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FROTH FLOTATION OF SILICA FROM IRON ORE WITH ANIONIC COLLECTOR

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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 vegetable tannin extracts or acidic polyhydroxy aromatic compounds derived therefrom by hydrolysis.

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 and 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 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 vegetable tannin extracts or related acidic polyhydroxy aromatic organic compounds, such as catechol, hydroquinone, pyrogallol, gallic acid, and tannic acid, derived from vegetable tannins by hydrolytic decomposition.

"Tannin" is a class name applied to a group of astringent products of vegetable origin employed for the tanning of animal hides to yield leather. Tannins occur widely distributed in nature in the bark, wood, leaves, roots, and fruits of various trees and plants. They are found in commercial quantities, for example, in the bark and wood of the quebracho, oak, chestnut, pine, hemlock, acasia, mangrove, mimosa, and other trees; in the leaves of sumac and gambier; the roots of canaigre and palmetto; the fruits of myrobalans and Turkish oak; and in gall-nuts, the warty masses which grow on trees as a result of insects puncturing the bark.

The tannins are extracted from these and other plants and trees by comminution of the tannin-bearing material, leaching with water, and recovering the extracted solids by evaporation. The tannins are unavoidably diluted by other water soluble substances present in the bark or wood, such as mineral salts, carbohydrates, etc., and the extracts vary in the nature and proportion of tannin and non-tannin materials. The extracts may also be contaminated with suspended insoluble matter and appear turbid or muddy. The crude extracts may be treated by different methods before evaporation to yield a purified extract. Suspended solids may be removed by filter-pressing, centrifuging, or by settling and decanting. Another method of treatment is to add blood albumin and heat the extract to about 70° C., at which temperature the albumin coagulates and carries down with it the suspended matter and some of the deeply colored non-tannin bodies. Other methods of purification involve treatment with chemical agents, such as sulfur dioxide and sodium bisulfite. The purified extracts are usually evaporated under vacuum to yield concentrated liquid extracts or substantially dehydrated residues for marketing. Commercial liquid extracts may contain 50 to 60 percent or more of water, and the powdered or solid commercial extracts may contain from 5 to 15 percent water.

Although the exact chemical structure of the

tannins is not yet fully known, it is generally believed that they are rather complex glucosides of various polyhydroxy aromatic acids. Hydrolysis of the tannins, as by fusion with alkali, yields among other entities glucose and gallic, ellagic, or protocatechuic acid. The acid formed from hydrolysis furnishes a basis for simple classification of the tannin materials:

(1) The gallol tannins hydrolyze to yield gallic acid, with di-gallic (tannic) acid as an intermediate, which is convertible by heat into pyrogallol. These tannins give a distinguishing blue-black color with ferric chloride, and yield no precipitate with bromine water. This class includes the tannins of gall-nuts, sumac, oak wood, and chestnut wood.

(2) The catechol tannins hydrolyze to yield protocatechuic acid, which is convertible by heat into catechol. These tannins give a distinguishing green-black color with ferric chloride, and yield a precipitate with bromine water. This class includes the tannins of oak bark, hemlock bark, and quebracho wood. Arbutin, a glucoside, yields a catechol isomer, hydroquinone, and belongs to this class.

(3) The ellagi tannins yield ellagic acid on hydrolysis with dilute sulfuric acid. This class includes the tannins of divi-divi, myrobalans, and valonia.

This simple classification is arbitrary, however, as many of the natural tannins are quite complex and appear to be mixtures or combinations of the various classes.

We have found that various vegetable tannin extracts of the above designated classes are effective depressants for iron oxides during anionic flotation of the activated siliceous materials. The tannins which we have used and found satisfactory in the practice of our invention include the liquid and solid extracts of quebracho wood, chestnut wood and bark, hemlock wood and bark, oak wood and bark, acacia (Borneo cutch), sumac, mangrove, and myrobalans. The liquid and solid extracts were used interchangeably in our method of flotation, and, based on their respective tannin contents, were about equally effective. The non-tannins in the various extracts were inactive diluents and exerted no deleterious effect on flotation of the silica or retardation of the iron oxides.

In the practice of our invention, we may also employ as iron oxide depressants the acidic polyhydroxy aromatic compounds resulting from hydrolytic decomposition of natural vegetable tannin materials. These compounds, which may also be prepared by well known methods of organic synthesis, include catechol, hydroquinone, pyrogallol, gallic acid, and tannic (di-gallic) acid. While we prefer to employ the natural tannin extracts because of their lower cost, the acidic polyhydroxy aromatic compounds may be used if desired. In describing our invention, we shall for convenience use the term "vegetable tannin extract" to include the liquid and solid forms of natural tannin extracts of commerce and the acidic polyhydroxy aromatic compounds which may be derived therefrom or prepared by organic synthesis.

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 the vegetable tannin extracts. We prefer to employ caustic alkalies, such as sodium or potassium hydroxides, 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 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 in our flotation method to keep the pH in the range of 10 to 12.

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, presumedly 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 the 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 vegetable tannin extracts.

In the practice of our 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 suffices for complete activation of the siliceous gangue in most iron ores. The usual 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 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 of lime 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 100 parts per million of hydrated lime in solution, equivalent to about 0.8 pounds of dissolved hydrated lime per ton of solids in our tests, we prefer that the flotation pulp be substantially free of dissolved hydrated 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 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 usual requirements for most ores being 1 to 2 pounds per ton of solids, precipitates the lime remaining in solution and gives a pulp of the desired caustic alkalinity for flotation. Additional caustic soda may be added to the pulp, however, to establish and maintain the desired pH during 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 dissolved lime in the pulp 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 vegetable tannin extract 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 as they insure complete activation of the siliceous constituents to flotation.

The anion active collecting agents which we have found suitable for flotation of 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 tallols and sulfate soaps derived from sulfate paper mill black liquors. The tallols, which as mixtures of fatty and resin acids, are relatively inexpensive and are the preferred collectors in the practice of our invention.

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.

We have discovered that various addition agents may be advantageously employed to supplement the vegetable tannin extracts 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; 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 dextrins; and various crude and purified lignin sulphonates such as may be recovered from paper mill sulfite liquors. 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 vegetable tannin extracts 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 vegetable tannin extract may result 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 tannin extract 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 tests, 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 tests 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 retreated by conventional methods in continuous flotation operations to yield an even higher grade concentrate without departing from the spirit of the invention.

Our 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 amounts 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 "insoluble" or "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 to 200 mesh or finer, depending on the degree of liberation of 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 should be selected accordingly. 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, essentially free of slime and coarser than 20 microns, was then 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 tallol as the collector, and "Purex SM brand," a quebracho extract marketed by The Tannin Corp., 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
Caustic soda	1.6			0.6	0.6
Purex SM brand quebracho extract	0.5				
Tallol		0.8			
Time, min	2.5	2.5	1.5	1.5	1.5
Pulp pH	11.15	11.15	10.9	10.75	10.8

The substantially deslimed pulp was first conditioned with the caustic soda (commercial lye) and quebracho extract to establish the alkalinity desired for flotation and to retard the iron oxides. Tallol was chosen for the collector in the test. The pulp was conditioned with the tallol, and 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 1.5 minutes, whereupon flotation was complete. The rougher froth was cleaned twice by re-floating in the same cell using tap water with additional caustic to maintain alkalinity. The final silica rejects, the combined iron concentrates from the cleaning steps (middlings), the rougher iron concentrates (tailings), and the untreated slime were dried, weighed, and assayed. The results of the test follow:

Product	Weight, per cent	Assay, percent			Distribution, percent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher	36.4	52.4	5.1	11.6	52.5	17.0	17.1
Cleaner	11.8	33.1	15.8	17.2	10.8	17.2	8.3
Slime	27.0	43.2	10.7	15.1	32.1	26.6	16.5
Composite	75.2	46.1	8.8	13.7	95.4	60.8	41.9
Silica rejects	24.8	6.9	17.2	57.7	4.6	39.2	58.1
Composite feed	100.0	36.3	10.9	24.6	100.0	100.0	100.0

The flotation silica rejects accounted for 24.8 weight percent of the feed, and contained 58.1 percent of the insoluble and only 4.6 percent of the iron. The untreated slime and cleaner iron concentrates were sufficiently low in insoluble to be considered finished grade. The composited iron concentrates represented a recovery of 95.4 percent of the iron in the feed and assayed 46.1 percent Fe, 8.8 percent CaO, and 13.7 percent insoluble.

The results of the recorded test are typical of those obtained on deslimed charges of the calcareous red ore ground to pass 65, 100, or 200 mesh in a pebble mill, iron ball mill, or iron rod mill. Good flotation of the activated silica was achieved by using a moderate quantity of tallol, sulfate soap, oleic acid, sodium oleate, or similar anionic collecting agents in caustic alkaline pulps in conjunction with the "Purex SM Brand" quebracho extract to retard the iron oxides. A moderate quantity of the quebracho extract sufficed for the separation and control of the depressant was not critical.

Example II

The summarized results of several flotation tests on the calcareous red ore using various vegetable tannin extracts as the iron oxide depressant are given below. The ore charges were ground to pass 100 mesh, deslimed at 20 microns, and floated by the procedure described in Example I. The tests were made employing 1.0 pound per ton of the designated vegetable tannin extract together with 0.8 pound of tallol per ton as the collector, and 2.0 to 3.0 pounds per ton of caustic soda as needed to give a pulp pH of about 11 for the roughing operation. The rougher froths were double-cleaned in the tests using additional caustic soda and tannin to retard the remaining iron oxides; the quantities employed in the cleaning steps were 0.8 and 0.1 pound per ton, respectively. The grade of the composited flotation iron concentrates from the roughing and cleaning steps and the percentage of iron recovered from the flotation feed in the tests are as follows:

Test No.	Vegetable tannin extract employed	Weight, per cent	Assay, per cent			Recovery, per cent Fe
			Fe	CaO	Insol.	
	Flotation feed	100.0	33.4	11.4	28.2	100.0
1	"C, F, del C" brand quebracho extract.	78.2	41.6	11.8	11.6	97.4
2	"Hy-Test" brand quebracho extract.	66.1	47.7	7.7	13.0	93.1
3	Oak bark extract	72.7	44.2	10.5	12.5	96.1
4	Borneo cutch	79.9	41.5	11.7	14.8	97.9
5	Hemlock extract	66.5	47.4	9.3	12.1	93.9
6	Chestnut extract	69.9	45.4	10.2	12.1	94.8
7	Myrobalan extract	65.1	47.4	8.4	12.8	93.5

The various tannin extracts employed in the

tests were of the dry, powdered forms and were selected as being typical of the gallol, catechol, and ellagi classes of tannins commercially available. Based on their respective tannin content, the various commercial extracts were equally effective for retarding the iron oxides during anionic flotation of the silica.

Example III

In the two preceding examples we have considered the utility of various commercial tannin extracts as iron oxide depressants in our method of silica flotation. We shall now consider the results of similar flotation tests on deslimed portions of the calcareous red ore wherein various polyhydroxy benzenes and benzoic acids were employed to retard the iron oxides. These polyhydroxy aromatic compounds are closely related to the vegetable tannins and may be derived from the extracts by hydrolysis of the glucosides. Acid hydrolysis or fusion of the dry extract with alkali yields the hydroxy acids which may be recovered. The acids decompose on heating to yield the polyhydroxy benzenes. The compounds may also be conveniently prepared from benzene and its derivatives by well known methods of organic synthesis.

The flotation charges were ground to pass 100 mesh, deslimed at 20 microns, and floated by the procedure given in Example I. The comparative tests were made using 1.0 pound per ton of the designated polyhydroxy compound to retard the iron oxides together with 0.8 pound per ton of tallol as the silica collector and 2.0 to 3.0 pounds per ton of caustic soda as needed to establish a pulp pH of about 11 for the roughing separation. The rougher froths in the tests were triple-cleaned using 0.8 pound per ton of caustic soda to maintain the pulp alkalinity in each step. The grade of the flotation concentrates from the roughing and cleaning steps and the percentage of iron recovered from the flotation feed in the various tests are as follows:

Test No.	Polyhydroxy compound employed as depressant	Weight, per cent	Assay, per cent			Recovery, per cent Fe
			Fe	CaO	Insol.	
	Flotation feed	100.0	33.8	11.4	27.7	100.0
1	Gallic acid	67.8	46.7	9.2	14.3	94.9
2	Tannic acid (di-gallic acid)	67.8	46.3	8.0	15.0	93.1
3	Catechol	57.2	50.0	4.7	16.2	86.7
4	Hydroquinone	52.8	51.8	3.8	15.3	83.2
5	Pyrogallol	65.0	47.4	7.2	15.9	91.7

The results of the test are of interest and demonstrate that the polyhydroxy benzenes and benzoic acids may be employed if desired as iron oxide depressants. The polyhydroxy benzenes (poly-phenols) are particularly advantageous when rejection of the calcite or other calcareous materials with the silica is sought. While we prefer to use the vegetable tannin extracts as depressants in the practice of our invention because of their high degree of effectiveness and relatively low cost, the acidic polyhydroxy aromatic compounds resulting from hydrolysis of natural or treated tannin extracts of commerce, or prepared by organic synthesis, may likewise be employed without departing from the spirit of our invention.

Example IV

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 iron oxides was effected by the following reagents expressed in conventional terms of pounds per ton of ore:

Reagent	Conditioner		Rougher	Cleaner		
	No. 1	No. 2		No. 1	No. 2	No. 3
Caustic soda	3.0			0.6	0.6	0.6
Purex SM brand quebracho extract	2.0					
Tallol		0.8				
Time, min.	2.5	2.5	2.5	2.5	2.5	2.5
Pulp pH	11.0	11.0	10.8	10.85	10.8	10.8

The slime-bearing pulp was conditioned with caustic soda (commercial lye) and quebracho extract. Tallol was then added and the pulp again briefly conditioned as indicated. The rougher froth was triple-cleaned by re-floating in the same cell using tap water for dilution together with caustic soda. The rougher and composited 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, percent			Distribution, percent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher	52.3	49.4	3.8	18.3	70.7	18.5	39.3
Cleaner	28.2	34.1	16.7	15.7	26.3	43.8	18.1
Composite	80.5	44.0	8.3	17.4	97.0	62.3	57.4
Silica rejects	19.5	5.6	20.8	53.1	3.0	37.7	42.6
Composite feed	100.0	36.5	10.8	24.3	100.0	100.0	100.0

Flotation of the silica from the slime-bearing pulp rejected 42.6 percent of the silica (insol.) with a loss of only 3.0 percent of the iron. It is therefore apparent that our method of flotation is applicable to iron ore pulp containing substantial quantities of slime.

Example V

In the previously described examples of practice, various vegetable tannin extracts and acidic polyhydroxy aromatic compounds which may be derived from the tannin extracts by hydrolysis were 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 vegetable tannin extracts in our method of flotation.

A 250-gram charge of the calcareous red ore ground to pass 100 mesh in a laboratory rod mill and the charge including slime was floated by the procedure described in Example IV. 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 quebracho extract and aid retardation of the iron oxides. The quantities of reagents employed in the test, expressed in conventional pounds per ton of ore, were as follows:

Reagent	Conditioner		Rougher	Cleaner	
	No. 1	No. 2		No. 1	No. 2
Caustic soda	2.5			0.8	0.8
Purex SM brand quebracho extract	1.0			0.04	0.04
Potato starch	1.0			0.04	0.04
Tallol		0.8			
Time, min	2.5	2.5	2.0	2.5	2.5
Pulp pH	11.0	11.0	10.8	10.75	10.75

The results of the test are as follows:

Product	Weight, per cent	Assay, percent			Distribution, percent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher	52.3	50.4	5.6	14.4	73.0	25.5	30.5
Cleaner	27.8	31.5	21.6	12.6	24.2	52.7	14.0
Composite	80.1	43.8	11.1	13.8	97.2	78.2	44.3
Silica rejects	19.9	5.1	12.5	69.8	2.8	21.8	55.7
Composite feed	100.0	36.2	11.4	25.0	100.0	100.0	100.0

The combination of quebracho extract and potato starch facilitated effective retardation of both the slime and granular iron oxides during anionic flotation of the silica. Additional quebracho supplemented by starch was employed in the cleaning steps to facilitate recovery of calcite in the composited iron concentrates and yield a substantially self-fluxing iron product. If desired, however, the calcite may be floated with the silica and rejected by use of a small additional quantity of collector in the cleaning steps together with reduced quantities of tannin extract.

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 quebracho and other vegetable tannin extracts. The results of the tests were similar to those recorded when optimum quantities of the starch and tannin were employed. 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., and assigned to the same assignee as the present application. 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 vegetable tannin extracts.

Example VI

In addition to the starches and hydrolyzed starch products, other useful auxiliary addition agents which have been employed in conjunction with the vegetable tannin extracts in the practice of this invention include the metaphosphates, the polyphosphates, and various crude and purified lignin sulphonates derived from paper mill sulfite liquors. We shall now consider the results of a typical test using Goulac, a commercial calcium lignin sulphonate product from dehydration of paper mill sulfite liquor marketed by the American Gum Products Company, in conjunction with Purex SM brand quebracho extract to retard the iron oxides during flotation of activated silica from a calcareous red iron ore.

The ore was ground to pass 100 mesh and the charge, including slime, was floated by the procedure described in Eample IV. The quantities of caustic, Purex SM brand quebracho, Goulac, and tallol employed in the roughing step were 3.0, 1.0, 2.0, and 0.8 pounds per ton of ore, respectively. The rougher froth was triple-cleaned using 0.8 and 0.04 pound per ton of caustic soda and quebracho, respectively, in each step. The composited rougher and cleaner flotation concentrates from the test assayed 46.6 percent Fe, 8.7 percent CaO, and 12.7 percent insol., and represented a recovery of 95.0 percent of the iron in the ore. The silica rejects assayed 6.5 percent Fe, 18.2 percent CaO, and 57.2 percent insol., and contained 63.2 percent of the silica (insoluble) in the ore.

Example VII

The utility of metaphosphates as auxiliary agents to supplement the tannin extracts in the practice of our invention was demonstrated by the following test.

A 250-gram portion of deslimed gravity plant fines from a bowl classifier operating in an iron ore concentrator of the Birmingham district, Alabama, was subjected to flotation to reject the silica, which was present largely as quartz, and recover an iron enriched product. The sample as received was substantially finer than 65 mesh. The reagent charge for flotation, expressed in pounds per ton of feed, was as follows:

Reagent	Conditioner		Rougher	Cleaner	
	No. 1	No. 2		No. 1	No. 2
Caustic soda	1.25			0.5	0.5
Purex SM brand quebracho extract	1.00				
Sodium hexametaphosphate	0.16			0.04	0.08
Sodium oleate		2.00			
Oleic acid		0.96			
Time, min	2.5	2.5	2.5	2.5	2.5
Pulp pH	11.1	11.1	10.95	10.8	10.9

The results of the test are as follows:

Product	Weight, per cent	Assay, percent			Distribution, percent		
		Fe	CaO	Insol.	Fe	CaO	Insol.
Iron concentrates:							
Rougher	78.8	48.2	8.5	12.2	89.3	74.1	49.7
Cleaner	10.7	36.0	17.0	13.0	9.0	20.1	7.2
Composite	89.5	46.7	9.5	12.3	98.3	94.2	56.9
Silica rejects	10.5	6.9	5.0	79.4	1.7	5.8	43.1
Composite feed	100.0	42.6	9.0	19.3	100.0	100.0	100.0

Example VIII

The flotation tests heretofore reported were made on typical calcareous iron ores and mill products which contained siliceous gangue materials naturally activated to anionic flotation due to the presence of soluble lime or magnesia salts in the ores. We shall now consider the application of our invention to iron ores containing unactivated siliceous gangue constituents. The weathered and siliceous red ores of the Birmingham district, for example, seldom contain sufficient lime or magnesia salts to activate the contained siliceous materials to anionic flotation. In applying our invention to such ores the silica may be activated and rendered floatable by the use of hydrated lime or metal-salt activating agents.

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

A 250-gram portion of the washer rejects was wet ground to pass 100 mesh and deslimed at 20 microns by sedimentation and decantation by the procedure described in Example I. The granular portion was transferred to a laboratory mechanical flotation cell and diluted with tap water to a pulp consistency of about 20 percent solids. The pulp was conditioned with hydrated lime to establish a pulp pH of about 11 and activate the silica to anionic flotation. Soda ash was then added to the pulp to precipitate the hydrated lime remaining in solution and simultaneously form caustic soda in the pulp. The resulting pulp, substantially free of dissolved lime, was then conditioned with quebracho extract and tallol and subjected to flotation. The lime-activated silica floated readily from the retarded iron oxides in a compact, heavily mineralized, siliceous froth. The rougher froth was cleaned once by re-floating in the same cell to retard the remaining iron oxides and give the final silica rejects. The quantities of reagents, expressed in pounds per ton of ore, employed in the test were as follows:

Reagent	Conditioner				Rougher	Cleaner No. 1
	No. 1	No. 2	No. 3	No. 4		
Hydrated lime	4.0					
Soda ash		0.9				
Caustic soda			1.0			0.4
Purex SM brand quebracho extract			1.0			0.2
Tallol				0.6		0.1
Time, min	2.5	2.5	2.5	2.5	4.0	4.0
Pulp pH	11.0	10.9	11.2	10.9	10.8	10.8

The grade of the flotation test products and the untreated slime fraction are as follows:

Product	Weight, per cent	Assay, per cent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates:					
Rougher	28.7	55.8	9.5	39.5	8.1
Cleaner	24.3	51.7	16.1	31.0	11.7
Composite	53.0	53.9	12.5	70.5	19.8
Silica rejects	20.5	11.9	80.8	6.0	49.4
Slime (untreated)	26.5	35.9	39.0	23.5	30.8
Composite	100.0	40.5	33.5	100.0	100.0

Activation and flotation of the granular silica in the deslimed sample yielded a composite iron concentrate from roughing and cleaning representing a recovery of 70.5 percent of the iron in the washer rejects. The slime was neither of concentrate nor tailing grade and contained 23.5 percent of the total iron in the sample. Flotation gave an excellent separation on the granular portion; 71.3 percent of the silica (insoluble) was rejected in the silica froth and 92.2 percent of the iron was recovered in the composited iron concentrates.

Example IX

Another 250-gram portion of the siliceous washer rejects was ground to pass 100 mesh in a laboratory rod mill. The ground charge, including slime, was transferred to a small mechanical flotation cell, diluted with tap water to give a pulp containing about 22 percent solids, and subjected to froth flotation using the following reagent charge expressed in pounds per ton of feed:

Reagent	Conditioner				Rougher	Cleaner		
	No. 1	No. 2	No. 3	No. 4		No. 1	No. 2	No. 3
Hydrated lime	4.0							
Soda ash		0.9						
Caustic soda			1.2			0.4	0.4	0.4
Purex SM brand quebracho extract			1.5			0.1	0.1	0.1
Tallol				1.0		0.2	0.2	0.2
Time, min	5.0	2.5	2.5	1.5	5	4.5	3.5	3.0
Pulp pH	10.9	10.9	11.0		10.7	10.8	10.9	10.9

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

Product	Weight, per cent	Assay, per cent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates:					
Rougher	28.4	51.2	14.2	36.2	11.7
Cleaner	43.4	53.5	14.6	57.7	18.2
Composite	71.8	52.6	14.5	93.9	29.9
Silica rejects	28.2	8.6	86.4	6.1	70.1
Composite feed	100.0	40.2	34.8	100.0	100.0

Activation and anionic flotation of the silica from the slime-bearing pulp rejected 70.1 percent of the silica (insoluble) in the washer rejects and yielded an iron enriched product which assayed 52.6 percent Fe and 14.5 percent insoluble and represented a recovery of 93.9 percent of the total iron. This test further demonstrates the utility of our method for floating silica from iron ore pulps containing substantial quantities of slime. While we prefer to employ deslimed pulps in the practice of our invention, desliming is not obligatory on many iron ores.

The results of the above recorded test were about average of those obtained on total charges of the ore. Various of the commercial tannin extracts were employed and found satisfactory for retarding the iron oxides during anionic flotation of the silica with oleic acid, sodium oleate, sulfate soap, tallol, and the fish oil fatty acids and soaps. Based on their respective tannin content, the liquid and solid tannin extracts, such as sulfited and non-sulfited quebracho extracts, oak extract, hemlock extract, chestnut extract, myrobalans, and Borneo cutch were about equally effective for retarding the iron oxides. Control of the tannin and collector was not critical and reasonable variation in the quantities employed did not adversely affect the separation. Considerable latitude was apparent both in the choice and quantities of tannin extract and collector employed.

Example X

The utility of auxiliary addition agents, such as the solubilized cereal and tuber starches, metaphosphates, and lignin sulphonates, to supplement the vegetable tannin extracts and aid retardation of iron oxides during anionic flotation of naturally activated silica from calcareous iron ore pulps has been described in previous examples. These addition agents are likewise useful and give an improved separation on many siliceous iron ores. We shall now consider the results obtained using causticized potato starch as an addition agent to supplement quebracho extract in the flotation of a siliceous ore.

A sample of tailing pond material from an operating plant in the Mesabi Range, Minnesota, was obtained for testing. The sample as received was substantially finer than 20 mesh and contained hematite as the predominant iron oxide together with some specular hematite and magnetite. The gangue was quartz together with some iron silicates and considerable clayey material. A head analysis of the sample gave 43.5 percent Fe and 31.8 percent acid insoluble.

A 250-gram portion of the sample was ground to 100 mesh and deslimed by the procedure given in Example VIII to reject the clay. The granular portion was transferred to a laboratory flotation cell and diluted with tap water to give a pulp containing about 20 percent solids for flotation. The pulp was conditioned with hydrated lime to activate the silica and then with soda ash to precipitate the lime remaining in solution as carbonate. The lime-activated silica was floated using tallol as the collector while retarding the iron oxides with a combination of quebracho extract and potato starch. The potato starch was solubilized by rupturing the granules with caustic soda at room temperature to give a solution containing 2.5 percent starch and 0.5 percent caustic soda. The reagent charge, expressed in pounds per ton, employed in the test was as follows:

Reagent	Conditioner				Rougher
	No. 1	No. 2	No. 3	No. 4	
Hydrated lime	6.0				
Soda ash		1.5			
Caustic soda			1.0		
Purex SM brand quebracho extract			1.0		
Potato starch			2.0		
Tallol				1.0	
Time, min.	5	5	2.5	1.5	2.5
Pulp pH	11.1	11.1	11.0		11.0

The combination of tannin and starch was particularly efficacious for retarding the iron oxides. A roughing treatment yielded a froth of sufficiently low iron content for rejection and a cleaning operation was unnecessary. The grade and distribution of iron and insoluble in the flotation products are as follows:

Product	Weight, per cent	Assay, per cent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates	68.6	61.6	5.3	92.7	12.2
Silica froth	31.4	10.6	83.0	7.3	87.8
Composite feed	100.0	45.6	29.7	100.0	100.0

Example XI

A sample of siliceous iron ore from a Michigan deposit was next examined. The ore resembled the weathered "taconites" of the Lake Superior district and consisted of hematite together with some magnetite finely disseminated in a siliceous gangue of quartz and various iron silicates. Grinding to 100 mesh was necessary for liberation of the iron oxides.

A 250-gram portion of the ore rolls-crushed to pass 20 mesh was wet ground in a laboratory rod mill to 100 mesh. The ground charge including slime and grind water was transferred to the small mechanical flotation cell and diluted with tap water to give a pulp containing about 20 percent solids. The pulp was conditioned for 10 minutes with hydrated lime equivalent to 16 pounds per ton of solids to activate the quartz and iron silicates to anionic flotation. The pH of the lime-conditioned pulp was 12.3. The pulp was withdrawn from the cell and allowed to settle whereupon the clear supernatant water was carefully decanted to avoid loss of slime. The settled ore was repulped with fresh water to about 10 percent solids and allowed to settle. The lime-bearing water was decanted and the washing operation again repeated to give a final pulp (pH—9.8) substantially free of dissolved hydrated lime. The lime-conditioned and washed solids were returned to the cell and diluted with tap water to give a pulp containing about 22

percent solids for flotation. Flotation of the activated silica from the retarded iron oxides was achieved with the following reagents, expressed in pounds per ton of ore:

Reagent	Conditioner		Rougher	Cleaner		
	No. 1	No. 2		No. 1	No. 2	No. 3
Caustic soda	2.0			0.8	0.8	0.8
Purex SM brand quebracho extract	1.0			0.08	0.04	0.04
Tallol		1.0		0.2	0.2	0.2
Time, min.	2.5	2.5	4.0	2.5	2.5	2.5
Pulp pH	11.2		11.0	10.7	10.8	10.8

The results of the test are as follows:

Product	Weight, per cent	Assay, per cent		Distribution, per cent	
		Fe	Insol.	Fe	Insol.
Iron concentrates:					
Rougher	27.7	57.8	12.0	41.1	8.3
Cleaner	33.5	54.5	16.8	46.9	14.1
Composite	61.2	56.0	14.6	88.0	22.4
Silica rejects	38.8	12.0	80.0	12.0	77.6
Composite feed	100.0	38.9	40.0	100.0	100.0

The results of the recorded test are typical of those obtained on lime-activated charges of the finely ground ore using various commercial tannin extracts as the depressants. Equally good activation of the quartz and iron silicate gangue minerals was achieved by either conditioning the pulp with a large quantity of hydrated lime and removing the excess dissolved lime by washing the pulp before flotation, or by conditioning the pulp with a lesser quantity of hydrated lime and precipitating the dissolved lime remaining in the pulp with soda ash prior to flotation as described in Example IX. Good flotation of the silica was achieved with moderate quantities of collector from both total and deslimed pulps of the ore containing not more than 100 parts per million of dissolved lime. Pulp containing larger quantities of dissolved lime or calcium salts invariably required excessive amounts of collector and flotation of the silica was incomplete.

Example XII

While we prefer to employ hydrated lime as the silica activating agent in the practice of our invention, the soluble salts of calcium, magnesium, barium, strontium, and lead may also be employed if desired. Addition of a moderate quantity of the metal salt to the caustic alkaline iron ore pulp suffices to activate the siliceous constituents to anionic flotation without impairing retardation of the iron oxides by the vegetable tannin extracts. Various ores require different quantities of the metal salt activating agents and the optimum quantity of activator is best determined by experimentation for any particular case. The utility of metal salts activating agents in the practice of our invention was demonstrated by the following experiment:

Three 250-gram charges of a siliceous iron ore from the Lake Superior district were ground to pass 100 mesh, deslimed at 20 microns, and floated by the reagent charge and procedure given in Example I. Lead nitrate, magnesium chloride, and calcium chloride were employed on the charges to activate the silica. The summarized results showing the grade of the flotation concentrates from the tests are as follows:

Method of activation	Weight, per cent	Assay, per cent		Recovery of Fe
		Fe	Insol.	
Flotation feed	100.0	38.6	41.5	100.0
$CaCl_2$—1.0 pound per ton	55.0	59.7	11.0	84.1
$MgCl_2 \cdot 6H_2O$—0.6 pound per ton	41.4	58.1	13.2	86.5
$Pb(NO_3)_2$—0.6 pound per ton	47.5	55.3	16.9	92.8

The results of the previously described flotation tests in the various examples of practice are typical of those we obtained on a variety of calcareous and siliceous iron ores using various vegetable tannin extracts, or acidic polyhydroxy aromatic compounds which may be derived from tannin extracts by hydrolytic decomposition, as the iron oxide depressants while floating activated siliceous gangue constituents from caustic alkaline iron ore pulps with oleic acid, sodium oleate, tallol, 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 iron ores containing siliceous gangue materials which comprises conditioning an aqueous pulp of the comminuted ore in the presence of 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 dissolved hydrated lime, adding thereto a quantity of caustic alkali to establish a pulp pH at least as alkaline as pH 10, and a vegetable tannin extract, and then 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.

2. A process for beneficiating iron ores containing siliceous gangue materials which comprises conditioning an aqueous pulp of the comminuted ore in the presence of hydrated lime to yield a pulp with a pH of at least 11, adding thereto a quantity of 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, thereafter adding a vegetable tannin extract and 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 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 pH 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 vegetable tannin extract, and then 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.

4. A process for the production of a beneficiated iron ore which comprises first subjecting an aqueous pulp of such an ore to a preliminary activating treatment with a soluble compound of a polyvalent metal selected from the class consisting of calcium, magnesium, strontium, barium, and lead; and thereafter subjecting the thus-activated pulp to agitation and aeration at a caustic alkaline pulp pH at least as high as pH 10 in the presence of a tannin substance selected from the group consisting of vegetable tannin extracts and polyhydroxyaromatic compounds derivable therefrom by hydrolytic decomposition, and in the concurrent presence of an anion-active collecting agent selected from the class consisting of higher fatty acids, resin acids and their soaps, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

5. A process for the production of a beneficiated iron ore which comprises first subjecting an aqueous pulp of such an ore to a preliminary activating treatment with sufficient lime to establish a pulp pH of at least 10, then incorporating with said pulp sufficient soda ash to precipitate excess lime while maintaining the desired caustic alkaline pulp for flotation, and thereafter subjecting the thus activated pulp of such an ore to agitation and aeration at a caustic alkaline pulp pH at least as high as pH 10 in the presence of a tannin substance selected from the group consisting of vegetable tannin extracts and polyhydroxyaromatic compounds derivable therefrom by hydrolytic decomposition, and in the concurrent presence of an anion-active collecting agent selected from the class consisting of higher fatty acids, resin acids and their soaps, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

6. A process for the production of a beneficiated iron ore which comprises first subjecting an aqueous pulp of such an ore to a preliminary activating treatment with excess lime, then removing the lime from the thus activated pulp to yield an activated pulp containing not more than 100 parts per million of residual dissolved lime, and thereafter subjecting the thus-treated ore pulp to agitation and aeration at a caustic alkaline pulp pH at least as high as pH 10 in the presence of a tannin substance selected from the group consisting of vegetable tannin extracts and polyhydroxyaromatic compounds derivable therefrom by hydrolytic decomposition, and in the concurrent presence of an anion-active collecting agent selected from the class consisting of higher fatty acids, resin acids and their soaps, whereby siliceous gangue is floated and beneficiated iron ore is depressed and recovered.

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