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(54) Title: SULFONATED MODIFIERS FOR FROTH FLOTATION

(57) Abstract: Improved sparge compositions for reverse froth flotation separation and uses thereof, and methods of reverse froth flotation are described. The sparge compositions comprise sulfonated polymeric modifiers which can act as dispersants and depressants, and the compositions are suitably used in the reverse froth flotation of particulate material containing ultrafine particles. For example, the compositions and methods can be used in the separation of iron oxide beneficiary from iron ores comprising silica, silicates, and the like.

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SULFONATED MODIFIERS FOR FROTH FLOTATION

Field of the Invention

[0001] The present invention relates to improved methods, modifiers, and compositions for froth flotation, in particular for separation of beneficiaries from mineral ores that require fine comminution.

Background of the Invention

[0001a] Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

[0002] The invention relates to novel materials, compositions, and methods for improving the effectiveness of froth flotation beneficiation processes. In a beneficiation process, two or more materials which coexist in a mixture of particulate material are separated from each other using mechanical processes with/without chemicals. Often one of the materials, the beneficiary, is more valuable or desired than the other material, the gangue.

[0003] One form of beneficiation is froth flotation separation. In froth flotation separation, to make a slurry a particulate material comprising an ore, such as ground or comminuted ore is slurried with water (or another solvent or solvent mix) along with chemicals such as collectors, modifiers, depressants and/or activators that assist in the separation of beneficiary from gangue. The role of the collector is to make targeted particles more hydrophobic, thereby assisting in their flotation from the slurry. The slurry is then doped with a frothing agent (frother) if necessary and sparged to form bubbles, which rise up out of the slurry carrying hydrophobic particles therewith and form a froth layer above the sparged slurry. The froth layer may then be deposited on a launder. The less hydrophobic material remains behind in the slurry, thereby accomplishing the froth flotation separation.

[0004] Two common forms of flotation separation processes are direct flotation and reverse flotation. In direct flotation processes, the froth comprises the beneficiary or concentrate while in reverse flotation processes, the froth comprises gangue or tailings. The object of the flotation in either process is to separate and recover as much as possible of the beneficiary from the particulate material in as high a concentration as possible, which is then made available for further downstream processing steps. In

froth flotation, a sparge composition comprising a slurry is sparged to form a froth layer and a sparged slurry. In a direct froth flotation, the froth layer comprises a concentrated beneficiary (a concentrate), and the sparged slurry comprises tailings (concentrated gangue). In reverse froth flotation, the froth layer comprises tailings and the sparged slurry comprises the concentrated beneficiary. In direct froth flotation, the froth comprises more beneficiary as a proportion of beneficiary plus gangue than beneficiary as a proportion of beneficiary plus gangue in the sparge composition prior to sparging; and the tailings comprise more gangue as a proportion of beneficiary plus gangue than gangue as a proportion of beneficiary plus gangue in the sparge composition prior to sparging. In reverse froth flotation, the froth comprises more gangue as a proportion of beneficiary plus gangue than gangue as a proportion of beneficiary plus gangue in the sparge composition prior to sparging; and the tailings therefore comprise more gangue as a proportion of beneficiary plus gangue than gangue as a proportion of beneficiary plus gangue in the sparge composition prior to sparging.

[0005] Froth flotation separation can be used to separate solids from solids (such as the constituents of mine ore), and liquids or semi-solids from solids (such as the separation of bitumen from oil sands).

[0006] Depressants are commonly used to assist collectors in the froth flotation separation of mineral ores. Depressants hinder the flotation of either tailings (in direct froth flotation) or beneficiary (in reverse flotation).

[0007] Sulfonate moieties have been used as depressants for gangue such as siliceous materials in the flotation of beneficiary such as phosphate in direct froth flotation.

[0008] US Patent 4,172,029 discloses a process for beneficiation of a siliceous phosphate ore by froth flotation with fatty acid and fuel oil reagents and conditioning the phosphate ore with an alkyl–substituted aromatic sulfonate before floating the phosphate ore.

[0009] US Patent 4,514,292 discloses gangue depressants that consist essentially of the combination of an inorganic sulfite and salts of certain sulfonated compounds for metallic ore and coal. The salts disclosed include the salts of benzene disulfonic acids, naphthalene disulfonic acids, condensates of formaldehyde and naphthalene sulfonic acids, naphthol sulfonic acids, lignin sulfonic acids, and sulfonated quebracho.

[0010] US Patent 4,719,009 discloses polyester materials containing ether groups and metal sulfonate groups useful as depressants for siliceous gangue in the froth flotation separation of zinc sulfide concentrates from complex ores.

[0011] US Patent 5,314,073 discloses a process for beneficiation of siliceous phosphate ore by conditioning an aqueous slurry of the ore at a pH of 7.5 to 10.5 with a fatty acid and a fuel oil and a water-dispersible sulfo-polyester, and aerating the conditioned phosphate slurry to float the phosphate.

[0012] US Patent 5,507,395 discloses a method of depression of siliceous gangue, wherein the depressant is a graft polymer of polyvinyl alcohol and an acrylamide. The depressants may include comonomers such as vinyl sulfonate, 2-acrylamido-2-methyl propane sulfonic acid, styrene sulfonic acid, and 2-sulfoethylmethacrylate.

[0013] US Patent 5,525,212 discloses a method for the depression of non-sulfide silicate gangue materials, wherein the depressant is a mixture of polysaccharide and a graft polymer of polyvinyl alcohol and an acrylamide. The acrylamide may include a comonomers such as vinyl sulfonate, 2-acrylamido-2-methyl propane sulfonic acid, styrene sulfonic acid, and 2-sulfoethylmethacrylate.

[0014] US Patent 5,531,330 discloses a method of depression of non-sulfide, silicate gangue. The depressant is a polymeric material comprising the polymerization residue of acrylamide residue(s), a hydroxyl containing polymer unit, and an anionic group containing polymer unit. The anionic group containing polymer unit may comprise the polymerization residue of vinyl sulfonate, 2-acrylamido-2-methyl propane sulfonic acid, styrene sulfonic acid, and 2-sulfoethylmethacrylate, *inter alia*.

[0015] US Patent 5,533,626 discloses a method of depression of non-sulfide silicate gangue, wherein the depressant is a mixture of a polysaccharide and a polymeric material comprising the polymerization residue of acrylamide residue(s), a hydroxyl containing polymer unit, and an anionic group containing polymer unit. The anionic group containing polymer unit may comprise the polymerization residue of vinyl sulfonate, 2-acrylamido-2-methyl propane sulfonic acid, styrene sulfonic acid, and 2-sulfoethylmethacrylate, *inter alia*.

[0016] Further, sulfonate moieties have been used as collectors. For example, US patent 3,164,549 discloses recovery of phosphate fraction from phosphate ore by employing fuel oil and sulfonic acid or it salt. US Patent 5,171,427 discloses dialkylated aryl sulfonic acids or salts thereof or their mixture used as collectors in the flotation of minerals, particularly oxide minerals.

[0017] From the foregoing, it will be seen that sulfonate moieties have been used as depressants for gangue minerals, especially for siliceous gangue and in processes in which beneficiary such as phosphate is floated.

[0018] The prerequisite for flotation separation is the liberation of particles. For flotation of mineral ores, therefore, comminuting (grinding the solids up by such techniques as dry-grinding, wet-grinding, and the like) is required to liberate minerals. Extensive grinding or comminution can result in better liberation of particles for the separation of beneficiary and gangue in a froth flotation process. However, such grinding or comminution can result in a relatively large proportion of ultrafine particles (less than 10μm). The presence of ultrafine particles represents a challenge for froth flotation such as slime coating, which can lead to lower recovery of beneficiary. In slime coating, particles of ultrafines coat larger particles of ore. This issue is especially serious for the flotation of non-sulfide mineral ores such as industrial mineral ores, phosphate ores, potash ores, and metallic oxide ores: Ultrafine particles of gangue or gangue-rich material may coat particles of beneficiary or beneficiary-rich material—in such a case, beneficiary-rich material may be separated with the gangue in a froth flotation process. Such an eventuality can undesirably result in lower recovery of the beneficiary. Similarly, for example, ultrafines of beneficiary may coat particles of gangue—the particles of gangue may thus be separated with beneficiary. Such an eventuality can undesirably result in a lower purity of beneficiary. In order to avoid such problems, desliming processes are commonly implemented before and in preparation for froth flotation, to remove ultrafine particles. However, ultrafines often nevertheless enter the froth flotation process and cause slime coating and other issues that have deleterious effects on separation of beneficiary and gangue. Therefore dispersants are often employed in froth flotation processes to mitigate the detrimental effect of ultrafines in froth flotation by dispersing ultrafines of beneficiary and gangue and/or reducing the availability of ultrafines to coat the larger particles in desliming processes and/or conditioning processes or otherwise mitigate loss of beneficiary and/or reduction of the purity of beneficiary.

[0018a] It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

[0019] In view of the above issues, it would be an advantage to provide for froth flotation improved methods and/or compositions that can be implemented in existing froth flotation installations for separation of beneficiary from ores. It would be an advantage to provide improved methods and/or compositions that can be used effectively to concentrate beneficiaries from materials that contain ultrafine particles. It

would be an advantage to provide one or more dispersants to effectively disperse both beneficiary and gangue particles in the grinding process, desliming processes, conditioning processes, or any combination thereof of ores and/or slurries of comminuted ores for froth flotation separation.

[0019a] Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

[0019b] Although the invention will be described with reference to specific examples it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

Summary of the Invention

[0019c] According to a first aspect of the present invention there is provided a sparge composition comprising:

(i) a medium;

(ii) a metal oxide ore comprising a gangue and a beneficiary;

(iii) an amine collector comprising a C12-C24 fatty amine, a C12-C24 fatty diamine, a C6-C13 ether amine, a C6-C13 ether diamine, or any combination thereof; and

(iv) a modifier comprising one or more sulfonated polymers, wherein at least one of the one or more sulfonated polymers is a sulfonated guar gum, a sulfonated xanthan gum, or comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, styrene sulfonate, or any combination thereof, wherein the at least one of the one or more sulfonated polymers has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole, wherein the at least one of the one or more sulfonated polymers further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, a maleic acid ester, or any combination thereof, and

wherein the beneficiary comprises an iron oxide and the gangue comprises a silicate, silica, a carbonate, or any combination thereof.

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[0019d] According to a second aspect of the present invention there is provided a method of froth flotation comprising:

forming a sparge composition, the sparge composition comprising

(i) a medium,

(ii) a metal oxide ore comprising a beneficiary and a gangue, the beneficiary comprising an iron oxide, and the gangue comprising silicate, silica, carbonate, or any combination thereof,

(iii) an amine collector, and

(iv) a modifier comprising one or more sulfonated polymers, wherein at least one of the one or more sulfonated polymers is a sulfonated guar gum, a sulfonated xanthan gum, or comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, styrene sulfonate, or any combination thereof, wherein the at least one of the one or more sulfonated polymers has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole, and wherein the at least one of the one or more sulfonated polymers further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, a maleic acid ester, or any combination thereof; and

sparging the sparge composition to yield a sparged composition, the sparged composition comprising a froth and a sparged slurry, wherein the sparged slurry comprises a concentrate of the beneficiary and wherein the froth comprises tailings of the gangue.

[0019e] According to a third aspect of the present invention there is provided a sparge composition comprising:

(i) a medium;

(ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof, the ore comprising a gangue and a beneficiary;

(iii) a collector; and

(iv) a sulfonated polymer, wherein the sulfonated polymer

(a) has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole,

(b) comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, or any combination thereof, and

(c) further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, maleic acid esters, or any combination thereof.

[0019f] According to a fourth aspect of the present invention there is provided a method of froth flotation comprising:

forming a sparge composition, the sparge composition comprising

(i) a medium,

(ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof, the ore comprising a gangue and a beneficiary,

(iii) a collector, and

(iv) a sulfonated polymer, wherein the sulfonated polymer

(a) has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole,

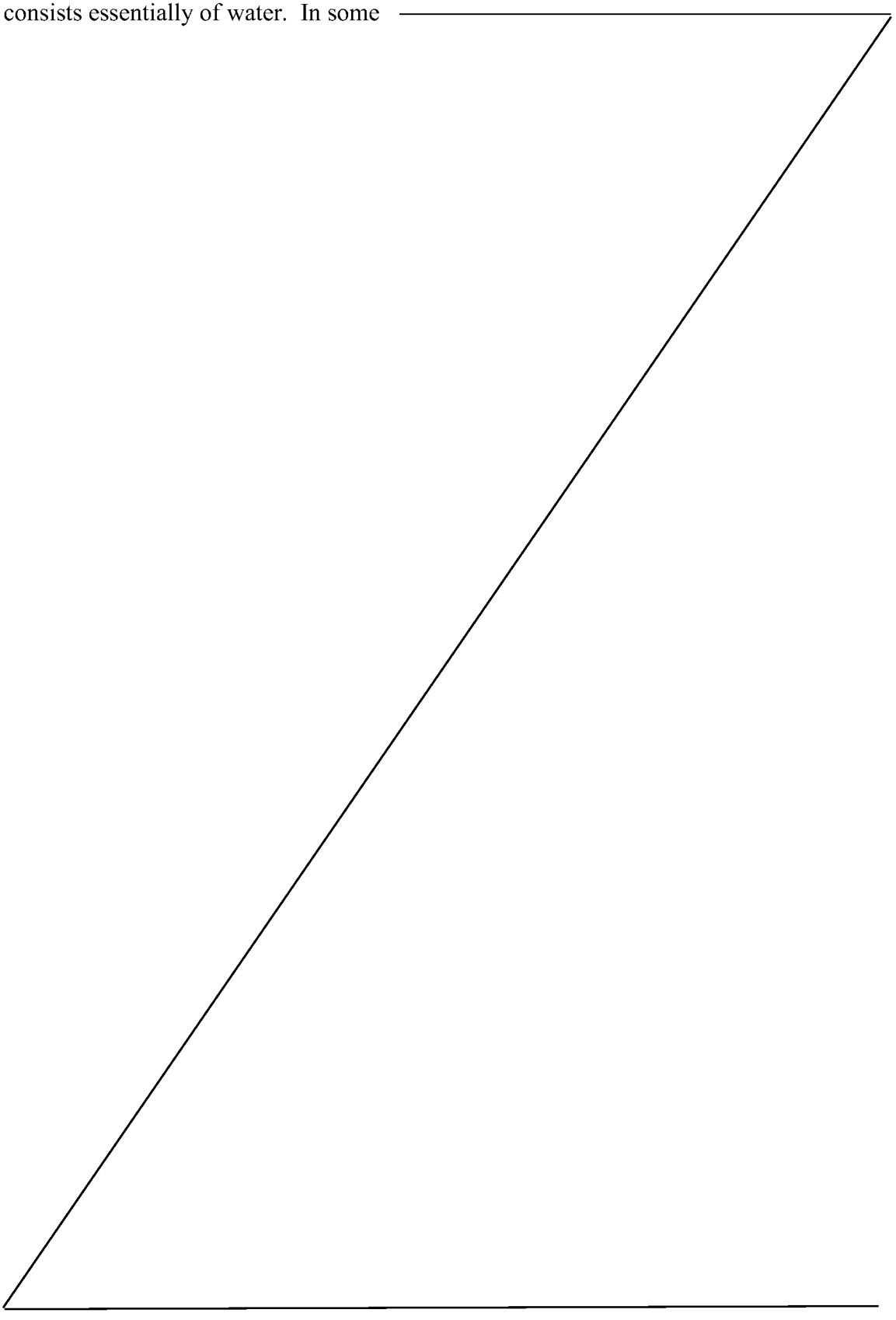
(b) comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, or any combination thereof, and

(c) further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, maleic acid esters, or any combination thereof; and

sparging the sparge composition to yield a sparged composition, the sparged composition comprising a froth and a sparged slurry.

[0020] Disclosed herein is a sparge composition comprising, consisting of, or consisting essentially of (i) a medium; (ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof; (iii) an amine collector; and

(iv) a modifier comprising one or more sulfonated polymers, wherein the ore comprises a beneficiary and a gangue. In embodiments, the medium comprises, consists of, or consists essentially of water. In some



embodiments, the ore comprises, consists of, or consists essentially of a metal oxide ore. In embodiments, the beneficiary comprises, consists of, or consists essentially of an iron oxide. In embodiments, the iron oxide is selected from magnetite, hematite, goethite, and limonite and any combination thereof. In embodiments, the beneficiary comprises, consists of, or consists essentially of a magnetite. In embodiments, the gangue comprises a silicate, silica, carbonate, or any combination thereof. In embodiments the amine collector comprises, consists of, or consists essentially of a C12-C24 fatty amine, a C12-C24 fatty diamine, a C6-C13 ether amine, a C6-C13 ether diamine, or any combination thereof. In some such embodiments, the amine collector comprises, consists of, or consists essentially of C13 ether diamine. In embodiments, the sparge composition has a pH of 4 to 7.

[0021] In embodiments, the modifier has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole. In some such embodiments, the modifier comprises, consists of, or consists essentially of a polymer comprising a first residue comprising the polymerized residue of acrylic acid and/or a salt thereof, and a second residue comprising the polymerized residue of acrylamido-2-methylpropane sulfonic acid and/or a salt thereof (collectively, ATBS), sulfomethylated acrylamide, or both ATBS and sulfomethylated acrylamide.

[0022] Also disclosed herein is a method of froth flotation, the method comprising forming a sparge composition, the sparge composition comprising, consisting of, or consisting essentially of (i) a medium, (ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof, (iii) a collector, and (iv) a modifier comprising one or more sulfonated polymers; and sparging the sparge composition to yield a sparged composition comprising a froth and a sparged slurry, wherein the sparged slurry comprises a concentrate of a beneficiary and wherein the froth comprises tailings of a gangue, the gangue comprising silica, a silicate, carbonate, or any combination thereof. In embodiments, the ore comprises, consists of, or consists essentially of a metal oxide ore. In embodiments, the medium comprises, consists of, or consists essentially of water. In embodiments, the metal oxide ore comprises, consists of, or consists essentially of an iron ore. In some such embodiments, the froth comprises silica, silicate, carbonate, or a combination thereof and the concentrate of the beneficiary comprises iron oxide. In embodiments, the modifier comprises, consists of, or consists essentially of a sulfonated natural polymer, a sulfonated synthetic polymer, or a combination thereof. In some such embodiments, the modifier

comprises, consists of, or consists essentially of a sulfonated synthetic polymer having a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole. In some such embodiments, the sulfonated synthetic polymer comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, a salt of 2-acrylamido-2-methylpropane sulfonic acid, styrene sulfonic acid, a salt of styrene sulfonic acid, or any combination thereof. In some such embodiments, the sulfonated synthetic polymer further comprises a residue of acrylic acid, a salt of acrylic acid, methacrylic acid, a salt of methacrylic acid, acrylamide, vinyl alcohol, maleic acid, a salt of maleic acid, an ester of maleic acid, or any combination thereof. In some embodiments, the sulfonated synthetic polymer comprises a first residue of acrylic acid and/or a salt thereof; and a second residue of 2-acrylamido-2-methylpropane sulfonic acid and/or a salt thereof (ATBS), a sulfomethylated acrylamide, or a combination thereof. In some such embodiments, the sulfonated synthetic polymer has a weight average molecular weight of about 300 g/mole to about 100,000 g/mole. In embodiments, the method further includes separating at least a portion of the concentrate of the beneficiary from the sparged slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 shows a plot of the percentage grade of iron recovered versus % silica removal for three froth flotation tests.

DETAILED DESCRIPTION

[0024] Although the present disclosure provides references to preferred embodiments, persons skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention. Reference to various embodiments does not limit the scope of the claims attached hereto. Additionally, any examples set forth in this specification are not intended to be limiting and merely set forth some of the many possible embodiments for the appended claims.

[0025] **Definitions**

[0026] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control.

[0027] As used herein, the terms "comprise(s)," "include(s)," "having," "has," "can," "contain(s)," and variants thereof are intended to be open-ended transitional phrases, terms, or words that do not preclude the possibility of additional acts or structures. The singular forms "a," "and" and "the" include plural references unless the context clearly dictates otherwise. The present disclosure also contemplates other embodiments "comprising," "consisting of" and "consisting essentially of," the embodiments or elements presented herein, whether explicitly set forth or not.

[0028] As used herein, the term "optional" or "optionally" means that the subsequently described event or circumstance may but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not.

[0029] As used herein, the term "about" modifying, for example, the quantity of an ingredient in a composition, concentration, volume, process temperature, process time, yield, flow rate, pressure, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used for making compounds, compositions, concentrates or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods, and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Where modified by the term "about" the claims appended hereto include equivalents to these quantities. Further, where "about" is employed to describe a range of values, for example "about 1 to 5" or "about 1 to about 5", the recitation means "1 to 5" and "about 1 to about 5" and "1 to about 5" and "about 1 to 5" unless specifically limited by context.

[0030] As used herein, "ore" means any solid terranean material of economic value that is obtained by excavation such as quarrying, open-cast mining, or pit mining: "ore" is construed herein to include not only rock, minerals, and mineral aggregates containing one or more metals in elemental and/or chemically compounded forms, but also coal and other solid terranean substances.

[0031] As used herein, "carbonate", unless specified to the contrary, means inorganic carbonate such as material containing CO_3^{2-}, HCO_3^- ions and counterions.

[0032] As used herein, "phosphate", unless specified to the contrary, refers to inorganic phosphate such as material containing PO_4^{3-}, $H_2PO_4^{2-}$, and $H_2PO_4^-$ ions and counterions.

[0033] As used herein, "medium" means a material that is liquid at 20 °C and 1 atmosphere pressure. In any of the embodiments herein, the medium can comprise, consist of, or consist essentially of water.

[0034] As used herein, a "collector" means a material that selectively adheres to targeted particles in a sparge composition, and increases adhesion or association of the targeted particles to bubbles of a gas during sparging. "Targeted particles" are gangue-rich particles (in reverse froth flotation) or beneficiary-rich particles (in direct froth flotation).

[0035] As used herein, "amine collector" means an organic moiety comprising an amine group and/or an ammonium group. Non-limiting examples of amine collectors include C12-C24 fatty amines, C12-C24 fatty diamines, C6-C13 ether amines, C6-C13 ether diamines, or any combination thereof, further wherein the term "amine" refers to the free amine, the conjugate acid thereof, or a combination thereof.

[0036] As used herein, "particulate" or "particulate material" means a plurality of particles.

[0037] As used herein, "particle" means a discreet, solid object to which can be ascribed physicochemical properties such as volume or mass, wherein a particle has a largest maximum dimension in any direction of about 0.001 μm to about 5 mm.

[0038] As used herein, "ultrafine particles" or "ultrafines" means a particulate having a particle size of less than 10 μm as measured by throw-action sieve analysis carried out wet. The procedure for sieve analysis is outlined in American Society for Testing and Materials (ASTM) C 136[2].

[0039] As used herein, "comminute" means to reduce the particle size of a particulate. In embodiments, comminuted means powdered, pulverized, ground, or otherwise divided by mechanical means.

[0040] As used herein, "sparge composition" means a composition comprising a particulate material, a collector, and a liquid medium. Such a composition has a liquid surface and comprises a slurry of the particulate material in the medium. Such a composition, after being sparged, comprises froth at the liquid surface and a sparged slurry. In direct froth flotation, the froth comprises a concentrate, and the sparged slurry comprises tailings. In reverse froth flotation, the froth comprises tailings and the sparged slurry comprises a concentrate.

[0041] As used herein, "sparge", "sparged", or "sparging" refers to the introduction of a gas into a sparge composition for the purpose of creating a plurality of bubbles that migrate upwards within the liquid. In embodiments, the gas is air.

[0042] As used herein, "concentrate" refers to a material in which a beneficiary has been concentrated by a froth flotation process. The concentrate has a higher concentration of the beneficiary (as a ratio by weight of beneficiary to beneficiary plus gangue) than the particulate material of the sparge composition before sparging.

[0043] As used herein, "tailings" refers to a material in which a gangue has been concentrated by a froth flotation process. The tailings have a higher concentration of the gangue (as a ratio by weight of gangue to beneficiary plus gangue) than the particulate material of the sparge composition before sparging.

[0044] As used herein, "sparged slurry" means the liquid body of a sparge composition that has been sparged, wherein a froth has formed at the air-liquid interface. As used herein, the sparged slurry excludes or substantially excludes the froth.

[0045] As used herein "slurry of particles" means a composition comprising a liquid medium and particulate material, wherein the particulate material is dispersed and/or suspended in the medium, and wherein the composition excludes or substantially excludes a collector. In embodiments, the liquid medium consists essentially of water.

[0046] As used herein, a "depressant" means a material that selectively reduces the adhesion or association of untargeted particles in a sparge composition to bubbles of a gas during sparging. Untargeted particles are gangue-rich particles in direct froth flotation or beneficiary-rich particles in a reverse froth flotation. A depressant acts to decrease the migration of untargeted particles to the surface of a sparged composition.

[0047] As used herein, a "frother" or "frothing agent" means a composition of matter that reduces the surface tension of water and enables the formation of a froth at air-liquid interface of a sparge composition during sparging.

[0048] As used herein, "dispersant" means a material that facilitates dispersion of particles of an ore in a liquid medium, assists in the dispersion of particles of an ore in a liquid medium, stabilizes a dispersion of particles of an ore in a liquid medium, or any combination thereof. In embodiments, a dispersant is a material that disperses ultrafine particles of the ore in a medium.

[0049] As used herein, a "modifier" means a material that is, acts as, or is effective as a dispersant, a depressant, or both a dispersant and depressant. In embodiments, the modifiers of the invention are, act as, or are effective as both dispersants and depressants.

[0050] As used herein, "ATBS" means 2-acrylamido-2-methylpropane sulfonic acid and/or salts thereof, except where otherwise specified as follows: as used herein, "ATBS sulfonic acid" means 2-acrylamido-2-methylpropane sulfonic acid; as used herein an "ATBS salt" means a salt of 2-acrylamido-2-methylpropane sulfonic acid.

[0051] As used herein, "flotation" of a material refers to a process in froth flotation in which during the sparging of a slurry of a comminuted ore in a liquid medium, the material migrates at least partially into a froth layer that forms at the liquid-air interface.

[0052] As used herein, "depression" of a material refers to a process in froth flotation in which during the sparging of a slurry of a comminuted ore in a liquid medium, the material remains substantially within the sparged slurry and does not tend to migrate into the froth layer.

[0053] As used herein, "sulfonated monomer" means a polymerizable compound comprising at least one sulfonate or sulfate group ($-SO_3H$, $-SO_3R$, $-SO_3^-$, $-O-SO_3H$, $-O-SO_3R$, or $-O-SO_3^-$, where R is alkyl, aryl, alkaryl, or another organic group).

[0054] As used herein, "sulfonated monomer residue" and like terms mean a polymerized residue of a monomer, wherein the residue comprises at least one sulfonate or sulfate moiety.

[0055] As used herein, "sulfonate moiety", "sulfonate", "sulfonate group", "sulfonated" and like terms means a moiety comprising at least one sulfonate or sulfate group ($-SO_3H$, $-SO_3R$,

$-SO_3^-$, -O-SO_3H, -O-SO_3R, or –O-SO_3^-, where R is alkyl, aryl, alkaryl, or another organic group).

[0056] As used herein, "sulfonated polymer" means a polymer comprising at least one sulfonate or sulfate group (-SO_3H, -SO_3R, $-SO_3^-$, -O-SO_3H, -O-SO_3R, or –O-SO_3^-, where R is alkyl, aryl, alkaryl, or another organic group).

[0057] As used herein, "metal oxide ore" means an ore in the form of a particulate comprising metal ions and oxide ions. Non-limiting examples of metal oxide ores include comminuted magnetite, hematite, goethite, and limonite.

[0058] As used herein, "iron ore" refers to those ores comprising iron ions. Examples include but are not limited to those comprising magnetite, hematite, goethite, limonite, or any combination thereof.

[0059] **Discussion**

[0060] Preferred methods and materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing of the present invention. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and examples disclosed herein are illustrative only and not intended to be limiting.

[0061] Applicants have found that sulfonated polymers having a weight average molecular weight of about 100,000 g/mole or less unexpectedly improve the floating of gangue minerals in the reverse flotation of metal oxide ores, and have found that sulfonated polymers act as dispersants for both beneficiary and gangue particles for metal oxide ores. Therefore, sulfonated polymers can be used as dispersants in both direct and reverse froth flotation and can be applied before flotation in a grinding process, a desliming process, a conditioning process, or any combination thereof. In embodiments, the sulfonated polymers decrease slime coating in the froth flotation.

[0062] The polymers comprise one or more sulfonate and/or sulfate groups. Disclosed are methods and compositions for froth flotation that include modifiers that comprise, consist of, or consist essentially of one or more sulfonated polymers. The modifiers, compositions comprising the modifiers, and methods can be implemented in existing froth flotation installations for separation of beneficiary and gangue of a comminuted ore. The comminuted ore comprises particles of ore. In embodiments, the particles of ore comprise, consist of, or

consist essentially of ultrafine particles. Used in a reverse froth flotation process in a medium for the separation of beneficiary and gangue from a metal oxide ore, the modifiers of Applicant's invention unexpectedly provide improved separation and selectivity toward concentrate or tailings, improved recovery of beneficiary (as measured by weight of beneficiary recovered as a proportion of total beneficiary in the metal oxide ore), higher grade (as measured by weight of beneficiary in the concentrate), improved depressing action of depressant on the beneficiary (as measured by reduction of depressant dosage), improved dispersion of particles of ore, improved dispersion of ultrafines of ore, reduced slime coating of particles of ore, or any combination thereof.

[0063] **First Embodiments**

[0064] Therefore, in first embodiments, there is provided a sparge composition for froth flotation, the sparge composition comprising, consisting of, or consisting essentially of a medium, an ore comprising a beneficiary and a gangue, a collector, and a modifier comprising one or more sulfonated polymers. In embodiments, the sparge composition for froth flotation is a sparge composition for reverse froth flotation. In embodiments, the medium comprises, consists of, or consists essentially of water. In embodiments, the medium is water. In embodiments, the ore is selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof. In embodiments, the ore comprises, consists of, or consists essentially of a metal oxide ore. In embodiments, the ore comprises, consists of, or consists essentially of an iron ore. In embodiments, the metal oxide ore is an iron ore. In embodiments, the beneficiary comprises, consists of, or consists essentially of an iron oxide. In some such embodiments, the beneficiary comprises, consists of, or consists essentially of magnetite, hematite, goethite, limonite, or any combination thereof. In embodiments, the beneficiary comprises, consists of, or consists essentially of magnetite. In embodiments, the gangue comprises, consists of, or consists essentially of a silicate, silica, carbonate, or a combination thereof.

[0065] In alternative first embodiments, the metal oxide ore is selected from iron ore, wolframite-scheelite, copper oxide ore, zinc oxide ore, lead oxide ore, oxide ore comprising gold, bauxite, and any combination thereof.

[0066] In first embodiments, the amine collector is selected from C12-C24 fatty amines, C12-C24 fatty diamines, C6-C13 ether amines, C6-C13 ether diamines, or any combination thereof.

[0067] In first embodiments, the amine collector is selected from one or more fatty amines having the structure (I)

$$R_6NH_2,$$

(I)

wherein R_6 is C12-C24 linear or branched alkyl; one or more fatty diamines having the structure (II)

$$R_6—NH—R_7—NH_2$$

(II),

wherein R_6 is C12-C24 linear or branched alkyl and R_7 is a linear or branched hydrocarbon chain, in some embodiments $(CH_2)_3$; one or more ether amines having the structure (III)

$$R_8—O—R_7—NH_2$$

(III),

wherein R_8 is C6-C13 branched or linear alkyl and R_7 is a linear or branched hydrocarbon chain, in embodiments $(CH_2)_3$; one or more ether diamines having the structure (IV)

$$R_9—O—R_7—NH—R_7—NH_2$$

(IV),

wherein R_9 is C8-C13 branched or linear alkyl and R_7 is a linear or branched hydrocarbon chain, in embodiments $(CH_2)_3$.

[0068] In first embodiments, the amine collector comprises, consists of, or consists essentially of the C13 ether diamine having the structure (V)

$$H_2N—(CH_2)_3—NH—(CH_2)_3—O—(CH_2)_{10}—CH(CH_3)_2$$

(V).

[0069] In first embodiments, the one or more sulfonated polymers is selected from a sulfonated natural polymer, a sulfonated synthetic polymer, and a combination thereof.

[0070] In first embodiments the weight average molecular weight of the one or more sulfonated synthetic polymers is from about 300 to about 5,000,000, in embodiments about 300 to about 1,000,000, in embodiments about 300 to about 500,000, in embodiments about 300 to about 100,000, in embodiments about 300 to about 50,000, in embodiments about 300 to about 35,000, in embodiments about 300 to about 30,000, in embodiments about 300 to about 25,000, in embodiments from about 500 to about 5,000,000, in embodiments about 500 to about 1,000,000, in embodiments about 500 to about 500,000, in embodiments about 500 to about 100,000, in embodiments about 500 to about 50,000, in embodiments about 500 to

about 25,000, in embodiments from about 700 to about 5,000,000, in embodiments about 700 to about 1,000,000, in embodiments about 700 to about 500,000, in embodiments about 700 to about 100,000, in embodiments about 700 to about 50,000, in embodiments about 700 to about 25,000, in embodiments from about 1,000 to about 5,000,000, in embodiments about 1,000 to about 1,000,000, in embodiments about 1,000 to about 500,000, in embodiments about 1,000 to about 100,000, in embodiments about 1,000 to about 50,000, in embodiments about 1,000 to about 40,000, in embodiments about 1,000 to about 35,000, in embodiments about 1,000 to about 30,000, in embodiments about 1,000 to about 25,000, in embodiments about 500 to about 20,000, in embodiments about 500 to about 15,000, in embodiments about 500 to about 10,000, in embodiments about 500 to about 7,000, in embodiments about 500 to about 5,000, in embodiments about 500 to about 3,000, in embodiments about 500 to about 1,000, in embodiments about 1,000 to about 25,000, in embodiments about 700 to about 20,000, in embodiments about 700 to about 15,000, in embodiments about 700 to about 10,000, in embodiments about 700 to about 7,000, in embodiments about 700 to about 5,000, in embodiments about 700 to about 3,000, in embodiments about 700 to about 1,000, in embodiments about 1,000 to about 25,000, in embodiments about 1,000 to about 20,000, in embodiments about 1,000 to about 15,000, in embodiments about 1,000 to about 10,000, in embodiments about 1,000 to about 7,000, in embodiments about 1,000 to about 5,000, in embodiments about 1,000 to about 3,000, or in embodiments about 1,000 to about 2,000.

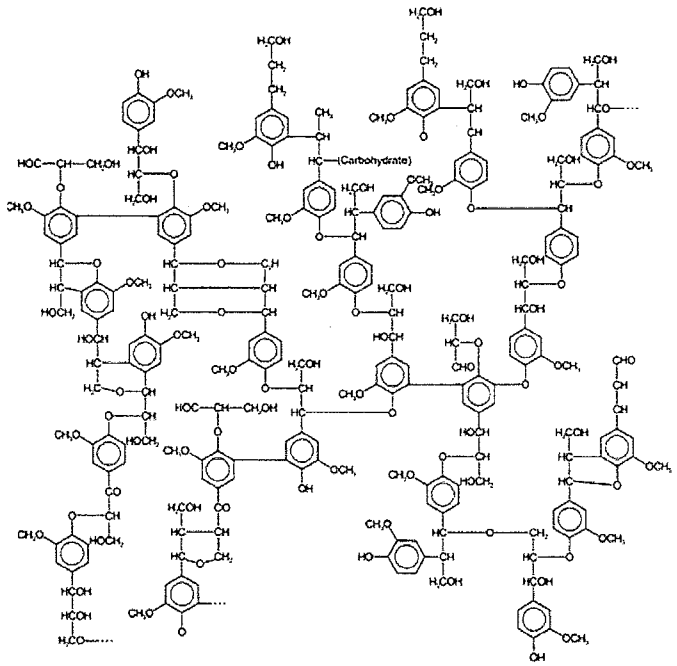
[0071] In first embodiments, the weight ratio of the one or more sulfonated polymers to the particles of mineral ore is from about 1g to about 1000g of the one or more sulfonated polymers per ton of particles of mineral ore, in embodiments from about 5g to about 500g, in embodiments, from about 10g to about 500g, in embodiments from about 20g to about 300g, in embodiments from about 50g to about 300g, in embodiments from about 50g to about 200g, in embodiments from about 10g to about 100g, in embodiments from about 10g to about 70g, in embodiments from about 30g to about 70g of the one or more sulfonated polymers per ton of ore.

[0072] The metal oxide ore is in the form of a particulate. In embodiments, 1% to 99% by weight of the particulate has a particle size from about 38 microns to about 250 microns, in embodiments 50% to 80% by weight of the comminuted ore has a particle size from about 38 microns to about 250 microns, in embodiments 60% to about 70% has a particle size from about 38 microns to about 250 microns, in embodiments 65% to 75% has a particle size from about 38 microns to about 250 microns, or in embodiments about 68% to about 72% has a

particle size from about 38 microns to about 250 microns as measured by throw-action sieve analysis carried out wet. The procedure for sieve analysis is outlined in American Society for Testing and Materials (ASTM) C 136[2]ASTM C136 / C136M – 14.

[0073] **Second Embodiments**

[0074] In second embodiments, the modifier of the composition of any of the first embodiments comprises, consists of, or consists essentially of a sulfonated lignin. Lignin is a class of complex organic polymers. Without limitation thereto and solely for the purposes of illustration, lignin may be represented by the structure (VI).



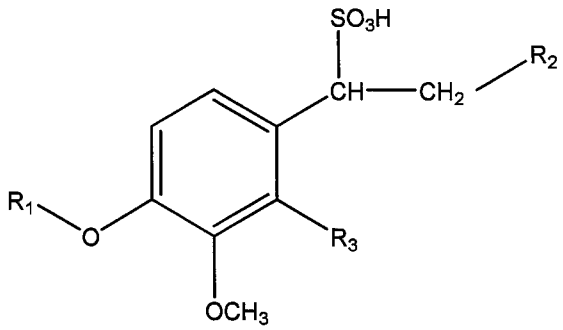
(VI)

[0075] In second embodiments the sulfonated lignin has a broad range of molecular weight. In embodiments, the sulfonated lignin has a weight average molecular weight range of from about 1,000 to about 140,000.

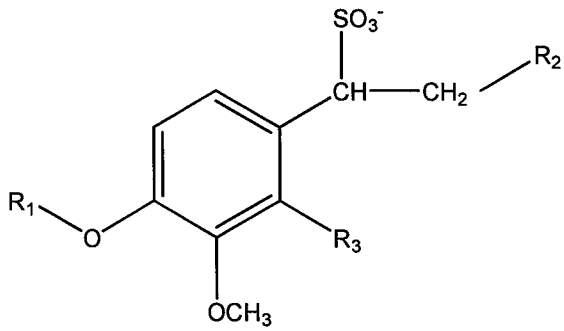
[0076] In second embodiments, the sulfonated lignin comprises, consists of, or consists essentially of a byproduct of production of wood pulp using sulfite pumping. In some embodiments, the sulfonated lignin is the reaction product of lignin with one or more sulfites, one or more bisulfites, or a combination thereof.

[0077] In second embodiments, the sulfonated lignin has comprises a modification of structure (VI) wherein one or more of the $-CH_2OH$ groups is replaced with $-CH_2SO_3H$, $-CH_2SO_3^-$, or a combination thereof.

[0078] In second embodiments, the sulfonated lignin has a structure comprising structure (VII), structure (VIII), or both structure (VII) and structure (VIII):



(VII)



(VIII),

wherein R_1 is hydrogen or one of a wide variety of organic structures found in the structure of lignin; R_2 is one of a wide variety of organic structures found in the structure of lignin; and R_3 is hydrogen or one of a wide variety of organic structures found in the structure of lignin.

[0079] **Third Embodiments**

[0080] In third embodiments, the modifier of the composition of any of the first embodiments comprises, consists of, or consists essentially of a sulfonated starch. In embodiments, the sulfonated starch comprises amylopectin wherein one or more of the –OH groups is replaced with a sulfonate group (-SO_3H and/or -SO_3^-), amylose wherein one or more of the –OH groups is replaced by a sulfonate group (-SO_3H and/or -SO_3^-), or a combination thereof.

[0081] **Fourth Embodiments**

[0082] In fourth embodiments, the modifier of the composition of any of the first embodiments comprises, consists of, or consists essentially of a sulfonated cellulose, wherein

one or more of the –OH groups in cellulose molecules is replaced by a sulfonate group (-SO_3H and/or -SO_3^-).

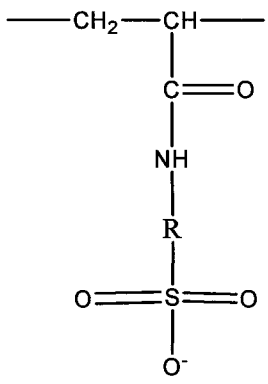
[0083] **Fifth Embodiments**

[0084] In fifth embodiments, the modifier of the composition of any of the first embodiments comprises, consists of, or consists essentially of a sulfonated lignin, a sulfonated starch, a sulfonated cellulose, a sulfonated guar gum, a sulfonated xanthan gum, or any combination thereof.

[0085] **Sixth Embodiments**

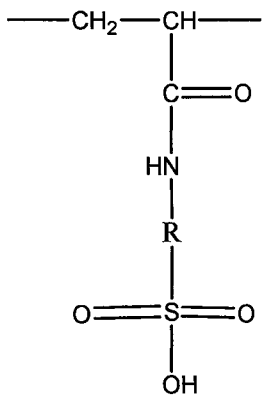
[0086] In sixth embodiments, the modifier of the composition of any of the first embodiments comprises one or more sulfonated synthetic polymers. In sixth embodiments, the modifier of the sparge composition of any of the first embodiments comprises one or more sulfonated synthetic polymers, wherein at least one of the one or more sulfonated synthetic polymers comprises a residue of a sulfonated monomer, wherein the sulfonated monomer is selected from sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, a salt of 2-acrylamido-2-methylpropane sulfonic acid, styrene sulfonic acid, a salt of styrene sulfonic acid, and any combination thereof.

[0087] In sixth embodiments, the at least one of the one or more sulfonated synthetic polymers comprises a monomer residue having the structure (IX)



(IX),

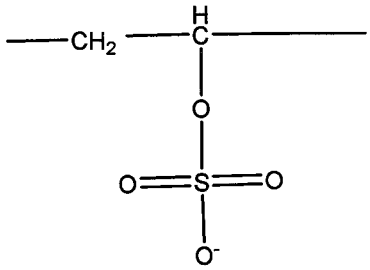
wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, quaternary organic ammonium; a monomer residue having the structure (X)



(X);

or a combination thereof.

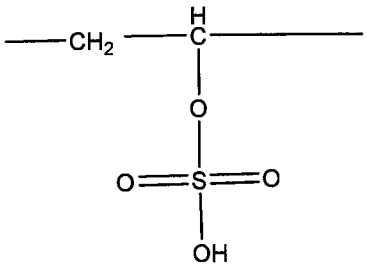
[0088] In sixth embodiments, the at least one of the one or more sulfonated synthetic polymers comprises a monomer residue having the structure (XI)



(XI),

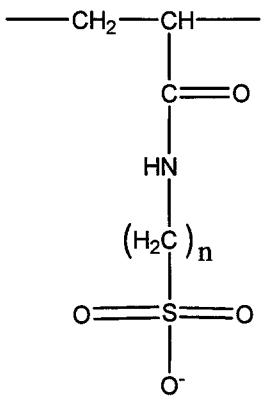
wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium;

the monomer residue having the structure (XII)



(XII);

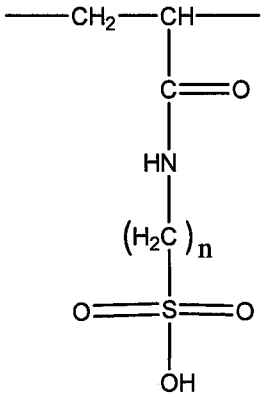
the monomer residue having the structure (XIII)



(XIII),

wherein n is 1, 2, or 3 and the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium;

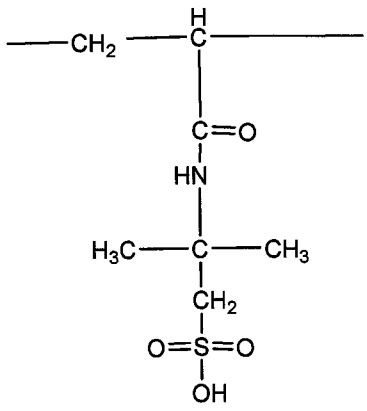
the monomer residue having the structure (XIV)



(XIV),

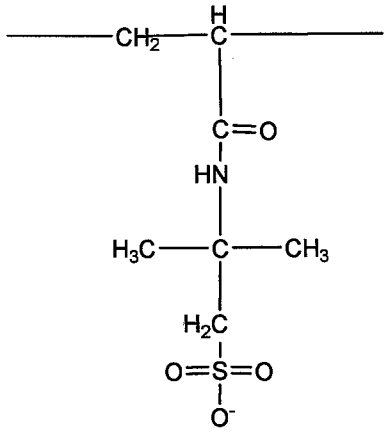
wherein n is 1, 2, or 3;

the monomer residue having the structure (XV)



(XV);

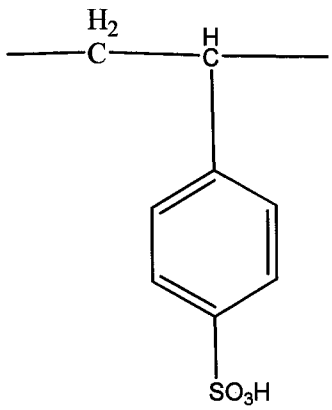
the monomer residue having the structure (XVI)



(XVI),

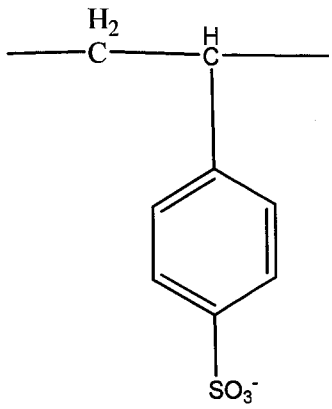
wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium;

the monomer residue having the structure (XVII)



(XVII);

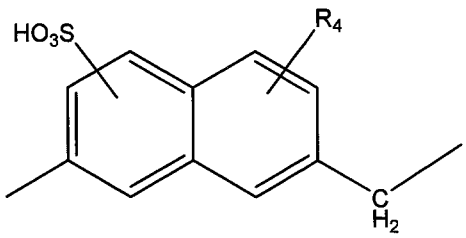
the monomer residue having the structure (XVIII)



(XVIII),

wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium;

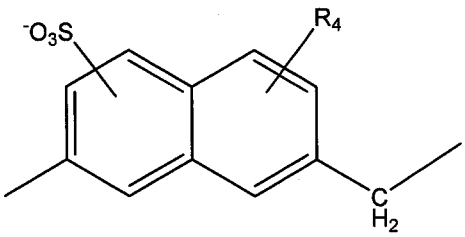
the monomer residue having the structure (XIX)



(XIX),

wherein R_4 is alkyl;

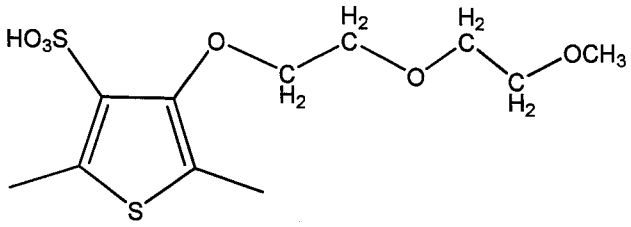
the monomer residue having the structure (XX)



(XX),

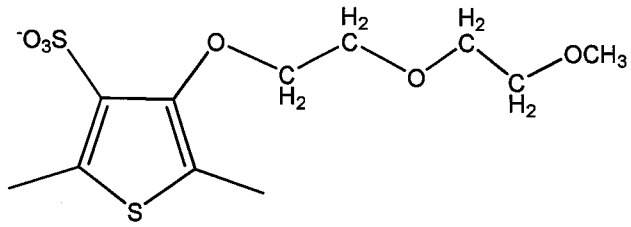
wherein R_4 is alkyl and wherein the sulfonate counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium;

the monomer residue having the structure (XXI)



(XXI);

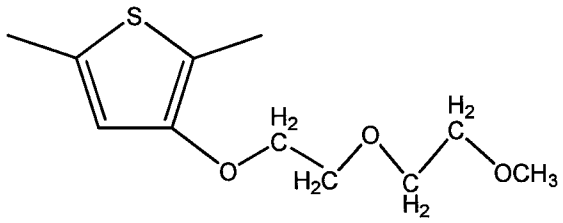
the monomer residue having the structure (XXII)



(XXII),

wherein the sulfonate counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; or any combination thereof.

[0089] In some such sixth embodiments, the at least one of the one or more sulfonated synthetic polymers further comprises the residue of acrylamide, the residue of acrylic acid, the residue of an acrylic acid salt, the residue of methacrylic acid, the residue of a methacrylic acid salt, the residue of maleic acid, the residue of a salt of maleic acid, the residue of a monoester of maleic acid, the residue of salt of a monoester of maleic acid, the residue of a diester of maleic acid, the residue having the structure (XXIII)



(XXIII),

or any combination thereof. In embodiments, the cation of the acrylic acid salt, the residue of the methacrylic acid salt, the residue of the salt of maleic acid, or the residue of the salt of the monoester of maleic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

[0090] In sixth embodiments, the modifier of the sparge composition of any of the first embodiments comprises, consists of, or consists essentially of a copolymer of acrylic acid and/or a salt of acrylic acid with ATBS. In embodiments, the cation of the salt of the acrylic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium. In embodiments, the ATBS is an ATBS salt, wherein the cation is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

[0091] In embodiments, the modifier of the sparge composition of any of the first embodiments comprises, consists of, or consists essentially of a terpolymer of acrylic acid and/or a salt of acrylic acid, ATBS, and acrylamide. In embodiments, the cation of the salt of the acrylic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium. In embodiments, the ATBS is an ATBS salt, wherein the cation is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

Seventh Embodiments

[0092] In seventh embodiments, there is provided a method comprising sparging the sparge composition of any one of the first to sixth embodiments to yield a froth comprising tailings of gangue and a sparged slurry comprising a concentrate of beneficiary; and separating at least a portion of the concentrate from the sparged slurry. In embodiments, the sparging the sparge composition yields a sparged composition, the sparged composition comprising, consisting of, or consisting essentially of an upper froth layer and a lower slurry layer. In some such embodiments, the lower slurry layer comprises water and a slurry of the concentrate and the upper froth layer comprises the tailings. In some such embodiments, the method comprises separating the upper froth layer from the lower slurry layer. Therefore the separating the at least the portion of concentrate from the tailings is accomplished by means known in the art. In embodiments, the separating comprises, consists of, or consists essentially of: tapping off at least a portion of the upper froth layer, skimming off at least a portion of the upper froth layer, depositing at least a portion of the upper froth layer onto a launder, decanting at least a portion of the upper froth layer, or any combination thereof.

[0093] **Eighth Embodiments**

[0094] In eighth embodiments, there is provided a method of froth flotation, the method comprising, consisting of, or consisting essentially of forming a sparge composition, the sparge composition comprising (i) a medium, (ii) an ore, (iii) an amine collector, and (iv) a modifier comprising one or more sulfonated polymers; and sparging the sparge composition to yield a sparged composition, the sparged composition comprising, consisting of, or consisting essentially of a froth and a sparged slurry, wherein the sparged slurry comprises a concentrate of a beneficiary and wherein the froth comprises tailings of a gangue, and the gangue comprises, consists of, or consists essentially of a silicate silica, carbonate, or any combination thereof. In embodiments, the ore comprises, consists of, or consists essentially of an iron ore. In embodiments, the beneficiary comprises, consists of, or consists essentially of an iron oxide. In embodiments, the iron oxide is selected from magnetite, hematite, goethite, limonite, or any combination thereof. In embodiments, the beneficiary comprises, consists of, or consists essentially of magnetite. In embodiments, the method further comprises separating at least a portion of the concentrate of the beneficiary from the sparged composition. In embodiments, the medium comprises, consists of, or consists essentially of water.

[0095] In eighth embodiments, the gangue comprises, consists of, or consists essentially of calcite, dolomite, clay, or any combination thereof. In embodiments, the metal oxide ore comprises, consists of, or consists essentially of an iron ore. In some such embodiments, the iron ore comprises magnetite.

[0096] In eighth embodiments, the sparge composition has a pH from 1-3, in embodiments 3-6, in embodiments 4-7, in embodiments 6-10, in embodiments 11-14, in embodiments 4.5 to 5.5, in embodiments, 4.7 to 5.3, or in embodiments 5.0 to 5.2.

[0097] In eighth embodiments, the sparge composition of the method comprises, consists of, or consists essentially of: water; a metal oxide ore comprising magnetite and further comprising silica, a silicate or a combination thereof; the amine collector; and the modifier comprising the one or more sulfonated polymers.

[0098] In eighth embodiments, the one or more sulfonated polymers is selected from a sulfonated natural polymer, a sulfonated synthetic polymer, and a combination thereof.

[0099] In eighth embodiments the weight average molecular weight of the sulfonated synthetic polymer is from about 300 to about 5,000,000, in embodiments about 300 to about 1,000,000, in embodiments about 300 to about 500,000, in embodiments about 300 to about

100,000, in embodiments about 300 to about 50,000, in embodiments about 300 to about 35,000, in embodiments about 300 to about 30,000, in embodiments about 300 to about 25,000, in embodiments from about 500 to about 5,000,000, in embodiments about 500 to about 1,000,000, in embodiments about 500 to about 500,000, in embodiments about 500 to about 100,000, in embodiments about 500 to about 50,000, in embodiments about 500 to about 25,000, in embodiments from about 700 to about 5,000,000, in embodiments about 700 to about 1,000,000, in embodiments about 700 to about 500,000, in embodiments about 700 to about 100,000, in embodiments about 700 to about 50,000, in embodiments about 700 to about 25,000, in embodiments from about 1,000 to about 5,000,000, in embodiments about 1,000 to about 1,000,000, in embodiments about 1,000 to about 500,000, in embodiments about 1,000 to about 100,000, in embodiments about 1,000 to about 50,000, in embodiments about 1,000 to about 40,000, in embodiments about 1,000 to about 35,000, in embodiments about 1,000 to about 30,000, in embodiments about 1,000 to about 25,000, in embodiments about 500 to about 20,000, in embodiments about 500 to about 15,000, in embodiments about 500 to about 10,000, in embodiments about 500 to about 7,000, in embodiments about 500 to about 5,000, in embodiments about 500 to about 3,000, in embodiments about 500 to about 1,000, in embodiments about 1,000 to about 25,000, in embodiments about 700 to about 20,000, in embodiments about 700 to about 15,000, in embodiments about 700 to about 10,000, in embodiments about 700 to about 7,000, in embodiments about 700 to about 5,000, in embodiments about 700 to about 3,000, in embodiments about 700 to about 1,000, in embodiments about 1,000 to about 25,000, in embodiments about 1,000 to about 20,000, in embodiments about 1,000 to about 15,000, in embodiments about 1,000 to about 10,000, in embodiments about 1,000 to about 7,000, in embodiments about 1,000 to about 5,000, in embodiments about 1,000 to about 3,000, or in embodiments about 1,000 to about 2,000.

[0100] In eighth embodiments, the weight ratio of the one or more sulfonated polymers to the particulate comprising the metal oxide ore in the sparge composition of the method of the eighth embodiments is from about 1g to about 1000g of the one or more sulfonated polymers per ton of particulate, in embodiments from about 5g to about 500g, in embodiments, from about 10g to about 500g, in embodiments from about 20g to about 300g, in embodiments from about 50g to about 300g, in embodiments from about 50g to about 200g, in embodiments from about 10g to about 100g, in embodiments from about 10g to about 70g, or in embodiments from about 30g to about 70g of the one or more sulfonated polymers per particulate.

[0101] **Ninth Embodiments**

[0102] In ninth embodiments, the modifier of the composition of the method of the seventh or eighth embodiments comprises, consists of, or consists essentially of a sulfonated lignin. Lignin is a class of complex organic polymers.

[0103] In ninth embodiments the sulfonated lignin has a broad range of molecular weight. In embodiments, the sulfonated lignin has a weight average molecular weight range of from about 1,000 to about 140,000.

[0104] In ninth embodiments, the sulfonated lignin comprises, consists of, or consists essentially of a byproduct of production of wood pulp using sulfite pumping. In some embodiments, the sulfonated lignin is the reaction product of lignin with one or more sulfites, one or more bisulfites, or a combination thereof.

[0105] In ninth embodiments, the sulfonated lignin has comprises a modification of structure (I) wherein one or more of the $-CH_2OH$ groups is replaced with $-CH_2SO_3H$, $-CH_2SO_3^-$, or a combination thereof.

[0106] In ninth embodiments, the sulfonated lignin has a structure comprising structure (II), structure (III), or both structure (II) and structure (III), wherein R_1 is hydrogen or one of a wide variety of organic structures found in the structure of lignin; R_2 is one of a wide variety of organic structures found in the structure of lignin; and R_3 is hydrogen or one of a wide variety of organic structures found in the structure of lignin.

[0107] **Tenth Embodiments**

[0108] In tenth embodiments, the modifier of the composition of the method of the seventh or eighth embodiments comprises, consists of, or consists essentially of a sulfonated starch. In embodiments, the sulfonated starch comprises amylopectin wherein one or more of the –OH groups is replaced with a sulfonate group ($-SO_3H$ and/or $-SO_3^-$), amylose wherein one or more of the –OH groups is replaced by a sulfonate group ($-SO_3H$ and/or $-SO_3^-$), or a combination thereof.

[0109] **Eleventh Embodiments**

[0110] In eleventh embodiments, the modifier of the composition of any of the methods of the seventh or eighth embodiments comprises, consists of, or consists essentially of a sulfonated cellulose, wherein one or more of the –OH groups in cellulose molecules is replaced by a sulfonate group ($-SO_3H$ and/or $-SO_3^-$).

[0111] **Twelfth Embodiments**

[0112] In twelfth embodiments, the modifier of the composition of any of the methods of the seventh or eighth embodiments comprises, consists of, or consists essentially of a sulfonated natural polymer selected from sulfonated lignin, sulfonated starch, sulfonated cellulose, sulfonated guar gum, sulfonated xanthate gum, and any combination thereof.

[0113] **Thirteenth Embodiments**

[0114] In thirteenth embodiments, the modifier of the composition of the methods of the seventh or eighth embodiments comprises a sulfonated synthetic polymer. In thirteenth embodiments, the modifier of the sparge composition of any of the methods of the seventh or eighth embodiments comprises a sulfonated synthetic polymer, wherein the sulfonated synthetic polymer comprises a residue of a sulfonated monomer, wherein the sulfonated monomer is selected from sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonic acid and/or a salt thereof (ATBS), styrene sulfonic acid and/or a salt thereof, and any combination thereof.

[0115] In thirteenth embodiments, the sulfonated synthetic polymer comprises a monomer residue selected from the monomer residue having the structure (IX), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; the monomer residue having the structure (X); the monomer residue having the structure (XI), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; the monomer residue having the structure (XII); the monomer residue having the structure (XIII), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, quaternary organic ammonium; the monomer residue having the structure (XIV); the monomer residue having the structure (XV); the monomer residue having the structure (XVI), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; the monomer residue having the structure (XVII); the monomer residue having the structure (XVIII), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; the monomer residue having the structure (XIX), wherein R_4 is alkyl; the monomer residue having the structure (XX), wherein R_4 is alkyl and wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic

ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; the monomer residue having the structure (XXI); the monomer residue having the structure (XXII), wherein the counterion is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium; and any combination thereof.

[0116] In some such thirteenth embodiments, the sulfonated synthetic polymer further comprises the residue of acrylamide, the residue of acrylic acid, the residue of an acrylic acid salt, the residue of methacrylic acid, the residue of a methacrylic acid salt, the residue of maleic acid, the residue of a salt of maleic acid, the residue of a monoester of maleic acid, the residue of salt of a monoester of maleic acid, the residue of a diester of maleic acid, the residue having the structure (XXIII), or any combination thereof. In embodiments, the cation of the acrylic acid salt, the residue of the methacrylic acid salt, the residue of the salt of maleic acid, or the residue of the salt of the monoester of maleic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

[0117] In thirteenth embodiments, the modifier of the sparge composition of the methods of the seventh or eighth embodiments comprises, consists of, or consists essentially of a copolymer of acrylic acid and ATBS. In embodiments, the cation of the salt of the acrylic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium. In embodiments, the ATBS is an ATBS salt, wherein the cation is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

[0118] In thirteenth embodiments, the modifier of the sparge composition of any of the methods of the seventh or eighth embodiments comprises, consists of, or consists essentially of a terpolymer of acrylic acid, ATBS, and acrylamide. In embodiments, the cation of the salt of the acrylic acid is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium. In embodiments, the ATBS is an ATBS salt, wherein the cation is selected from NH_4^+, Na^+, K^+, primary organic ammonium, secondary organic ammonium, tertiary organic ammonium, and quaternary organic ammonium.

[0119] In thirteenth embodiments, at least one of the one or more sulfonated polymers of any one of the methods of the seventh or eighth embodiments comprises a residue of a monomer, wherein the monomer is selected from sulfonated vinyl alcohol, sulfonated acrylamide,

sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonic acid and/or a salt thereof (ATBS), styrene sulfonic acid and/or a salt thereof, and any combination thereof. In some such embodiments, the at least one of the one or more sulfonated polymers further comprises a residue of a monomer selected from acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, maleic acid esters, and any combination thereof. In some such embodiments, the at least one of the one or more sulfonated polymers further comprises a residue acrylic acid, a salt of acrylic acid, or a combination thereof. In some such embodiments, the at least one of the one or more sulfonated polymers comprises the residue of ATBS, the residue of a sulfomethylated acrylamide, or both the residue of ATBS and the residue of sulfomethylated acrylamide.

[0120] In embodiments, the modifier of any of the methods of the seventh and eighth embodiments comprises a naphthalene sulfonate formaldehyde condensate, sulfonated poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl), or a combination thereof.

[0121] **Fourteenth Embodiments**

[0122] In fourteenth embodiments, at least one of the one or more sulfonated polymers of any of the first to thirteenth embodiments is tagged with a fluorescent tag. In embodiments, the fluorescent tag is copolymerized into the backbone of the at least one of the one or more sulfonated polymers or the fluorescent tag is otherwise covalently bonded to the at least one of the one or more sulfonated polymers. In embodiments, the fluorescent tag is selected from the group consisting of hydroxy allyloxy propyl naphthalimide (HAPNQ), pyrene tetrasulfonic acid (PTSA), naphthalene disulfonic acid, and 4-methoxy-N-(3-dimethylaminopropyl)-naphthalimide vinylbenzyl chloride quat (VBNQ). In embodiments, the fluorescent tag is about 2% to about 5% by weight of the one or more sulfonated polymers.

[0123] In fourteenth embodiments, the modifier of any of the first to thirteenth embodiments comprises a fluorescent tag material. In such embodiments, the ratio by weight of the fluorescent tag material to the one or more sulfonated polymers is from about 2:98 to about 5:95. In some such embodiments, the fluorescent tag material is selected from the group consisting of hydroxy allyloxy propyl naphthalimide (HAPNQ), pyrene tetrasulfonic acid (PTSA), naphthalene disulfonic acid, and VBNQ.

[0124] **Fifteenth embodiments**

[0125] In fifteenth embodiments, the method of any one of the seventh to fourteenth embodiments further comprises grinding a mineral ore to form the particulate comprising the metal ore.

[0126] **Sixteenth embodiments**

[0127] In sixteenth embodiments, the method of the fifteenth embodiments further comprises the step of combining the particulate with at least a portion of the medium to form a medium-ore slurry.

[0128] **Seventeenth embodiments**

[0129] In seventeenth embodiments, the method of any one of the sixteenth embodiments further comprises desliming the metal ore.

[0130] **Eighteenth embodiments**

[0131] In eighteenth embodiments, the method of any one of the sixteenth or seventeenth embodiments further comprises combining the particulate with at least a portion of the modifier, the amine collector, or the modifier and the amine collector to form a modifier/collector-ore slurry, and conditioning the particulate.

[0132] **Nineteenth embodiments**

[0133] In nineteenth embodiments, the method of any of the seventh to eighteenth embodiments comprises grinding a mineral ore to form the particulate comprising the metal ore; and combining the particulate with the modifier, the amine collector, and the medium to make the sparge composition.

[0134] **Twentieth embodiments**

[0135] In twentieth embodiments, there is provided a use of any of the sparge compositions of the first to sixth embodiments in the beneficiation of iron ore by reverse froth flotation to furnish a beneficiary comprising iron oxide.

[0136] The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the invention. In particular the examples demonstrate representative examples of principles innate to the invention and these principles are not strictly limited to the specific condition

recited in these examples. As a result it should be understood that the invention encompasses various changes and modifications to the examples described herein and such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

EXAMPLES

[0137] Separation of an iron ore into a concentrate and tailings was conducted using a sulfonate polymer as modifier. The iron oxide comprised magnetite and a silica gangue.

[0138] **Example 1: Aqueous polymers**

[0139] Six aqueous polymers were synthesized as in TABLE 1:

[0140] Table 1: Aqueous polymers

Aqueous Polymer	**Composition**	**Actives, wt %**	**Weight average molecular weight, g/mole**
E	Sodium salt of poly(acrylic acid-co-sulfomethylated acrylamide)	35	25,000-30,000
F	Sodium salt of poly(acrylic acid-co-sulfomethylated acrylamide), tagged with less than 2% hydroxyl allyloxy propyl naphthalimide quaternary salt (HAPNQ)	35	25,000-30,000

[0141] **Example 2: Sparge Test of Iron Ore Sample**

[0142] A sample of flotation feed slurry was taken an iron ore beneficiation plant. The iron ore sample was mainly composed of magnetite with silica impurity. Its main composition, solids concentration, pH, and size are shown in TABLE 2.

Table 2: Composition of Iron Ore Slurry

Composition		Solids %	pH	Size*
Total Fe %	SiO_2 %			
66.7-67	5.6-5.8	39-40	7.9-8	85% -325 mesh

*As measured by throw-action sieve analysis carried out wet.

[0143] Reverse flotation was performed in a Denver D-12 flotation machine. Iron ore slurry at pH 7.9-8 was used for flotation without further dilution. Four separate reverse flotation tests were performed as shown in TABLE 3. A C13 ether diamine having the formula (V) was used as collector in each of the tests. Tests 1 and 2 were performed without modifier, Test 3 with Polymer E as modifier, and Test 4 with Polymer F as modifier. Each of the modifiers and collectors was prepared as a 1% solution in deionized water. The concentrate and tailings (froth) were filtered, dried, weighed, and sent for total iron and SiO_2 assay by X-ray analysis.

The tests results are shown in TABLE 3 and FIG. 1. In comparison, addition of sulfonated polymer E and F improves silica removal and iron recovery.

Table 3: Sparge Tests with Iron Ore Slurry

Test #	Modifier		Collector	Concentrate				
	Aqueous polymer	Aqueous Polymer g/t	kg/t	Yield, %	Grade of Fe, %	Grade of SiO_2, %	Recovery of Fe, %	Removal of SiO_2
1	None	0	20	94.29	91.06	7.15	95.37	16.61
2	None	0	30	92.21	91.38	6.86	93.6	21.74
3	E	50	30	92.89	92.39	6.5	94.59	24.61
4	F	50	30	93.16	91.55	6.66	94.69	23.03

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A sparge composition comprising:

(i) a medium;

(ii) a metal oxide ore comprising a gangue and a beneficiary;

(iii) an amine collector comprising a C12-C24 fatty amine, a C12-C24 fatty diamine, a C6-C13 ether amine, a C6-C13 ether diamine, or any combination thereof; and

(iv) a modifier comprising one or more sulfonated polymers, wherein at least one of the one or more sulfonated polymers is a sulfonated guar gum, a sulfonated xanthan gum, or comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, styrene sulfonate, or any combination thereof, wherein the at least one of the one or more sulfonated polymers has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole, wherein the at least one of the one or more sulfonated polymers further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, a maleic acid ester, or any combination thereof, and

wherein the beneficiary comprises an iron oxide and the gangue comprises a silicate, silica, a carbonate, or any combination thereof.

2. The sparge composition of claim 1, wherein the beneficiary comprises magnetite and the gangue comprises a silicate, silica, or a combination thereof.

3. The sparge composition of claim 1 or claim 2, wherein the modifier further comprises a sulfonated lignin, a sulfonated starch, a sulfonated cellulose, or any combination thereof.

4. The sparge composition of any one of claims 1-3, wherein the one or more sulfonated polymers comprises a copolymer of acrylic acid and a sulfomethylated acrylamide.

5. The sparge composition of any one of claims 1-4, wherein the amine collector comprises a C13 ether diamine.

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6. A method of froth flotation comprising:

forming a sparge composition, the sparge composition comprising

(i) a medium,

(ii) a metal oxide ore comprising a beneficiary and a gangue, the beneficiary comprising an iron oxide, and the gangue comprising silicate, silica, carbonate, or any combination thereof,

(iii) an amine collector, and

(iv) a modifier comprising one or more sulfonated polymers, wherein at least one of the one or more sulfonated polymers is a sulfonated guar gum, a sulfonated xanthan gum, or comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, styrene sulfonate, or any combination thereof, wherein the at least one of the one or more sulfonated polymers has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole, and wherein the at least one of the one or more sulfonated polymers further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, a maleic acid ester, or any combination thereof; and

sparging the sparge composition to yield a sparged composition, the sparged composition comprising a froth and a sparged slurry, wherein the sparged slurry comprises a concentrate of the beneficiary and wherein the froth comprises tailings of the gangue.

7. The method of claim 6, wherein the modifier further comprises a sulfonated lignin, a sulfonated starch, a sulfonated cellulose, or any combination thereof.

8. The method of claim 6 or claim 7, wherein the beneficiary comprises magnetite, hematite, goethite, limonite, or any combination thereof.

9. The method of any one of claims 6-8, wherein the amine collector comprises a C12-C24 fatty amine, a C12-C24 fatty diamine, a C6-C13 ether amine, a C6-C13 ether diamine, or any combination thereof.

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10. The method of any one of claims 6-9, wherein the one or more sulfonated polymers comprises a copolymer of acrylic acid and sulfomethylated acrylamide; the amine collector comprises C13 ether diamine; the beneficiary comprises magnetite; and the gangue comprises silica, a silicate, or any combination thereof.

11. Use of a composition of any one of claims 1-5 to concentrate a beneficiary comprising magnetite, hematite, goethite, limonite, or any combination thereof.

12. A sparge composition comprising:

(i) a medium;

(ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc, zircon, fluorite, and any combination thereof, the ore comprising a gangue and a beneficiary;

(iii) a collector; and

(iv) a sulfonated polymer, wherein the sulfonated polymer

(a) has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole,

(b) comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, or any combination thereof, and

(c) further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, maleic acid esters, or any combination thereof.

13. The sparge composition of claim 12, wherein the gangue comprises a silicate, silica, a carbonate, or any combination thereof..

14. A method of froth flotation comprising:

forming a sparge composition, the sparge composition comprising

(i) a medium,

(ii) an ore selected from potash ore, coal, metal oxide ore, limestone, clay, sand, gravel, diatomite, kaolin, bentonite, silica, barite, gypsum, talc,

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zircon, fluorite, and any combination thereof, the ore comprising a gangue and a beneficiary,

(iii) a collector, and

(iv) a sulfonated polymer, wherein the sulfonated polymer

(a) has a weight average molecular weight of from about 300 g/mole to about 100,000 g/mole,

(b) comprises a residue of sulfonated vinyl alcohol, sulfonated acrylamide, sulfomethylated acrylamide, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, or any combination thereof, and

(c) further comprises a residue of acrylic acid, methacrylic acid, acrylamide, vinyl alcohol, maleic acid, maleic acid esters, or any combination thereof; and

sparging the sparge composition to yield a sparged composition, the sparged composition comprising a froth and a sparged slurry.

15. The method of claim 14, wherein the gangue comprises a silicate, silica, a carbonate, or any combination thereof.

Dated this 19th day of August 2021

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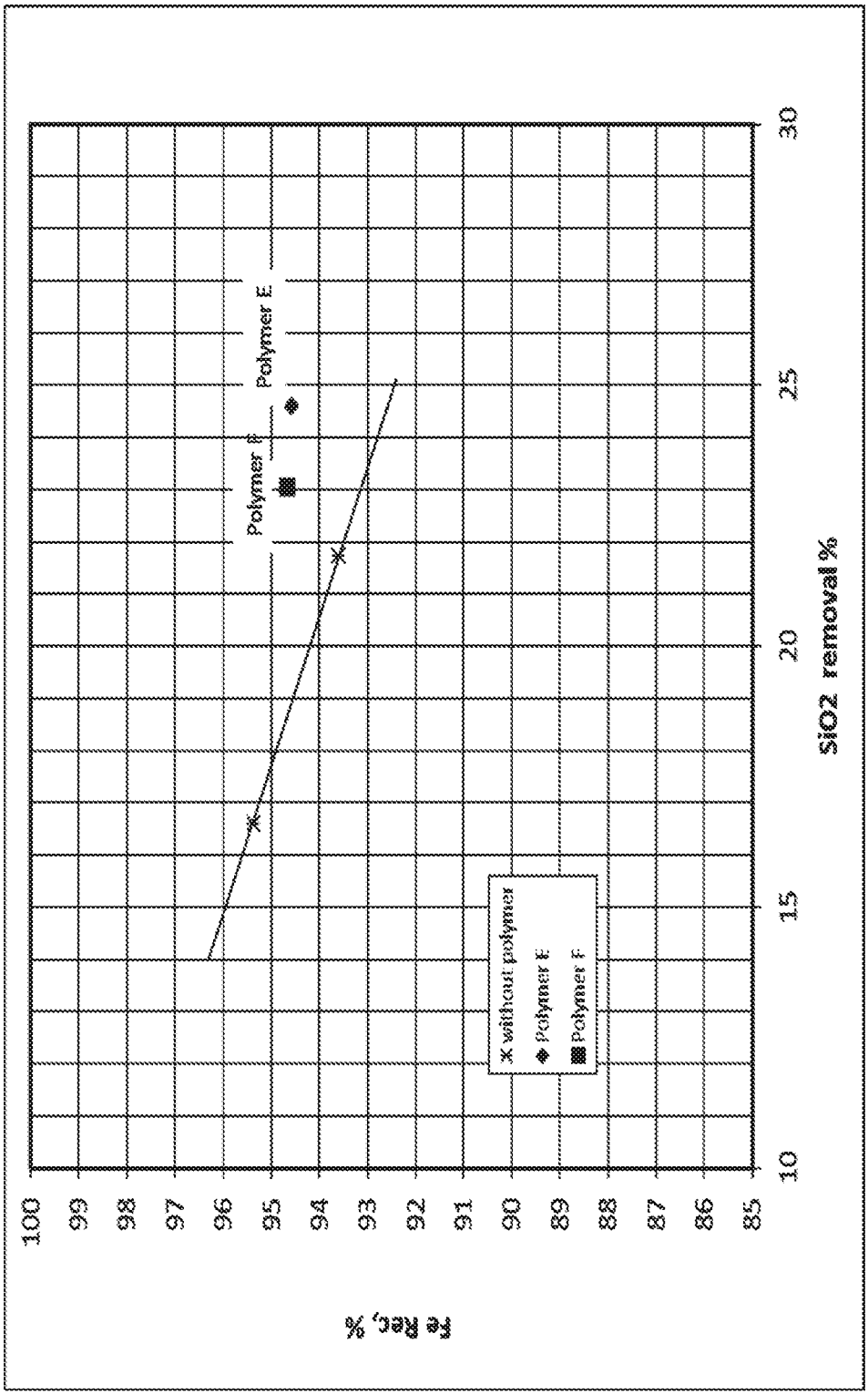

Fe Rec, %
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
10
15
20
25
30
SiO2 removal %
without polymer
Polymer E
Polymer F
Polymer F
Polymer E

FIG. 1