of calcite and magnesite particles of about 1/2 inch size was washed to remove surface fines. The amount of calcite and magnesite in the sample was in the ratio 1:1. The sample after desliming was conditioned with an aqueous suspension of about 2 percent oleic acid in which about 2 percent fluorescent dye, fluoranthene, was dissolved. Good fluorescent coating on calcite and poor coating on magnesite was obtained. Based on the difference in fluorescence under ultraviolet light, magnesite (nonfluorescent) was separated from calcite (fluorescent).

Example XI

A synthetic sample of dolomite and magnesite in the ratio 1:1 was deslimed. Particle size of dolomite and magnesite was about 1/2 inch. After desliming, the material was conditioned with an aqueous suspension of about 2 percent oleic acid in which about 2 percent fluoranthene was dissolved. Good fluorescent coating was obtained on dolomite. Poor coating was obtained on magnesite. The difference in intensity of fluorescence was improved upon rinsing the material with water. Separation of dolomite (fluorescent) was achieved from magnesite (nonfluorescent) under ultraviolet light.

The method of the present invention can also be used in optical, nonfluorescent separation systems by substituting for the fluorescent dye described herein, a dye that provides a distinct color within the visible spectrum.

WHAT IS CLAIMED IS:

1. A method for the separation of calcium-containing material from non-calcium-containing material including siliceous material present in a particulate ore comprising the steps of:

a) conditioning the particulate ore with a coupling agent selected from the group consisting of at least one carboxylic acid selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms for selectively coating calcium-containing material on the particulate ore to the substantial exclusion of coating siliceous material, at least one aliphatic amine containing from about 8 to about 22 carbon atoms for selectively coating siliceous material in the particulate ore to the substantial exclusion of coating calcium-containing material, and at least one beta amine containing from about 7 to about 21 carbon atoms for selectively coating siliceous material in the particulate ore to the substantial exclusion of coating calcium-containing material;

b) providing at least one tagging agent to the coupling agent; and

c) separating the coupling agent-coated material from the non-coupling-agent coated material.

2. A method as recited in claim 1 wherein the tagging agent is a coloring agent.

3. A method as recited in claim 1 wherein the tagging agent is a fluorescent dye and the conditioned particulate is radiated with electromagnetic radiation for inducing fluorescence of the fluorescent dye.

4. The method of claim 3 wherein said fluorescent dye is selected from the group consisting of fluorenthene, fluorescent yellow G and mixtures thereof.

5. A method as recited in claim 1 wherein calcium-containing material is separated from magnesite by selecting a coupling agent comprising at least one carboxylic acid selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms for selectively coating calcium-containing material to the substantial exclusion of coating magnesite.

6. The method of claim 1 wherein the particulate limestone ore is of a particle size of from about 1/4 inch to about 8 inches.

7. The method of claim 6 wherein the particulate limestone ore is of a particle size of from about 1/2 inch to about 3 inches.

8. The method of claim 1 wherein said tagging agent is provided to the coupling agent prior to the conditioning of the ore.

9. The method of claim 1 wherein said tagging agent is provided to the coupling agent after the conditioning of the ore.

10. The method of claim 1 wherein said tagging agent is oil soluble.

11. A method for the separation of higher-grade limestone from lower-grade limestone and the gangue present in particulate limestone ore which comprises: conditioning the particulate limestone ore with at least one coupling agent selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms, said coupling agent selectively coating the calcium carbonate in the limestone to the substantial exclusion of coating gangue in combination with providing at least one fluorescent dye to said coupling agent; radiating the conditioned particulate limestone ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the coated higher-grade limestone particles from the coated lower-grade limestone and the substantially non-coated gangue particles and separating the fluorescing coated higher-grade limestone particles from the coated lower-grade limestone and nonfluorescing gangue particles.

12. The method of claim 11 wherein said coupling agent is at least one carboxylic acid containing from about 8 to about 18 carbon atoms.

13. The method of claim 11 wherein said coupling agent is oleic acid.

14. The method of claim 11 wherein said coupling agent is caprylic acid.

15. The method of claim 11 wherein said coupling agent is a tall oil fatty acid.

16. A method for the separation of higher-grade limestone from lower-grade limestone and/or the silicate-containing gangue present in particulate limestone ore, comprising: conditioning the particulate limestone ore with at least one coupling agent selected from the group consisting of aliphatic amines containing from about 8 to about 22 carbon atoms and beta amines containing from about 7 to about 21 carbon atoms, said coupling agent selectively coating the silicates in the gangue particles to the substantial exclusion of coating the calcium carbonate particles, in combination with providing at least one fluorescent dye to said coupling agent; radiating the conditioned particulate limestone ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the coated gangue particles and partially coated lower-grade limestone from the lesser coated higher-grade limestone particles and separating the fluorescing, coated gangue and lower-grade limestone particles from the higher-grade limestone particles.

17. The method of claim 16 wherein the coupling agent is at least one aliphatic amine containing from about 8 to about 22 carbon atoms.

18. The method of claim 17 wherein said aliphatic amine is n-dodecyl amine.

19. The method of claim 16 wherein said coupling agent is at least one beta amine containing from about 7 to about 21 carbon atoms.

20. The method of claim 16 wherein the aliphatic and/or beta amine coupling agent is provided by a water soluble salt of such an aliphatic and/or beta amine.

21. A method for the separation of higher-grade magnesite from lower-grade magnesite and dolomite and/or calcite present in particulate ore which comprises:

a) conditioning the particulate ore with at least one coupling agent selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms, said coupling agent selectively coating the calcite and/or dolomite in the ore to the substantial exclusion of coating magnesite in combination with providing at least one fluorescent dye to said coupling agent;

b) radiating the conditioned particulate ore to excite and induce fluorescence of the fluorescent dye to a degree sufficient to distinguish the substantially non-coated higher-grade magnesite particles from the greater coated lower-grade magnesite and the much greater coated dolomite and calcite particles and separating the higher-grade magnesite particles from the coated lower-grade magnesite and calcite and/or dolomite particles.

22. The method of claim 21 wherein said coupling agent is at least one carboxylic acid containing from about 8 to about 18 carbon atoms.

23. The method of claim 21 wherein said coupling agent is oleic acid.

24. The method of claim 11, 16 or 21 wherein the particulate limestone ore is of a particle size of from about 1/4 inch to about 8 inches.

25. The method of claim 24 wherein the particulate limestone ore is of a particle size of from about 1/2 inch to about 3 inches.

26. The method of claim 11, 16 or 21 wherein said fluorescent dye is provided to the coupling agent prior to the conditioning of the ore.

27. The method of claim 11, 16 or 21 wherein said fluorescent dye is provided to the coupling agent after the conditioning of the ore.

28. The method of claim 11, 16 or 21 wherein said fluorescent dye is oil soluble.

29. The method of claim 11,16 or 21 wherein said fluorescent dye is selected from the group consisting of fluoranthene, fluorescent yellow G and mixtures thereof.

30. The method of claim 1 wherein the particulate ore is first conditioned with a coupling agent selected from the group consisting of at least one aliphatic amine containing from about 8 to about 22 carbon atoms and at least one beta amine containing at least from about 7 to about 21 carbon atoms for selectively coating siliceous material in the particulate ore to the substantial exclusion of coating non-siliceous material, separating the coated siliceous from the substantially non-coated, non-siliceous material, conditioning the resultant separated non-siliceous material with a coupling agent selected from the group consisting of at least one carboxylic acid selected from saturated and unsaturated carboxylic acids containing from about 4 to about 22 carbon atoms for selectively coating calcium-containing material in the particulate ore to the substantial exclusion of coating non-calcium-containing material and separating the coated calcium-containing material from the substantially non-coated, non-calcium-containing material.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 7900246

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. B07C 5/10, 5/34 2, 5/346

U.S. CL. 209/3.1,3.2,3.3,1,3,4,9,578

WO 79/00950

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	209/3.1,3.2,3.3,1,3,4,9,578

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US,A,3,356,211 Published 05 Dec. 1967	
A	US, A,3,795,310 Published 05 March. 1974	
A	US, A,3,472,375 Published 14 Oct. 1969	
A	US, A,3,936,188 Published 03 Feb 1976	
A	US, A,1,678,884 Published 31 July, 1928	
A	US, A,2,967,614 Published 10 Jan. 1961	
A	US, A,3992,287 Published 16 Nov. 1976	
A	US, A,3,346,111 Published 10 Oct. 1967	
A	US, A,3,901,793 Published 26 Aug. 1975	

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
5/7/79	22 MAY 1979
International Searching Authority [1]	**Signature of Authorized Officer [20]**
US	A. Knowles Allen U. Knowles

Form PCT/ISA/210 (second sheet) (October 1977)