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BENEFICIATION OF GARNET ORES BY FROTH FLOTATION WITH WATER-DISPERSIBLE PETROLEUM SULFONATES

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This invention relates to the beneficiation of ores containing garnet.

The practical recovery of garnet from ores is quite a serious problem because the commercial uses of garnet which are mainly in the abrasive field require a high grade material. This has greatly reduced the available garnet deposits and many garnet ores have been considered unsuitable for commercial exploitation because the beneficiation problem up to now has proven unsurmountable.

According to the present invention garnets are floated away from silicate gangues such as hornblende, serpentine, and various other gangues by means of water dispersible sulfonated petroleum hydrocarbons. Where garnet is the valuable mineral in the ore the preferred modification of the present invention includes subjecting the ore to a treatment with an acid having a dissociation constant of at least 10^{-7} in the conditioning step when the reagent is added. The practical beneficiation by the use of water dispersible sulfonates of liquid petroleum hydrocarbons, which will be referred to as petroleum sulfonates, and acid is all the more surprising because in the fatty acid or soap flotation of garnet the latter is depressed by acid as is described for example by Coghill & Clemmer, Transactions of the American Institute of Mining and Metallurgical Engineers, volume 112 (1934), page 458. The preferred modification of the present invention also runs counter to the recently developed iron ore flotation processes using acid treated ore with petroleum sulfonates. In these processes which are described and claimed in the copending patents of Booth and Herkenhoff, Patent No. 2,410,376, October 29, 1946, filed April 5, 1943, and Patent No. 2,410,377, October 29, 1946, filed June 18, 1943, the flotation procedure of the present invention is applied to iron ores. It would, therefore, be assumed that the use of petroleum hydrocarbon sulfonates with acid treatment would tend to float preferentially minerals containing iron. We have found, however, that in the case of the garnets it is apparently the particular silicate type which is floated. Thus, for example, a garnet which is free from iron such as grossularite and pyrope can be floated away from iron containing gangue such as hornblende or tremolite. The process of the present invention is, however, applicable to the flotation of all types of garnets both those which are free from iron and the iron containing garnets such as almandite and andradite. The reason for this peculiar behaviour of water dispersible hydrocarbon sulfonates in the flotation of garnet

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has not been determined fully. However, it would appear that the action may be bound up with the silicate structure of the garnet minerals. Otherwise it would be highly unlikely that silicates of such radically different chemical constitution should float in the same manner. The present invention is, therefore, not limited to any theory of the peculiar operation of the process of the present invention.

In many cases it is desirable to associate the water dispersible petroleum sulfonate with an unsulfonated oil such as for example fuel oil. This appears to be desirable in many cases but it has not been definitely determined whether the action of the unsulfonated oil is primarily one of dispersion of the sulfonate over the ore particles or whether it may act as a froth modifying agent. It seems likely that both functions may be performed. Most water dispersible oil soluble petroleum hydrocarbon sulfonates are commercially obtained in an oil solution and, of course, this oil solution may be used as such. Ordinarily best results are obtained with somewhat more oil and it is, therefore, frequently desirable to add additional fuel oil. Fuel oil, for example ordinary 20° Bé. fuel oil, gives excellent results as an additional oiling agent and because of its low cost and ready availability constitutes the preferred addition agent from economic standpoints. However, the invention is in no sense limited, and on the contrary other unsulfonated oils may be used, such as liquid fatty acids and the like. Among them talloel, because of its cheapness, is particularly useful. In the present case this reagent is claimed only in connection with the subject matter of the present invention, namely the beneficiation of garnet ores by froth flotation.

It is an advantage of the present invention that the choice of acids to be used in treating the ore is quite wide. Practically any acid stronger than those having a dissociation constant of 10^{-7} may be used, provided the acidic anion does not itself exert depressing or other undesirable effects on garnets. Sulfuric acid gives excellent results and because of its cheapness constitutes the preferred acid. Strongly acid salts may also be used.

Dispersion of the water dispersible petroleum sulfonate is sometimes improved by using inert organic solvents such as lower paraffin alcohols, and reagent mixtures containing such solvents are included in the scope of the present invention.

It is desirable to effect conditioning of the flotation feed at high solids, for example 60–85%, followed by dilution to flotation pulp density, for which even as high as 40% solids gives excel-

lent results in efficient mechanical flotation cells.

Where garnets are to be floated from silicious gangue such as hornblende, quartz and the like, the pH of the flotation circuit is not at all critical; however, the circuit should be distinctly acid having a pH below 5. This is a further advantage of the present invention. It is preferable to operate in an acid circuit, but the exact acidity may vary over fairly wide ranges. When there is associated with the garnet very readily floatable material such as for example certain iron minerals like ilmenite the separation is somewhat more difficult and requires careful control of pH. The preferred embodiment of the present invention in which the ore is treated with an acid in addition to the sulfonated reagent is necessary where garnet concentrates of commercial grade are desired in reasonable recovery. There are certain special conditions, however, where it is necessary to remove garnet as an impurity in other ores and where the grade of the concentrate is not of importance. In such cases, it is possible to omit the acid, good recoveries of a lower grade concentrate being obtainable with the water dispersible petroleum sulfonate alone, particularly oil-soluble sulfonated petroleum hydrocarbons. Where the acid treatment is unnecessary the added advantage is obtained that equipment need not be made of acid resistant material.

The flotation procedure of the present invention behaves normally with respect to slime; that is to say, in common with many anionic flotations it is desirable to deslime, but slime is not critical as in silica flotation operations employing cationic flotation reagents.

The invention will be described in greater detail in conjunction with the following specific examples.

Example 1

Screen undersize from garnet ore from northeastern United States containing approximately 26% garnet principally in the form of almandite

associated with a gangue containing hornblende as a principal constituent, with smaller amounts of feldspar and a minor amount of quartz, was ground in a rod mill at 67% solids to approximately the following screen size:

Mesh	Per cent Weight Distribution
+35	2.25
+48	13.21
+65	24.12
+100	17.50
+150	11.17
+200	9.00
+325	5.58
−325	17.17

The ground ore was then deslimed and then conditioned at 80–85% solids with 5 lbs per ton of sulfuric acid and 1 lb. per ton of an oil-soluble petroleum hydrocarbon sulfonate. Various tests were made with different reagent combinations, utilizing oil-soluble petroleum sulfonates from various sources. In each case the conditioned ore was diluted to froth flotation density and subjected to froth flotation in Fagergren flotation machines. A rougher concentrate was obtained which was then conditioned for a short time with an additional 0.5 lb. per ton of sulfuric acid and cleaned twice for odd numbered tests and once for even numbered tests. Where re-cleaning was effected the cleaner concentrate was conditioned with an additional 1 lb. per ton of sulfuric acid prior to re-cleaning. The following table shows the metallurgical results:

Test No.	Assays per cent Garnet		Recovery Garnet in Final Conc.	Reagent Tested 1.0 Lb./ton	pH		
	Rgh. Tail.	Final Conc.			Rgh. Float	Clean Float 1	Clean Float 2
1	7.5	95.4	79.82	50 Parts SP-302 (Stanco Distrib.), 5 Parts Sec. Butyl Alcohol	2.5		3.0
2	8.5	97.5	71.97	50 Parts Calol Sodium Sulfonate (Std. Oil of Calif.), 50 Parts SP-1 (Stanco Distrib.), 10 Parts Sec. Butyl Alcohol.	2.7	3.2	
3	4	92.2	81.56	100 Parts Calol Sodium Sulfonate (Std. Oil of Calif.), 10 Parts Sec. Butyl Alcohol.	2.5		3.0
4	5	95	83.80	50 Parts Ultranate No. 2 (Atlantic Ref. Co.), 5 Parts Sec. Butyl Alcohol.	2.5	2.8	
5	2	94.5	89.06	50 Parts Petronate (Sonneborn Sons), 5 Parts Sec. Butyl Alcohol	2.5	2.8	2.8

Example 2

The garnet ore of Example 1 was treated with various reagent combinations employing water-soluble sulfonated petroleum hydrocarbons associated with unsulfonated oils. The concentrate from the first test was re-cleaned, the second test cleaned three times, and the others cleaned only once. Acid was used as in Example I. The metallurgical data appear in the following table:

Assays per cent Garnet		Recovery Final Conc.	Sulfonate Tested	Addition Agent	pH			
Rgh. Tail	Final Conc.				Rgh. Float	Clean. Float 1	Clean. Float 2	Clean. Float 3
2.5	92.5	57.70	SP-702 (Stanco Distrib. Inc.) 1.0 Lb./ton.	22° Bé. Fuel Oil 0.5 Lb./ton	2.3	2.5	2.8	
4	63	90.48	Green Acids (Sonneborn Sons) 1.0 Lb./ton.	do	2.4	2.5	2.8	3.1
13.3	98	40.36	Green Sulfonic Acid Residue (20%) (Sun Oil Co.) 3.0 Lbs./ton of 20% solution.	No. 2 Fuel Oil 3.5 Lbs./ton	2.5	2.8		
7	97	33.30	SP-702 (Stanco Distrib. Inc.) 0.75 Lb./ton.	Talloel 0.52 Lb./ton	2.7	2.8		
4	98	67.94	SP-702 (Stanco Distrib. Inc.) 0.75 Lb./ton.	California Crude Oil 0.50 Lb./ton	2.5	2.3		
3	80	89.16	Green Acids (Sonneborn Sons) 1.0 ton	Oleic Acid 0.53 Lb./ton	2.5	2.8		
10	85	68.75	Green Acids (Sonneborn Sons) 0.75 Lb./ton.	Coconut Oil 0.5 Lb./ton	2.4	2.8		
10	96	69.50	MP-189 (du Pont) 1.0 Lb./ton.	22° B°. Fuel Oil 1.5 Lbs./ton	2.6	2.9		

It will be apparent that while a high grade was obtained with practically all of the foregoing reagent combinations there was considerable variation in the recovery. This is typical of the present invention as it has been found that while the sulfonates are generally useful there are differences between various sulfonates.

Example 3

The effect of various acids in the conditioning step was determined by following the procedure of Example 1, conditioning the ore at high solids with 1 lb. per ton of 50 parts of Petronate and 5 parts of secondary butyl alcohol using various amounts of acid. The results appear in the following table:

Assays per cent Garnet		Per cent Recovery Garnet in Final Conc.	Acid Used	Lbs./ton Acid		pH	
Rgh. Tail.	Final Conc.			Rgh. Float	Clean. Float	Rgh. Float	Clean. Float
2	92.3	92.08	Sulfuric	5.0	0.5	2.5	2.8
22	90	33.57	Hydrochloric 36%	5.0	2.0	4.1	2.9
20	97	39.70	Hydrofluoric 48%	7.5	3.0	4.4	3.5
7	50	87.72	Nitric	5.0	1.0	2.6	2.8
15	96	60.32	Citric	15.0	2.0	3.4	3.5
15	83	43.72	Saturated Carbonic	(1)	(1)	7.0	7.1
3	60	90.26	Boric	15.0	2.0	7.4	7.4

[1] All water used for flotation was saturated with CO_2 (pH 5.0). One cleaning of all rougher concentrates.

It will be apparent that when acids weaker than carbonic acid are used the grade is not satisfactory and apparently nitric acid contains an anion which adversely affects the flotation. In this respect nitric acid behaves very differently with garnet than with iron ore. It apparently does not have any deleterious effect on iron ore flotation. The reason for this difference in behaviour has not yet been determined.

Example 4

The procedure of Example 3 was followed substituting strongly acid salts for acids. The metallurgical results appear in the following table:

Assays per cent Garnet		Per cent Recovery Garnet in Final Conc.	Acid Salt Tested	Lbs./ton Salt		pH	
Rgh. Tail.	Final Conc.			Rgh. Float	Clean. Float	Rgh. Float	Clean. Float
11	95	70.89	Sodium Silicofluoride	15.0	3.0	4.4	4.0
8	95	79.08	Sodium Chlorosulfonate	15.0	2.0	2.3	2.7
7	98	80.45	Potassium Bisulfate	15.0	2.0	2.5	2.8

It will be apparent that acid salts give results practically the same as those obtained with strong acids, but much larger quantities are required.

Example 5

The procedure of Example 1 was followed using an ore containing pyrope with a serpentine gangue. The conditioning was with 7 lbs. per ton of sulfuric acid and 1.04 lbs. per ton of a mixture of 50 parts of an oil soluble petroleum sulfonate (Petronate) with 5 parts of secondary butyl alcohol. A rougher concentrate was obtained using an additional 2 lbs. per ton of the sulfonate reagent and then cleaned. The metallurgical results are as follows:

Product	Per cent Weight	Assay per cent Pyrope	Per cent Distribution Pyrope
Flot. Feed	100.00	7	100.00
Rgh. Conc	46.32	14.9	94.14
Rgh. Tail	53.68	0.8	5.86
Clean. Conc	33.20	20	90.59
Clean. Tail	13.12	2	3.55

Example 6

The procedure of Example 5 was followed but andradite with a hornblende-quartz gangue was substituted for the pyrope. The metallurgical results appear in the following table:

Product	Per cent Weight	Assay per cent Andradite	Per cent Distribution Andradite
Flot. Feed	100.00	28	100.00
Rgh. Conc	20.80	91.3	67.59
Rgh. Tail	79.20	11.5	32.41
Clean. Conc	20.67	91.5	67.27
Clean. Tail	0.13	66	0.32

Example 7

An ore containing grossularite with a hornblende gangue was conditioned as in the preceding examples using, however, 10 lbs. of sulfuric acid per ton instead of 7. The rougher float was carried on in series with stage oiling of an additional 2 lbs. per ton of sulfonate reagent. The combined rougher concentrates were then conditioned with an additional 2 lbs. per ton of sulfuric acid and a cleaner flotation carried out. The metallurgical results appear in the following table:

Product	Per cent Weight	Assay per cent Grossularite	Per cent Distribution Grossularite
Flot. Feed	100	36	100.00
Comb. Rgh. Concs	41.57	85.1	98.69
Rgh. Tail	58.43	0.8	1.31
Clean. Conc	40.06	88	98.38
Clean. Tail	1.51	7	0.31

Example 8

The procedure of Example 5 was followed with an ore containing rhodolite with a gangue of mixed talc, biotite, quartz, hornblende and tremolite. The amount of sulfuric acid used in conditioning the original feed was 10 lbs. per ton and sulfonate reagent 1.77 lbs. per ton. A rougher concentrate was obtained which was conditioned with an additional 4 lbs. per ton of sulfuric acid and cleaned. The metallurgical results appear in the following tables:

Product	Per cent Weight	Assay per cent Rhodolite	Per cent Distribution Rhodolite
Flot. Feed	100.00	63	100.00
Rgh. Conc	78.86	79.9	99.73
Rgh. Tail	21.14	[1] 0.8	0.27
Clean. Conc	74.03	85	99.57
Clean. Tail	4.83	[2]	0.16

[1] High biotite.
[2] Primarily biotite and talc.

The metallurgical results appear in the following table:

First Conditioner Per cent Solids	Per cent Garnet			Per cent Recovery Garnet in Final Conc.
	Feed	Rgh. Tail.	Final Conc.	
85	28	2	92.3	92.08
40	27	3	94	90.43

It will be apparent that conditioning at high solids is not as essential in the present invention as in many other flotation operations and this is an additional advantage of the process of the present invention.

Example 11

A garnet ore such as used in Example 1 was conditioned with and without sulfuric acid. In each case the conditioning was with 1 lb. per ton of a reagent consisting of 50 parts of Petronate and 5 parts of secondary butyl alcohol. The rougher concentrate was cleaned once. The results appear in the following table:

Per cent Garnet		Per cent Recovery Garnet in Final Conc.	Alkalinity Regulator	Lbs./ton Acid Used		pH	
Rgh. Tail	Final Conc.			Rgh. Float	Clean. Float	Rgh. Float	Clean. Float
2	92.3	92.08	H_2SO_4	5.0	0.5	2.5	2.8
7.5	72.5	84.19	do	2.0	0.5	5.1	----
9	70	75.59	None	----	----	7.5	----

Example 9

The effect of temperature in conditioning and floating was tested out by following the procedure of Example 1, the petroleum sulfonate reagent containing 50 parts of Petronate and 5 parts of secondary butyl alcohol. One test was effected at 28° C. and the other at 8° C. The results appear in the following table:

Per cent Garnet		Per cent Recovery Garnet in Final Conc.	Pulp Temperature Throughout Test
Rgh. Tail.	Final Conc.		
			° C.
2	92.3	92.08	28
6	97	77.81	8

It will be apparent that there is considerable loss at lower temperature, although the grade is even higher. While it is difficult to determine the exact reasons, it seems probable that the lower temperature made distribution of the flotation reagent less complete.

Example 10

The effect of solids content in conditioning was determined by following the procedure of Example 1, using 1 lb. per ton of a mixture of 50 parts Petronate and 5 parts secondary butyl alcohol and 5 lbs. per ton sulfuric acid, followed by a second conditioning with 0.5 lb. per ton of sulfuric acid. In one test the conditioning was effected at 85% solids, the second at 40% solids.

It will be apparent that while maximum recovery of a high grade garnet concentrate required conditioning with 5 lbs. per ton of sulfuric acid more than 75% of the garnet was recovered in a 70% concentrate without the use of sulfuric acid. While this might not be an economical procedure in the case of an ore which was treated for its garnet content alone, the procedure is useful with ores where it is desired to eliminate a large portion of the garnet where the garnet is a gangue mineral. In such cases the elimination of sulfuric acid presents some economical advantages because the corrosion problem in the equipment is greatly reduced.

We claim:

1. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent water dispersible petroleum sulfonates and an effective amount of an acid substance, the anion of which is capable of forming an acid having a dissociation constant greater than 10^{-7}, said acid substance being substantially free from nitric acid, and the amount of the acid substance being sufficient to modify the flotation characteristics of the garnet particles, whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

2. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent oil soluble water dispersible petroleum sulfonates and an effective amount of an acid substance, the anion of which is capable of forming an acid having a dissociation constant greater than 10^{-7}, said acid substance being substantially free from nitric acid,

and the amount of the acid substance being sufficient to modify the flotation characteristics of the garnet particles, whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

3. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent water dispersible petroleum sulfonates and an effective amount of sulfuric acid, the amount of the latter being sufficient to modify the flotation characteristics of the garnet particles whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

4. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent oil soluble water dispersible petroleum sulfonates and an effective amount of sulfuric acid, the amount of the latter being sufficient to modify the flotation characteristics of the garnet particles whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

5. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent water soluble petroleum sulfonates and an effective amount of sulfuric acid, the amount of the latter being sufficient to modify the flotation characteristics of the garnet particles whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

6. A method according to claim 1 in which the petroleum sulfonate is associated with an unsulfonated oil.

7. A method according to claim 3 in which the petroleum sulfonate is associated with an unsulfonated oil.

8. A method according to claim 1 in which the sulfonated material is associated with an unsulfonated hydrocarbon oil.

9. A method of beneficiating garnet-containing ore which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent water soluble petroleum sulfonates and an effective amount of an acid substance, the anion of which is capable of forming an acid having a dissociation constant greater than 10^{-7}, said acid substance being substantially free from nitric acid, and the amount of the acid substance being sufficient to modify the flotation characteristics of the garnet particles, whereby a concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

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REFERENCES CITED

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

Guzeit, Selective Flotation Tests of Minerals Constituting Block Sands, 34 Chemical Abstracts 3139, May 20, 1940.

Handbook of Chemistry and Physics, 27th edition, published Feb. 1943, by Chemical Rubber Publishing Co., 2310 Superior Ave. N. E., Cleveland, Ohio.

Gutzeit, Essais de Flottation Selective des Mineraux Constituant les "Sable Noirs," Archives des Sciences Physiques et Naturales, vol. 21, pages 260–269 (1939). (Copy in Scientific Library.) 209–166.