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METHOD OF CONCENTRATING IRON ORE

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to an improved process for concentrating iron ores whereby froth flotation of the siliceous gangue constituents yields an iron enriched product; more particularly it relates to a froth flotation process employing anionic collecting agents to effect flotation of activated siliceous gangue constituents from caustic alkaline iron ore pulps while retarding flotation of the iron oxides with lignin sulphonates.

An object of this invention is to provide a froth flotation process for concentrating iron oxides in pulps containing them in the presence of siliceous gangue. A further object is to provide a flotation process for separating silica from iron oxides employing anion-active collecting agents. A still further object is to provide a flotation process for concentrating iron ores or products from the milling of iron ores containing both calcareous and siliceous gangue materials. Still other objects include the development of a flotation process which will have greater selectivity in separating siliceous materials from oxide iron ore pulps and thereby effect greater operating economies. Other objects, purposes, and advantages of the invention will hereinafter more fully appear or will be understood from the detailed description of its practice.

In a co-pending application, assigned to the same assignee as the present application, Serial No. 473,162, filed January 22, 1943, by Julius Bruce Clemmer and Ballard H. Clemmons, is described a process for beneficiating iron ores by froth flotation wherein anionic collecting agents are employed to float activated siliceous gangue constituents from caustic alkaline iron ore pulps with a pH of at least 10, while retarding flotation of the iron oxides with metaphosphates or polyphosphates.

As a result of further extended research and experimentation, we have discovered an improved method of concentrating iron ores by froth flotation of activated siliceous gangue constituents employing anionic collecting agents, such as the higher fatty acids, resin acids, mixtures of fatty and resin acids, and soaps thereof, to float the activated siliceous materials from caustic alkaline iron ore pulps with a pH of at least as high as 10, while retarding flotation of the iron oxides

with the lignin sulphonates. The metaphosphates and polyphosphates may be used as supplementary reagents in conjunction with various crude or purified lignin sulphonates, if desired, but are not obligatory in the practice of this invention.

The lignin sulphonates which we prefer to utilize as iron oxide depressants in this invention are present in and may be derived from the by-product of the sulfite process of paper making commonly known as "sulfite liquor." These liquors separated as waste from the cellulose pulp contain soluble salts of the lignin sulphonate acids and other non-ligneous organic substances, such as hydrolyzed carbohydrates, resulting from decomposition of the wood by the acid solutions used in the pulping process. In the sulfite process, the lignin in the wood is dissolved by digesting the wood chips with an acid calcium, magnesium, or sodium sulfite solution at an elevated temperature whereby the lignin forms soluble calcium, magnesium, or sodium lignin sulphonates depending on the base employed. The sulfite liquors containing the lignin sulphonates and non-ligneous materials may be used as the iron oxide depressants in the practice of our invention or the crude sulfite liquors may be purified by known methods to reject the non-ligneous substances and recover a substantially purified lignin sulphonate which may be employed to retard the iron oxides in our method of silica flotation.

The crude or whole sulfite liquor recovered from the sulfite pulping process and containing the lignin sulphonates and non-ligneous organic substances, such as hemi-cellulose and various sugars, may be evaporated to yield a concentrated liquid or dehydrated residue for marketing. The liquid forms as marketed contain about 50 percent water, whereas the powdered forms are substantially dehydrated. The liquid and powdered forms have been used interchangeably in our method of flotation and, based on their respective content of lignin sulphonate, are equally effective for retardation of iron oxides. Comparative tests using the calcium, magnesium, and sodium base sulfite liquors, or the respective dehydration residues thereof, gave substantially equivalent results. The non-ligneous materials present in the liquid or dehydrated residues appear to be inactive diluents and exert little or no deleterious effect in the froth flotation of activated siliceous gangue from iron oxides. The evaporated crude sulfite liquors or dehydration residues were slightly less effective pound per pound than the corresponding purified lignin sulpho-

nates relatively free of non-ligneous material, but were particularly attractive as iron oxide depressants in our method of flotation due to their lower cost.

The crude or evaporated sulfite liquors may be processed by numerous methods to reject the non-ligneous material and recover substantially purified lignin sulphonates. Fractional precipitation methods using sodium chloride, calcium chloride, mineral acids, lime water, basic lead acetate, or organic bases may be employed to recover the lignin sulphonate and reject the non-ligneous materials. The precipitated lignin sulphonate may be further purified by dissolution and reprecipitation, by dialysis, or other methods. The purified sulphonates are ordinarily marketed as the powdered forms but solutions containing from 15 to 50 percent of the lignin sulphonate are also available. Various of the commercially available purified lignin sulphonates containing the calcium, magnesium, sodium, barium, aluminum, zinc, and copper salts have been tested and found satisfactory as iron oxide retardants in the practice of our invention. The calcium, magnesium, and sodium sulphonates are less expensive than the heavy metal salts and were preferred. The liquid or powdered forms of either the crude or purified sulfite liquor materials may be used in our method of flotation, and the ultimate choice of the particular lignin sulphonate employed will largely depend upon economic factors.

A variety of liquid and powdered forms of both crude and purified sulfite liquor products are commercially available and have been found satisfactory for retarding iron oxides in our flotation method. Examples of the sulfite liquor materials which we have used successfully include those sold under the trade names "Bindarene Liquid," "Bindarene Flour," "Goulac," "T. D. A.," "Marathon Extracts M, T, NS, TanC, SL, DT-31, DT-32, DT-33, DT-34, and DT-35," and the "Daxads 11, 21 and 23." Other sulfite liquor products which we have found acceptable include the crude and purified magnesium lignin sulphonates, the acid, neutral, and basic calcium lignin sulphonates, and sodium, copper, zinc, aluminum, and barium lignin sulphonates. For convenience, we shall hereinafter use the term "lignin sulphonate" to include the crude and purified metal salts of lignin sulphonic acids, the crude and purified paper mill sulfite liquors, and dehydrated residues thereof.

While we have achieved satisfactory flotation of activated silica from iron ore pulps containing substantial quantities of slime by the practice of our invention, we prefer that the pulps be deslimed. Desliming of the iron ore pulp should be practiced whenever permissible as subsequent flotation of the activated silica is more rapid and complete, and less reagents are required.

A caustic alkaline pulp with a pH at least as high as 10, and preferably in the range of 10 to 12, is preferable in our method of flotation to facilitate effective retardation of the iron oxides by lignin sulphonates. We prefer to employ caustic alkalies, such as sodium or potassium hydroxide, or their equivalents, to establish the desired pH for flotation. Moderate quantities of other alkaline reagents, such as sodium sulfide, sodium carbonate, and sodium silicate, may be used in conjunction with the caustic alkalies if desired. A combination of hydrated lime and soda ash has been successfully employed in the flotation of many iron ores and served the dual purpose of activating the siliceous materials to

anionic flotation and establishing the desired caustic alkalinity for flotation by formation of caustic soda within the pulp. The optimum pH for anionic flotation of the activated silica and retardation of the iron oxides varies slightly for different ores but generally falls within the range of 10 to 12, and the proper pH for any particular case is best determined by experimentation. Poor flotation of the silica and incomplete retardation of the iron oxides invariably results if the pH of the pulp is much less than 10; a pulp pH greater than 12 is not particularly objectionable, but the froth is inclined to be voluminous and flotation of the silica is sluggish. We therefore prefer to keep the pH in the range 10 to 12 in our flotation method.

It is essential in the practice of this invention that the siliceous gangue constituents in the iron ore be activated and made floatable by the anionic collecting agents. The siliceous gangue materials in certain iron ores, such as the calcareous red ores of the Birmingham district, Alabama, are naturally activated to soap flotation presumably due to the presence of lime and/or magnesia salts in the ores. Siliceous iron ores, as exemplified by the weathered red ores of the Birmingham district and most siliceous ores of the Lake Superior district, seldom contain naturally activated siliceous materials, and the successful operation of our process requires that the silica in such ores be activated for anionic flotation. Extended research on a variety of siliceous iron ores demonstrated that our method of flotation lends itself readily to the use of silica activating agents.

Many alkaline earth and heavy metal salts exhibit the property of activating quartz and various silicate minerals to soap flotation if a proper quantity is employed at an optimum pH. We have found that conditioning of the caustic alkaline iron ore pulp with a moderate quantity of an activator selected from the group consisting of soluble calcium, magnesium, barium, strontium, and lead salts suffices to activate the siliceous constituents to anionic flotation by the higher fatty acids, resin acids, or their derived soaps without adversely affecting retardation of the iron oxides by the crude or purified lignin sulphonates. The commercial lignin sulphonates are generally marketed as calcium or magnesium salts of the lignin sulfonic acids and as such may contain sufficient lime or magnesia to activate part of the silica in iron ores to flotation. In general, however, the metal salts in the lignin sulphonates are insufficient for complete activation of the silica and supplementary metal salt activating agents may be needed for an improved separation.

In the practice of this invention, we prefer to employ hydrated lime for activation of the silica. Grinding or blunging the iron ore with sufficient hydrated lime to establish a pulp pH of about 11 will generally suffice on most ores for complete activation of the siliceous gangue. The quantity of hydrated lime required to activate the silica in iron ores varies from 1 to 4 pounds per ton of ore, but some ores containing acidic salts may require 8 pounds or more of hydrated lime per ton. Our experiments on a variety of calcareous and siliceous iron ores have revealed that only part of the hydrated lime added to the flotation pulp is consumed in activating the siliceous constituents to anionic flotation; part of the added lime may react with salts in the pulp and is precipitated as carbonate, another part is adsorbed by the iron oxides, still another part remains in solution to

satisfy the solubility requirements of the water, and finally any excess hydrated lime added to the pulp remains undissolved. The lime consuming capacity differs for different iron ores, and the proper quantity for activation of the silica is best determined by experimentation. Excessive quantities of dissolved lime in the conditioned pulp should be removed before flotation as they increase collector requirements. Although we have achieved by the practice of this invention good flotation of silica from iron ore pulps containing dissolved lime equivalent to 100 parts per million of hydrated lime or about 0.8 pound of hydrated lime per ton of solids in our tests, we prefer that the flotation pulp be substantially free of dissolved lime. The dissolved lime may be removed either by washing the conditioned pulp with fresh water, or by addition of sufficient soda ash to precipitate the lime as insoluble calcium carbonate. Brief conditioning of the iron ore with sufficient hydrated lime to give a pulp with a pH of about 11 generally suffices for complete activation of the silica. Subsequent addition of soda ash to the pulp, the requirements for most ores being 1 to 2 pounds per ton of solids, precipitates the lime in solution and gives a pulp of the desired caustic alkalinity for flotation. Should an excess of hydrated lime be inadvertently added to the pulp to activate the silica, as evidenced by a pH of about 12.3, the excess is best removed by settling and washing the pulp one or more times with fresh water to reduce the pH to 11, whereupon soda ash may be added to precipitate the remaining lime in solution before proceeding with flotation. If desired, however, the washing may be carried further to give a final pulp for flotation practically free of dissolved lime and having a pH of 9 to 10. Subsequent addition of a caustic alkali to the lime conditioned and washed pulp to establish the desired pH for flotation together with a lignin sulphonate and a fatty acid or soap collector enables flotation of the calcium-activated silica and retardation of the iron oxides.

It will be apparent to those skilled in the art that soft water free of lime or magnesia salts is not obligatory in the practice of this invention. Some lime or magnesia salts in the flotation pulp are permissible, and, in fact, are advantageous in that they insure complete activation of the siliceous constituents to flotation.

The anion-active collecting agents which we have found suitable for flotation of the activated siliceous gangue materials from iron oxides include the higher fatty acids such as oleic acid or red oil, the purified or crude sodium oleates, fish oil fatty acids, fish oil soaps, and various crude and purified talloels and sulfate soaps derived from sulfate paper mill black liquors. The talloels, which are mixtures of fatty and resin acids, are relatively inexpensive and are the preferred collectors in the practice of our invention.

We have discovered that various addition agents may be advantageously employed to supplement the crude or purified lignin sulphonates in the practice of our invention to enable an improved separation to be obtained. The various addition agents which we have employed and found useful include the metaphosphates; the polyphosphates; sodium silicate; sodium fluoride; starches of different botanical origin such as potato, wheat, corn, rice, arrow-root, or tapioca solubilized by heat and/or chemical treatment to yield starch solutions or gels of the ruptured granules; hydrolyzed starch products, such as British gum or dextrans; and various vegetable

tannin materials such as quebracho extract, oak extract, and Borneo cutch. These auxiliary addition agents are advantageous on some iron ores in that they enable more effective retardation of the iron oxides with minimal quantities of the lignin sulphonates during anionic flotation of the activated siliceous materials.

The proportions of the various reagents employed in the practice of this invention are subject to considerable variation, and the optimum quantities are best determined by experimentation for any particular case. Purity of the separated products is a reliable guide for reagent adjustment. An excess of collecting agent promotes flotation of a portion of the iron oxides with the siliceous gangue, whereas a deficiency of collector results in incomplete flotation of the siliceous gangue. Conversely, an excess of lignin sulphonate results in retardation of a portion of the siliceous materials, whereas a deficiency permits flotation of some of the iron oxides with the silica. Control of the collector and lignin sulphonate is not critical, however, and reasonable variation in the quantities employed is permissible without adversely affecting the separation.

To avoid possible confusion in describing the results of our flotation test, we shall hereinafter designate the iron enriched pulps from the roughing and cleaning steps as "iron concentrates, rougher" and "iron concentrates, cleaner," respectively. The floated silica products from the roughing and cleaning steps will be designated as "rougher froth" and "silica rejects," respectively. In describing the results of our test we shall consider and report the iron enriched pulps from the cleaning steps (middlings) as finished concentrates. It will be readily apparent to those skilled in the art that the middlings may be re-treated by conventional methods in continuous flotation operations to yield an even higher grade concentrate without departing from the spirit of the invention.

The invention will be further illustrated, but is not intended to be limited by the following examples of practice:

Example I

A sample of calcareous red iron ore was obtained from an operating mine in the Birmingham district, Alabama. The ore was typical of the district and contained hematite associated with a gangue composed predominately of quartz and calcite together with minor quantities of accessory calcareous and siliceous materials including shale and ferruginous clay. A head analysis gave 36.2 percent Fe, 10.6 percent CaO, and 24.6 percent hydrochloric acid insoluble (hereinafter referred to as "insol."). The sample was a typical calcareous iron ore containing siliceous gangue naturally activated to soap flotation. Pulps of the ground ore were alkaline (pH—8.6), and qualitative tests on the water showed presence of lime salts.

In carrying out the flotation process according to this invention, the iron ore or product to be treated is first ground to proper size for flotation, if not already of such size, by conventional methods. The fineness of grind may vary from 35 mesh to 200 mesh or finer depending on the degree of interlocking of the iron oxides and gangue constituents in the particular ore; substantially complete liberation of the iron oxides and siliceous gangue is essential for a satisfactory separation by flotation, and the fineness of grind for a particular ore should be selected ac-

cordingly. A limiting size of 100 mesh was chosen for this ore.

A 250-gram portion of the ore rolls-crushed to 20 mesh was wet ground to pass 100 mesh using 25 pounds of one-half inch steel rods as the grinding media with 250 ml. of tap water in a laboratory rod mill. The ground charge was diluted to a volume of 2.5 liters with additional tap water to give a pulp containing about 10 percent solids. The pulp which was flocculated was then dispersed using caustic soda and soda ash equivalent to 2.0 and 1.0 pounds per ton of ore, respectively. The dispersed charge was fractionated by sedimentation and decantation to remove the bulk of the slime finer than 20 microns. The granular portion, substantially free of slime and coarser than 20 microns, was repulped with additional tap water and transferred to a small mechanical flotation cell of standard design. Sufficient tap water was added to give a pulp for flotation containing about 20 percent solids.

Flotation of the naturally activated silica was effected from a caustic alkaline pulp using talloel as the collector, and Goulac, a commercial dehydrated sulfite liquid product marketed by American Gum Products Company, as the iron oxide depressant. The reagent charge expressed in conventional pounds per ton of ore was as follows:

Reagent	Conditioner		Rougher	Cleaner		
	No. 1	No. 2		No. 1	No. 2	No. 3
Caustic soda.....	1.2	-----	-----	0.4	0.4	0.4
Goulac.....	2.0	-----	-----	0.5	0.5	0.5
Talloel.....	-----	0.4	-----	0.1	0.1	0.1
Time, min.....	2.5	2.5	3	2.5	2.5	2.5
Pulp pH.....	10.8	10.8	10.5	10.5	10.5	10.5

The substantially deslimed pulp was first conditioned with the caustic soda (commercial lye) and Goulac to establish the alkalinity desired for flotation and to retard the iron oxides. Talloel was chosen for the collector in the test. The pulp was conditioned with the talloel as indicated. Air was then allowed to enter the cell and resulted in immediate formation of a compact, heavily mineralized froth of the siliceous materials. The froth was collected for 2.5 minutes, whereupon flotation was complete. The rougher froth was cleaned by re-floating in the same cell using tap water with additional caustic soda to maintain alkalinity, Goulac to retard the remaining iron oxides, and talloel to insure flotation of the siliceous gangue, in each cleaning step. The final silica rejects, the combined iron concentrates from the cleaning steps, the rougher iron concentrates, and the untreated slime were dried, weighed, and assayed.

The results of the test follow:

Product	Weight, per cent	Assay, per cent			Distribution, per cent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher.....	29.1	53.9	1.3	13.9	41.6	4.4	16.2
Cleaner.....	21.7	37.7	9.7	19.8	21.7	23.7	17.3
Slime (untreated).....	28.6	44.0	8.3	17.8	33.4	26.8	20.5
Composite.....	79.4	45.9	6.1	16.9	96.7	54.9	54.0
Silica rejects.....	20.6	6.0	19.4	55.5	3.3	45.1	46.0
Composite feed.....	100.0	37.7	8.9	24.9	100.0	100.0	100.0

The flotation silica rejects accounted for 20.6

percent of the weight of the feed and contained 46.0 percent of the insoluble and only 3.3 percent of the iron. The untreated slime and cleaner middlings were sufficiently low in insoluble to be considered as iron concentrates. The composite iron concentrates from the test represent a recovery of 96.7 percent of the iron in the feed and assayed 45.9 percent iron, 6.1 percent lime, and 16.9 percent insoluble.

The results of the recorded test were about average of those obtained on deslimed charges of the calcareous red iron ore ground in a pebble mill, iron ball mill, or iron rod mill to pass 65, 100, or 200 mesh, respectively. Good flotation of the activated quartz and granular silicates was achieved in the tests by using from 1 to 2 pounds per ton of an anionic collecting agent, such as oleic acid, sodium oleate, fish oil fatty acid, fish oil soap, or a crude or purified talloel or sulfate soap from sulfate paper mill black liquors, together with sufficient caustic alkali to give a pulp pH of about 11 and from 1 to 4 pounds per ton of a crude or purified lignon sulphionate to retard the iron oxides. Sodium hydroxide, potassium hydroxide, caustic soda (commercial lye), and combinations of hydrated lime and soda ash to form caustic soda in the pulp proved equally suitable for establishing the desired caustic alkalinity for flotation.

Example II

A 250-gram charge of the calcareous iron ore was ground to pass 100 mesh as in Example I. The ground charge, including slime, was transferred to a small mechanical flotation cell of standard design and sufficient tap water was added to give a pulp for flotation containing about 22 percent solids. Flotation of the silica from the slime-bearing pulp was effected by the following reagents expressed in conventional terms of pounds per ton of flotation feed:

Reagent	Conditioner		Rougher	Cleaner				
	No. 1	No. 2		No. 1	No. 2	No. 3	No. 4	No. 5
Caustic soda.....	3.4	-----	-----	0.8	0.8	0.8	0.8	0.8
Goulac.....	4.0	-----	-----	0.1	0.1	0.1	0.1	0.1
Talloel.....	-----	0.8	-----	-----	-----	-----	-----	-----
Time, min.....	2.5	2.5	2.5	3.0	2.0	1.5	1.5	1.5
Pulp pH.....	11.25	11.25	10.85	10.9	10.85	10.9	10.85	10.8

The slime-bearing pulp was conditioned with caustic soda (commercial lye) and Goulac. Talloel was then added and the pulp again briefly conditioned as indicated. The rougher froth was cleaned by re-floating in the same cell using tap water for dilution together with additional caustic soda and Goulac. The rougher and composite cleaner iron concentrates and final silica rejects were dried, weighed, and analyzed.

The results of the test are as follows:

Product	Weight, per cent	Assay, per cent			Distribution, per cent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher.....	33.1	51.8	3.3	16.1	47.5	10.1	21.4
Cleaner.....	36.9	43.9	6.7	20.1	44.9	22.8	29.8
Composite.....	70.0	47.7	5.1	18.1	92.4	32.9	51.2
Silica rejects.....	30.0	9.1	24.3	40.5	7.6	67.1	48.8
Composite feed.....	100.0	36.1	10.9	24.9	100.0	100.0	100.0

Flotation of the silica from the slime-bearing pulp rejected 48.8 percent of the silica (insol.) with a loss of only 7.6 percent of the iron. It is therefore apparent that our method of flotation is applicable to both total and deslimed iron ore pulps. While we prefer to employ deslimed pulps in the practice of our invention, desliming is not obligatory for a satisfactory separation of silica from the iron oxides.

Example III

In the previously described examples of practice, a lignin sulphonate (Goulac) was employed to retard the iron oxides during anionic flotation of the naturally activated silica from either deslimed or total charges of the ground calcareous red ore. We shall now consider the results of flotation tests wherein auxiliary addition agents are employed to supplement the lignin sulphonates in the practice of our invention.

The results of a typical flotation test on a 250-gram charge of the calcareous red iron ore ground to pass 100 mesh in a laboratory rod mill and the total charge floated by the procedure described in Example II are given below. Potato starch solubilized with caustic soda to rupture the granules at room temperature and form a starch solution was used as an auxiliary reagent in the test to supplement the lignin sulphonate and aid retardation of the iron oxides. The quantities of caustic soda, causticized potato starch, lignin sulphonate (Goulac), and talloel employed in the roughing step were 2.8, 2.0, 3.0, and 0.8 pounds per ton of feed, respectively. The rougher froth was cleaned 4 times using 0.5 and 0.1 pound per ton of caustic soda and Goulac, respectively, in each step to retard the remaining iron oxides and yield the final silica reject.

Product	Weight, per cent	Assay, per cent			Distribution, per cent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher-----	45.4	52.8	4.2	13.0	66.3	17.3	23.9
Cleaner-----	23.2	37.0	13.0	18.3	28.8	33.2	20.9
Composite--	73.6	46.8	7.6	15.0	95.1	50.5	44.8
Silica rejects:	26.4	6.7	20.7	51.7	4.9	49.5	55.2
Composite feed-----	100.0	36.2	11.0	24.7	100.0	100.0	100.0

A combination of the lignin sulphonate and causticized potato starch facilitated retardation of both the slime and granular iron oxides during anionic flotation of the activated silica. Other cereal and tuber starches, such as corn, wheat, rice, arrow-root, and tapioca, solubilized by heat and/or chemical treatment to yield solutions or gels of the ruptured starch granules were employed in other tests on the ore to supplement the lignin sulphonates. An optimum quantity of the starches and lignin sulphonate gave results substantially identical to those recorded. The utility of the starches and hydrolyzed starch products for retarding iron oxides during anionic flotation of activated silica from caustic alkaline iron ore pulps is described in a co-pending application, Serial No. 567,763, filed December 11, 1944, by Julius Bruce Clemmer and Milton Friel Williams, Jr. Although the starches and hydrolyzed starch products are not obligatory in the practice of this invention, they are advantageous addition agents and enable an improved retardation of the iron oxides with reduced quantities of the lignin sulphonates.

In addition to the starches and hydrolyzed starch products, other useful auxiliary agents which have been employed in conjunction with the lignin sulphonates in the practice of this invention include the metaphosphates, the polyphosphates, sodium silicate, sodium fluoride, and various vegetable tannin materials such as quebracho extract, oak extract, and Borneo cutch. The grade of the composited iron concentrates recovered from flotation tests on typical calcareous red ores using several of these auxiliary agents to supplement commercial lignin sulphonates are given below. The red ores were ground to pass 100 mesh and floated by the procedure described in Example II.

Depressant employed	Pounds per ton	Assay, percent			Recovery, per cent, Fe
		Fe	CaO	Insol.	
Daxad 21-----	2.0	46.9	9.1	11.8	97.4
Sodium hexametaphosphate.	0.16				
Daxad 21-----	1.0	46.6	8.6	11.5	95.3
Sodium hexametaphosphate.	0.16				
Goulac-----	1.0	49.0	6.8	11.6	94.2
Sodium hexametaphosphate.	0.16				
Bindarene Flour-----	4.0	43.2	12.3	12.5	97.8
Sodium hexametaphosphate.	0.4				
Marathon NS-----	1.0	49.7	6.0	13.3	83.7
Sodium hexametaphosphate.	0.4				
Goulac-----	2.0	47.8	5.1	16.7	92.8
Sodium fluoride-----	1.0				
Goulac-----	2.0	54.2	2.7	13.9	84.6
Dextrin-----	1.0				
Goulac-----	2.0	46.6	8.7	12.7	95.0
Quebracho-----	1.0				

Example IV

The flotation tests heretofore reported were made on a typical calcareous iron ore containing siliceous gangue constituents naturally activated to soap flotation. We shall now consider the application of our method of flotation to siliceous iron ores which contain unactivated siliceous materials; the silica in such ores is usually non-floatable by anionic collectors, but can be rendered floatable in the practice of our invention by the use of hydrated lime or metal-salt activating agents.

A sample of rejects was obtained from an iron ore washer in the Mesabi range, Minnesota. The sample as received was substantially finer than 48 mesh, and was a composite of classifier and dewatering device overflows impractical to treat by methods of flotation heretofore available. The sample contained hematite as the predominate iron oxide together with specular hematite and magnetite. The gangue was mainly quartz with some iron silicate minerals and clayey material. A head analysis gave 40.9 percent Fe and 33.8 percent insoluble.

A 250-gram portion of the washer rejects was wet ground to pass 100 mesh and deslimed at 20 microns by sedimentation and decantation using the procedure described in Example I. The granular portion was transferred to a laboratory mechanical flotation cell of standard design and diluted with tap water to give a pulp containing about 20 percent solids for flotation. The pulp was first conditioned with hydrated lime to establish a pulp pH of about 11 and activate the quartz and silicate minerals to soap flotation. The lime-conditioned pulp was subsequently conditioned with soda ash to precipitate the hydrated

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lime remaining in solution as insoluble calcium carbonate and simultaneously form caustic soda in the pulp. The resulting pulp, substantially free of dissolved lime, was then conditioned with Marathon M, a commercial magnesium lignin sulphonate marketed by the Marathon Chemical Company, and talloel, and then subjected to flotation. The rougher froth was double-cleaned by re-flotating in the same cell using tap water for dilution together with additional caustic soda, Marathon M, and talloel in each step to retard the remaining iron oxides and yield a final silica reject of low iron content. The quantities of reagents, expressed in conventional terms of pounds per ton of flotation feed, employed in the test were as follows:

Reagent	Conditioner				Rougher	Cleaner	
	No. 1	No. 2	No. 3	No. 4		No. 1	No. 2
Hydrated lime.....	5.4						
Soda ash.....		1.2					
Caustic soda.....							
Marathon M.....			4.0			1.1	1.1
Talloel.....				0.8		0.3	0.3
Time, min.....	2.5	2.5	2.5	2.5	4.0	0.1	0.1
Pulp pH.....	11.2	11.1	11.0	11.0	10.8	4.0	3.0
						10.8	10.8

The grade and distribution of iron and insoluble in the test products were as follows:

Product	Weight, per cent	Assay, per cent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates:					
Rougher.....	49.7	57.2	7.8	67.7	11.9
Cleaner.....	17.7	51.7	18.1	21.7	9.8
Composite.....	67.4	55.8	10.5	89.4	21.7
Silica rejects.....	32.6	13.6	78.3	10.6	78.3
Composite flotation feed.....	100.0	42.0	32.6	100.0	100.0

Activation and flotation of the silica from the ground and deslimed sample rejected 78.3 percent of the insoluble and enabled recovery of 89.4 percent of the iron in concentrates which assayed 55.8 percent Fe and 10.5 percent insoluble.

Similar results were obtained on the washer rejects using other commercial lignin sulphonates to retard the iron oxides during anionic flotation of the calcium activated silica from caustic alkaline pulps. The grade and yield of iron concentrates from comparative tests with several lignin sulphonates using the previously described flotation procedure are as follows:

Lignin sulphonate	Iron concentrates			
	Weight, per cent	Assay, per cent		Recovery, per cent Fe
		Fe	Insol.	
Acid calcium lignin sulphonate.....	70.0	54.9	12.2	90.5
Neutral calcium lignin sulphonate.....	70.5	55.6	10.5	92.9
Basic calcium lignin sulphonate.....	70.5	53.0	13.4	94.6
Sodium lignin sulphonate.....	69.1	54.4	12.7	89.1

Example V

A portion of the washer rejects containing unactivated silica was next floated using a solution of a commercial basic-calcium lignin sulphonate that contained 12.0 percent of CaO for the dual

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purpose of activating the silica to anionic flotation while retarding flotation of the iron oxides. A 250-gram charge of the rejects was ground and deslimed using the procedure described in Example I. The granular portion was floated in a mechanical flotation cell of standard design using the following reagents, expressed in conventional pounds per ton of flotation feed:

Reagent	Conditioner		Rougher	Cleaner	
	No. 1	No. 2		No. 1	No. 2
Caustic soda.....	4.4			0.8	0.8
Basic-calcium lignin sulphonate.....	6.0			0.4	0.4
Talloel.....		0.6		0.1	0.1
Time, min.....	2.5	2.5	2.5	2.5	2.5
Pulp pH.....	11.05	11.0	10.9	10.75	10.8

The composited iron concentrates recovered from the roughing and cleaning steps in the test assayed 58.4 percent Fe and 8.8 percent insol., and represented a recovery of 93.6 percent of the iron in the flotation feed. The silica rejects assayed 9.3 percent Fe and 84.8 percent insoluble and contained 80.6 percent of the silica in the feed. The calcium salts contained in the commercial basic calcium lignin sulphonate employed in the test was sufficient to activate the silica to anionic flotation and the lignin portion retard the iron oxides. In the practice of our invention, we prefer, however, to employ supplementary metal salt activating agents to insure more complete activation and flotation of the siliceous gangue constituents.

Example VI

A 250-gram portion of the Mesabi washer rejects was ground to pass 100 mesh and deslimed at 20 microns by the procedure described in Example I. The granular portion was froth floated in a mechanical cell to reject the silica and recover an iron enriched product using hydrated lime to activate the silica, Marathon NS, a commercial sodium lignin sulphonate marketed by the Marathon Chemical Company, to retard the iron oxides, and talloel as the collector for the activated silica. The reagent charge, expressed in pounds per ton of flotation feed, employed in the test was as follows:

Reagent	Conditioner			Rougher
	No. 1	No. 2	No. 3	
Hydrated lime.....	5.5			
Caustic soda.....		1.5		
Marathon NS.....		3.0		
Talloel.....			0.8	
Time, min.....	2.5	2.5	2.5	3.0
Pulp pH.....	10.6	11.0	11.0	10.85

A roughing treatment sufficed for an adequate separation of the activated silica from the retarded iron oxides. The rougher iron concentrates assayed 57.6 percent Fe and 8.1 percent insol., and represented a recovery of 85.7 percent of the iron in the feed. The silica rejects rougher froth assayed 16.0 percent Fe and 85.2 percent insol., and contained 62.2 percent of the insoluble in the flotation feed.

In the recorded test, it will be noted that good flotation of the silica was achieved from the iron oxides in the presence of hydrated lime. Supplementary experiments indicated that the flotation pulp contained about 0.8 pound of dissolved hydrated lime per ton of solids in the test. While

we prefer that the flotation pulp be substantially free of dissolved hydrated lime in the practice of our invention, it is not obligatory that the flotation pulps be completely free of hydrated lime or calcium salts. Some calcium salts in the flotation pulp are permissible, and, in fact, are advantageous in that they insure more complete flotation of the silica. In carrying on our invention we prefer that the flotation pulp contain not more than 100 parts per million of dissolved hydrated lime or calcium salts.

Example VII

A 250-gram portion of the washer rejects was ground and deslimed as previously described. The granular portion was conditioned with the equivalent of 17 pounds per ton of hydrated lime. The lime-conditioned pulp which had a pH of 12.3 was then washed three times with tap water to remove the hydrated lime remaining in solution. The resulting pulp which had a pH of 9.8 was subsequently transferred to a laboratory mechanical flotation cell and diluted with tap water to give a pulp for flotation containing about 20 percent solids. The pulp was conditioned with caustic soda, Goulac, and talloel, and then subjected to flotation to float the lime-activated silica from the retarded iron oxides. The rougher froth was triple-cleaned by re-floating in the same cell using tap water for dilution together with caustic soda, Goulac, and talloel. The quantities of reagents, expressed in terms of pounds per ton of flotation feed, employed in the test were as follows:

Reagent	Conditioner		Rougher	Cleaner		
	No. 1	No. 2		No. 1	No. 2	No. 3
Caustic soda	2.8	-----	-----	1.1	1.1	1.1
Goulac	4.3	-----	-----	0.6	0.6	0.6
Talloel	-----	0.9	-----	0.1	0.1	0.1
Time, min	2.5	2.5	5.5	4.0	3.5	2.5
Pulp pH	11.1	11.1	10.7	10.8	10.75	10.85

The grade and distribution of iron and insoluble in the test products were as follows:

Product	Weight, per cent	Assay, Percent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates:					
Rougher	38.8	55.6	9.9	51.5	11.8
Cleaner	33.4	54.0	14.6	43.0	15.4
Composite	72.2	54.8	12.3	94.5	27.2
Silica rejects	27.8	8.2	85.4	5.5	72.8
Composite flotation feed	100.0	41.8	32.6	100.0	100.0

Activation and flotation of the silica from the ground and deslimed sample rejected 72.8 percent of the silica and enabled recovery of 94.5 percent of the iron in concentrates which assayed 54.8 percent Fe and 12.3 percent insoluble.

The results of the previously described flotation tests are typical of those we obtained on a variety of calcareous and siliceous iron ores using various crude and purified lignin sulphonates as the iron oxide depressants while floating activated siliceous gangue constituents from caustic alkaline iron ore pulps with oleic acid, sodium oleate, talloel, sulfate soap, or similar anionic collecting agents. While we have disclosed the preferred embodiments of our invention, it will be readily apparent to those skilled in the art that

many variations and modifications may be made therein without departing from the spirit of the invention.

What is claimed:

1. A process for beneficiating calcareous iron ores containing siliceous gangue materials which comprises addition to an aqueous pulp of the comminuted ore a quantity of caustic alkali to establish a pulp pH at least as alkaline as pH 10 and a lignin sulphonate, together with an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, and mixtures of fatty and resin acids, and soaps thereof, and then subjecting said pulp to agitation and aeration whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

2. A process for beneficiating calcareous iron ores containing siliceous gangue materials which comprises addition to an aqueous pulp of the comminuted ore a quantity of caustic alkali to establish a pulp pH at least as alkaline as pH 10 an iron oxide depressant selected from the class consisting of crude and purified metal salts of lignin sulphonate, crude and purified paper mill sulfite liquors, and dehydrated residues thereof, together with an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty acids and resin acids, and soaps thereof, and then subjecting said pulp to agitation and aeration whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

3. A process for beneficiating iron ores containing siliceous gangue materials which comprises addition to an aqueous pulp of the comminuted ore a quantity of caustic alkali to establish a pulp at least as alkaline as pH 10 adding thereto a basic-calcium lignin sulphonate together with an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty and resin acids, and soaps thereof, and then subjecting said pulp to agitation and aeration whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

4. A process for beneficiating iron ores containing siliceous gangue materials which comprises conditioning an aqueous pulp of the comminuted ore in the presence of sufficient hydrated lime to yield a pulp with a pH of at least 10 and containing not more than 100 parts per million of dissolved hydrated lime, adding thereto a lignin sulphonate and subjecting said pulp to agitation and aeration in the presence of an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty and resin acids, and soaps thereof, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

5. A process for beneficiating iron ores containing siliceous gangue materials which comprises conditioning an aqueous pulp of the comminuted ore, in the presence of sufficient hydrated lime to yield a pulp with a pH of at least 11, thereafter washing the conditioned pulp with fresh water to yield a pulp containing not more than 100 parts per million of hydrated lime remaining in solution, adding thereto sufficient caustic alkali to establish a pulp at least as alkaline as pH 10, and a lignin sulphonate, thereafter subjecting said pulp to agitation and aeration in the presence of an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty and resin

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acids, and soaps thereof, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

6. A process of beneficiating iron ores containing siliceous gangue materials which comprises conditioning an aqueous pulp of the comminuted ore in the presence of sufficient hydrated lime to yield a pulp with a pH of at least 11, adding thereto soda ash to precipitate the dissolved hydrated lime and yield a pulp containing not more than 100 parts per million of hydrated lime remaining in solution, and adding thereto a lignin sulphonate and thereafter subjecting said pulp to agitation and aeration in the presence of an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty and resin acids, and soaps thereof, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered. 20

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7. A process for beneficiating iron ores containing siliceous gangue materials which comprises addition to an aqueous pulp of the comminuted ore a quantity of caustic alkali to establish a pulp at least as alkaline as pH 10, and a soluble compound of an inorganic anion combined with a polyvalent metal selected from the class consisting of calcium, magnesium, strontium, barium, and lead, together with a lignin sulphonate and thereafter subject said pulp to agitation and aeration in the presence of an anion active collecting agent selected from the class consisting of higher fatty acids, resin acids, mixtures of fatty and resin acids, and soaps thereof, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered. 15

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