

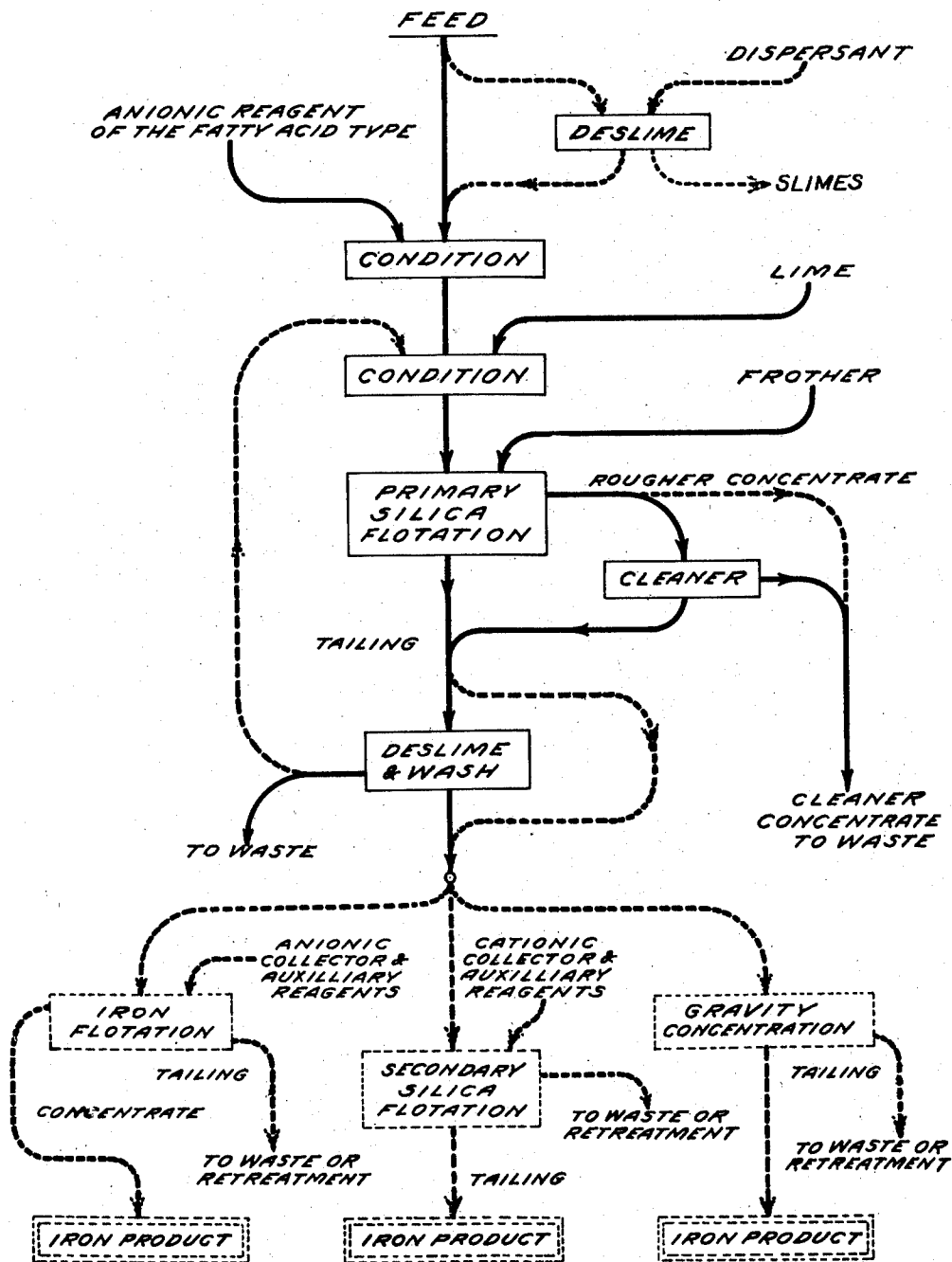
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FROTH FLOTATION OF SILICA FROM IRON ORE BY ANIONIC COLLECTORS

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FROTH FLOTATION OF SILICA FROM IRON
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This invention relates to a pretreating process in the beneficiation of iron ores and constitutes a continuation in part of my copending application for U. S. Letters Patent, Serial No. 468,523, filed December 10, 1942, now Patent No. 2,387,081, granted Oct. 16, 1945.

More particularly, the invention relates to a process of pre-treating low-grade ores by a process of conditioning and flotation. The present process is especially suitable for use on fines such as are found in the overflow from iron ore washer plants; in waste products from heavy-media separation processes and on those ores which must be finely ground in order to unlock the iron minerals from the gangue. Ores treated by the present process are in a particularly suitable condition for the production of a final iron concentrate by further treatment such as by gravity concentration or by further flotation.

Increasing amounts of the lower-grade iron ores, such as those with which the present invention is concerned, are coming into industrial importance because of the constantly decreasing amounts of available high-grade ore. Most of these ores are too low in iron and too high in silica-bearing gangue to be suitable for use in blast furnaces. Consequently, if they are to be used they must be beneficiated in some manner. Frequently, calcium carbonate and other alkaline earth carbonate minerals are also found in the ores. These, of themselves, are not ordinarily particularly objectionable, in fact being to a certain extent desirable, but in some cases it may be necessary to remove a portion of these constituents in order to raise the iron content.

The principal problem in the beneficiation of these low-grade ores is to raise the iron content to 50% or better and preferably to about 55-57%. Usually this involves the removal of silica. The necessary degree of beneficiation can be accomplished in any one of several ways, depending on the ore. In some cases, the necessary rise in iron content may be made by merely subjecting the ore to coarse crushing, followed by washing. Where the iron minerals and the gangue are so tightly locked that this can not be done, but the mineral values can be released without fine crushing or grinding, heavy-media separation is particularly useful.

Much of the naturally-occurring ore, however, requires fine grinding in order to enable separation of the objectionable gangue. After the necessary grinding is done, beneficiation by froth flotation is usually the preferable method of separating the gangue from the mineral values. In addition to the ores of this type, there are also two other sources of fines, which, although too low in iron content for ordinary use, because of the tremendous volumes involved, represent a very large amount of potentially useful iron mineral. These

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are the wastes from the washing and/or the heavy-media processes mentioned above.

As pointed out above, the principal objectionable constituent is usually a silica-bearing mineral of some type. Particularly from the point of view of susceptibility to froth flotation, this is unfortunate since the iron minerals and most silica-bearing gangues are generally difficult to separate. Because of this separational difficulty, a beneficiation process, to be successfully carried out, requires careful and relatively expensive handling, in the case of froth flotation usually also accompanied by a high reagent consumption. All of these factors tend to increase the cost of processing.

Yet iron ores, despite the fact that they must be handled in enormous quantities, are intrinsically cheap products and must be sold for but little more than the actual cost of mining. Therefore beneficiation, if it is to be carried out, must be done cheaply, easily and efficiently. This can not be said to be true of ordinary methods of beneficiating ores, particularly by froth flotation, when such methods are applied to low-grade iron ores.

Ordinarily, separation of mineral values from silica-bearing gangues takes one of two forms; methods which involve gravimetric separation and methods which involve flotation. In the latter case, either the mineral values are floated from the silica by the use of an anionic-type reagent or reagent combination, or the silica is floated from the mineral values by means of a cationic-type of reagent. In general, anionic flotation is the easiest and cheapest and is, therefore, used whenever possible. The general process is old and well known in conjunction with many ores.

Unfortunately, when applied to ordinary low-grade iron ores of the type with which the present invention is concerned, straight anionic flotation as previously practiced does not work well. The iron minerals and the gangue tend to float together. By using sufficient care and enough reagents a beneficiation can be carried out whereby some 30 to 40% of the iron values can be recovered but the grade is usually too low for blast furnace feed. Further, the cost is much higher than is practically desirable for the amount of mineral recovered at the maximum concentrations which are possible.

In like cases with other ores the reverse procedure is useful, i. e. silica is floated from the minerals by means of a cationic promoter. This process when it can be properly used is excellent. However, it suffers from several inherent drawbacks which must be capable of being overcome before the procedure can be said to be properly used. First of all, cationic reagents are expensive, the unit cost being several times that of

equal amounts of anionic-type reagents. They depend for competitive success on the fact that if they can be used effectively, they have a greater collecting power and so can be used in smaller amounts.

However, they must be very efficiently used and this involves a second difficulty, that of slimes. Cationic reagents are particularly sensitive to the presence of slimes, even a fraction of a percent in the pulp being often sufficient to impair the efficiency of the reagent to a point where the reagent cost becomes prohibitive. A balance must be made between the cost of preparing the ore such as the grinding, desliming, etc., the reagent cost, and the amount of mineral recovered. Unfortunately, with most of the low grade iron ores this balance works out unfavorably. The cost of the preparation required plus the reagent cost raises the total above that which can be expended for the amount of ore recovered if the latter is to be sold in a competitive market.

There remains, therefore, a demand for a suitable beneficiation process whereby the iron content of low grade ores, particularly the wastes from washer plants and the like, can be carried out at a cost which will permit the process to be used on a large scale.

It is, therefore, the principal object of the present invention to establish a procedure of preparing the ore for beneficiation by any subsequently desired method. At the same time, it is a further object to provide a method of obtaining the desired results of cheaper and more effective concentration of the iron minerals from low-grade starting materials.

In general, the objects of the present invention are obtained by the use of a new and novel pretreating process of conditioning and flotation. The ore is suitably prepared by conditioning with relatively inexpensive reagents and the bulk of the silica gangue, which may include much of the slimes is then floated away from the ore. Tailings from this procedure contain the bulk of the iron minerals and are in a very suitable condition for further beneficiation.

The exact method by which this final beneficiation is accomplished is not necessarily a limitation on the present process and may be carried out in any suitable manner. For example, it may involve a second flotation, either with an anionic or a cationic collector, or a gravity concentration procedure such as tabling, vanning or the like. Ores pretreated according to the present invention may be readily concentrated by any of these methods to give iron concentrates acceptable in grade for blast furnace feed. At the same time, the recovery is sufficiently high to make the process economically attractive.

The invention will be more fully set forth in conjunction with the accompanying illustration. This latter shows a flow scheme delineating the pretreating steps of the present process. Several optional modifications suitable for use in making the final ore product have also been delineated.

Ore is fed to the process in a size range suitable for use as flotation feed. Usually this will be about minus fourteen mesh, although this is not a limitation on the process. In the case of washer tailings and the like, the ore will ordinarily require no crushing or grinding by way of preparation. If untreated ore is being used it will ordinarily require some grinding to reduce the feed to a suitable size. Optionally, the feed material may be deslimed, making use, if neces-

sary, of a dispersing agent such as sodium silicate or the like to facilitate the separation.

This is followed by perhaps the most critical part of the pretreating process in which the ore is subjected to two successive conditioning steps. In the first of these, the ore is treated with an anionic reagent such as a fatty acid or the like. In the second, an alkaline earth metal oxide, preferably in its hydrated form, such as calcium hydroxide and the like, is incorporated. Addition of the lime or its equivalent in this order is critical, although its exact mode of operation is not fully understood.

A frother is then generally added, although it may be omitted if not required, and the conditioned ore is subjected to a flotation step. From the latter, a primary concentrate high in silica and low in iron is obtained. As shown in the illustration, this primary flotation concentrate may be directly discarded but is ordinarily cleaned before doing so. Although it is usually preferable to carry out this cleaning step by flotation, other methods such as gravity concentration, as for example tabling or vanning, may be employed with advantage on certain types of ores. The rougher tailings, together with the cleaner tailings if a cleaning step is used, may be deslimed and washed if necessary. The slimes are normally discarded but, as shown in the flow sheet may be recycled to the second conditioning step if so desired. The deslimed, washed sands are then ready for final concentration of the iron minerals.

As shown in the drawing, the final iron concentrating process may take any one of several forms. One of these is by the use of suitable anionic-type reagents to float an iron concentrate. One of the best of such procedures is that disclosed and claimed in my copending joint application with R. B. Booth, Serial No. 522,268, filed February 14, 1944, in which the ore is conditioned with a strong acid and the collector and is subjected to flotation. The iron minerals, as shown in that application, may be concentrated by means of a collector comprising a suitably sulfonated hydrocarbon, alcohol, fatty acid, resin acid, talloel, saponifiable glyceride oil and the like. The present process, however, is not meant to be limited thereto and any suitable anionic flotation may be employed. The iron product is collected by flotation and the tailings are ordinarily discarded but may be given further treatment.

Another highly useful process involves concentrating the silicious gangue by flotation using a cationic-type reagent, usually accompanied by a suitable frother. As shown by the flow sheet, these are added to the deslimed sands and the bulk of the residual silica is floated out. Again, the silica concentrate may be directly discarded or may be given additional treatment, as for example cleaned by flotation or the like. In the latter case the cleaner silica concentrate may be discarded and the cleaner tail may be either added to the rougher tail as iron product or may be recycled to the original conditioning step along with the fresh feed. This specific process is more fully described and claimed in my above-identified copending application for U. S. Letters Patent, Serial No. 468,523.

In other circumstances, it may be possible or even advantageous to employ some method of gravity concentration to make the final iron concentration. Tabling, for example, is a commonly used expedient for concentrating iron minerals.

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This has been indicated in the drawing. It was found that ores pretreated by the procedure of the present invention were particularly well suited for use as table feed, the silica being much more easily and thoroughly separated than when no pretreatment is used.

A number of modifications may be made without departing from the scope of the present invention. For example, the grinding step may be carried out after the feed material has been deslimed. Again, where the initial desliming step is not necessary, the grinding operation may be made to serve as the conditioning step, the grinding being carried out in the presence of a fatty-acid type of anionic reagent which is to be incorporated. A dispersant may be added if so desired. As pointed out, each flotation operation may be varied somewhat and the various cleaning operations may be done either by flotation or by gravity concentration or may not be even required. These considerations, however, fall within the skill of the operator and may be varied according to conditions for the particular ore being treated without departing from the scope of the present invention.

An anionic reagent is required in the primary silica flotation step. However, substantially any of the common non-sulfide promoting flotation reagents such as, for example, oleic acid, fish oil fatty acid, coconut oil fatty acid, linseed oil fatty acid, cottonseed oil fatty acid, crude and refined talloel, and the like, their sulfonated derivatives and the sodium, potassium and ammonium soaps and emulsions thereof may be used. These reagents, however, are illustrative only. Others of similar type may be substituted therefor if so desired. Further, oil- or water-soluble sulfonated petroleum hydrocarbons and mixtures of them may be used. Where the expression "anionic reagent of the fatty-acid type" has been used in the instant specification, these types of reagent are indicated thereby. The expression as so used is not intended to include the commonly-designated "non-sulfide" promoters such as the xanthates and the like.

While different ores may require different amounts of anionic reagent to produce an effective silica concentration during the primary silica flotation and the optimum may vary from one reagent to another, the use of the exact optimum is not highly critical. The presence of an excess may cause some overpromotion which in turn may require the use of slightly more lime. Ordinarily, however, a slight excess does not result in an excessive iron loss in the primary silica concentrate. Depending largely on the grade of the ore, the amount of slimes in the ore and the particular reagent chosen, amounts as little as 0.1 lb. per ton to as high as about 5-6 lbs. per ton may be required. For most of the commonly encountered ores, however, from about 0.25 to 3.0 lbs. per ton will be found to produce satisfactory results.

Similarly, substantially any frother which it is desirable to use, because of its cost or availability will give satisfactory results. Among the frothers which were found to be satisfactory are such materials as pine oil, synthetic pine oil, creylic acids, the commercial higher-aliphatic alcohol frothers and mixtures of these with each other or with various modifying agents.

Where a cationic reagent is to be used to carry out a secondary silica flotation the particular reagent chosen is principally dependent upon relative cost and availability. Among the reagents

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found suitable are various aliphatic amines having a carbon content of over about C₁₂ and their salts; quaternary "onium" compounds such as, for example, cetyl pyridinium bromide and the like; and polyalkylene-polyamine reaction product types. Again, these compounds are illustrative only, since many known compounds are commercially available for this purpose.

A particularly important feature of the pretreatment process is the fact that the ore, prior to the anionic flotation step, is conditioned with an alkaline earth metal oxide or hydroxide. The exact mechanism by which this reagent accomplishes its desired function is not fully understood. However, it appears to act in such a manner as not only to serve as a depressant for the iron minerals but also to cause the selective flotation of silica during the pretreatment flotation of part of the gangue. It would appear that it is not only necessary to add the oxide or hydroxide for the purpose of controlling the pH content of the pulp but the fact that the alkaline earth metal hydroxides tend to form insoluble soaps is for some reason of equal if not greater importance. Hydrated lime was found to give excellent results and since it is cheap and readily available is perhaps preferable. However, any of the alkaline earth metals which tends to form an insoluble soap with the fatty acid component of the anionic reagent may be used in the form of their oxides or hydroxides, if so desired.

The invention will be described in greater detail in conjunction with the following specific examples which are illustrative only and are not meant by way of limitation on the scope of the present invention.

EXAMPLE 1

In order to provide a standard to illustrate the advantages of pretreating the ore according to the present invention, a washer tailing sample was subjected to a straight anionic flotation. This material was about minus 48 mesh in size, assayed about 28% iron and contained principally hematite, quartz and some limonite. The ore was made up into a pulp of about 70% solids and then conditioned for 2 minutes with 3.5 lbs./ton of sulfuric acid, 4.6 lbs./ton of fuel oil and 4.0 lbs./ton of mixed oil-soluble petroleum sulfonates. The conditioned pulp was then floated for about 2½ minutes at 23% solids. A rougher concentrate containing about 34% of the iron in a 43% grade was obtained. This is fairly representative of the unsatisfactory results obtained by subjecting ores of this type to a straight anionic flotation.

EXAMPLE 2

By way of comparison, another sample of the same ore used in Example 1 was pretreated according to the present invention and then subjected to the same flotation operation used in Example 1, except that the rougher flotation was followed by cleaning without additional reagents for 1¼ minutes. The pretreating operation comprised conditioning the ore at 23% solids for 1 minute with 0.35 lb./ton of saponified talloel followed by a 10 minute conditioning with 2 lbs./ton of hydrated lime, after which 0.08 lb./ton of pine oil was added as a frother and the conditioned ore floated for 6 minutes. The tailing, which comprised the feed to the anionic flotation analogous to that of Example 1, was thickened by decanting the "fines" and then treated according to the same steps outlined in that example. The results are shown in Table I.

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Table I

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	28.31	100.00
Primary Silica Conc.....	21.60	22.05	16.82
Fines.....	0.94	22.77	0.76
Cl. Iron Conc.....	35.47	61.21	76.70
Cl. Tail.....	2.38	7.83	0.66
Tail.....	39.61	3.62	5.06
Rgh. Iron Conc.....	37.85	57.85	77.36

EXAMPLE 3

Another type of washer reject, minus 10 mesh in particle size, assaying about 40% Fe, principally as hematite associated with a quartz gangue most of which was in fine sizes, was subjected to a procedure similar to that of Example 2. At 23% solids the ore was conditioned successively for 2 minutes with 0.25 lb./ton of soda ash and 0.48 lb./ton of oleic acid and for 3 minutes with 3 lbs./ton of hydrated lime. The conditioned pulp, at a pH of 10.3, was then floated for about 10 minutes with 0.16 lb./ton of pine oil. The tailing was thickened by decanting the fines, made up into a 70% pulp and conditioned for 2 minutes with 5.0 lbs./ton of sulphuric acid, 4.4 lbs./ton of fuel oil and 4.0 lbs./ton of an oil-soluble sulfonated petroleum hydrocarbon. The concentrate was given a 1½ minute cleaning without additional reagents. The results are shown in Table II.

Table II

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	40.45	100.00
Primary Silica Conc.....	19.09	29.71	14.02
Fines.....	0.86	29.82	0.63
Cl. Conc.....	52.26	62.49	80.74
Cl. Tail.....	1.84	10.26	0.47
Tail.....	25.95	6.45	4.14

EXAMPLE 4

In order to show the advantages of the present pretreating process in a gravity separation another sample of the same ore used in Example 3 was pretreated by conditioning at 23% solids for 3 minutes with 2.0 lbs./ton of sodium silicate and 1.07 lbs./ton of saponified talloel and for an additional 3 minutes with 8.0 lbs./ton of hydrated lime. This was followed by a 6 minute flotation with 0.08 lb./ton of an alcohol frother. The tailing from this operation was treated on a Wilfley table. The results are shown in Table III.

Table III

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	40.50	100.00
Primary Silica Conc.....	33.77	23.02	19.19
Tailing.....	66.23	49.42	80.81
Table Conc.....	43.06	56.88	60.47
Table Tail.....	23.17	35.55	20.34

EXAMPLE 5

Another sample of the same ore used in Example 3 was subjected to the pretreating operation of the present invention without being initially deslimed. The ore was conditioned at 23% solids for 2 minutes with 2.0 lbs./ton of sodium silicate and 1.44 lbs./ton of oleic acid followed by a 3 minute conditioning with 5.0 lbs./ton of hydrated lime. The conditioned ore was then floated for 7 minutes with 0.08 lb./ton of an al-

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cohol frother, stage-added during the flotation. The pH in the cell after flotation was about 11. The fines were removed by decantation. The tailing comprised about 70% of the original feed and contained 82% of the iron in a 47% grade.

EXAMPLE 6

Example 5 was repeated on a sample of the same ore which was partially deslimed before being conditioned with 1.0 lb./ton of sodium silicate and 0.72 lb./ton of oleic acid, the test otherwise being identical. Substantially the same results were obtained as in Example 5.

EXAMPLE 7

Another sample of the ore used in Examples 5 and 6 was then quite fully deslimed before being conditioned with 0.5 lb./ton of sodium silicate and 0.72 lb./ton of oleic acid, the other conditions being the same as in Example 5. A concentrate comprising 57% of the weight of the feed and containing 76% of the iron in a 54% grade was obtained. It will be noted that this is good recovery and in a grade which requires but very little further beneficiation. One other distinction between the results in Example 5 and in this test was the reduction of the insoluble content of the tailing or iron product from 29.8 to 19.9.

Comparison of the results obtained in Examples 5, 6 and 7 indicates that the value of desliming and the extent to which it is carried out depends to a considerable extent on the conditions desired. Any of the concentrates obtained in these tests were in suitable condition to be used as feed for subsequent cationic or anionic flotation or as table feed, the principal advantages of the process being to pre-concentrate the ore and place it in a condition in which because of the surface conditions it is particularly susceptible to further treatment. Partial desliming appears to have a practical advantage in that it reduces the anionic reagent requirements in the pretreating process by about half without appreciably altering the results. Complete desliming produces a still further reduction in the required amount of reagents and enables the production of a lighter weight concentrate of higher grade and definitely lower insoluble content, but at the expense of a slightly lower recovery, only 76% of the iron being recovered as against 82% from the non-deslimed and the partially-deslimed ore.

EXAMPLE 8

In order to show the effect of varying the modifying agents during the fatty acid conditioning, a number of samples of a composite washer tailing, assaying about 23% iron and containing principally hematite and quartz with some limonite was subjected to a series of pretreating operations in which the conditions during the anionic reagent conditioning step were varied. In each case the ore was substantially deslimed, conditioned at 70% solids for 1 minute with an anionic fatty-acid reagent followed by a 2 minute conditioning with hydrated lime. The conditioned pulp was diluted to about 23% solids and subjected to a 2½ minute flotation with 0.027 lb./ton of an alcoholic frother. The rougher concentrate was conditioned for 1 minute at low solids with 1 lb./ton of hydrated lime and given a 1½ minute cleaner flotation. The tests principally differed in the reagents used in the first

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conditioning step. The conditioning reagents were as follows:

Sample 1.—0.65 lb./ton of saponified talloel followed by 4.0 lbs./ton of hydrated lime.

Sample 2.—0.50 lb./ton of sodium carbonate and 0.65 lb./ton of saponified talloel followed by 4 lbs./ton of lime.

Sample 3.—0.65 lb./ton of saponified talloel and 0.25 lb./ton of sulfuric acid followed by 5.0 lbs./ton of hydrated lime.

Sample 4.—0.65 lb./ton of saponified talloel, 0.25 lb./ton of sulfuric acid and 0.35 lb./ton of fuel oil followed by 5 lbs./ton of hydrated lime.

Illustrative results are shown in Table IV.

Table IV

	Per cent wt.	Per cent Fe	Per cent distribution
Sample 1:			
Feed.....	100.00	23.01	100.00
Cl. Conc.....	47.68	11.21	23.23
Cl. Tail.....	19.26	23.26	19.47
Tail.....	33.06	39.89	57.30
Comb. Tails.....	52.32	33.77	76.77
Sample 2:			
Feed.....	100.00	22.51	100.00
Cl. Conc.....	54.70	12.53	30.46
Cl. Tail.....	17.67	24.70	19.37
Tail.....	27.63	40.85	50.15
Comb. Tails.....	45.30	34.55	69.54
Sample 3:			
Feed.....	100.00	22.58	100.00
Cl. Conc.....	27.19	6.63	7.98
Cl. Tail.....	28.01	11.93	14.80
Tail.....	44.80	38.92	77.22
Comb. Tails.....	72.81	28.54	93.02
Sample 4:			
Feed.....	100.00	22.83	100.00
Cl. Conc.....	32.17	6.27	8.84
Cl. Tail.....	29.25	16.63	21.31
Tail.....	38.58	41.33	69.85
Comb. Tails.....	67.83	30.68	91.16

From these results it will be seen that in some cases the presence of acid and/or fuel oil during the first conditioning step may be of marked benefit in increasing the recovery.

EXAMPLE 9

In order to show the effect of varying the amount of lime, two additional samples of the same ore treated in Example 8 were deslimed and conditioned for one minute at 70% solids with 0.5 lb./ton of sodium silicate and 1.2 lbs./ton of sulfonated talloel followed by 2 minute conditioning respectively with 4 lbs./ton and with 12 lbs./ton of hydrated lime. The conditioned ore in each case was then floated for 2½ minutes with 0.54 lb./ton of an alcoholic frother and the rougher concentrate given a 1½ minute cleaner flotation without additional reagents. The pH of the rougher tail in the first test was 11.5 and in the second 11.8. The results are shown in Table V.

Table V

	Per cent wt.	Per cent Fe	Per cent distribution
4.0 lbs./ton of Lime:			
Feed.....	100.00	22.96	100.00
Cl. Conc.....	25.87	7.71	8.68
Cl. Tail.....	20.70	11.09	10.00
Tail.....	53.43	34.95	81.32
Comb. Tails.....	74.13	28.29	91.32
12.0 lbs./ton of Lime:			
Feed.....	100.00	22.77	100.00
Cl. Conc.....	30.28	7.47	9.93
Cl. Tail.....	19.72	12.05	10.43
Tail.....	50.00	36.27	79.64
Comb. Tails.....	69.72	29.42	90.07

Obviously the optimum amount of alkaline-earth metal oxide or hydroxide will vary with

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the nature of the ore, the particular fatty-acid type anionic reagent used, the use of acid in the first conditioning step and the like. However, it is only essential in order to depress the iron and activate the silica to have a sufficient amount present to form insoluble soaps of the fatty acid, or its equivalent, and to produce a basic pH. Fortunately, while the presence of an excess produces no particular advantage, it is not objectionable. Therefore a control is simply obtained by adding enough lime during the conditioning operation to insure the production of a pH of about 9.0 or higher. This amount may vary from as little as about 0.5 lb./ton in some cases to as much as about 20.0 lbs./ton in others. Ordinarily, however, from about 2.0 to 8.0 lbs./ton will be found satisfactory with the average feed.

EXAMPLE 10

Another sample of the same ore used in Example 9 was treated to show the critical requirement of conditioning first with the fatty acid reagent and then with the lime. The second test of Example 9 was repeated except that the conditioning with 12 lbs./ton of lime was carried out before the conditioning with the 1.2 lbs./ton of sulfonated talloel and 0.5 lb./ton of sodium silicate. The utility of such a procedure is practically negligible as shown by the results in Table VI.

Table VI

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	22.96	100.00
Conc.....	9.82	10.24	4.38
Tail.....	90.18	24.34	95.62

EXAMPLE 11

A sample of siliceous-hematite iron ore was ground in a wet rod mill at about 60% solids in the presence of about 2 lbs./ton of sodium silicate and 1.5 lbs./ton of talloel. The ground ore was transferred to a Fagergren flotation machine, diluted to about 23% solids, conditioned for 3 minutes with 4 lbs./ton of hydrated lime and floated for 5 minutes. The silica concentrate was given a 3 minute cleaner float, the cleaner silica concentrate being discarded. The rougher and cleaner tails were combined and deslimed by hydraulic classification. The deslimed sands were diluted to about 10% solids and floated for 5 minutes with 0.16 lb./ton of pine oil and 0.15 lb./ton of "Lorol" amine hydrochloride (about C₁₂). The silica concentrate was discarded and the tailing which constituted the iron concentrate was retained as product. The results are shown in Table VII.

Table VII

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	28.80	100.00
Primary Silica Conc.....	56.72	19.27	37.95
Slimes.....	5.16	48.11	8.62
Secondary Silica Conc.....	17.26	22.52	13.85
Product.....	20.86	54.67	39.58

EXAMPLE 12

A sample of an ore similar to that used in Example 11 was ground at 60% solids for 12 minutes using 2 lbs./ton of sodium silicate as a dispersant. The ground ore was then subjected to a desliming operation by hydraulic classification.

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The slimes were discarded and the deslimed sands subjected to a double conditioning step. In the first step the sands were conditioned for 3 minutes with 0.5 lb./ton of talloel and in the second step with 2.0 lbs./ton of hydrated lime. 0.054 lb./ton of pine oil were then added and the pulp floated for 4 minutes. The silica concentrate was cleaned using 1 lb./ton of hydrated lime and 0.027 lb./ton of pine oil, the silica cleaner concentrate being discarded. The combined rougher and cleaner tails were again deslimed, the slimes being discarded and the underflow subjected to flotation for 3 minutes at 13% solids in the presence of 0.189 lb./ton of pine oil and 0.15 lb./ton of n-octadecylamine. The silica concentrate was discarded and the tailing constituting the iron concentrate retained as product. The results are shown in Table VIII.

Table VIII

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	28.74	100.00
#1 Slimes.....	9.97	46.63	16.18
Primary Silica Conc.....	36.37	15.01	19.00
#2 Slimes.....	2.81	46.93	4.59
Secondary Silica Conc.....	27.51	16.37	15.66
Product.....	23.34	54.90	44.57

EXAMPLE 13

By way of comparison with Example 12 a sample of a similar ore was ground, deslimed, conditioned with a sufficient amount of the same cationic reagent to give the maximum recovery and grade, the amount being determined by experiment. Using several times the amount of cationic reagent required for the procedure of Example 2, an iron concentrate was obtained representing 18% by weight of the original ore, assaying 56.32% iron and containing 35% of the total iron. The much less expensive procedure of the present invention therefore gave a substantially higher recovery at a substantially equivalent grade.

EXAMPLE 14

A sample of tailings from a Minnesota iron ore washer plant principally composed of hematite and quartz and containing about 19.8% iron was deslimed with 1 lb./ton of sodium silicate as a dispersant. The deslimed sands were then treated according to the conditioning and flotation procedure of Example 2 using oleic acid as the anionic reagent and "Lorol" amine hydrochloride as the cationic reagent. The results are shown in Table IX.

Table IX

	Per cent wt.	Per cent Fe	Per cent distribution
Feed.....	100.00	19.85	100.00
#1 Slimes.....	19.21	18.71	18.11
Primary Silica Conc.....	35.20	8.24	14.61
#2 Slimes.....	1.20	18.47	1.12
Secondary Silica Conc.....	25.22	11.35	14.42
Product.....	19.17	53.57	51.74

Comparison of these results with the results obtained using the best single stage flotation procedure and employing cationic flotation reagents indicates that by the process of the present invention, even a low grade feed such as the washer wastes of Example 14, yields a greater quantity of concentrate of satisfactory grade. This concentrate is not only obtained from a

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poorer feed but was obtained at a much smaller cost. While the concentrate is two points less in grade, it represents a much greater proportion of the total iron content in the feed.

EXAMPLE 15

A sample of Arizona iron ore containing magnetite, hematite and quartz was ground at about 60% solids for 10 minutes in a wet rod mill. The conditioning and flotation procedure of Example 2 was carried out on the ground ore with the exception that 1 lb./ton of $\text{Fe}_2(\text{SO}_4)_3$ was added during the first conditioning stage in addition to the other reagents. The results are shown in Table X.

Table X

	Per cent Wt.	Assay		Distribution	
		Per cent Fe	Per cent Insol.	Per cent Fe	Per cent Insol.
Feed.....	100.00	32.48	45.09	100.00	100.00
Primary Silica Conc.....	39.30	20.70	62.00	25.05	54.05
Secondary Silica Conc.....	31.80	28.46	50.32	27.86	35.86
Product.....	28.90	52.92	16.32	47.09	10.47

I claim:

1. In a method of beneficiating iron ores containing silica-bearing gangue by froth flotation, an ore pretreatment process which comprises the steps of making a pulp of ore having a particle size suitable for use as flotation feed, subjecting the pulp to two successive conditioning operations, in the first with an effective amount of an anionic reagent selected from the group consisting of the long-chain, aliphatic fatty-acids, talloel, sulfonated derivatives of these materials, oil-soluble, sulfonated petroleum hydrocarbons, water-soluble, sulfonated petroleum hydrocarbons, the sodium, potassium and ammonium soaps of such materials and mixtures thereof, and in the second with at least a sufficient amount of an alkaline-earth metal oxide to convert the anionic reagent to insoluble soaps thereof and to produce an alkaline pH, and subjecting the conditioned pulp to a froth flotation operation whereby a concentrate relatively rich in silica and a tailing containing a major proportion of the iron minerals are produced.

2. A method according to claim 1 characterized in that the feed is at least partially deslimed prior to being conditioned with the anionic reagent.

3. A process according to claim 1 characterized in that the ore is ground to a size suitable for flotation and the first conditioning operation is carried out simultaneously with the grinding.

4. A process according to claim 1 in which the alkaline-earth metal oxide comprises calcined lime.

5. A method of beneficiating iron ores containing silica-bearing gangue by froth flotation which comprises the steps of making a pulp of ore having a particle size suitable for use as flotation feed, subjecting the pulp to two successive conditioning operations, in the first with an effective amount of an anionic reagent selected from the group consisting of the long-chain, aliphatic fatty-acids, talloel, sulfonated derivatives of these materials, oil-soluble, sulfonated petroleum hydrocarbons, water-soluble, sulfonated petroleum hydrocarbons, the sodium, potassium and ammonium soaps of such materials and mixtures thereof, and in the second with at least a suffi-

cient amount of an alkaline earth metal oxide to convert the anionic reagent to insoluble soaps thereof and to produce an alkaline pH, subjecting the conditioned pulp to a froth flotation operation, whereby a concentrate, relatively rich in silica and a tailing, containing a major proportion of the iron minerals are produced, subjecting the tailings to a desliming operation and subjecting the deslimed sands to further beneficiation to increase the iron content to at least that required for blast furnace feed.

6. A process according to claim 5 in which the further beneficiation comprises making a pulp of the pretreated ore, conditioning the pulp with a strong acid and an anionic reagent, selected from the group consisting of products obtained by sulfonating petroleum hydrocarbons, fatty acids, resin acids, talloel, saponifiable glyceride oils, and long-chain alcohols, and subjecting the conditioned pulp to froth flotation, whereby a concentrate rich in iron and relatively free from silica-bearing gangue is floated away from a tailing containing a major portion of the gangue.

7. A process according to claim 5 in which the further beneficiation comprises a gravity concentration operation in which a concentrate suitable for use as blast furnace feed is separated from a tailing relatively low in iron content and containing a major portion of the gangue remaining after the pretreating operation.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,914,695	Lange	June 20, 1933
2,230,565	Gaylor	Feb. 4, 1941
2,257,808	Phelps	Oct. 7, 1941
2,310,240	Keck	Feb. 9, 1943
1,979,324	Gaudin	Nov. 6, 1934
2,014,405	Weed	Sept. 17, 1935
2,195,724	Gaudin	Apr. 2, 1940
2,120,217	Harris	June 7, 1938
2,166,093	Harwood	June 11, 1939
2,162,494	Trotter et al.	June 13, 1939
2,028,742	Frantz	Jan. 28, 1936
2,331,722	Patch	Oct. 12, 1943
1,952,907	Christmann	Mar. 22, 1934
1,996,021	Klosky	Mar. 26, 1935
2,364,618	Brown et al.	Dec. 12, 1944
2,364,777	Brown et al.	Dec. 12, 1944
2,364,778	Brown et al.	Dec. 12, 1944
2,389,727	Herkenhoff	Nov. 27, 1945
2,387,081	Herkenhoff	Oct. 16, 1945

OTHER REFERENCES

- Keck et al., "Flotative Properties of Hematite,"
 30 A. I. M. E., T. P. 763 (1937), Mining Technology,
 p. 23.