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FROTH FLOTATION OF IRON IMPURITIES
FROM FELDSPARElmer William Gieseke, Old Greenwich, Conn.,
assignor to American Cyanamid Company, New
York, N. Y., a corporation of MaineNo Drawing. Application November 24, 1945,
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4 Claims. (Cl. 209-166)

1

This invention relates to the beneficiation of feldspars and feldspathic materials. In particular, it concerns an advantageous treatment of those ores of feldspathic materials in which excessive amounts of iron-bearing impurities must be reduced.

Feldspars and feldspathic materials, as used in the glass, pottery and other ceramic industries, are ordinarily subjected to specific limitations as to maximum iron content. This is done in order to eliminate undesired color which might be imparted to the finished articles by iron-bearing minerals during manufacture. The desired minerals are usually some form of aluminum-bearing silicates, accompanied in the ore by gangue comprising silica and other siliceous constituents, commonly iron-bearing. Therefore, in addition to the maximum "iron" limitations, a minimum alumina content is also frequently specified.

For these reasons the present invention may be considered as concerned with the separation of silica and iron-bearing silicates from non-ferrous silicates generally and non-ferrous aluminum-silicates specifically. Accordingly, in the present specification and claims the term "feldspathic materials" is used to include ores of feldspar, aplite, nepheline-syenite, kyanite, sillimanite and the like in which a feldspathic non-ferrous silicate or non-ferrous aluminum silicate constitutes the desired constituent.

Reference to the undesirable constituents as "iron minerals" or as "iron-bearing" substituents is quite general in commercial practice. This is true even though such substituents may not be oxidized iron minerals per se, although the latter, as for example in hematite, limonite, magnetite, ilmenite and the like are commonly present in varying amounts, ordinarily small. Most of the undesirable ferrous metal content is present in combination with other elements in silicates, particularly complex silicates containing in addition oxides such as those of lithium, potassium, barium, calcium, magnesium, aluminum and the like. In the present specification and claims, therefore, the expression "ferrous metal" is used to designate only minerals containing iron as an essential constituent of the composition, as for example in hematite or biotite, and "iron-bearing" is used to indicate a broad group including silicates such as pyroxenes, amphiboles, micas,

2

tourmaline, serpentine, and the like in which ferrous metal itself need not necessarily be a constituent but may be present. Small amounts of iron sulfide minerals such as pyrite and pyrrhotite also are frequently found.

Requirements as to maximum iron-bearing content and minimum aluminum content are becoming increasingly rigid. While abundant deposits of feldspathic materials are common, unfortunately it is becoming increasingly difficult to find natural deposits which meet industrial specifications. Beneficiation operations, as by tabling, flotation and/or magnetic separation, are therefore becoming increasingly important considerations in commercial practice. For a number of reasons beneficiation by froth flotation is generally accepted as preferable where it can be used.

However, in the past the beneficiation of lower grade natural deposits by froth flotation has been found to be neither simple nor inexpensive. Anionic flotation with the usual types of fatty-acid, resin-acid or soap type promoter has been found ineffective in separating the desirable from the undesirable silicates. While silica and some silicates, for example some clays, micas and the like, can be floated with a cationic type of reagent, the latter are not always effective in separating one silicate from another. Moreover, these reagents are not inexpensive, are not particularly effective on coarser sized particles and are extremely sensitive to slimes. To take advantage of their particular selectivity, they must be used carefully on an ore which has been properly ground and very completely deslimed. Desliming is so critical that the degree required may make the process economically impractical. Further, separation of some iron-bearing silicates, for example, iron-bearing tourmalines, biotite and the like from feldspar usually requires a secondary flotation and/or magnetic treatments. While such methods, or a combination of them, can often be worked out to produce an effective separation, such procedures in practice are both complicated and expensive.

There remains therefore a demand for a suitable operation, whereby the iron content may be reduced below the desired maximum in a simple, relatively-inexpensive operation and one which, if necessary, permits raising the aluminum con-

tent to a point above a specified minimum. Preferably also, the process should economically employ reagents which are readily obtainable and they should be used in a manner in which they are not hindered by the presence of slimes. It is, therefore, the principal object of the present invention to provide such a process together with suitable reagent combinations adapted to produce useful results when used therein.

Contrary to the most successful practice in the prior art of concentrating silica and silicates by froth flotation with a cationic promoter, followed if necessary by magnetic separation, the process of the present invention first employs an inexpensive, simple and effective anionic flotation of iron-bearing minerals from the feed. This is accomplished by using a promoter, comprising a suitable sulfonated organic compound in an acid circuit of the correct pH. To increase the aluminum content of the residual tailing, which may contain excessive amounts of silica and non-ferrous silicates, this is followed, if so desired, by a cationic flotation in which a concentration of the non-ferrous, aluminum-bearing silicates is carried out. The effectiveness of this treatment is particularly remarkable when it is considered that the iron content in the feed is considerably lower than that of the flotation tailings obtained in any practical treatment of commercial iron ores.

The problems solved by the process of the present invention are well illustrated in the beneficiation of feldspar itself. Feldspar is usually considered to be an aluminum silicate containing oxides of sodium, potassium or calcium. As found in natural deposits, feldspar minerals usually are accompanied by one or more impurities of a wide range including quartz or silica, micaceous and/or ferrous metal silicates such as biotite tourmaline and the like, and also by high aluminum content silicates such as kyanite and spodumene. In addition, at least traces of iron oxide minerals such as hematite, limonite and the like are almost always present. The problem, then, is to reduce the content of silica and ferrous metal oxides or silicates while retaining as high a content as possible of the desirable non-ferrous, aluminum silicates.

When an attempt is made to do this with ordinary anionic reagents of the fatty-acid, resin-acid or soap type, little or no selectivity is found. Use of various depressants, froth modifiers, supplementary promoters and the like have not been found satisfactory in effectively modifying the action of the usual anionic promoters. Nevertheless, because an anionic flotation is usually one which is less sensitive to slimes and generally employs less expensive reagents, it is to be industrially preferred.

It is, then, a feature of the present process that it successfully employs anionic flotation. The novel anionic promoters used may be designated generally as sulfonated petroleum hydrocarbons. Three types have been found to be particularly useful: (1) the oil-soluble, water-insoluble, water-dispersible, sulfonated petroleum hydrocarbons; (2) the water-soluble, sulfonated petroleum hydrocarbons of the "green acid" type; and (3) mixtures thereof.

Such sulfonated products are commercially available in a number of different forms. However, as shown, for example, in U. S. Patent 2,331,049, their principal source is as by-products from the refining of petroleum lubricating oil fractions in the course of treatment with fuming

sulfuric acids or sulfuric acids. When so produced, these by-products are generally found to be salts of the sulfonated hydrocarbons, most commonly the sodium salt although other salts may be encountered. In some cases no attempt has been made to neutralize the acid product. Even after neutralization, free sulfonates and/or sulfates are often found.

In general, the oil-soluble, water dispersible group of sulfonates used are those characterized as "mahogany sulfonates," or when neutralized with alkali, as "mahogany soaps," because of the characteristic color which is usually, though not necessarily, present in a solution thereof. The water-soluble products are derived from the water-soluble sulfonate portions which are separated from the same treatments. From their characteristic color which is normally present in solution, the water-soluble types are often designated as "green" acids, or when neutralized as "green soaps." They constitute an entirely different class of materials from the so-called "kerosene acid sludge" products. They differ not only in their different source, the refining of lubricating oils, but in appearing to have a much higher content of carbon atoms, apparently 18 or more and usually around 20-24 as compared with the 12-14 or less of the kerosene products, and even more importantly, in their effectiveness in use.

For many purposes in the process of the present invention it has been found desirable to use a mixture of both the mahogany and the green type of sulfonates. In this way it is possible to take advantage of the most useful properties of each to obtain a result which in general is better than either will produce when used alone.

Oil-soluble, water-dispersible, sulfonated petroleum hydrocarbons have been suggested for the concentration of non-metallic minerals, metallic sulfide minerals and certain oxidized metal ores. However, their direct substitution for such anionic promoters as resin acids, fatty acids, soaps and the like in an attempt to beneficiate feldspathic materials by the conventional anionic flotation of the prior art produces no particularly useful result. No useful separation of ferrous-metal silicates and/or silica from the desirable constituents is obtained. Nor is any better success obtained by trying as substitutes water-soluble, petroleum sulfonates of the green acid type, either alone or mixed with oil-soluble, water-dispersible sulfonates. It is a feature of the present invention that the effective separation of ferrous-metal silicates from the other constituents must be effected under acid conditions. Not only must the circuit be acidic but the degree of acidity must be controlled. If the pH is too high, for example, more than about 4.5 to 5.0 effective flotation of the ferrous-metal silicates may be obtained but in addition substantially all of the other silicates float therewith. On the other hand, if the pH becomes too low, lower than about 2.5-2.8, the depressing action of the acid begins to be noticeable not only on the non-ferrous-metal silicates but also on the ferrous-metal silicates. Again no separation of any particular utility is obtained. It is important therefore that the pulp to be treated have a pH in the range of about 2.5 to 5.0 at flotation densities.

Any acid or acid-liberating compound which will produce the desired pH may be used. It should be one which does not contain cationic

5

groupings which interfere with successful flotation. Of the material available, sulfuric acid is probably the most practical from a commercial point of view because of its low cost and availability. However, in some cases other acids such as hydrochloric or even acetic acid, because of particular local conditions, may be economically competitive.

Both or either of the oil-soluble, water-dispersible sulfonates or the water-soluble sulfonates may be used in a crude or semi-refined or fully refined condition. Usually the only noticeable effect of purification is in relation to the amount which is required for a given flotation. The expression "sulfonated" is generically used and does not exclude the presence of some of the sulfur in sulfate groupings since the latter are usually present, at least in small amounts. Similarly, the sulfonates may be wholly or partially neutralized, as with sodium, potassium or ammonium ions. All or part of the sulfonated material therefore may be present as a "soap" or salt. The sulfonated compounds are those customarily used because of their availability. Similar compounds which are phosphoretted rather than sulfonated are highly successful in use. However, their practical utilization is limited by the lack of a commercial source.

The amount of such reagent used will obviously vary in accordance with a number of conditions. The principal variants are occasioned by the amount of the undesirable constituents which must be removed, the physical condition of these constituents, and the content of available sulfonated compound in the particular reagent used, i. e., the degree of purity. For normal operation it is usually found that the amount of reagent required will be equivalent to about 0.1 to 3.0 lbs./ton of ore treated.

The larger amounts of reagent, even in some cases exceeding 3 lbs./ton, are usually found to be required when much of the undesirable material is present as slimes or when the ore to be beneficiated is particularly high in micaceous material. In such cases an economic balance will usually show that it is preferable to carry out a partial desliming operation, as by screening or hydraulic separation, before flotation, thereby reducing reagent consumption.

In some cases excessive reagent consumption also can be partially offset by the addition of an oiling agent. Particularly is this true in making use of the water-soluble sulfonates. In such a case the oiling agent not only aids in slimes control but also may act as a froth controlling agent and be of assistance in insuring a good separation. Substantially any oiling agent may be used. Probably the simplest, most readily available and cheapest are the petroleum hydrocarbon oils, as for example kerosene and fuel oils. If desired, however, these may be effectively replaced by saponifiable glyceride oils such as corn oil, coconut oil, fish oil and the like; or by higher certain fatty acids such as oleic acid and the like having oily characteristics or even by a fatty acid-resin acid mixture such as is found in talloel.

Obviously the degree to which beneficiation can be effected and still have a useful recovery will depend to considerable extent on the nature of the iron-bearing constituent which is to be removed. In an ore in which the iron-bearing constituent is relatively "free" or easily liberated, the extent to which it can be removed while still obtaining good recovery is quite high. Thus, for example, ores which may assay as high as 1.5-

6

2.0% of Fe_2O_3 in a free, or readily freed, condition may be readily reduced to below the maximum required for even the highest grades. On the other hand, when much of the iron is present, for example, as micaceous silicates meeting such low limits of iron content in the eventual product is much more difficult to obtain with a high recovery.

Preferably, but not necessarily, the ore to be treated should be conditioned with the reagents before being subjected to froth flotation. In so doing, better results are usually obtained if the conditioning is carried out on an aqueous pulp of the ore having a high solids content of 30-70% usually 50-60%. This pulp is then diluted to flotation density, usually before or during transfer to the flotation cell or cells. Where equipment is not available, acceptable results may usually be obtained by conditioning with the reagents at flotation density. Particularly is this true if the process water is recycled and reused. In some cases good results may be had even by adding the reagents directly to the flotation cells.

As noted above, it may be desirable to deslime the ore before conditioning it with the flotation reagents. It is, however, an advantage of the present process that this is not a limitation to the extent that it is in cationic flotation operations of the prior art. As noted above, the tendency of the presence of slimes is to increase reagent consumption and lower somewhat the effectiveness of separation. Where it is determined that desliming is more economical than to permit high reagent consumption, simple desliming, as by hydraulic classification, is usually adequate. Conventionally used reagents such as soluble silicates, alkaline phosphates and the like may be used as dispersants if so desired.

Ferrous-metal minerals frequently are present in the materials as stains of hematite or the like. In preparing ore for desliming, a scrubbing in the presence of a strong alkali, using from about 0.5 to 1.5 lbs./ton of caustic, or the equivalent, is often desirable. This not only is helpful in dispersing the slimes but also assists in the separation of at least a part of the staining iron.

The practice of the present invention will be illustrated in conjunction with the following examples which are intended to be illustrative only and not by way of limitation. All parts are by weight unless otherwise noted.

EXAMPLE 1

In order to illustrate the practice of the prior art in attempting to use soaps as a promotor for silicate minerals in the presence of lime or other alkaline metal ions, a sample of feldspar ore containing feldspar, quartz, mica, tourmaline and garnet and having considerable iron staining on the feldspar was ground, pulped with water to about 22% solids, conditioned for 1 minute with 3 lbs./ton of lime and floated for 4 minutes with 1 lb./ton of talloel sodium soap. Since it was apparent by visual observation that the full possibilities of concentration were not exhausted, 1 lb. of crude octadecylamine acetate was then added to the flotation cell and a second concentrate was taken over a period of 2 minutes. As shown in the following Table I, the test which is typical of attempts at either soap flotation or cationic flotation shows some selectivity. However, the Fe_2O_3 assay was not reduced to any great extent and the tailing contained only 26% of the alumina. The results are far from satisfactory.

7
Table I

	Per Cent Weight	Per Cent Assay		Per Cent Distribution	
		Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃
Feed.....	100.0	18.08	0.172	100.00	100.00
Conc. #1.....	42.7	15.62	0.248	41.48	61.63
Conc. #2.....	34.3	15.22	0.102	32.46	20.35
Rougher Tail.....	23.01	18.19	0.136	26.06	18.02

EXAMPLE 2

In order to show the effectiveness of the present process using sulfonated petroleum hydrocarbons in acid circuit, a series of tests was carried out on a feldspar ore which contained considerable quartz, mica and iron silicates. The ore was reduced to size for flotation feed, pulped to about 65% solids with water, and conditioned for 2 minutes with 0.60 lb./ton of sulfuric acid, 1.27 lbs./ton of fuel oil, 0.09 lb./ton of "Aerofloat 31" and with a promotor. The latter were various sulfonated petroleum hydrocarbons as shown in the following table, which also summarizes the metallurgical results. In the table, promotor A is an oil-soluble, water dispersible sulfonated petroleum hydrocarbon, and promotor B is essentially a water-soluble sulfonated petroleum hydrocarbon of the green type containing about 20-24 carbon atoms. The "Aerofloat 31" reagent used in this and subsequent tests comprises about 6% thiocarbanilid dissolved in dicresyl dithio phosphoric acid. As used in the process of the present invention it appears to have a beneficial effect on the froth quality.

Table II

	Assays, percent		Distribution, Fe ₂ O ₃ , percent	Promotor, lbs./ton	
	Weight	Fe ₂ O ₃		A	B
Test 1:					
Conc.....	5.20	2.91	61.38	0.75	-----
Tail.....	94.80	0.10	38.62		
Feed.....	100.00	0.246	100.00		
Test 2:					
Conc.....	5.93	2.69	67.80	0.50	0.50
Tail.....	94.07	0.081	32.20		
Feed.....	100.00	0.236	100.00		
Test 3:					
Conc.....	5.99	2.46	68.69	0.25	0.75
Tail.....	94.01	0.071	31.31		
Feed.....	100.00	0.214	100.00		
Test 4:					
Conc.....	6.13	2.25	64.49	0.10	0.90
Tail.....	93.87	0.081	35.51		
Feed.....	100.00	0.214	100.00		
Test 5:					
Conc.....	4.54	2.53	48.12	-----	1.00
Tail.....	95.46	0.13	51.88		
Feed.....	100.00	0.239	100.00		

From the foregoing table it will be seen that even when no particular attempt is made to obtain the best possible combination of steps, the reagent combination comprising about 25% oil-soluble, water-dispersible and 75% water-soluble petroleum sulfonates produced the best results. It should be noted, however, that the other reagent combinations are all definitely superior to the results obtained in Example 1. The results indicated in the above table were found to be generally applicable to the concentration of feldspar ores, i. e., mixtures containing from about 50% to about 85 or 90% of water-soluble sulfonates and from about 10 or 15% to about 50% oil-soluble, water-dispersible sulfonates generally give better results. The exact proportions, however, vary somewhat with the amount of oiling

8

agent used. Where in the following examples and claims a mixture of oil-soluble, water-dispersible and water-soluble petroleum sulfonates is indicated, a mixture within this range of 15 to 50% of oil-soluble sulfonates is that used.

TREATMENT OF SLIMES AND STAINS

EXAMPLE 3

As was pointed out above, under certain circumstances the reagent consumption may be advantageously decreased by partial desliming. In order to illustrate this, a sample of feldspar ore containing mica and iron silicates with considerable iron oxide staining of the feldspar was subjected to a number of treatments. The ore before treatment had approximately the following chemical analysis.

	Percent
SiO ₂	74.00
Al ₂ O ₃	16.11
Fe ₂ O ₃	0.19
CaO.....	0.90
MgO.....	(trace)
K ₂ O.....	4.59
Na ₂ O.....	4.59
Na ₂ O.....	4.34

In the first test the ore was reduced to a suitable size for froth flotation, pulped with water, and without further treatment conditioned at 68% solids for 2 minutes with 0.66 lb./ton of H₂SO₄, 0.77 lb./ton of fuel oil, 0.05 lb./ton of "Aerofloat 31" and 1.67 lbs./ton of mixed petroleum sulfonates, approximately 25% being oil-soluble, water-dispersible. The treated pulp was then reduced to flotation density and subjected to froth flotation for 3 minutes. Visual observation indicated that insufficient iron was floated to be useful and the products were discarded.

EXAMPLE 4

Another sample of the same ore, after being size reduced and pulped with water, was deslimed hydraulically in the presence of 0.135 lb./ton of caustic soda. The deslimed sands were then conditioned in the same way with the same reagents as in Example 3 and given the same flotation. The results are shown in the following Table III.

Table III

	Per Cent Wt.	Assays, Per Cent		Distribution, Per Cent	
		Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃
Feed.....	100.00	16.11	0.26	100.00	100.00
Conc.....	8.36	1.78	1.78	57.63	57.63
Tail.....	89.89	14.22	0.11	79.33	38.22

The above results indicate the beneficial effect of treating the ore with caustic soda and desliming prior to flotation.

EXAMPLE 5

A third sample of the same ore, after being size reduced and pulped to about 64% solids, was scrubbed for 2 minutes with 0.13 lb./ton of caustic soda in a flotation machine with the air inlet closed. The treated pulp was then deslimed hydraulically and the sands conditioned and floated with the same reagents and in the same way as in Examples 3 and 4. As shown in the following Table IV, the results are considerably better than simple desliming in the presence of caustic soda. Presumably, but not necessarily,

this is due to the effect of the scrubbing action on the iron staining.

Table IV

	Per Cent Wt.	Assays, Per Cent		Distribution, Per Cent	
		Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃
Feed.....	100.00	16.11	0.25	-----	-----
Conc.....	12.77	-----	1.50	-----	76.10
Tail.....	84.58	14.55	0.053	76.41	17.92

EXAMPLE 6

Because acid leaching as well as caustic leaching is practiced in the treatment of feldspar ores, the preceding example was repeated on another sample of the same ore except that 0.25 lb./ton of sulfuric acid rather than the caustic soda was used in the scrubbing treatment. The results were very poor and the products were discarded without analyzing them.

The observations obtained in the preceding tests were found generally applicable to the beneficiation of feldspar ores in which there is appreciable iron staining and/or in which there is a considerable excess of micaceous silicates. The scrubbing with caustic soda followed by desliming is generally found to produce better results than straight desliming either with or without alkali. Scrubbing in the presence of acid in general proved to be rather ineffective.

EFFECT OF VARIATING pH AND AMOUNT OF PROMOTER ON IRON FLOTATION

EXAMPLE 7

In order to illustrate the effect of varying the amount of promoter for the iron, a series of tests were carried out in which additional samples of the same ore treated in Examples 3 to 6 were scrubbed with caustic soda and deslimed as in Example 5. Sample A was conditioned at about 65-70% solids with 0.33 lb./ton of sulfuric acid, 0.77 lb./ton of fuel oil (22° Bé.), and 0.56 lb./ton of an approximately 1-3 mixture of oil-soluble, water-dispersible, and water-soluble petroleum sulfonates. After dilution to about 29% the pulp

was subjected to froth flotation for 4 minutes and the concentrate collected. Sample B was then treated in the same manner but the amount of petroleum sulfonates was increased to 1.12 lbs./ton. Sample C was also treated in the same way but using 1.67 lbs./ton of the mixed petroleum sulfonates. The metallurgical results are shown in Table V. It will be noted from Table V that because of the acidic nature of these particular sulfonates, varying the amount thereof has an effect on the pH of the pulp. When this occurs in plant practice where the pH is controlled it must be allowed for in regulating amounts of acid to be added. It will also be noted that while the recovery of iron in the concentrate was better in the case of Sample C than for Sample B, the alumina assay of the tail of Sample C is poorer, indicating the optimum quantity of promoter to lie between 1.12 and 1.67 lbs./ton in the case of this particular ore. Ordinarily, however, the lower iron content in the tailing is more important at this stage than the question of recovery. In plant practice, therefore, the results obtained with Sample C would probably be preferable as producing a tailing assaying less than 0.1% of Fe₂O₃.

Table V

Sample	Promoter, lbs./ton	pH pulp	Per cent Wt.	Assays, Per cent		Distribution, Per cent	
				Fe ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃
A.....	0.33	5.2	(Poor float—discarded)				
B.....	1.12	4.6	Feed.....	100.00	0.25	16.11	100.00
			Conc.....	7.41	1.88	-----	55.82
			Tail.....	89.99	0.10	15.29	37.35
C.....	1.67	4.0	Feed.....	100.00	0.32	16.11	100.00
			Conc.....	8.94	2.64	-----	75.40
			Tail.....	89.72	0.08	15.23	21.72

EXAMPLE 8

In order to show the effect of varying the amount of acid used, the test procedure used in Example 7, Sample C, was repeated on additional samples of the same ore except that different amounts of acid were present during the conditioning operation. The conditions otherwise were identical to those in the treatment of Sample C. The results are shown in the following Table VI. It also will be seen therefrom that while, within limits, a continued decrease in the Fe₂O₃ content of the tailing can be effected, it is done at the expense of the Al₂O₃ content. Therefore the amount of acid used must be considered from the point of view of the maximum Fe₂O₃ permitted by the specifications to be met. Ordinarily, however, as noted above low iron content is preferable to high recovery since untreated ore is both cheap and unsaleable. In most plant operations the results obtained on Sample E would be preferred.

Table VI

Sample	H ₂ SO ₄ , lb./ton	Per cent Wt.	Assays, per cent		Distribution	
			Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃
D.....	0	(Poor float—discarded)				
C.....	0.33	Feed.....	100.00	0.32	100.00	100.00
		Conc.....	8.94	2.64	-----	75.40
		Tail.....	89.72	0.08	84.79	21.72
E.....	0.66	Feed.....	100.00	0.25	100.00	100.00
		Conc.....	12.77	1.50	-----	76.10
		Tail.....	84.58	0.05	76.41	17.92

11 EXAMPLE 9

To illustrate further that sufficient acid to activate the ferrous metal silicates must be used but excessive amounts do little if any good, the following tests on another ore of similar type were conducted. Samples were ground to suitable size, pulped with water to about 60% solids, scrubbed for two minutes with 0.133 lbs./ton of NaOH and deslimed hydraulically. Four samples were then conditioned for two minutes at about 60-70% solids with 1.11 lbs./ton of the mixed sulfonates used in Examples 7 and 8, 0.77 lb./ton of fuel oil (22° Bé.) and varying amounts of H₂SO₄. The pulp was then diluted to about 27% solids, subjected to froth flotation, the concentrate removed and the rougher tailing collected. The results are shown in Table VII.

For comparison of the effect of varying the other reagents, additional samples were also treated by the procedure used on Sample G except for the changes footnoted at the bottom of Table VII.

Table VII

Sample	H ₂ SO ₄ , lbs/ton	pH	Percent, Wt.	Assays, percent		Percent, Distribution Al ₂ O ₃	Percent, Assay Fe ₂ O ₃
				Al ₂ O ₃	Fe ₂ O ₃		
F	0.00			(Poor float—discarded)			
G	0.66	3.3	87.47	13.67	0.185	11.95	0.162
H	1.48	3.1	88.42	14.23	0.19	12.58	0.175
I	2.96	2.7	83.11	13.99	0.19	11.63	0.165
J	0.66	3.0	83.75	13.81	0.093	11.57	0.078
K	0.66	3.05	81.37	13.64	0.085	11.10	0.069
L	0.66	3.3	79.26	13.62	0.067	10.80	0.053
M	0.66		78.60	13.52	0.071	10.63	0.071
N	0.66		83.33		0.068		0.054
O	0.66		81.69		0.07		0.058

¹ Sulfonate reagent replaced by 1.23 lbs./ton of a 2-1 mixture of oil-soluble water dispersible and water-soluble sulfonates.

² Sulfonate reagent replaced by 1.67 lbs./ton of 1-1 mixture of oil-soluble water-dispersible and water-soluble sulfonates.

³ Repeat of sample K using 0.05 lb./ton of Aerofloat 31 as a froth conditioning agent.

⁴ Repeat of sample G using 1.67 lbs./ton of sulfonates and 0.05 lb./ton of Aerofloat 31 as a froth conditioning agent.

⁵ Repeat of sample M raising oil content to 1.54 lbs./ton and 0.10 lb./ton of Aerofloat 31.

⁶ Repeat of sample M raising oil content to 2.31 lbs./ton and 0.10 lb./ton of Aerofloat 31.

INCREASING Al₂O₃ CONTENT OF PRODUCT

The foregoing examples have been primarily concerned with the demonstration of that part of the present invention which is concerned with producing an iron-bearing concentrate of ferrous-metal silicates, thereby reducing the overall ferrous-metal content of the tailing. In most industrial uses of feldspar, it is desirable that the Fe₂O₃ assay be less than 0.10%. In some of the above examples this grade has been produced, in others it has not. In addition a 16% or better content of Al₂O₃ is often required. While no special effort has been made in the foregoing examples to complete the production of a high grade spar concentrate, in actual practice this latter is an important part of the present process.

In general, the second stage in the present process comprises reversal of the first operation. It is primarily concerned with concentrating non-ferrous metal silicates and non-ferrous metal aluminum silicates from the residual silica and ferrous-metal silicates in the iron flotation tailing. A cationic reagent is used to produce the promoting and/or concentrating action. In this way the cationic reagent is employed to best advantage on a feed which is substantially free from slimes and which has been reduced in the iron-bearing substituents.

Substantially any cationic type of promoter

may be used in this part of the process. Various agents of this type are well known and commercially available in many forms. Typical illustrations include for example: many quarternary ammonium compounds such as cetyl pyridinium bromide and the like; reaction products of poly-alkylenepolyamines and fatty acids such as the reaction product diethylenetriamine and oleic acid; and, used illustratively in the following examples because of their typical action and comparatively greater availability, the long-chain fatty-acid amines of 14 or more carbon atoms. These amines are usually insoluble in water and to assist in distribution in the flotation feed are preferably used in the form of an acid salt such as the acetate, citrate or hydrochloride.

As in the iron flotation, the feed, i. e., the rougher iron flotation tailing, before being subjected to concentration by froth flotation is conditioned with the promoter. This is quite important in obtaining optimum separation for the amount of reagent used. Whether this condi-

tioning is carried out at high or low solids is optional, although an operation at high solids tends to produce somewhat better results. Usually the amount required is between 0.25 and 0.75 lbs./ton although as much as 1.0 lb./ton or more may be occasionally required.

To assist in disseminating the cationic reagent, which is usually employed in comparatively small quantities, an oiling or diluting agent is also desirable in this operation. As in the iron flotation, the most practical oil is a light petroleum distillate such as kerosene or light fuel oil. The amounts used are usually about the same as in the iron flotation although this amount may not be actually required. From about 0.5-1.5 lbs./ton are usually suitable. As in the iron flotation, the petroleum oil may be replaced with other organic oils if so desired.

In addition to the cationic promoter, a surface conditioner for the feldspathic materials is usually found necessary. For this purpose hydrofluoric acid is generally found to be preferable. The amount used will vary somewhat with the concentration of acid available and with the nature of the ore with 48% acid for example, usually ranges from about ½ lb. to about 4 lbs./ton, although with particularly recalcitrant ores as much as 6-8 lbs./ton may be required. The amount may be adjusted as the acid used in higher or lower in concentration. Since it is a condition-

ing agent, it is the primary reason for using a conditioning step, although, as noted, the latter also is helpful in disseminating the cationic reagent.

the same except that the hydrofluoric acid used was increased to 3.33 lbs./ton. The results are shown in Table IX. Both the iron and alumina content are highly satisfactory.

Table IX

	Per Cent Wt. Original Feed	Per Cent Assays		Per Cent Distribution		
				Original Feed		Spar Float Al_2O_3
		Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	
Rougher Iron Tailing.....	84.58	14.55	0.053	76.41	17.92	100.0
Spar Concentrate.....	61.09	19.50	0.06	73.93	14.74	96.75
Quartz Tailing.....	23.49	1.72	0.035	2.48	3.18	3.25

A frothing agent also is usually desirable. Any standard frothers such as natural or synthetic pine oil or the 7-8 carbon atomaliphatic alcohol frothers may be used alone or in mixtures. If so desired, they may be added directly to the cells

EXAMPLE 12

The procedure of Example 10 was repeated on the tail obtained in the treatment of Sample C in Example 7. The results are shown in the following Table X.

Table X

	Per Cent Wt. Original Feed	Per Cent Assays		Per Cent Distribution		
				Original Feed		Spar Float Al_2O_3
		Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	
Rougher Iron Tailing.....	89.72	15.23	.07	84.79	21.72	100.00
Spar Concentrate.....	65.97	19.80	.09	81.07	18.85	95.61
Quartz Tailing.....	23.75	2.52	.04	3.72	2.87	4.39

during the flotation operation, but for simplicity in operation they are preferably incorporated during the same conditioning operation in which the hydrofluoric acid and the cationic promoter are added. Additional frother added after flotation has proceeded for some time is effective in promoting the last traces of valuable mineral.

EXAMPLE 10

In order to illustrate the feldspar flotation operation in the process of the present invention the rougher tail obtained in Example 4 above was dewatered to about 65% solids and conditioned for 1 minute with 0.77 lb./ton of fuel oil, 2.0 lbs./ton of 48% hydrofluoric acid, 0.07 lb./ton of pine oil and 0.50 lb./ton of octadecylamine acetate. The metallurgical results are shown in the following table:

Table VIII

	Percent Weight Original Feed	Assays Percent			Percent Distribution		
		Al_2O_3	Fe_2O_3	SiO_2	Original Feed		Spar Float Al_2O_3
					Al_2O_3	Fe_2O_3	
Rougher Iron Tailing.....	89.89	14.22	0.11	76.50	79.33	38.22	100.00
Spar Concentrate.....	67.82	18.54	0.13	69.34	78.09	33.98	98.44
Quartz Tailing.....	22.06	0.89	0.05	98.56	1.24	4.24	1.56

EXAMPLE 11

As shown in Example 10, a satisfactory Al_2O_3 assay was obtained in good recovery. However, the Fe_2O_3 content is a little higher than usually desired. Accordingly, the procedure of Example 10 was repeated on the rougher concentrate obtained in Example 5 above. The conditions were

EXAMPLE 13

In order to illustrate the overall procedure, another sample of the same ore treated in Example 11 was ground to size for flotation feed, pulped with water to about 65% solids, scrubbed for 15 seconds with 0.13 lb./ton of NaOH and delimed hydraulically. The sands were then conditioned at about 60-70% solids with 0.67 lb./ton of H_2SO_4 , 1.67 lbs./ton of a 3-1 mixture of oil-soluble, water-dispersible and water-soluble sulfonated petroleum hydrocarbons; 2.31 lbs./ton of fuel oil and 0.05 lb./ton of "Aerofloat 31". The conditioned pulp was diluted to 29-30% solids, floated for 3 minutes and iron concentrate removed.

The rougher iron tailing was then conditioned for one minute at 26% solids with an additional 0.75 lb./ton of fuel oil, 1.33 lb./ton of 48% hydro-

fluoric acid, 0.50 lb./ton of octadecylamine acetate, 0.07 lb./ton of pine oil and 0.03 lb./ton of a commercial alcoholic frother. The conditioned pulp was given a rougher spar float at 26% solids for two minutes and a cleaner float at about 20% solids for 1½ minutes. The results are shown in the following Table XI.

Table XI

	Per cent Wt.	Assays, per cent			Distribution, per cent	
		Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃ (Whole feed)	Al ₂ O ₃ (spar float)
Feed.....	100.00	16.11	0.19	79.00	100.00	-----
Ro. Iron Conc.....	12.62	-----	1.76	-----	-----	-----
Ro. Iron Tail.....	85.70	15.05	-----	75.13	80.07	100.00
Ro. Spar Conc.....	62.67	19.31	-----	68.05	75.11	93.80
Cl. Spar Conc.....	56.38	20.10	0.06	66.70	70.33	87.83
Quartz Tail.....	22.03	3.47	-----	94.40	4.98	6.20

From the foregoing it will be apparent that the process of the present invention represents a true combination of steps into a unitary whole. In so doing neither operation is pushed to its extreme limit so far as that particular step is concerned. By combining them a flexible procedure is obtained which enables the production of a uniform product of high grade and in higher recovery than can be obtained by the practice of either alone.

In treating the average feldspar ore in accordance with the present invention, the usual treatment consists in reducing the ore to -20 mesh as flotation feed. However, it may be economically advantageous in some cases to treat only the smaller sized fractions, for example, the -35 mesh particles, by flotation. This results in lowered reagent consumption. Often much of the iron-bearing content of the ore is in that fraction which is most easily reduced to small sizes. This can be taken advantage of in the present process by crushing the ore to -20 mesh, removing the +35 mesh fraction and subjecting only the -35 mesh fraction to froth flotation. This may be done in those cases where the +35 mesh sands are sufficiently high in aluminum and low in iron so that they may be mixed with the flotation concentrates to produce saleable products, particularly when only the iron content requirement is to be met. This is illustrated in the following example.

EXAMPLE 14

A sample of feldspar ore contaminated with iron stainings, quartz and several mixed iron-bearing silicates was crushed to about -20 mesh and the crushed ore pulped with water to about 37% solids and scrubbed for 2 minutes with 1 lb./ton of the caustic soda. It was then screened at 35 mesh, the +35 mesh fraction being retained and the -35 mesh fraction being deslimed hydraulically. The deslimed fraction was conditioned for 4 minutes at 65-70% solids with 1 lb./ton of sulfuric acid, 0.35 lb./ton of fuel oil and 1.0 lb./ton of mixed petroleum sulfonates (about 75% "green" acids). The conditioned pulp was diluted to about 20% solids and floated for 8 minutes with 0.02 lb./ton of pine oil, 0.03 lb./ton of "Aerofloat 31" and 0.10 lb./ton of a higher alcohol frother. The rougher iron concentrate was removed. The rougher iron tailing was floated for 2 minutes with 0.02 lb./ton of pine oil, 3.0 lbs./ton of 48% hydrofluoric acid and 0.31 lb./ton of crude octodecylamine acetate. The results are shown in the following table.

Table XII

	Percent Weight	Assays, percent			Percent Distribution Fe ₂ O ₃
		Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	
Original.....	100.00	15.85	0.179	71.70	100.00
Plus 35 Mesh.....	42.82	15.50	0.071	72.68	16.76
Minus 35 Mesh.....	57.18	-----	-----	-----	83.24
Slimes.....	11.52	19.20	0.775	66.59	49.72
Minus 35 Mesh Sands.....	45.66	-----	-----	-----	35.52
Iron Conc.....	4.87	-----	1.01	-----	27.37
Feldspar Conc.....	33.34	18.66	0.031	67.36	5.59
Quartz Tail.....	7.45	3.24	0.017	95.90	0.56
Plus 35 Mesh+Fe Tailing.....	83.61	15.67	0.049	72.62	-----
Plus 35 Mesh+ Feldspar Conc.....	76.16	16.89	0.053	70.35	-----

I claim:

1. In a concentration by froth flotation of a feldspathic-materials ore, too low in Al₂O₃ assay and too high in ferrous metals oxides and silicates, in which a pulp of the ore is floated with an anionic promoter to produce an enriched feldspathic-materials tailing and a feldspathic-materials concentrate is floated from said tailing with a cationic promoter; the improved method of reducing the ferrous-metals silicates content which comprises the steps of pulping the ore with water; simultaneously conditioning the pulp with a sufficient amount of a member of the group consisting of the water-soluble acids and acid salts yielding free acidic radicals in solution to produce a pH of from about 2.5-5.0 in the pulp at flotation density and with an effective amount of a promoter selected from the group of sulfonated petroleum hydrocarbons obtained in the manufacture of lubricating oil stocks consisting of the oil-soluble, water-dispersible sulfonates of the "mahogany" type, the water-soluble sulfonates of the "green" type and mixtures thereof; subjecting the conditioned pulp to froth flotation and removing the flotation concentrate.

2. A process according to claim 1 in which the ore after pulping with water is scrubbed with about 0.1 lb.-1.0 lbs. per ton of caustic soda and then deslimed before being conditioned with the reagents.

3. A process according to claim 1 in which the ore after pulping with water is scrubbed with about 0.1-1.0 lbs. per ton of caustic soda and then deslimed before being conditioned with the reagents, the conditioning being carried out at a solids content of about 30-70% and the conditioned pulp being diluted to flotation density before being subjected to froth flotation.

4. A process according to claim 1 in which the promoter comprises a mixture of from about

2,488,192

17

50-85% water-soluble and 15-50% oil-soluble, water-dispersible sulfonated petroleum hydrocarbons.

ELMER WILLIAM GIESEKE.

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Certificate of Correction

Patent No. 2,483,192

September 27, 1949

ELMER WILLIAM GIESEKE

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 8, line 24, strike out " K_2O -----4.59"; column 12, line 74, for the words "used in" read *used is*; column 14, line 44, for "60-70%" read *65-70%*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of February, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.