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(57) Abrégé/Abstract:

Processes for treating a tailings stream which comprises water and solids, include: (i) adding one or more anionic polymer flocculants and one or more salts of organic acids to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream.

ABSTRACT

Processes for treating a tailings stream which comprises water and solids, include: (i) adding one or more anionic polymer flocculants and one or more salts of organic acids to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream.

PROCESSES FOR TREATING TAILINGS STREAMS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present disclosure claims priority to U.S. Provisional Application No. 61/922,501, filed December 31, 2013.

FIELD OF THE ART

[0002] The present disclosure relates to processes for the treatment of tailings streams from oil sands ore.

BACKGROUND

[0003] Bituminous sands, or oil sands, are a type of unconventional petroleum deposit. The sands contain naturally occurring mixtures of sand, clay, water, and a dense and extremely viscous form of petroleum technically referred to as bitumen (or colloquially "tar" due to its similar appearance, odor, and color). Oil sands are found in large amounts in many countries throughout the world, but are found in extremely large quantities in Canada and Venezuela. Oil sand deposits in northern Alberta in Canada (Athabasca oil sands) contain approximately 1.6 trillion barrels of bitumen, and production from oil sands mining operations is expected to reach 1.5 million barrels of bitumen per day by 2020.

[0004] Oil sands reserves have only recently been considered to be part of the world's oil reserves, as higher oil prices and new technology enable them to be profitably extracted and upgraded to usable products. They are often referred to as unconventional oil or crude bitumen, in order to distinguish the bitumen extracted from oil sands from the free-flowing hydrocarbon mixtures known as crude oil traditionally produced from oil wells.

[0005] Conventional crude oil is normally extracted from the ground by drilling oil wells into a petroleum reservoir, and allowing oil to flow into them under natural reservoir pressure, although artificial lift and techniques such as water flooding and gas injection are usually required to maintain production as reservoir pressure drops toward the end of a field's life. Because extra-heavy oil and bitumen flow very slowly, if at all, toward producing wells

under normal reservoir conditions, the sands may be extracted by either strip mining or the oil made to flow into wells by in situ techniques which reduce the viscosity such as by injecting steam, solvents, and/or hot air into the sands. These processes can use more water and require larger amounts of energy than conventional oil extraction, although many conventional oil fields also require large amounts of water and energy to achieve good rates of production.

[0006] The original process for extraction of bitumen from the sands was developed by Dr. Karl Clark, working with the Alberta Research Council in the 1920s. Today, producers using surface mining processes use a variation of the Clark Hot Water Extraction (CHWE) process. In this process, the ores are mined using open-pit mining techniques. The mined ore is then crushed for size reduction in relatively large tumblers or conditioning drums. Hot water at 40–80 °C is added to the ore, forming a slurry. The formed slurry may be conditioned and transported, for example using a piping system called hydrotransport line, to extraction units, for example to a primary separation vessel (PSV) in which a flotation process is used to recover bitumen as bitumen froth. The hydrotransport line may be configured to condition the oil sands stream while moving it to the extraction unit. The water used for hydrotransport is generally cooler (but still heated) than that in the tumblers or conditioning drums.

[0007] The displacement and liberation of bitumen from the sands is achieved by wetting the surface of the sand grains with an aqueous solution containing a caustic wetting agent, such as sodium hydroxide. The resulting strong surface hydration forces operative at the surface of the sand particles give rise to the displacement of the bitumen by the aqueous phase. For example, sodium hydroxide is added to the slurry to maintain a basic pH, e.g., in the range of 8.0 to 10. This has the effect of dispersing fines (particle size of less than 44 µm) and clays from the oil sands and reducing the viscosity of the slurry, thereby reducing the particle size of the minerals in the oil sands.

[0008] Once the bitumen has been displaced and the sand grains are free, the components can be separated. Gravity can cause sand and rock from the slurry to settle to a bottom layer. A portion of the bitumen can float to the top based on the natural hydrophobicity exhibited by the free bituminous droplets at moderate alkaline pH values, and be removed as bitumen froth. An intermediate portion, often referred to as middlings, is relatively viscous and typically contains dispersed clay particles and some trapped bitumen which is not able to rise due to the viscosity. The middlings may then be exposed to froth flotation techniques to recover

additional bitumen. (Hot water extraction of bitumen from Utah tar sands, Sepulveda *et al.* S. B. Radding, ed., Symposium on Oil Shale, Tar Sand, and Related Material - Production and Utilization of Synfuels: Preprints of Papers Presented at San Francisco, California, August 29 - September 3, 1976; vol. 21, no. 6, pp. 110–122 (1976)).

[0009] The recovered bitumen froth generally consists of 60% bitumen, 30% water and 10% solids (sand and clay fines) by weight. The recovered bitumen froth may be cleaned to reject the contained solids and water to meet the requirement of downstream upgrading processes. Depending on the bitumen content in the ore, between 70 and 100% of the bitumen can be recovered using modern hot water extraction techniques from high grade ores.

[0010] Hydrophilic and biwetttable ultrafine solids, mainly clays and other charged silicates and metal oxides, tend to form stable colloids in water and exhibit a very slow settling behavior, resulting in tailings ponds that take several years to dewater. The slow settling of fine (<44 μm) and ultrafine clays (<1 μm) and the large demand of water during oil sand extraction process have promoted research and development of new technologies during the last 20 years to modify the water release and to improve settling characteristics of tailings streams. These include process modifications such as variations in pH, salinity and addition of chemical substances. Currently, two technologies commonly used in the oil sands industry are the consolidated tailings (CT) process and the paste technology process. In the CT process, gypsum is used as a coagulant. In the paste technology process polyelectrolytes, generally polyacrylamides of high density, are used as flocculants. Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles.

SUMMARY

[0012] Processes for treating a tailings stream which comprises water and solids, include: (i) adding one or more polymer flocculants and one or more salts of organic acids to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream.

DETAILED DESCRIPTION

[0013] Disclosed herein are processes for enhancing separation of solids from tailings streams. Exemplary processes utilize blends of polymer flocculants and salts of organic acids to enhance flocculation and separate the solids. The exemplary processes may provide a faster settling rate and a more complete separation of the solids from the water, and improved process efficiency relative to conventional processes for treating tailings streams. The processes may be used to enhance settling of solids, especially ultrafine solids, in oils sands ore tailings streams. The processes may be readily incorporated into current processing facilities and may provide economic and environmental benefits.

[0025] Exemplary processes for treating a tailings stream which comprises water and solids, include: (i) adding one or more polymer flocculants and one or more salts of organic acids to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream. In exemplary embodiments, the addition of the one or more polymer flocculants and one or more salts of organic acids to the tailings stream results in the formation of flocculated solids. In exemplary embodiments, the process further comprises adding one or more coagulants to the tailings stream.

[0026] The expressions “tailings”, “tailings stream”, “process oil sand tailings”, or “in-process tailings” as used herein refer to tailings that are directly generated as bitumen is extracted from oil sands. Generally, tailings are the discarded materials generated in the course of extracting the valuable material from ore. In tar sand processing, tailings comprise the whole tar sand ore and any net additions of process water thus missing the recovered bitumen. Any tailings fraction obtained from the process, such as tailings from primary separation cell, primary flotation and secondary flotation, process tailings and mature fine tailings or combination thereof, may be treated by the exemplary processes described herein. The tailings may comprise a colloidal sludge suspension containing clay minerals and/or metal oxides/hydroxides. In exemplary embodiments, the tailings stream comprises water and solids.

[0027] Oil sands process tailings contain mineral solids having a variety of particle sizes. Mineral fractions with a particle diameter greater than 44 microns are referred to as “coarse” particles or “sand.” Mineral fractions with a particle diameter less than 44 microns are

referred to as “fines” and are essentially comprised of silica and silicates and clays that can be easily suspended in the water. Ultrafine solids (<1 µm) may also be present in the tailings stream and are primarily composed of clays. The tailings may include one or more of the coarse, fine tailings, or ultrafine solids.

[0028] The tailings can include one or more of any of the tailings streams produced in a process to extract bitumen from an oil sands ore. In exemplary embodiments, the tailings may comprise paraffinic or naphthenic tailings, for example paraffinic froth tailings. The tailings may be combined into a single tailings stream for dewatering or each tailings stream may be dewatered individually.

[0029] In exemplary embodiments, the tailings stream is produced from an oil sands ore and comprises water and solids, for example sand and fines. In exemplary embodiments, the tailings stream comprises at least one of the coarse, fine tailings, and ultrafine solids. In particular, the processes may be used to treat ultrafine solids. In exemplary embodiments, the tailings stream comprises a fine (particle size <44 µm) content of about 10 to about 100 wt%, about 20 to about 100 wt%, about 30 to about 100 wt%, or about 40 to about 90 wt% of the dry tailings. In exemplary embodiments, the tailings stream contains about 0.01 to about 5 wt% of bitumen. In exemplary embodiments, the oil sands ore tailings stream comprises process tailings.

[0030] Flocculants

[0031] As used herein, the terms “polymer,” “polymers,” “polymeric,” and similar terms are used in their ordinary sense as understood by one skilled in the art, and thus may be used herein to refer to or describe a large molecule (or group of such molecules) that contains recurring units. Polymers may be formed in various ways, including by polymerizing monomers and/or by chemically modifying one or more recurring units of a precursor polymer. A polymer may be a “homopolymer” comprising substantially identical recurring units formed by, e.g., polymerizing a particular monomer. A polymer may also be a “copolymer” comprising two or more different recurring units formed by, e.g., copolymerizing two or more different monomers, and/or by chemically modifying one or more recurring units of a precursor polymer. The term “terpolymer” may be used herein to refer to copolymers containing three or more different recurring units. A polymer may also be linear, branched, or crosslinked.

[0032] In exemplary embodiments, the one or more polymer flocculants include, for example, flocculant-grade homopolymers, copolymers, and terpolymers prepared from

monomers. In exemplary embodiments, the one or more polymer flocculants may be linear, branched, or crosslinked. In exemplary embodiments, the polymer flocculant is a commercially available flocculant. In exemplary embodiments, one or more polymer flocculants may have a molecular weight of greater than about 1,000,000; about 5,000,000; about 10,000,000; about 15,000,000; about 20,000,000; or about 25,000,000 Daltons. In exemplary embodiments, one or more polymer flocculants may have a molecular weight in the range of about 1,000,000 to about 30,000,000 Daltons.

[0033] In exemplary embodiments, the one or more polymer flocculants comprise one or more anionic polymer flocculants. In exemplary embodiments, the one or more polymer flocculants are prepared by the polymerization of one or more anionic monomers or monomers comprising anionic functionality. In exemplary embodiments, the one or more anionic polymer flocculants are prepared by the polymerization of one or more anionic monomers or monomers comprising anionic functionality combined with nonionic co-monomers. In exemplary embodiments, the one or more anionic polymer flocculants comprise one or more monomers selected from monomers which comprise a carboxylic acid group, a sulfonic acid group or both.

[0034] In exemplary embodiments, the one or more anionic polymer flocculants may comprise monomers selected from the group consisting of acrylic, methacrylic, acrylamido, methacrylamido, vinyl, allyl, ethyl, maleic monomers and the like, all of which may be substituted with a carboxylic acid group, a sulphonic acid group, or both. In exemplary embodiments, monomers which may be substituted with a carboxylic acid group include, for example, acrylic acid, and methacrylic acid. In exemplary embodiments, monomers having a sulphonic function may include, for example, 2-acrylamido-2-methylpropane sulfonic acid (AMPS). The monomer may be a derivative or salt of a monomer according the embodiments. In exemplary embodiments, the one or more anionic polymer flocculants is a copolymer comprising monomers of acrylic acid and acrylamide.

[0035] In exemplary embodiments, the one or more polymer flocculants comprise one or more nonionic polymer flocculants. In exemplary embodiments, the one or more nonionic polymer flocculants are prepared by the polymerization of one or more nonionic monomers. In exemplary embodiments, the one or more nonionic polymer flocculants may comprise one or more hydrophobic monomer. In exemplary embodiments, the one or more nonionic polymer flocculants may comprise one or more polar functional groups.

[0036] In exemplary embodiments, the one or more nonionic polymer flocculants may comprise monomers selected from the group consisting of acrylic, methacrylic, acrylamido, methacrylamido, vinyl, allyl, ethyl or maleic monomers and the like, all of which may be substituted with a side chain selected from, for example, an alkyl, arylalkyl, dialkyl, ethoxyl, and/or hydrophobic group. In exemplary embodiments, the one or more nonionic monomers are selected from the group consisting of: acrylamide, methacrylamide, N-vinyl pyrrolidone, N-vinyl formamide, N,N dimethylacrylamide, N-vinyl acetamide, N-vinylpyridine, N-vinylimidazole, isopropyl acrylamide and polyethelene glycol methacrylate.

[0037] In exemplary embodiments, the one or more polymer flocculants consists of one or more anionic polymer flocculants. In exemplary embodiments, the one or more polymer flocculants consists of one or more nonionic polymer flocculants. In exemplary embodiments, the one or more polymer flocculants consists of one or more anionic polymer flocculants and one or more nonionic polymer flocculants.

[0038] In exemplary embodiments, the one or more polymer flocculants comprise one or more cationic polymer flocculants, for example a poly(diallyl dimethyl ammonium chloride) compound or an epi-polyamine compound.

[0039] In exemplary embodiments, the one or more anionic polymer flocculants are in an aqueous solution or in an emulsion. In exemplary embodiments, the one or more nonionic polymer flocculants are in an aqueous solution or in an emulsion or inverse emulsion. In exemplary embodiments, the one or more anionic polymer flocculants are in dry form. In exemplary embodiments, the one or more nonionic polymer flocculants are in dry form. In exemplary embodiments, the one or more polymer flocculants are premixed, for example as a dry blend or in an aqueous solution or emulsion.

[0040] In exemplary embodiments, the one or more polymer flocculants may be added to the tailings stream in dry form, in an emulsion, or in an aqueous solution.

[0041] In the exemplary embodiments, the total dosage of the one or more polymer flocculants can be any dosage that will achieve a necessary or desired result. In other exemplary embodiments, the total dosage of the one or more polymer flocculants added to the tailings stream are in the range of about 100 to about 100,000 grams per dry ton (g/t) of dry tailings. In exemplary embodiments, the total dosage of the one or more polymer flocculants is from about 500 to about 10000 g/t, about 1000 to about 10000 g/t, or about 1000 to about 5000 g/t. In

exemplary embodiments, the total dosage of the one or more polymer flocculants is about 500 g/t, about 700 g/t, about 1000 g/t, about 1500 g/t, about 2000 g/t, about 2500 g/t, about 3000 g/t, about 3500 g/t, about 4000 g/t, about 4500 g/t, or about 5000 g/t dry tailings.

[0042] Salts of Organic Acids

[0043] In exemplary embodiments, one or more salts of organic acids can be used in any of the processes described herein. Exemplary salts of organic acids include, for example carboxylate salts. Exemplary carboxylate salts include, but are not limited to, C₁-C₇ alkyl carboxylate salts. In exemplary embodiments, the one or more salts of organic acids comprises one or more sodium, potassium, ammonium or calcium salts of C₁-C₇ alkyl carboxylates, for example sodium formate, potassium formate, ammonium formate, calcium formate, sodium acetate, potassium acetate, ammonium acetate, calcium acetate, sodium chloroacetate, potassium chloroacetate, ammonium chloroacetate, calcium chloroacetate, sodium dichloroacetate, potassium dichloroacetate, ammonium dichloroacetate, calcium dichloroacetate, sodium trichloroacetate, potassium trichloroacetate, ammonium trichloroacetate, calcium trichloroacetate, sodium propanoate, potassium propanoate, ammonium propanoate, calcium propanoate, sodium butanoate, potassium butanoate, ammonium butanoate, calcium butanoate, sodium pentanoate, potassium pentanoate, ammonium pentanoate, calcium pentanoate, sodium hexanoate, potassium hexanoate, ammonium hexanoate, calcium hexanoate, sodium heptanoate, potassium heptanoate, ammonium heptanoate, calcium heptanoate, sodium oxalate, calcium oxalate, sodium benzoate, potassium benzoate, and mixtures thereof. In exemplary embodiments, the one or more salts of organic acids is selected from the group consisting of salts of formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, propionic acid, butyric acid, pentanoic (e.g. valeric) acid, hexanoic (e.g. caproic) acid, heptanoic (e.g. enanthic) acid, oxalic acid, benzoic acid, and the like.

[0044] In one embodiment, the one or more salts of an organic acid comprises a monocarboxylate salt. In one embodiment, the one or more salts of an organic acid comprises a dicarboxylate salt. The cation or cations of the salt of an organic acid are not intended to be limited and can be, for example, sodium, potassium, cesium, ammonium, calcium, magnesium and the like. In certain embodiments, one cation may be the counterion to two carboxylate groups, for example calcium formate (Ca(HCOO)₂), calcium acetate (Ca(CH₃COO)₂), calcium propanoate (Ca(C₂H₅COO)₂) and the like.

[0045] In exemplary embodiments, the one or more salts of organic acids is selected from the group consisting of: sodium formate, potassium formate, sodium acetate, potassium acetate and mixtures thereof. In a particular embodiment, the one or more salts of organic acids comprises sodium formate. In another particular embodiment, the one or more salts of organic acids sodium acetate.

[0046] In exemplary embodiments, the one or more salts of organic acids are a dry powder, aqueous solution, suspension in water, or emulsion. In exemplary embodiments, if two or more salts of organic acids are used in a process described herein, the salts may be added to the tailing stream as individual compositions in any of the forms described herein (e.g. a dry powder, aqueous solution, suspension in water, or emulsion) or as a combined preparation (e.g. mixture, solution, suspension or dry blend). In exemplary embodiments, if two or more salts of organic acids are used in a process described herein, the salts may be added to the tailing stream simultaneously or sequentially. In exemplary embodiments, several doses of one or more organic salts, the same or different as the previous dose, may be added to the tailings stream.

[0047] In the exemplary embodiments, the total dosage of the one or more salts of organic acids can be any dosage that will achieve a necessary or desired result. In other exemplary embodiments, the total dosage of the one or more salts of organic acids added to the tailings stream are in the range of about 10 to about 100,000 grams per dry ton (g/t) of dry tailings. In exemplary embodiments, the total dosage of the one or more polymer flocculants is from about 100 to about 10000 g/t, about 500 to about 10000 g/t, about 500 to about 5000 g/t, or about 100 to about 5000 g/t. In exemplary embodiments, the total dosage of the one or more salts of organic acids is about 100 g/t, 500 g/t, about 700 g/t, about 1000 g/t, about 1500 g/t, about 2000 g/t, about 2500 g/t, about 3000 g/t, about 3500 g/t, about 4000 g/t, about 4500 g/t, or about 5000 g/t dry tailings.

[0048] In exemplary embodiments, the ratio of dosage of the one or more polymer flocculants to the dosage of the one or more salts of organic acids can be any dosage that will achieve a necessary or desired result. In exemplary embodiments, the ratio of the dosage of the one or more polymer flocculants to the one or more salts of organic acids is from about 5:1 to about 1:100, about 5:1 to about 1:50, about 5:1 to about 1:10, about 5:1 to about 1:5, or about 5:1 to about 1:1 by weight.

[0049] Coagulants

[0050] In exemplary embodiments, the process optionally comprises adding one or more coagulants to the tailings stream. Exemplary coagulants include, for example cationic coagulants or cationic flocculants. In exemplary embodiments, the one or more coagulants may be added to the tailings stream before, after or at the same time as the one or more polymer flocculants are added to the tailings stream. In exemplary embodiments, the one or more coagulants may be added to the tailings stream before, after or at the same time as the one or more salts of organic acids are added to the tailings stream. In exemplary embodiments, the one or more coagulants may be added to the tailings stream after the one or more polymer flocculants and the one or more salts of organic acids are added to the tailings stream.

[0051] Exemplary coagulants include, but are not limited to, a poly(diallyl dimethyl ammonium chloride) compound; an epi-polyamine compound; a polymer that contains one or more quaternized ammonium groups, such as acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, methacrylamidopropyltrimethylammonium chloride, acrylamidopropyltrimethylammonium chloride; or a mixture thereof. In exemplary embodiments, one or more inorganic coagulants may be added to the tailings stream. An inorganic coagulant may, for example, reduce, neutralize or invert electrical repulsions between particles. Exemplary inorganic coagulants include inorganic salts such as aluminum sulfate, ferric chloride, lime, calcium chloride, magnesium chloride, or various commercially available iron or aluminum salts coagulants.

[0052] In exemplary embodiments, the one or more coagulants may be added to the tailings stream in dry form, in an emulsion, or in an aqueous solution.

[0053] In the exemplary embodiments, the total dosage of the one or more coagulants can be any dosage that will achieve a necessary or desired result. In other exemplary embodiments, the total dosage of the one or more coagulants added to the tailings stream are in the range of about 100 to about 100,000 grams per dry ton (g/t) of dry tailings. In exemplary embodiments, the total dosage of the one or more coagulants is from about 500 to about 10000 g/t, about 1000 to about 10000 g/t, or about 1000 to about 5000 g/t. In exemplary embodiments, the total dosage of the one or more coagulants is about 500 g/t, about 700 g/t, about 1000 g/t, about 1500 g/t, about 2000 g/t, about 2500 g/t, about 3000 g/t, about 3500 g/t, about 4000 g/t, about 4500 g/t, or about 5000 g/t dry tailings.

[0054] In exemplary embodiments, the ratio of the dosage of the one or more polymer flocculants to the one or more coagulants is from about 1:20 to about 20:1, or about 1:2 to about 2:1 by weight.

[0055] Processes for Treating Tailings Streams

[0056] In exemplary embodiments, a process for treating a tailings stream which comprises water and solids; includes: (i) adding one or more polymer flocculants and one or more salts of organic acids to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream.

[0057] In exemplary embodiments, a process is provided for treating a tailings stream which comprises water and solids; the process comprising (i) adding one or more polymer flocculants, one or more salts of organic acids and one or more coagulants to the tailings stream; (ii) allowing at least a portion of the solids to flocculate; and (iii) separating at least a portion of the flocculated solids from the tailings stream.

[0058] In exemplary embodiments, the addition of the one or more polymer flocculants and one or more salts of organic acids to the tailings stream results in the formation of flocculated solids. In exemplary embodiments, the addition of the one or more polymer flocculants, one or more salts of organic acids and one or more coagulants to the tailings stream results in the formation of flocculated solids.

[0059] In exemplary embodiments, the one or more polymer flocculants are added to the tailings stream before the one or more salts of organic acids. In exemplary embodiments, the one or more polymer flocculants are added to the tailings stream after the one or more salts of organic acids. In exemplary embodiments, the one or more polymer flocculants are added to the tailings stream before the one or more coagulants. In exemplary embodiments, the one or more polymer flocculants are added to the tailings stream after the one or more coagulants. In exemplary embodiments, the one or more polymer flocculants and the one or more salts of organic acids are premixed, for example as a dry blend or in an aqueous solution, before being added to a tailings stream. In exemplary embodiments, the one or more polymer flocculants and the one or more salts of organic acids are added to the tailings stream simultaneously or substantially at the same time. In exemplary embodiments, the one or more coagulants are added to the tailings stream after the one or more polymer flocculants and the one or more salts of organic acids are added to the tailings stream. In exemplary embodiments, the one or more

coagulants are added to the tailings stream before the one or more polymer flocculants and after the one or more salts of organic acids are added to the tailings stream. In exemplary embodiments, the one or more polymer flocculants are added to the tailings stream after the one or more salts of organic acids. In exemplary embodiments, the one or more coagulants are added to the tailings stream after the one or more salts of organic acids.

[0060] In exemplary embodiments, separating the flocculated solids from the tailings stream may be accomplished by any means known to those skilled in the art, including but not limited to centrifuges, hydrocyclones, decantation, filtration, thickeners, or another mechanical separation method.

[0061] In exemplary embodiments, the process may provide enhanced flocculation of solid materials in the tailings, better separation of the solids from water, an increased rate of separation of the solids from the water, and/or may expand the range of operating conditions which can be tolerated while still achieving the desired level of separation of solids from the water within a desired period of time.

[0062] The exemplary processes described herein may provide flocculated beds with higher densities, leading to compact beds that can dewater faster and build yield strength faster than comparable treatments without the addition of the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants. In an exemplary embodiment, the processes accelerate dewatering of the tailings stream.

[0063] In certain embodiments, the processes may achieve a clarified water phase with less than 0.5% solids within 8 hours. In exemplary embodiments, the processes may achieve a clarified water phase with less than 0.01% solids within 24 hours.

[0064] In exemplary embodiments, the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants can be added prior to and/or during a bitumen extraction process. In exemplary embodiments, the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants are contacted with the oil sands ore at a primary separation step or in a primary separation vessel.

[0065] In exemplary embodiments, the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants may be added in any mixing, conditioning, or separation step in the bitumen extraction process or treatment of oil sand ore tailings stream process. In view of the embodiments described herein, it will be understood that the one or more

anionic polymer flocculants and the one or more nonionic polymer flocculants could be added at other points in the bitumen recovery/extraction process as necessary or desired.

[0066] In exemplary embodiments, the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants may be added to the tailings stream before or after desanding. Desanding is a process wherein the tailings are settled for a period of time to form desanded tailings as the supernatant. Desanding can be done also for example by using a hydrocyclone.

[0067] In exemplary embodiments, the processes may be used in the presence, or with the addition of, one or more additives. Exemplary additives include but are not limited to surfactants, anti-foaming agents, polymers, flocculants, mineral oils, mixture thereof, and other necessary or desired additives. In exemplary embodiments, the additives are in an amount of 0.01 to 50 weight percent based on a total weight of dry ore or tailings. The addition of other additives to the tailings stream may occur at any point in the process as necessary or desired, including simultaneously, before or after the step of adding the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants.

[0068] In exemplary embodiments, the process provides efficient dewatering of the tailings and no other chemicals are necessary as the one or more anionic polymer flocculants and the one or more nonionic polymer flocculants are sufficient.

[0069] According to the exemplary embodiments, the clays in the supernatant, which may be present as a very dilute suspension, can be flocculated and separated from the tailings stream.

[0070] In exemplary embodiments, the processes may be used to dewater the tailings to provide a solid material having any necessary or desired yield strength. For example, the dewatered tailings may have sufficient yield strength so as to provide trafficable solids, such as solids which possess a yield stress of greater than about 5000 Pa after one year, or a yield stress of greater than about 10000 Pa within five years.

[0071] In the exemplary embodiments, the dewatered solids may be handled or processed in any manner as necessary or desired. In one embodiment, the dewatered solids should be handled in compliance with governmental regulations. In some embodiments, the resultant solids may be disposed of, sent to a tailings pond for additional settling, or when solids are a concentrated source of minerals, the solids may be used a raw materials or feed to produce

compounds for commercial products. In the exemplary embodiments, the separated water may be handled or processed in any manner as necessary or desired. In one embodiment, the separated water may be recycled to the process (“recycled water”). For example, the recycled water may be added to the crushed oil sands ore for bitumen extraction. Recycled water may also be added to the process at any point where water is added.

[0072] In exemplary embodiments, the processes may be carried out at broad pH conditions, such as a pH of about 6 to about 12, or about 8.5 to about 10.5. In exemplary embodiments, the pH of the tailings stream is adjusted prior to the addition of the flocculants. In exemplary embodiments, the pH of the tailings stream is not adjusted prior to the addition of the flocculants.

[0073] In the exemplary embodiments, the processes may be carried out at temperature of about 0°C to about 100°C, or about ambient temperature to about 90°C, or about 20°C to about 90°C.

[0074] In one embodiment, the processes produce at least about 20 %, at least about 25 %, about 30 %, about 35 %, about 40 %, or about 50 %, by weight, of bed solids.

[0075] In one embodiment, the processes produce less than about 2 wt%, about 1.5 wt%, about 1 wt%, about 0.5 wt%, or about 0.3 wt% solids in the supernatant.

[0076] In order that the disclosure may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention, but not limit the scope thereof.

EXAMPLES

[0077] **Example 1. Effect of Exemplary Salts of Organic Acids on Bitumen Extraction**

[0078] To evaluate the use of exemplary salts of organic acids as process aids, a low-grade ore sample was tested using laboratory-scale Denver flotation cell (Metso Minerals, Danville, PA) under semi-batch conditions (batch water, continuous air). The composition of these ores as determined by Dean-Stark Soxhlet extraction can be found in Table 1.

[0079] Table 1: Composition of Low- Grade Oil Sands Ore

Component	Percent by weight
Bitumen	9.03 %
Water	4.10 %
Total Solids	86.87 %
Fines content (<45µm)	32.12 %

[0080] For each experiment, 300 g of oil sands ore was added to 1.5 L of pre-heated water at 50 °C at an impeller speed of 1000 rpm in a 2-L rectangular tank. The flotation tank was kept at 50 °C with a hot water circulating bath. Prior to the addition of ore, the exemplary salts of organic acids (for example, sodium formate) were added to the test water. Upon ore addition, the slurry was pre-conditioned for 5 min before aeration began at an airflow rate of 200 mL/min. At 2, 5, 10, 20, and 60 minutes after the start of aeration, the agitation was paused for 30 sec and all froth which had developed was collected in order to simulate both primary and secondary bitumen recoveries. The slurry which remained after froth collection, referred to as the tailings, was transferred to a 2 L graduated cylinder to monitor whether the fine clays settled or remained in suspension. For each froth, the concentrations of bitumen, water, and solids were determined by toluene solvent extraction using standard Dean-Stark Soxhlet extractor units. Triplicate experiments indicated recovery rates being reproducible within ±5%.

[0081] The addition of the exemplary salts of organic acids at a range of doses (e.g. 3-10 kg/t) was applied in the Denver cell tests for ore samples. The results for bitumen recovery were compared to a test using the addition of sodium hydroxide to pH 8.5.

[0082] It was observed that the addition of the exemplary salts of organic acids at each of the concentrations performed similar to the use of NaOH at a slurry pH of 8.5. This indicated that the upfront addition of the exemplary salts of organic acids did not interfere with the liberation and aeration of bitumen in a way that would reduce bitumen recovery.

[0083] Further, when the tailings were observed for 24 hours, for samples treated with at least 3 kg/t of the exemplary salts of organic acids, the clarity of the supernatant began to improve and a secondary settled bed of fine solids was observed to form on top of the sedimented coarse tailings. The segregation was also observed to be within the fine solids which

settled. As the concentration of the exemplary salts of organic acids increased, the degree of segregation within the fines was reduced and a more uniform settled bed was observed.

[0084] Example 2. Effect of Exemplary Salts of Organic Acids on Settling of Coarse and Fine Solids

[0085] When processing the exemplary salts of organic acids in the Denver cell or hydrotransport (HT) loop, the majority of the solids in the slurry are coarse solids, i.e. larger than 45 μm in diameter. In order to more closely observe the interaction of the exemplary salts of organic acids with fine solids, additional testing was performed by processing a low-grade oil sand in the laboratory scale HT loop without additional process aids. The slurry remaining after a 60 minute flotation experiment was collected. After allowing the coarsest fraction to settle for approximately 1 minute, the unsettled slurry (supernatant) was collected. These tailings were transferred to 100 or 250mL graduated cylinders to conduct additional settling experiments. The exemplary salts of organic acids was added to tailings, based on the amount of ore used in the flotation process, by capping and inverting the graduated cylinder fifteen times, with each inversion cycle lasting approximately one second. The settling was monitored for a minimum of 24 hours and observed for the type of settling and the initial settling rate (ISR). The supernatant and settled beds were sampled and analyzed by additional techniques.

[0086] Particle size distributions (PSD) were determined with a Malvern Mastersizer S, which measures the angular dependence of scattered light (mainly in the forward direction). The original and treated tailings were dispersed in the impeller driven flow loop of the Mastersizer. The flow loop contained deionized water without additional chemical dispersants. Particle size distributions were computed as equivalent-sphere size distributions based on Mie scattering and Fraunhofer diffraction formalisms applied to the scattering data. The optical constants ($\lambda = 432.8 \text{ nm}$) used for these computations were a complex refractive index of 1.5295, 0.100i for the solids and a real refractive index of 1.3300 for the continuous phase. Measurements were taken during each test at 30, 60, and 120 seconds after addition of the solids to the diluent under continuous agitation at a single impeller speed. This procedure was used to assess whether a steady-state size distribution had been achieved. Typically the size distributions after 120 sec of mixing were used for comparisons, since steady state was achieved by this time.

[0087] Particle zeta potentials were measured using a Brookhaven ZetaPALS equipped with a 659 nm laser. Samples of settled beds were diluted to approximately 0.5 wt% with water from their corresponding supernatants to a volume of 1.5 mL, and then added to 1 cm² acrylic cuvettes. Scans were collected every minute for 10 minutes at a temperature of 24.8 °C and were averaged to give the final results.

[0088] The ability of flocs formed by the addition of the exemplary salts of organic acids to reform after being subjected to additional shear was investigated by agitating the flocculated bed once it had initially settled for 24 hours. In the first test, the process of inverting the cylinder was repeated to simulate a low-shear agitation, and the ISR was followed for an additional 24 hours. A second test was then performed by vigorously shaking the sample for 60 seconds to simulate the higher shear conditions which might be encountered during transport in a pipeline to a tailings pond. The settling was then followed for an additional 24 hours.

[0089] A more comprehensive range of the exemplary salts of organic acids concentration was monitored in the post-treatment of process tailings acquired from the HT-loop.

[0090] At a concentration of 100 g/t of the exemplary salts of organic acids, the ISR appeared to increase from 150 to 180 min. The increase was believed to be due to suspended fines being destabilized and joining the coarser particles in the settling process. Below 100 g/t of the exemplary salts of organic acids, it was observed that the sedimentation occurred as a rising settled zone where the solids accumulated on the bottom and began to stack on top of each other. This type of sedimentation was also much slower and was not observed within the initial 3 hours of settling, but was noticed and monitored after the cylinders settled overnight. Above the 100 g/t dose, the sedimentation existed as a falling front which collapsed quickly and resulted in a clear supernatant after 24 hours.

[0091] The type of settling could also be described by the level of segregation in the settled bed. It was observed that at the lower concentrations of the exemplary salts of organic acids where a rising-bed sedimentation dominated, two distinct zones were noticed. Notably, even though the coarsest material was removed before this stage of testing, there was still a size fraction which would settle on its own after a few hours, as can be seen in the control experiment. As the concentration of the exemplary salts of organic acids increased beyond certain concentrations, the stratification was no longer observed and a single, non-segregated bed existed. This was also observed in the Denver cell tailings where higher concentrations of the

exemplary salts of organic acids produced less stratification. Minimizing the amount of segregation can significantly improve the dewatering capability of the settled bed. (Farinato et al. "Segregation and Differential Settling in Flocculated Tailings." Proceedings of the Second International Oil Sands Tailings Conference, pp. 87-95, 2010, Edmonton, AB Canada.)

[0092] For the tests which produced a settled bed after 24 hours, a sample was removed and dried in an oven at 105°C for a minimum of three hours. To prevent the solids which settled naturally from being included in the solids content measurement, the excised sample was taken from the upper portion of the floc bed. It was observed that as the amount of the exemplary salts of organic acids increased, the solids content of the settled bed also increased. At a higher dose, the coarse particles were more evenly distributed throughout the settled bed.

[0093] PSDs were determined for the untreated tailings sample as well as several of the settled beds. It was observed that the distributions of the settled beds from these samples were unchanged from the original tailings.

[0094] Aggregates which formed through the addition of the exemplary salts of organic acids were dispersed by the impeller of the Mastersizer, indicating that they were weakly attracted with a low resistance to shear. A flocculated structure with strong interactions would show resistance to the shear induced by the Mastersizer impeller and demonstrate a shift in distribution to larger particle sizes after treatment. (Farinato et al. "Segregation and Differential Settling in Flocculated Tailings." Proceedings of the Second International Oil Sands Tailings Conference, pp. 87-95, 2010, Edmonton, AB Canada.)

[0095] The zeta potential results supported the findings of the PSD measurements. The addition of the exemplary salts of organic acids reduced the intensity of the surface charge. As the fine solids began to form aggregates with coarse material, an improvement in supernatant clarity was observed.

[0096] Example 3. Effect of Exemplary Salts of Organic Acids in Combination with Exemplary Flocculants on Settling of Coarse and Fine Solids

[0097] The effects of a combination treatment including exemplary salts of organic acids and exemplary polymer flocculants on the settling behavior of coarse and fine solids were assessed. The exemplary polymer flocculant used in these experiments was an anionic polyacrylamide flocculant. The flocculant concentration was ranged from 100 g/t to 5000 g/t. For

tests involving both exemplary salts of organic acids and exemplary polymer flocculants, the exemplary salts of organic acids was initially added with the inversion method, immediately followed by the addition of the and exemplary flocculants and a second inversion step.

[0098] The use of an exemplary polymer flocculant alone was able to provide an improvement in ISR, although the supernatants demonstrated that a fraction of the fine solids were unaffected by flocculant addition.

[0099] Addition of the exemplary salts of organic acids at a concentration of 50 g/t had previously shown poor results. The addition of an exemplary flocculant enhanced the settling but left a fraction of the fine solids unsettled. After 24 hours, the remaining fines had settled, but as a separate bed with low solids content.

[00100] Table 2: Settled bed solids content with and without flocculant addition (values in table indicate % of bed solids)

Flocculant	Flocculant + 50 g/t Salt of Organic Acid		Flocculant + 150 g/t Salt of Organic Acid	150 g/t Salt of Organic Acid
	Top Bed	Bottom Bed		
9.8	1.5	8.3	5.8	5.4

[00101] Comparing to the use of exemplary salts of organic acids alone at 160 g/t, the combination with the exemplary polymer flocculant was able to improve the ISR of the tailings and still provide a clear supernatant, although the bed was not as compact as the use of flocculant alone. Exemplary salts of organic acids improved the treatability of the fine solids so that settled beds could be formed which contained both fine and coarse solids.

[00102] Example 4. Effect of Exemplary Salts of Organic Acids in Combination with Exemplary Flocculants and Exemplary Coagulants on Settling of Coarse and Fine Solids

[0058] Samples of mature fine tailings (MFT) and tailings pond water (TPW) were obtained from a major oil sand producer in Alberta, Canada. The MFT were diluted to 30 wt% with TPW. Each 100 g sample was treated with 2000 g/t of a blend of exemplary acrylamide polymer flocculants (1800 g/t anionic polyacrylamide flocculant A and 200 g/t anionic polyacrylamide flocculant B) polymer flocculant). Some samples were also treated with an exemplary coagulant or an exemplary coagulant and an exemplary salt of organic acid (for

example, sodium formate or sodium acetate). Generally, the salt was added to the sample first, if included, the coagulant was added next, and the flocculant was added last. The sample was mixed, then transferred to a 50 mL centrifuge tube and centrifuged at a G-Force of 2000 for 2 minutes. Finally, the centrate was decanted from the sample and the centrate and cake solids were calculated gravimetrically. Yield stress measurements (rheological investigations) were conducted at 22°C on an Anton-Paar rheometer equipped with a six—lade Anton Paar ST 22-6V-16/106 spindle (equivalent to the Haake FL-100 spindle). The supernatant was decanted from the 50 mL centrifuge tube, and the 50 mL tube was placed into the rheometer sample holder and clamped in place to ensure immobility during testing. The spindle was lowered until it was one millimeter about where the taper starts in the centrifuge tube. The rotational shear stress was steadily increased until the sample began to yield, defined as the moment the strain began to increase as the sample began to deform (Barnes, 1999

[0059] The results are summarized in Table 3. It was observed that yield stress of the resulting solids was significantly improved when an exemplary salt of organic acid was included in the treatment.

[00103] Table 3. Centrifugation of MFT treated with exemplary flocculants, coagulants and salts of organic acids.

Coagulant Dose (g/t)	Salt of an Organic Acid Dose (g/t)	Centrate Solids (wt%)	Cake Solids (wt%)	Yield Stress (Pa)
0	0	1.85	40.0	1032
1000	0	1.10	40.0	642
1000	500	0.85	39.9	1860
1000	1000	0.87	43.5	1935
2000	0	0.70	40.0	881
2000	500	0.91	41.0	2505

[00104] In the preceding specification, various exemplary embodiments have been described. It will, however, be evident that various modifications and changes may be made thereto, and additional embodiments may be implemented, without departing from the broader scope of the exemplary embodiments as set forth in the claims that follow.

We Claim:

1. A process for treating a tailings stream which comprises water and solids, the process comprising:

(i) adding one or more anionic polymer flocculants and one or more salts of organic acids to the tailings stream, wherein the one or more salts of organic acids comprise sodium, potassium or ammonium carboxylate salts;

(ii) allowing at least a portion of the solids to flocculate; and

(iii) separating at least a portion of the flocculated solids from the tailings stream.

2. The process of claim 1, wherein the process further comprises adding one or more coagulants to the tailings stream.

3. The process of claim 1, wherein the one or more anionic polymer flocculants is added before the one or more salts of organic acids.

4. The process of claim 1, wherein the one or more anionic polymer flocculants is added after the one or more salts of organic acids.

5. The process of claim 1, wherein the one or more anionic polymer flocculants is added simultaneously with the one or more salts of organic acids.

6. The process of claim 2, wherein the one or more anionic polymer flocculants and one or more salts of organic acids are added before the one or more coagulants.

7. The process of claim 2, wherein the one or more anionic polymer flocculants are added to the tailings stream after the one or more coagulants.

8. The process of claim 2, wherein the one or more coagulants are added to the tailings stream before the one or more anionic polymer flocculants and after the one or more salts of organic acids are added to the tailings stream.

9. The process of claim 1, wherein the one or more anionic polymer flocculants and the one or more salts of organic acids are premixed before being added to a tailings stream.
10. The process of claim 1, wherein the addition of the one or more anionic polymer flocculants and the one or more salts of organic acids accelerates the consolidation and/or sedimentation of the flocculated solids in the tailings streams.
11. The process of claim 1, wherein the one or more anionic polymer flocculants are a dry blend, in an emulsion or in an aqueous solution.
12. The process of claim 1, wherein the one or more salts of organic acids are a dry blend, in an emulsion or in an aqueous solution.
13. The process of claim 1, where in the ratio of the dosage one or more anionic polymer flocculants to the one or more salts of organic acids is from about 5:1 to about 1:100 by weight.
14. The process of claim 2, where in the ratio of the dosage of one or more anionic polymer flocculants to the one or more coagulants is about 1:2 to about 2:1 by weight.
15. The process of claim 1, wherein the total dosage of the one or more anionic polymer flocculants is about 500 to about 10000 g/t dry tailings.
16. The process of claim 1, wherein the total dosage of the one or more salts of organic acids is about 100 to about 10000 g/t dry tailings.
17. The process of claim 2, wherein the total dosage of the one or more coagulants is about 500 to about 10000 g/t dry tailings.
18. The process of claim 1, wherein the separation of the solids from the tailings stream is by centrifuge, hydrocyclone, decantation, filtration, thickening or another mechanical separation.

19. The process of claim 1, wherein the process further comprises a desanding step.
20. The process of claim 1, wherein the one or more anionic polymer flocculants comprise anionic polyacrylamide.
21. The process of claim 1, wherein the one or more salt of organic acid comprises sodium formate or sodium acetate.