Patented Apr. 6, 1948 2,439,200

UNITED STATES PATENT OFFICE

2,439,200

FLOTATION OF IRON WITH ORGANIC ACID AND PETROLEUM SULFONATE

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No Drawing. Application January 5, 1946, Serial No. 639,434

10 Claims. (Cl. 209—166)

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This invention relates to the beneficiation of iron ores by froth flotation processes.

Low grade iron ores have presented a very serious beneficiation problem because the unit value of iron concentrates is not high and flotation procedures in the past have not given commercially useful results. Iron ores containing hematite, magnetite, or similar iron minerals can be subjected to froth flotation in the presence of the typical fatty acid collectors used with oxide ores, but, while some beneficiation takes place, the grade obtained and recovery are not sufficiently high to make the process commercially feasible.

It has been proposed to float oxide ores with oil soluble petroleum sulfonates obtained as waste products from the refining of petroleum lubricating oil stocks with sulfonating agents such as strong sulfuric acid, oleum, chlorosulfonic acid and the like. These reagents give somewhat better results than fatty acids, but the results are not commercial, particularly when iron ores are treated.

According to the present invention oxidized iron ore pulps are treated with a strong organic acid having a dissociation constant of not less than 10^{-7}, selected from the group consisting of aliphatic monobasic acids, aromatic sulfonic acids, and aliphatic dibasic acids, the carboxyl groups of which are separated by at least one carbon atom. The acid treated pulp can then be floated with oil soluble, and preferably water dispersible, petroleum sulfonates, such as mahogany soaps or mahogany acids, to give high grades and good recoveries. The present process permits transforming rejected tailings, waste products from washers, and other low grade ores into commercially acceptable concentrates. Preferably, although not necessarily, the oil-soluble petroleum sulfonates are dispersed in or associated with unsulfonated oil, such as petroleum hydrocarbons, alcohols, or other oily solvents.

The mechanism of the present invention is not completely known and it is not desired to limit it to any particular theory of operation. The acids falling within the groups enumerated above may be used generally, although, of course, some of the acids are somewhat more effective than others. Acids falling outside the group, in general, do not give the improved results of the present invention. For example, aromatic carboxylic

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acids, such as benzoic and salicylic and phthalic acid, give inferior recoveries and grades but little better than can be obtained with oil soluble petroleum sulfonates alone. Hydroxy aromatic acids of the gallic and tannic acid type are actually deleterious, presumably because of their deflocculating effect, and do not permit any float at all. Hydroxy monobasic aliphatic acids and dibasic aliphatic acids, however, are not objectionable, and some of them give excellent results. Hydroxy tri-basic acids, such as citric acid, however, cannot be used, nor can dibasic acids such as oxalic acid be used where there is no carbon atom between carboxyl groups.

The rather general effectiveness of such wide groups of acids leads us to believe that probably one factor of the present reaction may be the action of the acid on the particles of iron ore. It is possible that another factor may be action on stained gangue, such as iron stained quartz. However, it is not intended to limit the invention to any particular theories, the above being advanced only as possible explanations.

While it is possible to obtain fair results when the conditioning with acid and petroleum sulfonate is effected at flotation density, best results are obtained when this conditioning is effected at high solids, for example, 50–70%, and the conditioned pulp then diluted to flotation density before flotation is effected.

It is an advantage of the present invention that the amount of acid to be used is not critical. This does not mean that acids may be used in unlimited quantities. With every acid and every ore the effect generally increases at first with the addition of more acid, reaches a maximum, and then may decline when more acid is used. In general amounts of acid from 1½ to 5 lbs. per ton of flotation feed constitute the range of best operation, with an optimum depending on the ore and other conditions of about 2½ to 3 lbs. per ton. These figures apply to processes in which the pulp is conditioned at high solids. Where conditioning at low solids is employed, such as for example, at flotation pulp density, acceptable results can be obtained, but the amount of acid required is greatly increased, ranging from 5 to 10 lbs. per ton of feed. A commercially acceptable product is obtained, but, because of the better results and smaller reagent consumption, it is

preferred to condition at high solids, although the invention is not limited thereto. The action does not appear to be one due solely to the pH of the circuit, although this may be a contributing factor. In general the pH of the rougher tailing will run from slightly below 2 to a little below 6, there being little correlation between changes of pH in this range and metallurgical efficiency. This is an added reason for believing that at least one factor in the process is some surface effect of the acid on the ore particles.

Oil soluble, water-insoluble reaction products of sulfuric acid and petroleum hydrocarbons from lubricating oil stock vary quite widely with different crude oils and different refining procedures. The compositions are somewhat indefinite and are ordinarily considered to be mixtures containing both sulfonate and sulfate esters. We have found that practically all of these products can be used in the present invention, although there is some difference in effectiveness between mahogany soaps of different petroleum companies. When no acid is used in treating the pulp, there is a very wide difference between mahogany soaps of different origins. It is a surprising effect of the present invention, however, that the acid treatment of the ore to a very great extent adjusts differences between mahogany soaps of different origins. They all give improved results with acid and the difference between various ones is definitely lessened. This curiously different behaviour with and without acid of various mahogany soaps is an additional reason for believing that one factor of the present invention is a surface alteration of the iron ore and possibly of the gangue. It seems reasonable to believe that the acid treatment may so alter the surface of iron mineral particles that good adherence is obtained with almost any mahogany sulfonate.

It is necessary to coat the mineral particles with the active mahogany soap. This makes it necessary to use some precautions in mixing the promoter with the ore. We have found that it is desirable to have the active ingredients in solution or dispersion in organic solvents. Commercial mahogany soaps are sold as an oil solution or dispersion of the sulfuric acid reaction products and, therefore, are already dispersed in a hydrocarbon solvent.

These commercial products may be mixed with the ores directly or they may be further diluted with other organic solvents. The nature of the solvent does not appear to be critical. Excellent results are obtained with hydrocarbon solvents, such as petroleum hydrocarbons which are naturally present in the commercial mahogany soaps, the latter being normally sold in the form of a solution in petroleum hydrocarbons. Glyceride oils, of which cocoanut oil is a typical example, also give good results and it is possible to get good feeding with solutions in various alcohols and other organic materials. This leads us to believe that the main, if not only, function of the solvent is to effect more uniform distribution in the ore pulp, but it may also have other effects, because when it is attempted to feed the active constituents of the mahogany soaps in the form of hot water dispersions the results are not as good. Therefore, it is preferred to introduce the collector in solution in an organic solvent without limiting the invention broadly to this preferred modification.

The question of froth is present as in any froth flotation process, and various mahogany soaps show different frothing powers. Where adequate frothing can be obtained they may be used alone. However, in many cases it is desirable to use one or more frothers, for which the standard types of frothers such as pine oil, cresylic acid, mixtures of higher paraffine alcohols from 7 to 10 carbon atoms and synthetic frothers prepared from mixtures of these higher alcohols with hydrocarbons, may be used. We have also found that water-soluble reaction products of sulfuric acid with petroleum hydrocarbons from lubricating oil stock, the so-called green acids, may also be used as frothers and also show some promoting effect. When used alone with acid treatment, fair results are obtained, but not as good as with the mahogany soaps or acids of the present invention.

The technique of froth flotation is not materially changed by the use of the present invention, and this is an advantage because the operator does not have to learn new techniques, and standard flow-sheets and equipment may be used in most cases. Examples of typical flotation procedures are the use of the process of the present invention in rougher floats, cleaner floats, and the like.

It is also possible to utilize the principles of the present invention in a so-called double-flotation process in which a rougher float is effected with the mahogany soaps or acids on acid treated pulp, adjusting conditions for maximum recovery at some slight sacrifice of grade. The concentrate is then treated with chemicals or agents to remove the collector from the surface of the particles. Typical of such agents are quebracho and other dispersing agents. The concentrate with collector removed is then subjected to a cleaning operation using a cationic flotation reagent to float out silica or siliceous gangue. This double float presents a more expensive procedure, but with some highly refractory ores it is an economically attractive procedure.

It is an advantage of the present invention that it may be used in such various manners so as to obtain the best results economically with various ores, taking into consideration the nature of the ore and the economic factors at the mines, such as availability of fuel, shipping costs and the like. In every case the present invention will be used to obtain the best economic results with any particular ore, and the wide latitude given to the ore dressing engineer by the non-critical character of the present invention is of real advantage in permitting optimum results with a wide variety of iron ores.

The problem of slime is not greatly different in the process of the present invention than in the general run of flotation processes. Here, as elsewhere, slime is never desirable. However, it is an advantage of the present invention that it is not peculiarly critical as far as slime is concerned and it is possible to operate with undeslimed ore, or, which is more important, with ore, which has been only partially deslimed, thus permitting more economical desliming procedures. The effect of slime is normal and manifests itself primarily in added consumption of reagent. As the reagents are fairly cheap it is sometimes desirable to use relatively economical desliming procedures which do not remove the slime completely and such procedures are permissible by reason of the relative lack of sensitivity of the present process to the presence of small amounts of slime. More involved desliming procedures, such as those employing a polishing

or scrubbing of the ore particle followed by desliming, are not normally necessary although they may be used and do effect some economy of reagent. The extent to which the desliming is to be effected is largely one of economic compromise and the degree of desliming to produce optimum results with minimum costs will be determined in the case of each ore.

Within wide limits the purity of the acid does not seem to play any decisive result in the present invention, which permits the use of lower purity acids which are sometimes available at considerably reduced prices and the possibility of using cheap material in the present invention constitutes a further economic advantage.

It is an advantage of the present invention that the addition of acid may take place at various points in the flotation procedure. Thus it may be added in the conditioner and in most cases this is preferable, or it may be used in desliming, or added directly to the flotation circuit. Obviously, of course, the acid may be added in portions at various points in the flotation operation. The fact that the acid addition is not critical permits a great deal of flexibility in setting up a flow sheet for any given iron ore.

The present invention will be described in greater detail in conjunction with the following specific examples, which are typical of the invention, and which have been chosen to illustrate certain of the ranges within which the invention gives good results. The parts are by weight.

EXAMPLE 1

A typical ore from the Mesabi Range containing about 40% Fe was ground for one minute on a steel rod mill. The ore contained primarily hematite and quartz. The screen analysis of the flotation feed is as follows:

TABLE I

Screen analyses of flotation feed

Tyler Screen Mesh	1 Minute Grind
−48	None
+65	13.14
+100	19.83
+150	16.60
Etc.	Etc.

Two series of tests were made with various organic acids, the first series using Oronite Sodium Sulfonates No. 1, typical mahogany soap sold by the Oronite Chemical Company, and the second series Sherosope L, sold by the Sherwood Refining Company. Both oil soluble petroleum sulfonates were used in the form of 12% aqueous dispersions. The sulfonates, the organic acids and 22° Bé. fuel oil were incorporated with the ore in a conditioner operating at high solids. In each case 3 lbs. per ton of the petroleum sulfonate was used with 4.4 lbs. per ton of the fuel oil and varying amounts of the organic acids. Flotation was effected in a Fagergren flotation machine with one cleaning. Pulp density was standard, about 22% solids, and the rougher float was slightly longer than the cleaner float, in each case being carried out to give optimum results. In each series of tests there was a blank which used the same amount of petroleum sulfonate but no added acid. Conditioning and flotation procedure was otherwise identical.

The following table shows the metallurgical results.

TABLE II

Flotation tests with various organic acids

Acid Used		Cleaner Concentrate			Cleaner Tailing		Rougher Tailing		pH	
Type	Lb./ton	Assay Insol.	Assay Fe	Dist. Fe	Assay Fe	Dist. Fe	Assay Fe	Dist. Fe	Rough. Tail.	Clean. Tail.
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*		
Series 1										
None	None	7.76	58.97	48.94	34.39	13.73	15.58	37.33	7.2	7.4
Formic	3.0	10.82	57.24	80.81	17.89	6.02	6.58	13.17	2.0	2.4
Acetic	3.0	14.74	54.47	75.90	12.41	4.26	10.39	19.84	2.7	3.1
Propionic	3.0	13.54	55.51	67.44	15.88	7.10	13.21	25.46	2.7	3.2
Monochlor Acetic	3.0	9.94	57.64	73.67	19.62	7.65	9.58	18.68	2.8	3.8
CFB α-Hydroxy-Isobutyric	3.5	10.98	57.01	67.97	29.77	15.00	8.89	17.03	3.0	3.4
Amino-acetic	3.5	10.42	57.18	55.56	23.54	9.26	15.58	35.18	4.5	4.7
Series 2										
None	None	5.64	59.83	41.91	36.70	10.97	17.89	47.12	7.2	7.3
Tartaric	3.0	4.38	61.05	51.02	40.68	15.11	14.08	33.87	2.6	3.3
Citric	3.0	4.84	59.89	25.00	48.18	23.05	18.98	51.95	2.9	4.1
Oxalic	3.0	4.48	60.82	41.29	44.31	22.67	14.77	36.04	2.9	4.2
d-Malic	3.0	5.38	60.76	61.17	38.54	15.72	10.56	23.11	2.8	3.6
Lactic	3.0	7.60	58.97	71.51	26.83	10.62	8.89	17.87	3.0	4.6
Toluene	3.0	9.30	57.93	71.22	27.98	8.38	9.81	20.40	3.2	3.2
Sulfonic Maleic Anhydride	3.5	11.50	56.60	76.62	12.92	3.63	10.04	19.75	2.2	2.5
Tannic	3.0	(1)							7.4	7.5
Naphthalene-sulfonic	3.0	5.12	60.76	56.08	33.54	9.41	14.77	34.51	5.7	6.5
Benzoic	3.0	27.86	46.22	48.12	17.25	10.68	21.35	41.20	3.4	4.9
Gallic	3.3	(2)								
Salicylic	3.3	17.34	53.08	49.99	21.00	11.31	18.29	38.70	3.8	6.4
Phthalic	3.3	19.66	51.47	59.06	20.60	13.68	15.06	27.26	3.0	5.0

[1] 1.5% weight in rougher concentration.
[2] 4.3% weight in rougher concentration.
CFB-Acid added in stages as follows:
α-Hydroxy-isobutyric acid—2.5 lb./ton to conditioning; 0.5 lb./ton to cleaning flotation.
CFB p-Toluene sulfonic acid—2.5 lb./ton to conditioning; 0.5 lb./ton to cleaning flotation.
Maleic anhydride—2.5 lb./ton to conditioning; 1.0 lb./ton to cleaning flotation.
Naphthalene β-sulfonic acid—2.5 lb./ton to conditioning; 0.5 lb./ton to cleaning flotation.
In all other tests acid added to conditioning only.

EXAMPLE 2

A low grade Minnesota iron ore having only about 14½% Fe was deslimed, conditioned at

high solids with 2.2 lbs./ton of an equal mixture of Calol, a mahogany soap sold by the Standard Oil Company of California, and SP-1, a mahogany soap sold by the Stanco Distributors, Inc. The mixture was diluted with 10% secondary butanol. Various acids were used as appear below. Rougher flotation only was used. The results appear in the following table:

TABLE III

Acid Used		Concentrate			Tailing	
Type	Lbs./ton	Per cent wt.	Per cent Fe		Assay, per cent Fe	pH
			Assay	Dist.		
Formic	2.5	29.96	38.37	91.22	1.58	2.8
Acetic	2.5	30.51	37.15	89.32	1.95	3.0
Acrylic	2.5	26.70	42.69	90.30	1.67	3.5
Lactic	2.5	26.49	41.67	88.66	1.92	3.5
Tartaric	2.5	19.82	55.54	88.92	1.71	2.8
Maleic anhydride	2.5	22.31	49.10	86.61	2.18	3.5
p-Toluene sulfonic	2.5	23.23	48.08	90.45	1.54	3.1

The examples show the beneficiation of typical high and low grade hematite ores such as are found in the Lake Superior District. Similar results are obtained with ores in which the iron is present in the form of martite, limonite, goethite, magnetite, siderite and ilmenite.

Fuel oil is a satisfactory hydrocarbon to use in conjunction with the oil soluble petroleum sulfonates and because of its cheapness is preferred. However, almost any unsulfonated organic oil may be used instead, results being substantially the same with oleic acid, talloel, cottonseed oil, coconut oil, toluene, or chlorinated kerosene. All of these products being more expensive than fuel oil they are economically less desirable as the results obtained are no better. Apparently the unsulfonated oil acts as a solvent or distributor of the oil soluble petroleum sulfonate and its exact chemical constitution does not appear to materially affect its operation.

The amount of acid is determined by the conditions obtaining in the conditioner itself. However, a rough measure of the amount of acid in its strength is given by the pH of the rougher tailing in the absence of any added alkali. This pH is in the range of 2 to 6, the actual acidity in the conditioning step being, of course, slightly higher, since the dilution to flotation density reduces the hydrogen ion concentration and therefore raises the pH a few points. As it is very difficult to measure pH in the conditioner where the operation is being carried out at high solids, the indirect measure based on the acidity of the rougher tailing is practically more useful. It should be understood, however, that the effect is not due to the pH of the rougher circuit, as this can be altered considerably after conditioning without changing the improved results obtained by the present invention.

All of the oil soluble petroleum sulfonates referred to in the examples under the trade names are typical petroleum sulfonates of the mahogany soap or acid type, as commercially obtained from the treatment of petroleum lubricating oil fractions with sulfonating agents such as sulfuric acid, oleum and the like.

This application is in part a continuation of our copending application, Serial No. 481,906, filed April 5, 1943, Patent No. 2,410,376, issued October 29, 1946.

We claim:

1. A method of beneficiating oxidized iron ores by froth flotation of the ore in the form of an aqueous pulp, which comprises conditioning the ore with an organic acid, having a disassociation constant of at least 10 to the minus 7, said acid being selected from the group consisting of water soluble lower aliphatic monobasic carboxylic acids and aromatic sulfonic acids, the amount of said acid being such that on dilution to froth flotation density and floating, the rougher tailing in the absence of added alkali shows a pH in the range of 2 to 6, and subjecting the aqueous pulp of said treated ore to froth flotation in the presence of a collector for oxidized iron minerals, the major constituent of which is an oil soluble petroleum sulfonate obtained in the refining of petroleum lubricating oils, and removing a concentrate relatively rich in iron and a tailing relatively poor in iron.

2. A method of beneficiating oxidized iron ores by froth flotation of the ore in the form of an aqueous pulp, which comprises conditioning the ore with an unsulfonated oil and an organic acid having a disassociation constant of at least 10 to the minus 7, selected from the group consisting of water soluble lower aliphatic monobasic carboxylic acids and aromatic sulfonic acids, the amount of said acid being such that on dilution to froth flotation density and floating, the rougher tailing in the absence of added alkali shows a pH in the range of 2 to 6, and subjecting the aqueous pulp of said treated ore to froth flotation in the presence of a collector for oxidized iron minerals, the major constituent of which is an oil soluble petroleum sulfonate obtained in the refining of petroleum lubricating oils, and removing a concentrate relatively rich in iron and a tailing relatively poor in iron.

3. A method of beneficiating oxidized iron ores by froth flotation of the ore in the form of an aqueous pulp, which comprises conditioning the ore with acetic acid, the amount of said acetic acid being such that on dilution to froth flotation density and floating, the rougher tailing in the absence of added alkali shows a pH in the range of 2 to 6, and subjecting the aqueous pulp of said treated ore to froth flotation in the presence of a collector for oxidized iron minerals, the major constituent of which is an oil soluble petroleum sulfonate obtained in the refining of petroleum lubricating oils, and removing a concentrate relatively rich in iron and a tailing relatively poor in iron.

4. A method of beneficiating oxidized iron ores by froth flotation of the ore in the form of an aqueous pulp, which comprises conditioning the ore with formic acid, the amount of said formic acid being such that on dilution to froth flotation density and floating, the rougher tailing in the absence of added alkali shows a pH in the range of 2 to 6, and subjecting the aqueous pulp of said treated ore to froth flotation in the presence of a collector for oxidized iron minerals, the major constituent of which is an oil soluble petroleum sulfonate obtained in the refining of petroleum lubricating oils, and removing a concentrate relatively rich in iron and a tailing relatively poor in iron.

5. A method of beneficiating oxidized iron ores by froth flotation of the ore in the form of an aqueous pulp, which comprises conditioning the ore with toluene sulfonic acid, the amount of said toluene sulfonic acid being such that on dilution to froth flotation density and floating, the rougher tailing in the absence of added alkali shows a pH in the range of 2 to 6, and subjecting the

aqueous pulp of said treated ore to froth flotation in the presence of a collector for oxidized iron minerals, the major constituent of which is an oil soluble petroleum sulfonate obtained in the refining of petroleum lubricating oils, and removing a concentrate relatively rich in iron and a tailing relatively poor in iron.

6. A method according to claim 1 in which the conditioning is effected at high solids with both collector and acid substance and the thus conditioned pulp is then diluted to froth flotation density before froth flotation.

7. A method according to claim 2 in which the conditioning is effected at high solids with both collector and acid substance and the thus conditioned pulp is then diluted to froth flotation density before froth flotation.

8. A method according to claim 3 in which the conditioning is effected at high solids with both collector and acid substance and the thus conditioned pulp is then diluted to froth flotation density before froth flotation.

9. A method according to claim 4 in which the conditioning is effected at high solids with both collector and acid substance and the thus conditioned pulp is then diluted to froth flotation density before froth flotation.

10. A method according to claim 5 in which the conditioning is effected at high solids with both collector and acid substance and the thus conditioned pulp is then diluted to froth flotation density before froth flotation.

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