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FLOTATION METHOD AND REAGENT

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This invention relates to improved methods for flotation of iron oxide minerals from silicious minerals and to improved flotation reagents. As used herein, the term "iron oxide minerals" includes hydrated oxides, such as the various limonites and goethite, as well as hematite and magnetite. The term "silicious minerals" includes quartz and various silicates, such as feldspar.

The flotation methods of the present invention are particularly applicable for beneficiating low-grade iron ores, such as taconites of the Mesabi range. Taconites vary greatly in physical structure and chemical composition. Previously known flotation methods can make a fairly satisfactory separation between the iron oxide and the silicious components in some grades of taconite, but in most instances they require relatively expensive reagents and they float the silicious minerals and direct the iron oxide minerals to the underflow. For practical operation, it would be essential to employ inexpensive reagents, such as collectors of the fatty acid type, and it would be desirable to float the iron oxide minerals, since they are less voluminous than the silicious minerals and it is easier to recover them when they are a float product than when they are dispersed as an underflow product. Although it is known that collectors of the fatty acid type are capable of floating iron oxide minerals, they have not been used to any extent for this purpose because with previously known methods they do not generally furnish clear separations of the iron oxide minerals from the silicious minerals.

An object of the present invention is to provide improved flotation methods which utilize relatively inexpensive reagents and yet furnish a satisfactory separation between iron oxide minerals and silicious minerals, and which can be applied to some ores that previously have been difficult to beneficiate, and which float iron oxide minerals and direct silicious minerals to the underflow.

A further object of the invention is to provide flotation methods which utilize relatively inexpensive collectors of the fatty acid type for floating iron oxide minerals, in conjunction with an improved agent for wetting and thereby depressing silicious minerals, namely colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1.

A further object of the invention is to provide improved prepared flotation reagents which consist of an emulsion of a collector of the fatty acid type and colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1, and preferably having a pH value of 3 to 6 to promote stability.

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I define the term "collectors of the fatty acid type" as used herein to include higher fatty acids, such as oleic acid, palmitic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, stearic acid, and tariric acid; esters of the higher fatty acids, such as their glyceryl and glycol esters; resin acids, such as abietic acid; and naphthenic acids; and various mixtures of the foregoing, but in each instance being substantially free of ions of alkali metals such as would be found in the sodium soaps of the various acids. Practically I prefer crude mixtures of fatty acids and resin acids, such as tall oil, because such mixtures are readily available at low cost, for example, under the trade names "Opoil" and "Facoil."

For the successful practice of the present invention, it is essential that the reagents have a very low content of ions of alkali metals and alkaline earth metals, although appreciable amounts of the latter often occur in the ore. It would be desirable that such ions be absent entirely, since they weaken the wetting action of colloidal silica on particles of silicious minerals. It is known that alkaline earth metal ions, such as calcium ions, tend to activate silicious minerals and to cause fatty acid collectors to float them. The colloidal silica wetting agent must overcome this tendency. Practically it is difficult to obtain reagents that are entirely free of such ions and I find that certain small amounts can be tolerated. Therefore the mol ratio of silica to alkali metals should be at least 25 to 1.

The colloidal silica which I employ can be prepared by neutralizing commercial sodium silicate with an acid, such as sulphuric acid, using concentrations that form a gel, and then washing out the sodium salt. Another way is by treating sodium silicate with an acid type ion exchange medium which replaces the sodium ions of the silicate with hydrogen ions. The resulting colloidal silica in the first instance is a gel and in the second instance a sol. The silica gel remains effective for my purpose if it is dried at moderate temperatures (e. g. 105° C.) and ground. A suitable colloidal silica is available commercially under the trade name "Ludox." The analysis of this commercial material as furnished by the producer is as follows:

SiO ₂ -----	29 to 31%.
Na ₂ O-----	0.31 to 0.41%.
Sulphates (as Na ₂ SO ₄)-----	0.15% maximum.
pH-----	9.5 to 10.5.
Specific gravity-----	24.7 to 26.4° Bé.
Viscosity at 25° C-----	2.0 to 3.3 cps.

Since methods of preparing such material are known and per se are not part of the present

invention, no more detailed description is believed necessary.

A preferred way of practicing the present invention is to pre-mix a reagent which consists of a collector of the fatty acid type and colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1. The colloidal silica functions as an emulsifying agent for the collector. The ratio of colloidal silica solution of approximately 30% SiO₂ content to collector can vary from about 0.2 to 2.0 parts by weight of aqueous colloidal silica solution to one part by weight of collector. I find a ratio of about 1 to 1 is convenient practically. On an anhydrous basis, the ratio of silica to collector can vary from about 0.06 to 0.6 part by weight of silica to 1 part by weight of collector. A satisfactory reagent also can be formed by mixing dried and ground silica gel with fatty acid type collector. If the pre-mixed reagent is used promptly, it can have any pH value within the range of about 3 to 8, but it is more stable if acidified to a pH value of about 3 to 6, preferably with sulphuric acid, although other equivalent acids work just as well.

The reagent is then intimately mixed with a pulp of the ore containing about 10 to 85 per cent solids by weight. The quantity of reagent can vary from 1 to 15 pounds of pre-mixed reagent per long ton of crude ore, or on an anhydrous basis, from about 0.5 to 5.0 pounds of collector and from about 0.2 to 3.0 pounds of silica per long ton of ore. For many ores I find about 4 to 5 pounds of the 1:1 pre-mixed reagent is satisfactory. In general an excess of colloidal silica would tend to depress iron oxide minerals and an excess of collector would tend to float silicious minerals. Conveniently at least part of the reagent can be added to the pulp in the ball-mill and the remainder in the flotation cell. Where the pulp is re-treated after the first flotation treatment, make-up reagent can be added as needed. Also it is apparent that the collector and the colloidal silica can be introduced to the pulp separately. If the silica gel first is dried, the grinding and mixing with the collector conveniently can take place in the ball-mill, either with or without ore present. The pulp pH can vary from about 5.5 to 7.5. As is usual in flotation processes, the optimum quantities of reagent within the foregoing ranges, the best mode of introducing the reagent, the optimum pulp pH and other operating conditions vary with different ores and should be determined by experiment in each instance.

In some instances it is desirable to introduce a small quantity of a hydrocarbon oil to modify the froth. I find that Bunker C fuel oil is an inexpensive and satisfactory hydrocarbon for the purpose, although many equivalents are possible. Colloidal silica and fatty acid type collectors produce a fast-forming dry froth which can mechanically entrap silicious particles and thus the float product may require several re-treatments. By introducing hydrocarbon oil in an amount within the range of about 0.5 to 4.0 pounds per long ton of crude ore, I produce a froth which does not entrap undesired particles to nearly as great an extent.

To assist in describing the present invention, I have compiled the following specific examples of treatments of ores in accordance with the invention.

Example I

The ore treated was Spruce taconite, which is representative of a common type, and in this

instance contained 34.8% iron and 48.6% silica. The iron minerals were chiefly hematite and goethite with a minor content of magnetite, and the gangue was chiefly quartz with a minor content of carbonates and iron silicates. Previously this ore had not been beneficiated satisfactorily with fatty acid type collectors.

A reagent was compounded by mixing 10 grams of colloidal silica solution (about 30% SiO₂) substantially free of ions of either alkali metals or alkaline earth metals ("Ludox") and 10 grams of oleic acid and agitating the mixture until it was emulsified. A sample of the ore was crushed dry to pass a 14-mesh screen and then ball-milled with water and a quantity of emulsion equivalent to 1 pound each of colloidal silica solution (about 30% SiO₂) and oleic acid per long ton of ore. The solids in the milled pulp were 85% minus 325 mesh.

The pulp was transferred to a small Denver flotation cell with additional water and was treated by flotation in the usual way. No other materials were introduced, except make-up quantities of the reagent emulsion. The total reagent including that added to both the ball mill and the flotation cell, was equivalent to two pounds each of colloidal silica solution and oleic acid per long ton of ore. The float product or concentrate was returned to the cell and re-cleaned four times. The original underflow and the first cleaner underflow were combined as a tailing. The second, third and fourth cleaner underflows were combined as a middling which might in actual operation be returned to the mill circuit.

The results were as follows:

Product	Percent wt.	Analysis, percent Fe	Distribution, percent Fe
Heads (calculated)	100.0	34.44	100.0
Concentrate	45.8	61.61	81.9
Middling	5.3	31.71	4.9
Tailing	48.9	9.28	13.2

It is to be noted that no conditioning agents of any kind were used in the test. The pH of the flotation pulp was about 7.30, which is approximately the same as the pH obtained on grinding the ore in water in the absence of reagent.

Example II

The ore treated was the same as in Example I and the reagent was the same except that crude tall oil ("Opoll") was substituted for oleic acid as the collector. A 500 gram sample of the ore was crushed dry to pass a 14-mesh screen and ball-milled for 25 minutes with 500 ml. water and 50 drops of the reagent. The solids in the milled pulp were 90.8% minus 325 mesh.

The milled pulp was transferred to a 500 gram Denver sub-A flotation cell with water and conditioned 3 minutes with 12 drops additional reagent. The total reagent including that added to the mill was equivalent to 2½ pounds each of colloidal silica solution and tall oil per long ton of ore. The pulp was subjected to a flotation treatment for a seven minute period during which air admission to the cell was regulated to avoid excessive froth volume. The concentrate was returned to the cell and re-cleaned seven times with small additions of the pre-mixed reagent and colloidal silica for the last four cleanings. The total reagents for the entire test were equivalent to 3.3 pounds of collector and 4 pounds of colloidal silica solution per long ton of ore.

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The results were as follows:

Product	Percent Wt.	Analysis		Distribution, Percent Fe
		Percent Fe	Percent Insol.	
Heads (calculated).....	100.0	34.53	-----	100.0
Concentrate.....	48.1	61.09	9.84	85.1
Combined Tailings.....	51.9	9.94	-----	14.9

Example III

The ore treated was the same as in Examples I and II. The iron oxide minerals are about 90% freed from the gangue when the ore is crushed to minus 150 mesh, but it has been the usual practice to grind the ore finer than this for flotation with other reagent combinations. In the present example the ore was treated in a somewhat coarser state.

500 grams of the ore was crushed dry to pass a 14-mesh screen and then transferred to a ball mill with 500 ml. of water. Crude tall oil and colloidal silica substantially free of ions of either alkali metals or alkaline earth metals were added to the ball mill separately in an amount equivalent to two pounds of each per long ton of ore. The whole was milled for 15 minutes and the charge transferred to a 500 gram Denver flotation cell with water. A screen analysis on an identically prepared sample was as follows:

Mesh	Wt. Percent	Cumulative Percent
+100.....	0.3	-----
+200.....	9.6	9.9
+325.....	14.9	24.8
Minus 325.....	75.2	100.0

The flotation and re-cleaning were carried out

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example anionic combinations which employ soap, starch, lime and caustic, or cationic combinations which employ organic amines. Taconite ores commonly contain silicate and carbonate minerals that have highly adsorptive properties, a tendency to slime on grinding, and pronounced ion exchange capacity. Silicious siderite is a typical ore component of this sort. Previously it not only has been impossible to obtain a satisfactory concentrate from silicious siderite alone, but when silicious siderite is present with cleaner ores, it prevents recovery of iron oxide. Whereas Spruce taconite used in Examples I, II and III has a cation exchange capacity of 0.55 milliequivalents per 100 grams by the ammonium acetate method (Bray) and 0.46 milliequivalent by a calcium chloride method, typical corresponding values for silicious siderite are 6.20 and 8.35 milliequivalents per 100 grams. I have found that the ability of taconites to be concentrated diminishes greatly with increase in ion exchange capacity.

400 grams of taconite as used in the preceding examples and 100 grams of silicious siderite were crushed dry to pass a 14-mesh screen and introduced to a ball mill with 500 ml. of water and a pre-mixed reagent emulsion which consisted of the equivalent of 2½ pounds of tall oil, 2½ pounds of colloidal silica solution (about 30% SiO₂) and 0.12 pounds of oleic acid per long ton of ore. The mixture was milled for 15 minutes and the ore pulp transferred to a 500 gram Denver flotation cell with water. Flotation and re-cleaning were carried out in a fashion similar to Examples II and III. The total reagent additions including those made to the mill were equivalent to 2.67 pounds each of colloidal silica solution and tall oil and 0.13 pounds of oleic acid per long ton of ore.

The results were as follows:

Product	Percent Wt.	Analysis		Distribution		
		Percent Fe	Percent Insol.	Units Fe	Percent Fe, Total	Percent Fe, Spruce Portion
Total calculated heads.....	100.0	33.46	-----	33.46	-----	-----
Spruce ore content.....	80.0	35.00	-----	28.00	-----	-----
Concentrate.....	40.2	58.79	10.48	23.63	70.6	54.4
Combined tailings.....	59.8	16.44	-----	9.83	29.4	15.6

in the fashion as in Example II. The total reagent additions for the entire operation were equivalent to 2.67 pounds each of collector and colloidal silica solution per long ton of ore.

The results were as follows:

Product	Percent Wt.	Analysis, percent Fe	Distribution, percent Fe
Heads (calculated).....	100.0	35.23	100.0
Concentrate.....	53.7	69.04	91.6
Combined Tailings.....	46.3	6.46	8.4

This test demonstrates that the method is capable of making a satisfactory separation without the extremely fine grinding of Examples I and II and with smaller quantities of reagent than in Example II.

Example IV

Although the taconite used in Examples I, II and III had not previously been treated successfully for recovery of the iron oxides with collectors of the fatty acid type, it is considered a relatively clean taconite and can be treated successfully with other known flotation methods, for

Example V

In practice the seven re-cleaning operations of Examples II, III and IV might prove disadvantageous. The need for such a large number of re-cleaning operations is believed due to mechanical entrapment of silicious mineral particles in the fast-forming dry froth, which is characteristic of the flotation when only colloidal silica and the fatty acid collector are used. In the present example a hydrocarbon oil is introduced as a froth modifier and substantially reduces the number of cleaning operations needed.

500 grams of taconite like that used in the preceding examples was dry crushed to pass a 14-mesh screen and added to a ball mill with 500 ml. of water and a reagent consisting of tall oil and colloidal silica solution equivalent to 2 pounds of each per long ton of ore. The mixture was milled for 15 minutes and the pulp transferred to a 500 gram Denver flotation cell with water. A hydrocarbon oil, in this instance Bunker C fuel oil, was added to the charge in the cell in an amount equivalent to 0.9 pounds per long ton of ore. The mixture was condi-

tioned for 5 minutes and froth removed for 5 minutes. The concentrate was returned to the cell and re-cleaned three times without further reagent addition. Each re-cleaning was completed in 3½ minutes. The original tailing and first two cleaner tailings were combined. The third cleaner tailing was less than 8% of the weight and in continuous operation would be returned to the circuit for re-flotation.

The results were as follows:

Product	Percent Wt.	Analysis, percent Fe	Distribution, percent Fe
Heads (calculated).....	100.0	34.72	100.00
Concentrate.....	48.6	60.05	84.04
Middling.....	7.9	28.31	6.45
Tailing.....	43.5	7.59	9.51

From the foregoing description it is seen that the present invention provides flotation methods and reagents which utilize only inexpensive materials and yet furnish better separations of iron oxide minerals from silicious minerals than methods and reagents previously known. As previously suggested, it is of the essence of the invention that the reagents be substantially free of alkali metal ions, that is, that they have a mol ratio of silica to alkali metals of at least 25 to 1. Once this condition is met, a wide choice of inexpensive collectors and colloidal silica can be used.

While I have described in detail only certain preferred modes of carrying out the invention and certain preferred reagent compositions, it is apparent modifications may arise. Therefore I do not wish to be limited to this disclosure, but only to the scope of the appended claims.

I claim:

1. A method for floating iron oxide minerals from silicious minerals comprising adding to an ore pulp, which contains about 10 to 85% solids by weight, about 0.5 to 5.0 pounds of a collector of the fatty acid type per long ton of solids in the pulp and about 0.2 to 3.0 pounds of colloidal silica on an anhydrous basis per long ton of solids, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions the colloidal silica having a mol ratio of silica to alkali metals of at least 25 to 1, and subjecting the pulp to a flotation treatment.

2. A method for beneficiating low grade iron ores comprising adding to an ore pulp which contains about 10 to 85% solids by weight, about 0.5 to 5.0 pounds of a collector of the fatty acid type per long ton of solids in the pulp and about 0.2 to 3.0 pounds of colloidal silica on an anhydrous basis per long ton of solids, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, the colloidal silica having a mol ratio of silica to alkali metals of at least 25 to 1, and subjecting the pulp to a flotation treatment which floats the iron oxide minerals.

3. A method for beneficiating low grade iron ores comprising adding to an ore pulp which contains about 10 to 85% solids by weight, about 0.5 to 5.0 pounds of a collector of the fatty acid type per long ton of solids in the pulp, about 0.2 to 3.0 pounds of colloidal silica on an anhydrous basis per long ton of solids, and about 0.5 to 4.0 pounds of a hydrocarbon oil per long ton of solids, the collector being of the group which consists

of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, the colloidal silica having a mol ratio of silica to alkali metals of at least 25 to 1, and subjecting the pulp to a flotation treatment which floats the iron oxide minerals.

4. A pre-mixed flotation reagent consisting of an aqueous emulsion of a collector of the fatty acid type and colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, the ratio of colloidal silica to collector on an anhydrous basis being from about 0.06 to 0.6 part by weight of silica to 1 part by weight of collector.

5. A pre-mixed flotation reagent consisting of an aqueous emulsion of a collector of the fatty acid type and colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, said colloidal silica acting as the emulsifying agent, the ratio of colloidal silica to collector on an anhydrous basis being from about 0.06 to 0.6 part by weight of silica to 1 part by weight of collector, the emulsion being acidified to a pH value of about 3 to 6.

6. A method for floating iron oxide minerals from silicious minerals comprising adding to an ore pulp, which contains about 10 to 85% solids by weight, a pre-mixed reagent consisting of an aqueous emulsion of a collector of the fatty acid type and colloidal silica which has a mol ratio of silica to alkali metals of at least 25 to 1, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, the quantity of collector being about 0.5 to 5.0 pounds per long ton of solids in the pulp and the quantity of colloidal silica being about 0.2 to 3.0 pounds per long ton of solids on an anhydrous basis, and subjecting the pulp to a flotation treatment.

7. A method for floating iron oxide minerals from silicious minerals comprising adding to a coarse ore pulp, which contains 10 to 85% solids by weight, about 0.5 to 5.0 pounds of a collector of the fatty acid type per long ton of solids in the pulp and about 0.2 to 3.0 pounds of dried silica gel per long ton of solids, the collector being of the group which consists of higher fatty acids, esters of the higher fatty acids, resin acids, naphthenic acids and mixtures of the foregoing, but being substantially free of alkali metal ions, the silica gel having a mol ratio of silica to alkali metals of at least 25 to 1, grinding and mixing the pulp, collector and silica gel, and subjecting the resulting ground and mixed pulp to a flotation treatment.

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