(54) PROCESSING AIDS FOR ENHANCED HYDROCARBON RECOVERY FROM OIL SANDS, OIL SHALE AND OTHER PETROLEUM RESIDUES

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(57) ABSTRACT

A method of improving hydrocarbon recovery from oil sands, oil shale, and petroleum residues includes adding a polymeric or nonpolymeric processing aid capable of sequestering cations, such as the multivalent calcium, magnesium and iron cations. The hydrocarbons are preferably contacted with the processing aid before a primary separation of the hydrocarbons in order to increase bitumen recovery. A processing aid is provided in an effective amount to increase the liberation of the hydrocarbons from inorganic solids, particularly when the source is a poor processing ore. Preferred processing aids include citric acid or a polymeric acid selected from polyacrylic acid, polymethacrylic acid, salts of these acids, partial salts of these acids, and combinations thereof. The processing aids significantly increase the hydrocarbon recovery typically with concentrations less than 50 ppm and the polymeric processing aids can also provide beneficial flocculation of solids in tailings slurry.
FIG. 1

Crushed Sand Ore

Primary Separation

Air

Water

Processing Aid

Transfer Agent

Middlings

Water

Bitumen

Solids

Water

Bitumen

Solids

Froth

Tailings

12

14

16

18

20

10
FIG. 2
FIG. 3
FIG. 4
FIG. 5
Dosage: 50 ppm citric acid

No addition after 60 minutes of flotation

B/W or B/S Ratio

Recovery

Flotation time, min

FIG. 6

Bitumen Recovery, %
PROCESSING AIDS FOR ENHANCED HYDROCARBON RECOVERY FROM OIL SANDS, OIL SHALE AND OTHER PETROLEUM RESIDUES

[0001] This application claims priority from U.S. provisional applications 60/505,083 filed on Sep. 22, 2003 and 60/604,212 filed on Aug. 25, 2004.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to the recovery of hydrocarbons from tar sands, oil shale and other petroleum residues. The invention also relates to the settling of solids from the tailings slurry of a hydrocarbon recovery process. More specifically, the invention relates to compositions and methods for improving the recovery of hydrocarbons and, in some cases, also the settling of solids in the tailings.

[0004] 2. Description of the Related Art

[0005] The Athabasca Oil Sands Deposit is, by itself, the largest petroleum resource in the world. These oil sands or tar sands are located in northwestern Alberta, Canada and represent the equivalent of roughly 1.6 to 2.7 trillion barrels of oil. Oil sand is visible on the banks of the Athabasca River, north and south of Fort McMurray, but most of the oil sand in the area lies buried 50 meters or deeper under muskeg and overburden.

[0006] To utilize this resource, as one means, truck and shovel operations first mine the oil sand and deliver it to a crusher. The crushed oil sand is then conveyed to a mixing operation that combines the oil sand with hot water to create an aqueous slurry that is pumped via pipeline to a bitumen extraction plant.

[0007] Bichard (U.S. Pat. No. 3,330,757) discloses a bitumen extraction process that mixes water at a temperature between 140°F and 200°F with the tar sand to remove most of the sand and other solids. Under these conditions, a froth or emulsion comprising water, nonseparated solids and oil is produced. This froth is introduced into a secondary processing zone where the froth is contacted with a combination of water, a transfer agent and a chelating agent in order to obtain a froth that is substantially solids-free. Bichard states that this process results in substantially 100% of the sand being removed from the froth. The froth can then be further processed to recover hydrocarbons.

[0008] Tipman et al. (U.S. Pat. No. 5,876,592) discloses that bitumen separation and recovery from sand may be accomplished by following what is known as the Clark hot water extraction process. In the front end of this process, the oil sand is mixed with hot water and caustic in a rotating tumbler to produce an aqueous slurry. The slurry is screened to remove large rocks and the like. The screened slurry is diluted with additional hot water and the product is then temporarily retained in a primary separation vessel (PSV). In this vessel, bitumen globules contact and coat air bubbles that are entrained in the slurry in the tumbler. The buoyant bitumen-coated air bubbles rise through the slurry and form bitumen froth. The sand in the slurry settles and is discharged from the base of the vessel, together with some water and bitumen. This stream or portion is referred to as the “PSV underflow” or tailings. A “middlings” portion may also be obtained, the middlings comprising water with non-buoyant bitumen and fines, collected from the middle of the PSV. The froth overflows the lip of the vessel and is recovered as the primary froth, typically comprising 65 wt. % bitumen, 28 wt. % water and 7 wt. % particulate solids.

[0009] The PSV underflow is introduced into a deep cone vessel, referred to as the tailings oil recovery vessel (“TORV”). Here the PSV underflow is contacted and mixed with a stream of aerated middlings from the PSV. Again, bitumen and air bubbles contact and unite to form buoyant globules that rise and form froth. This “secondary” froth overflows the lip of the TORV and is recovered. The secondary froth typically comprises 45 wt. % bitumen, 45 wt. % water and 10 wt. % solids. The middlings from the TORV are withdrawn and processed in a series of sub-aerated, impeller-agitated flotation cells. Secondary froth, typically comprising 40 wt. % bitumen, 50 wt. % water and 10 wt. % solids, is produced from these cells.

[0010] The primary and secondary froth streams are combined to yield a product froth stream, typically comprising 60 wt. % bitumen, 32 wt. % water and 8 wt. % solids. This stream will typically have a temperature of about 80°C. The water and solids in the froth are contaminants which need to be reduced in concentration before the froth can be treated in a downstream refinery-type upgrading facility. This cleaning operation is carried out using what is referred to as a “dilution centrifuging circuit”.

[0011] More particularly, the combined froth product is first deaerated and then diluted with sufficient solvent, specifically naphtha, to provide a solvent to froth (“S/F”) ratio of about 0.45 (w/w). This is done to increase the density differential between the bitumen on the one hand and the water and solids on the other. The diluted froth is then processed in a scroll-type centrifuge to remove coarse solids. The bitumen product from the scroll machine is subsequently processed in a disc-type centrifuge to remove water and fine clay solids.

[0012] However, the process of separating bitumen from sand, clay, and water is complicated by variations in the composition of the oil sand deposits. While the amount of sand, clay, water and bitumen in the oil sands are quite determinable, variations in the processability that are experienced between different oil sands are not self-evident. In fact, various oil sands have been classified as “problem ores” or “poor processing ores” while others are referred to as “good processing ores.” Problem ores, such as transition ores, oxidized ores, “type-X” ores and those having high fines or clays, bring about reduced bitumen yield or increased bitumen losses to waste streams. These problem ores typically yield only 40 to 60% recovery of their total bitumen content. By contrast, good processing ores typically yield around 58% recovery of their total bitumen content. Because of the relative amounts of problem ores and good processing ores, the problem ores reduce the industry average recovery to about 92% of total bitumen content. Therefore, there has been no explanation for why these problem ores are difficult to process and there has been no solution that allows these ores to be processed efficiently. As a result, problem ores are avoided or pushed aside in the mining operation in order to take advantage of the good processing ores. Eventually, the problem ores must be processed.

[0013] Therefore, there remains a need for a bitumen recovery process that improves the separation of bitumen...
from other constituents of the oil sands. It would be desirable if the process allowed problem ores to be processed in due order as encountered in the mining operation. It would be further desirable to identify a processing aid that would allow problem ores to be processed in the same extraction plant as good processing ores without any major redesigns, additional equipment, or process interruptions. Additional benefits would be enjoyed if there were a method for controlling the addition of the processing aid as needed to effectively recover bitumen from oil sands of different quality.

SUMMARY OF THE INVENTION

[0014] One embodiment of the present invention provides a method, comprising contacting a hydrocarbon-containing source with a processing aid, and separating the hydrocarbon-containing source from a hydrocarbon-containing froth and a tailings portion. Preferably, the method further comprises determining an amount of hydrocarbons in the tailings portion, and varying the amount of the processing aid added to the hydrocarbon-containing source to control the amount of hydrocarbons in the tailings portion. Most preferably, the hydrocarbon-containing source is separated in the presence of water and a transfer agent, such as a caustic, phosphate, silicate, carbonate, or combinations thereof. An exemplary hydrocarbon-containing source is selected from tar sand, oil shale, petroleum residues, and combinations thereof. Without being limited to a single theory, it is believed that the processing aids are effective by associating with or sequestering one or more cations selected from calcium, magnesium, iron, alumina, silica, titanium, zirconium, and combinations thereof.

[0015] The invention provides a method comprising the step of providing a processing aid to sequester cations in an aqueous mixture of hydrocarbons and inorganic solids and liberating the hydrocarbons from the inorganic material. It is preferred to then separate the aqueous mixture into a hydrocarbon-containing froth portion and a tailings portion, for example by mechanical separation including a centrifuge. Optionally, the method may further include determining an amount of hydrocarbons in the tailings portion, such as by fluorescence, and varying the amount the processing aid added to the aqueous mixture to control the amount of hydrocarbons in the tailings portion. The hydrocarbons may be liberated in the presence of water and a transfer agent. Suitable transfer agents are selected from a caustic, a phosphate, a silicate, a carbonate and combinations thereof. Furthermore, the aqueous mixture may include a hydrocarbon-containing source selected from tar sand, oil shale, petroleum residues, and combinations thereof. The hydrocarbon-containing source may be characterized by having a combined concentration of calcium ions, magnesium ions and iron ions that is greater than 40 parts per million.

[0016] The processing aid may be a carboxylic acid or a salt or partial salt thereof. The processing aid may be a carboxylic acid derivative of a nitrogen containing organic compound, or a salt or partial salt thereof. The processing aid may be a carboxylic acid, a salt of the carboxylic acid, or a combination thereof. The processing aid may be selected from amines, nitrilotriacetic acid, ethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, di(carboxymethyl)glutamic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, hydroxyethyliminodiacetic acid, hydroxyethylaminodiacetic acid, hydroxyethylethylenediaminetetraacetic acid, and combinations thereof. The processing aid may be a carbohydrate. The processing aid may be an organic alcohol. The processing aid may be an organic amine, a derivative of an organic amine, a salt of an organic amine, or a combination thereof, for example wherein the organic amine is selected from a hydroxy amine, an aromatic amine, derivatives or salts of the amines, and combinations thereof, or wherein the organic amine is selected from ethylene diamine, benztriazole, triethanolamine, 2,2'-dipyridyl, or combinations thereof. The processing aid may be an organic acid selected from acetic acid, maleic acid, citric acid, isocitric acid, humic acid, fulvic acid, salts of these acids, and combinations thereof. The processing aid may be a hydrogenated organic acid selected from glycolic acid, malic acid, gluconic acid, glucoheptonic acid, tartaric acid, maleic acid, fumaric acid, salicylic acid, salts of these acids, partial salts of these acids, and combinations thereof. The processing aid may be a polymeric acid selected from polyacrylic acid, polymethacrylic acid, salts of these acids, partial salts of these acids, and combinations thereof. The processing aid may be a phosphoric acid derivative selected from sodium tripolyphosphate, potassium polyphosphate, sodium polyphosphate, disodium dihydrogenphosphosphate, and combinations thereof. The processing aid may be an organophosphate selected from methylphosphonic acid, hydroxyethylidene phosphonic acid, any of the salts or partial salts of these acids, and combinations thereof. The processing aid may be an organophosphate based on a nitrogen containing organic compound selected from aminomethane phosphonic acid, nitrotris(methylene)triposphonic acid, ethylenediaminetetra(methylene phosphonic acid), diethylenetriaminepenta(methylene phosphonic acid), hexamethylenediaminetetra(methylene phosphonic acid), hydroxy containing derivatives thereof, and combinations thereof. The processing aid may be an organic compound containing both carboxylic and phosphonic functional groups, the organic compound selected from 2-phosphonobutane 1,2,4-tricarboxylic acid, any of the salts or partial salts of these acids, and combinations thereof. The processing aid may be a polymer selected from a homo polymer, a co-polymer, a salt or partial salt of these polymers, and combinations thereof, wherein the polymer includes a functional group selected from hydroxy, carboxylic amine, or combinations thereof. The processing aid may be a sulfonate-containing organic acid selected from 2,3-dimercaptopropanoic acid, sulfosalicylic acid, lignosulfonate, a salt or partial salt thereof, and combinations thereof. The processing aid may be an oxalkylate derivative of an amine. The processing aid may be used to control the amount of hydrocarbons in the tailings portion. The processing aid may be suitable for sequestering cations selected from calcium, magnesium, iron, alumina, silica, titanium, zirconium, and combinations thereof.

[0017] Another embodiment of the invention provides a method that includes providing a polymeric processing aid to sequester cations in an aqueous mixture of hydrocarbons and selectively flocculate inorganic solids, and liberating the hydrocarbons from the inorganic material. Preferably, the
polymeric processing aid is provided in an amount that is effective to increase the liberation of the hydrocarbons. The hydrocarbons and inorganic solids may optionally be obtained from oil sand, oil shale, petroleum residue, or a combination thereof. The process is especially beneficial for use wherein the hydrocarbons and inorganic solids are obtained from a poor processing ore.

[0018] The method may also include recovering liberated hydrocarbons from the mixture, such as by forming a froth having the hydrocarbons attached to air bubbles. Furthermore, the method may include separating the inorganic solids into a tailings portion. Optionally, an additional amount of a polymeric processing aid may be added to the tailings portion to flocculate solids. The polymeric processing aid provided to the tailings may or may not be the same polymeric processing aid provided to the aqueous mixture. Preferably, the polymeric processing aid separates along with the tailing portion in order to also flocculate solids.

[0019] Preferably, the aqueous mixture is provided with between 1 and 150 ppm of the polymeric processing aid, more preferably between 10 and 100 ppm, and most preferably between 15 and 60 ppm. The addition of the polymeric processing aid has been shown to increase the bitumen recovery by at least 5 percent, or even at least 10 percent.

[0020] The cations in the aqueous mixture may originate from the source of the hydrocarbons and inorganic material and the cations may include multivalent ions selected from calcium, magnesium, iron and combinations thereof. Depending upon the specific hydrocarbon source and/or water source, the aqueous mixture may have greater than 10 ppm, or even greater than 30 ppm of these cations. Still further, the aqueous mixture can have a combined concentration of calcium ions, magnesium ions and iron ions that is greater than 40 parts per million.

[0021] Accordingly, the processing aids of this invention should be suitable for sequestering cations selected from calcium, magnesium, iron, alumina, silica, titanium, zirconium, and combinations thereof. Preferably, the method is characterized by a reduction in the cation concentration and allows greater bubble attachment of the hydrocarbons. Optionally, the method includes reducing the concentration of unsequestered multivalent ions in the aqueous mixture to less than 30 ppm. Still, the method may further comprise monitoring the efficiency of the hydrocarbon recovery and varying the amount of processing aid added to the aqueous mixture to control the efficiency.

[0022] Suitably, the polymeric processing aid may comprise a polymer, copolymer or terpolymer based on monomers selected from acrylic acid, acrylamide, acrylonitrile, or substituted derivatives of these monomers. Optionally, these polymeric processing aids may be a derivative selected from sulfonates, phosphates, phosphonates, betaines, sulfobetaines, and combinations thereof. Furthermore, the polymeric processing aid may be a salt selected from amine salts, ammonium salts, phosphonium salts, thiourea salts, and combinations thereof. The polymeric processing aids may be oil soluble or water soluble. In one embodiment, the polymeric processing aid is supplied or provided as an aqueous solution.

[0023] In another embodiment, the polymeric processing aid comprises an acrylic acid-based polymer or a polymer based on a substituted polyacrylic acid. Preferred examples include polyacrylic acid or polymethacrylic acid. Furthermore, the polymeric processing aid may be a polymeric acid selected from polyacrylic acid, polymethacrylic acid, salts of these acids, partial salts of these acids, and combinations thereof.

[0024] In a further embodiment, the polymeric processing aid comprises an acrylamid-based polymer or a polymer based on a substituted acrylamide, such as polyacrylamide or polymethacrylamide. Optionally, the polymeric processing aids of these embodiments may have a hypophosphite in the polymer backbone. An example of this is where the hypophosphate backbone is formed by reacting the polyacrylic acid or the polymethacrylic acid with hypophosphorus acid.

[0025] In a still further embodiment, the polymeric processing aid is a hydrolysis product or salt capable of sequestering calcium. Optionally, such a polymeric processing aid hydrolyzes under conditions of the aqueous mixture.

[0026] In a yet further embodiment, the polymeric processing aid comprises a methylene sulfonate modified polyacrylamide, a methylene sulfonate modified polymethacrylamide, a hydroxamic acid modified polyacrylamide, or a hydroxamic acid modified polymethacrylamide.

[0027] The polyacrylamides useful to the present invention should not be limited by molecular weight, anionic character, or cationic character. However, a suitable polyacrylamide processing aid may be prepared by the reaction of polyacrylamide with water. The polyacrylamide processing aid is preferably characterized by forming a polyacrylamide acid at alkaline pH. Specifically, the polymeric processing aid may be a hydrolysed polyacrylamide polymer characterized by an ability to sequester cations and an ability to flocculate solids. The polyacrylamide may have a molecular weight between that of an acrylamide monomer and 1 billion, preferably between 1 and 50 million, and more preferably between 1 and 30 million. It should be noted that while this discussion refers primarily to polymers, acrylamide monomers, dimers, trimers and other acrylamide polymers may be used in accordance with the invention. The polyacrylamide may have any percentage anionic or cationic character, depending upon the intended function(s) of the polyacrylamide, but preferably has between 10 and 90 percent anionic charge. In a polyacrylamide prepared primarily for water softening (cation removal), the percentage anionic charge will be higher, such as 50 to 100 percent, and the molecular weight will be lower, such as a between a monomer and 8 million. One preferred polyacrylamide for water softening has a molecular weight of about 5 million and an anionic charge of about 80% and is preferably added at the front end of the process to improve bitumen liberation. In a polyacrylamide prepared primarily for flocculation, the percentage anionic charge will be lower, such as 10 and 30 percent, and the molecular weight will be higher, such as 50 million and 1 billion. One preferred polyacrylamide for flocculating has a molecular weight of 20 million and an anionic charge of about 30% and is preferably added into the primary separation vessel. Alternatively, a cationic polyacrylamide is useful for the removal of fine silica particles that carry a positive charge. Still further, the polyacrylamide may be further selected to optimize pH and/or viscosity effects, such as increasing the pH or reduc-
ing the viscosity. Any of the acrylamides may be used alone or in combinations. It should be recognized that the exact composition of the acrylamide may be tailored to the given conditions.

[0028] The polymeric processing aid may be a polymer with a nitrogen functionality, such as a polyetheramine that has been reacted with methylchloride or salted with a polycarboxyl or a triethanolamine-based polymer having a molecular weight up to 150,000.

[0029] The polymeric processing aid may be a polymer selected from a homo polymer, a co-polymer, a salt or partial salt of these polymers, and combinations thereof, wherein the polymer includes a functional group selected from hydroxyl, carboxylic, amine, or combinations thereof. The polymeric processing aid may also be a polymer based on monomers of maleic anhydride.

[0030] In further embodiments, the liberation is performed at a pH between about 7 and about 10, between about 8 and about 9, between about 8.2 and about 8.7, or between about 8.2 and about 8.5. Similarly, the method may include adjusting the pH of the aqueous mixture to between about 8 and about 9.

[0031] Optionally, the polymeric processing aid is added into a pipeline transporting the aqueous mixture and/or into a separation vessel. The method may further include supplying a transfer agent to the aqueous mixture. An exemplary transfer agent may be selected from a caustic, a phosphoric acid, a silicate, a carbonate, and combinations thereof. Examples of suitable caustics include sodium hydroxide, potassium hydroxide, and combinations thereof.

[0032] The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention, as illustrated in the accompanying drawing wherein like reference numbers represent like parts of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] FIG. 1 is a schematic process flow diagram of a simplified embodiment of a bitumen recovery process.

[0034] FIG. 2 is a graph of bitumen liberation at various HPAM dosages.

[0035] FIG. 3 is a graph of cumulative bitumen recovery after 50 minutes flotation at various HPAM dosages.

[0036] FIG. 4 is a graph of initial settling rate of the tailings slurry at various HPAM dosages.

[0037] FIG. 5 is a graph of the concentrations of calcium ions (Ca++) and magnesium ions (Mg++) in Aurora process water showing the concentrations without treatment and after treatment with various concentrations of HPAM.

[0038] FIG. 6 is a graph of bitumen recovery percentage as a function of the flotation time using 50 ppm citric acid.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

[0039] The present invention is a method for recovering hydrocarbons. The method comprises contacting a hydrocarbon-containing source with a processing aid, and separating the hydrocarbon-containing source into a hydrocarbon-containing froth portion and a tailings portion. Preferably, the hydrocarbon-containing source is separated in the presence of water and a transfer agent. The hydrocarbon-containing source is contacted with the processing aid before, during and/or after the primary separation, but the contact most preferably occurs before the primary separation in order to increase bitumen recovery. The contact may even occur before or during an optional hydrotransport step used to move hydrocarbon-containing slurries (such as oil sand slurries) to an extraction plant. Providing the processing aid early in the process stream allows for better mixing and longer contact time with the hydrocarbons, resulting in greater bitumen recovery effectiveness of the processing aid.

[0040] The processing aids of the present invention include polymeric compounds or agents, non-polymeric compounds or agents, and combinations thereof. The advantages or disadvantages of the various polymeric and non-polymeric processing aids may dictate their individual use under certain processing conditions or hydrocarbons sources, or benefit from their combined use in any beneficial ratios or amounts. At the present time, it has been confirmed that the polymeric processing aids not only improve bitumen recovery, but also improve the settling rate in the tailings. Other advantages or benefits of polymeric or non-polymeric processing aids may be discovered over time that may provide a basis for using one or the other, using mixtures of one or the other, using mixtures of both, or optimizing the ratios of components in a mixture.

[0041] The non-polymeric processing aids of this invention include, for example, any one of the following chemical families:

[0042] 1. Carbohydrates, including polysaccharides, or organic salts such as octyl, mannitol, etc., or organic amines such as ethylene diamine or benzotriazole, etc.

[0043] 2. Organic amines such as ethylene diamine, or hydroxy amines such as triethanolamine, or aromatic amines such as 2,2'-dipyridyl, etc., or derivatives or salts of the amines.

[0044] 3. Organic acids such as acetic acid, malonic acid, citric acid, isocitric acid, etc., or hydroxy organic acids, such as glyceric acid, maleic acid, gluconic acid, glucoheptonic acid, tartaric acid, etc., or unsaturated hydroxy organic acids, such as maleic acid, fumaric acid, etc., or aromatic hydroxy acids such as salicylic acid, or complex mixtures of organic acids such as humic acid, vulvac acid, etc., or polymeric acids such as polyacrylic acid, polymethacrylic acid or polymers based on monomers such as maleic anhydride, etc., or any of the salts, or partial salts of these acids, with cations such as sodium, potassium, etc.

[0045] 4. Carboxylic acid derivatives of nitrogen containing organic compounds, such as glycine, or such as nitrilotriacetic acid, NTA, or such as ethylenediaminetetraacetic acid, EDTA, or such as diethylenetriaminepentaacetic acid, DTPA, or such as dicarboxymethyl glutamic acid, etc., or cyclic derivatives such as trimethylcyclohexane-N,N',N'-
tetraacetic acid, CDTA, etc., or ether derivatives such as ethylenediamine(N,N,N,N-tetraacetic acid, EDTA, etc., or hydroxy containing derivatives such as hydroxyethyliminodiacetic acid, hydroxyethyliminodiaminotetraacetic acid, HEDTA, etc., or any of the salts, or partial salts of these acids, with cations such as sodium, potassium, etc.

5. Phosphoric acid derivatives or salts, such as sodium triphosphate, potassium triphosphate, sodium polyphosphate, disodium dihydrogenpyrophosphate, etc.

6. Organophosphonates such as methylphosphonic acid, etc., or hydroxy containing derivatives such as hydroxyethylidene diphasphonic acid, etc. or any of the salts, or partial salts of these acids, with cations such as sodium, potassium, etc.

7. Organophosphonates based on nitrogen containing organic compounds such as amino tri(lower alkyl ene phosphonic acids), such as amionmethanesphosphonic acid, AMPH, nitritolri(methyl)triphasphonic acid, ATMP, ethylenediaminetetra(methylphosphonic acid), EDTMP, diethylene triamine penta(methylene phosphonic acid), DTPMP, hexamethylene-diaminetetra(methylphosphonic acid), etc., or hydroxy containing derivatives, such as

8. Organic compounds containing both carboxylic and phosphoric functional groups, such as 2-phosphobutane-1,2,4-tricarboxylic acid, PBTC, etc., or any of the salts, or partial salts of these acids, with cations such as sodium, potassium, etc.

9. Homo polymers containing hydroxyl, or carboxyl or amine functional groups or co-polymer containing any combination of these functional groups, or mixtures of these polymers or any of the salts, or partial salts of these polymers, with cations such as sodium, potassium, etc.

10. Sulfur containing organic acids such as 2,3-dimercapto-1-propanol, etc., or sulfur containing aromatic hydroxy acids such as sulfosaliclyc acid, etc., or sulfonates, such as lignosulfonate or any of the salts, or partial salts of these polymers, with cations such as sodium, potassium, etc.

11. Oxyalkylate derivatives of amines such as tetraethylenediamine, etc.

However, a presently preferred processing aid includes ethylene diamine tetracetic acid or a salt thereof, citric acid or a salt thereof, or combinations thereof. Furthermore, it is believed that the chelating agents disclosed in U.S. Pat. No. 3,330,757, which patent is incorporated by reference herein, may be effective as processing aids when used in accordance with the present invention.

The polymeric processing aids include, without limitation, the following:

1. Acrylic acid-based polymers, such as polyacrylic acid, and polymers based on substituted polyacrylic acids, such as polymethacrylic acid.

2. Acrylamid-based polymers, such as polyacrylamides, and polymers based on substituted acrylamides, such as polymethacrylamid.
agent such as sodium hydroxide. Accordingly, the polycarboxylic acids serve as a chelating agent that improves hydrocarbon recovery.

[0065] In addition to improving hydrocarbon recovery, polymeric processing aids provide the benefit of flocculating fine inorganic particles in the tailings stream. This flocculation results in faster settling of solids and improved recovery of water. In order to accomplish this flocculation, the processing aids may be provided directly to the tailings stream. However, it is preferable to supply polymeric processing aids into the process as disclosed above with respect to all processing aids, such as before the primary separator. By supplying polymeric processing aids early in the process, the polymeric processing aids can chelate troublesome cations to improve the primary separation of bitumen or other hydrocarbons from inorganic solids. Any unreacted portion of the polymeric processing aids remains in the process stream and can subsequently serve as a flocculating agent in the tailings stream. In this manner, the polymeric processing aids may serve dual purposes to a greater extent than other processing aids described herein. The polymeric processing aids, as well as their chelated calcium or magnesium cations and flocculated mineral solids, will separate out in the tailings stream of the separator.

[0066] The processing aids may be formulated with other agents, additives or solvents. Optionally, the processing aid may be provided as an aqueous solution, such as a 30 weight percent solution of citric acid in water. Preferred additives for use in cold weather or climates include antifreeze, such as methanol. Accordingly, an aqueous solution containing the processing aid may further include between 10 and 15% antifreeze.

[0067] The processing aids are particularly beneficial when they make contact with the hydrocarbon slurry before or during the primary separation, although the agents are also beneficial in any secondary separations and any further separations (tertiary, etc.) of the hydrocarbons from sand, clay and other inorganic materials when the hydrocarbons do not efficiently separate from the inorganic solids. However, it should be emphasized that the method may be used to avoid the loss of hydrocarbons in a tailings or waste stream and that using the processing aid at appropriate injection points will improve the overall hydrocarbon recovery efficiency, as well as processability. The processing aids may also be used to treat middlings, which may include both hydrocarbons and sand, although the volume of primary middlings may be reduced if the processing aid is used before or during the primary separation. It should be recognized that the processing aids described herein may be introduced to the oil sands in various manners. For example, the processing aids may be injected directly into an aqueous oil sand stream, or mixed with other processing aids, such as transfer agents. In one embodiment, it is preferable to inject the processing aid into the process at a point located before the air is introduced into the transport pipeline. Specifically, it is anticipated that the processing aids can be beneficially used in contactors, hydrotransport lines, tumbler, primary separators and secondary separators. Other processing vessel types and processing stages may also benefit from the use of these processing aids.

[0068] The addition of the processing aid into the process may be achieved manually or automatically, using batch, intermittent or continuous processes, and other techniques known in the art. It is preferred to provide the processing aid automatically using a process control scheme. For example, the process control may include determining an amount of hydrocarbon in the tailings portion, and varying the amount the processing aid added to the hydrocarbon-containing source to control the amount of hydrocarbons in the tailings portion. This type of process control can be accomplished with an analog or digital microcontroller or computer-based process control system having an input signal for the hydrocarbons in the tailings and an output signal to a flow control valve providing the processing aid into the process. The input signal may be from a detector that measures the fluorescence of the tailings as an indicator of hydrocarbon content. Such a detector may provide continuous detection by placing the detector in fluorescent communication with the process stream, or provide periodic detection by taking samples out of the process stream.

[0069] The term “control” as used herein means that one factor is used to exert some effect over another factor, and is not limited to a definite and known relationship between the factors. Accordingly, it is recognized that the use of a processing aid to “control” hydrocarbon-content in a tailings portion does not mean that a given amount of the processing aid will necessarily produce a direct, measurable and known change in the hydrocarbon-content, since other factors may change in a manner that offsets the use of the processing aid. For example, a good processing ore having a low calcium or magnesium ion concentration may easily separate to produce a tailings portion having little or no hydrocarbons even without use of a processing aid. By contrast, a problem ore having a higher calcium or magnesium ion concentration may produce a tailings portion having significant hydrocarbon content. While the use of a processing aid will reduce the hydrocarbons in the tailings portion of the problem ore, the hydrocarbon-content may still be higher than in the tailings of the good processing ore without using a processing aid. Still, the hydrocarbon-content in the tailings portion when processing a problem ore will be reduced with use of a processing aid relative to the hydrocarbon-content in the tailings portion when processing the same problem ore without a processing aid.

[0070] The concentration of processing aids used may vary accordingly to the type and condition of the hydrocarbon source being processed and the specific processing aid(s) being used. However, a processing aid is preferably added in an amount effective to improve hydrocarbon recovery. Preferably, the processing aid is provided into an aqueous slurry containing tar sands at a concentration between 1 and 150 parts per million (ppm) based on the slurry. The processing aid concentration in the slurry is more preferably between 10 and 100 ppm and most preferably less than 100 ppm, such as between 15 and 60 ppm. Concentrations exceeding 100 ppm have not presently been found to provide any additional recovery of bitumen, but may actually recover less bitumen than with 100 ppm or less of processing aid. It should be recognized that the processing aid(s) may be used in sufficient concentrations to provide improved hydrocarbon recovery as well as improved consolidation of solids in the tailings.

[0071] Without being limited to a particular theory, it is believed that the processing aids of the present invention are effective to improve hydrocarbon recovery because of the
ability of the aids to associate with cations in the hydrocarbon-containing source, such as calcium, magnesium, iron, alumina, silica, titanium, zirconium, and combinations thereof. It is considered that these cations (positively charged) may be responsible for attracting both hydrocarbons and sand or clay particles (having a slightly negative surface charge) due to a charge association. By introducing a processing aid that associates with these cations, the charge association can be broken so that the hydrocarbons can more easily separate from the sand or clay. The exact mechanism of the attraction between the processing aid and the cations has not been determined, and is therefore referred to as an “association.” This association is intended to encompass partial associations and perhaps chelation.

0072 The terms “oil,” “bitumen,” and “hydrocarbons” are used interchangeably herein to identify the hydrocarbon content of the tar sand, oil shale, crude oil or petroleum source or residue. These terms encompass hydrocarbons based on carbon chains or rings and also containing hydrogen with or without oxygen, nitrogen, sulfur or other elements, regardless of the color, viscosity, or condition of the hydrocarbons. These carbon chains or rings specifically encompass functional groups selected from alkyl, aryl, alkynyl and combinations thereof.

0073 The hydrocarbon-containing source may be various types of materials. For example, the source may be oil sand (also referred to as “tar sand”), oil shale, petroleum residues, and combinations thereof. The hydrocarbon-containing sources are typically mixtures of hydrocarbons and inorganic materials, such as sand, clay or rock. The process of the invention may also be beneficial in enhancing the recovery of other hydrocarbons that require separation from a mixture with inorganic substrates or particulates. Furthermore, the terms “oil,” “bitumen,” and “hydrocarbons” are used interchangeably herein to broadly identify the hydrocarbon content of the tar sand, oil shale, or petroleum source or residue. These terms encompass hydrocarbons based on carbon chains or rings and also containing hydrogen with or without oxygen, nitrogen, sulfur or other elements, regardless of the color, viscosity, or condition of the hydrocarbons. These carbon chains or rings specifically encompass functional groups selected from alkyl, aryl, alkynyl and combinations thereof.

0074 The processing aids may be suitable for use in various hydrocarbon recovery processes. Even in the extraction of hydrocarbons from oil sands, there are various processes, equipment and conditions that can be used, each process having its own advantages and disadvantages. For example, there are hot water extraction processes and solvent extraction processes. The processing aids disclosed may also prove beneficial in hydrocarbon recovery processes not mentioned herein. It is anticipated that the processing aids may find use in a variety of applications, especially where hydrocarbons must be separated from sand or other inorganic substrates or particulate components. Furthermore, it is believed that the processing aids would improve interface control in treaters, specifically for heavy crude oils containing asphaltenes and naphthenic acids.

0075 However, many of the separation processes include a hot water separation that is at least similar to that described by Tipman in U.S. Pat. No. 5,876,592 as the Clark Hot Water Extraction Process (discussed above). Accordingly, one particularly preferred embodiment of the invention provides for the use of the processing aids in the hot water extraction process. It is an important discovery that processing aids will enhance the separation of hydrocarbons from sand to provide improved hydrocarbon yields and reduce environmental hazards associated with handling the tailings.

0076 The most preferred transfer agents are caustics, such as sodium hydroxide, potassium hydroxide or combinations thereof. However, a suitable transfer agent may include a phosphate, such as sodium tripolyphosphate, tetraceladon acid, hydroxyphosphate, trisodium phosphate, sodium hexametaphosphate and condensed phosphates. A further suitable transfer agent is sodium silicate or silicatized having SiO₂:Na₄O moduli of less than or equal to one. Still other chemicals that may be used as transfer agents includes sodium bicarbonate, sodium carbonate, sodium sulphide, sodium hydrosulphide, sodium cyanide, sodium hydroxide with carboxymethylcellulose, ammonium hydroxide (and similar salts of other alkali metal cations, e.g. potassium).

0077 In another embodiment, the processing aid may be used with lower concentrations of a transfer agent than is typically used, possibly even in the absence of a transfer agent. Reductions in the use of a transfer agent may be possible if the beneficial effects of the transfer agent can be achieved with the processing aids at a lower cost of operation.

0078 FIG. 1 is a schematic process flow diagram of a simplified embodiment of a bitumen recovery process 10. Oils sand ores are removed from natural deposits and crushed. The crushed oil sand ore 12 is contacted with water and an optional transfer agent to form a slurry that will typically be passed through a hydrotreatment line to a hydrocarbon recovery facility. A processing aid is also added to the slurry, preferably at the upstream end of the hydrotreatment line. At the hydrocarbon recovery facility, air is injected into the slurry in association with a primary separation 14 of the hydrocarbon from the sand or other inorganic material, such as clay. During the primary separation 14, the components of the oil sand ore are separated into froth, middlings and tailings. The froth comprises hydrocarbons attached to the surfaces of air bubbles, typically accompanied by small but undesirable amounts of water and solids. The tailings comprise inorganic material, such as sand and clay, along with water. However, the tailings may also include a significant amount of hydrocarbons. The middlings typically comprises less hydrocarbon, more water and more solids than the froth, yet more hydrocarbon, less water and less solids than the tailings. While the froth, middlings and tailings commonly undergo further separation processes 16, 18, 20, respectively, in order to increase the overall hydrocarbon recovery efficiency and to increase the quality or purity of each stream. For example, it is desirable to further process the hydrocarbons without water or solids, reuse the water without high solids content and dispose of the inorganic materials without excessive amounts of water. These objectives are achieved while avoiding large capital investments, avoiding further processing steps, and maintaining or increasing processing capacity through the use of the present processing aids. Specifically, the processing aids serve to increase bitumen separation from organic material leading to greater bitumen content and less solids in the froth. The processing aids separate out into the tailings where the aids improve consolidation of the solids from the water. The improved quality of the froth and
the tailings may result in higher process capacities or throughput for a given processing facility.

EXAMPLE 1

Bitumen Yields Using a Polymeric Hydrolysed Polyacrylamide Processing Aid

[0079] Bitumen extraction experiments were conducted in a laboratory hydrotransport extraction system capable of simulating commercial production conditions. Two CCD (charge coupled device) cameras were used for on-line monitoring of bitumen liberation and bubble surface loading, respectively, and a computer automatically recorded the signals.

[0080] Samples of oil sands, called transition ore that is one of poor processing ores, and Aurora recycle process water were obtained from an Aurora commercial plant operated by Syncrude Canada Ltd. The bulk ore sample was homogenized, packed in 600 g plastic bags and stored in a freezer at −29°C to prevent oxidation. This ore sample consisted of 9.2 wt % bitumen, 73.3 wt % water and 83.5 wt % solids. The solids contain 33% clay fines (less than 44 μm in size). The water used for the bitumen extraction experiments is called Aurora process water. Atomic absorption spectrometer (AAS) analysis showed that this water contained 47 ppm calcium and 15 ppm magnesium. The water had a pH of 8.2.

[0081] A polymeric hydrolysed polyacrylamide, PERCOL 777, was purchased from Ciba Specialty Chemicals. Each polymer solution was prepared at 0.04 wt % with deionized water just before the extraction experiment. All polymer dosages were recorded as mg of polymer per liter of slurry. Unless otherwise stated, all bitumen extraction experiments were carried out with Aurora industrial process water at a slurry temperature of 35°C.

[0082] For each bitumen extraction experiment, 1 kg oil sand was prepared and fed into the laboratory hydrotransport pipeline containing 3 L Aurora process water pre-heated to around 35°C. Bitumen extraction usually involves two steps, bitumen liberation and bitumen flotation. Bitumen liberation takes place in the slurry conditioning stage (oil sands plus Aurora process water with chemicals added), which runs for 5 min before air is introduced into the pipeline. When the air is introduced into the slurry through a stainless steel needle with a blunt end and adjusted to 195 mL/min, bitumen flotation and flotation timing begin. Six froth samples were collected at times of 3, 10, 20, 30, 40, and 60 minutes. Pulp slurry pH values were measured by a pH meter and slurry temperature was measured by a digital thermometer.

[0083] To evaluate the effect of chemical addition on bitumen liberation from the sand grains, an interactive image analysis technique was used. A high-speed black and white CCD camera was mounted in front of a specially designed square section of the glass pipeline. Images of oil sand slurry were captured and analyzed by image analysis software (obtained from Sigman Scan Pro), which used grey scale intensity to differentiate bitumen from the grayish background. The degree of “darkness” of the slurry was taken as an inverse measure of bitumen liberation degree from the sand grains.

[0084] After each experiment, the weight percent of bitumen, solids and water was determined for both the froth and the feed samples. The froth bitumen recovery i.e. aerated bitumen, was calculated based on the ratio of bitumen content in the froth to that in the feed. This procedure gives bitumen recovery as a function of flotation time. The tailings slurry was used for tailings settling tests. Tailings water was taken from tailings slurry after standing and was used for AFM measurement and was analyzed by AAS (Spectr AA 220FS) for calcium and magnesium concentrations.

[0085] Bitumen liberation plays an important role in bitumen extraction. Generally, bitumen liberation is controlled by the interaction between bitumen and sand grain surfaces. FIG. 2 shows a plot of bitumen recovery during the bitumen extraction experiments at various HPAM dosages. Compared to the case of no chemical addition, the use of HPAM significantly improved bitumen liberation degree from 80% to almost 100% at a flotation time of 60 minutes using a low dosage, e.g., 15 or 30 ppm. However, bitumen liberation deteriorated beginning at 60 ppm and declined to 60% when 150 ppm HPAM was added. So, a preferred HPAM dosage for bitumen extraction would be limited to about 30 ppm or less from the standpoint of bitumen liberation. A direct benefit obtained from improved bitumen liberation is increased bitumen recovery.

[0086] When air is introduced and dispersed into the slurry in the form of air bubbles after conditioning (bitumen liberation), bitumen droplets and air bubbles attach to each other and bitumen flotation takes place. FIG. 3 shows the final bitumen extraction results after 50 minutes flotation at dosages of 0, 15, 30, 60 and 150 ppm. The recovery is represented by the cumulative bitumen recovery (total bitumen amount recovered in froth).

[0087] On the recovery curve, the cumulative bitumen recovery was found to increase with the addition of HPAM at low dosages, and a peak value of 84% recovery appears at about 30 to 40 ppm. This indicates an increase of about 20% in bitumen recovery as compared to the 64% recovery achieved without chemical addition. As the polymer dosage was increased further, the bitumen recovery decreased and dropped below 50% when a much higher dosage of 150 ppm HPAM was added.

EXAMPLE 2

Tailings Settling Using a Polymeric Hydrolysed Polyacrylamide Processing Aid

[0088] Tailings samples taken directly from the bitumen extraction experiments of Example 1, with or without chemical addition, were used to conduct settling tests in closed cylinders. The descent of the solid/solution interface (mud line) was recorded as a function of time. A plot of the thickness of the supernatant layer versus time was used to determine the initial settling rate from the slope of the initial linear portion of the plot.

[0089] A Nanoscope E atomic force microscope (AFM) with a fluid cell was used for the surface force measurements. Force measurements were performed in the fluid cell where a colloidal probe (a silica sphere or a clay fine particle) interacted with a flat silica plate or a bitumen surface in various tailings waters taken from bitumen extraction experiments as soon as a clean layer of water was
available. All force measurements were conducted after an incubation time of 30 minutes at a room temperature 22±1°C.

[0090] FIG. 4 shows the variation of the initial settling rate with HPAM polymer dosage. With no polymer addition as well as with a polymer dosage of 150 ppm, the initial settling rates were fairly low. A maximum in the settling rate occurred at about 30 ppm polymer dosage. FIG. 4 shows a large improvement in the slurry settling rate due to an optimal polymer dosage addition. Note that the HPAM dosage is referring to the amount of HPAM that was added for bitumen liberation with no additional HPAM added during bitumen recovery. A distinct layer of clear supernatant was observed at HPAM dosages of 15 and 30 ppm, but no such clear supernatant was obtained at 150 ppm at a settling time of 150 minutes.

EXAMPLE 3

Effect of a Polymeric Hydrolysed Polyacrylamide Processing Aid on the Concentration of Divalent Cations in Process Water

[0091] A sample of Aurora process water at a pH of 8.5 was obtained and divided into four equal aliquots. Three of the aliquots received a treatment with HPAM at dosages of 15, 45 and 150 mg/L, respectively. The fourth aliquot was not treated. The concentrations of calcium ions (Ca++) and magnesium ions (Mg++) in each of the aliquots were measured using an Atomic Absorption Spectrometer and the results are plotted in the graph of FIG. 5. The untreated aliquot showed that the process water had initial calcium and magnesium ion concentrations of 39 ppm and 13 ppm, respectively. The treated aliquots showed a linear reduction of both calcium and magnesium ions with increasing HPAM concentration over the range investigated. The reduction of calcium and magnesium ion concentrations indicates ion intake by HPAM. It is believed that this ion absorption not only improves bitumen liberation, but leads to cation bridging between HPAM and fines in the tailings to improve settling.

EXAMPLE 4

Effect of Citric Acid on Bitumen Recovery

[0092] A bitumen extraction experiment was conducted in accordance with Example 1, except that the processing aid was 50 ppm citric acid. FIG. 6 shows the bitumen recovery percentage as a function of the flotation time for up to 60 minutes. The recovery is represented by the cumulative bitumen recovery (total bitumen amount recovered in froth). On the recovery curve, the cumulative bitumen recovery was found to increase over time with the addition of 50 ppm citric acid. The peak recovery of about 90% was obtained at 60 minutes of flotation. When the same experiment was run without a processing aid, the bitumen recovery was approximately 64%. This indicates an increase of about 26% in bitumen recovery attributable to the use of 50 ppm citric acid. The amount of solids and water in the recovered bitumen was also measured and the bitumen-to-solids ratio and the bitumen-to-water ratio were calculated and plotted on the same graph using the right-hand axis. These bitumen ratios increased over time with the addition of 50 ppm citric acid by about 50% and 25%, respectively. Accordingly, citric acid was found to increase the froth quality as well as the bitumen recovery efficiency.

[0093] The significance of the bitumen recovery results (Example 1) and tailings settling results (Example 2) is that they reveal the surprising and beneficial effect of HPAM as a bitumen (hydrocarbon) processing aid as well as a solids flocculant that accelerates the tailings slurry settling rate.

[0094] Aside from the successful results of Examples 1 and 2, other polymeric processing aids disclosed herein may enhance both bitumen recovery and solids settling derived from tailings streams. It is also possible that certain polymeric processing aids would also enhance froth treatment through demulsification of the water droplets in the diluted bitumen.

[0095] The terms “comprising,” “including,” and “having,” as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term “consisting essentially of,” as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms “a,” “an,” and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. For example, the phrase “a solution comprising a hydrocarbon-containing compound” should be read to describe a solution having one or more hydrocarbon-containing compound. The term “one” or “single” shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as “two,” are used when a specific number of things is intended. The terms “preferably,” “preferred,” “prefer,” “optionally,” “may,” and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention.

[0096] It should be understood from the foregoing description that various modifications and changes may be made in the preferred embodiments of the present invention without departing from its true spirit. It is intended that this foregoing description is for purposes of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

What is claimed is:
1. A method, comprising:
   providing a processing aid to sequester cations in an aqueous mixture of hydrocarbons and inorganic solids; and
   liberating the hydrocarbons from the inorganic material.
2. The method of claim 1, further comprising separating the aqueous mixture into a hydrocarbon-containing froth portion and a tailings portion.
3. The method of claim 1, further comprising:
   determining an amount of hydrocarbons in the tailings portion; and
   varying the amount the processing aid added to the aqueous mixture to control the amount of hydrocarbons in the tailings portion.
4. The method of claim 1, wherein the hydrocarbons are liberated in the presence of water and a transfer agent.
5. The method of claim 1, wherein the aqueous mixture includes a hydrocarbon-containing source selected from tar sand, oil shale, petroleum residues, and combinations thereof.

6. The method of claim 3, wherein the transfer agent is selected from a caustic, a phosphate, a silicate, a carbonate, and combinations thereof.

7. The method of claim 3, wherein the transfer agent is a caustic selected from sodium hydroxide, potassium hydroxide, and combinations thereof.

8. The method of claim 3, wherein the amount of hydrocarbons is determined by fluorescence.

9. The method of claim 4, wherein the hydrocarbon-containing source is characterized by having a combined concentration of calcium ions, magnesium ions and iron ions that is greater than 40 parts per million.

10. The method of claim 1, wherein the processing aid is a carboxylic acid or a salt or partial salt thereof.

11. The method of claim 1, wherein the processing aid is a carboxylic acid derivative of a nitrogen containing organic compound, or a salt or partial salt thereof.

12. The method of claim 1, wherein the processing aid is a carboxylic acid, a salt of the carboxylic acid, a partial salt of the carboxylic acid, or a combination thereof.

13. The method of claim 1, wherein the processing aid is selected from glycine, nitrotroic acid, ethylenediamine-tetraacetic acid, diethylenetriaminepentaacetic acid, dicarboxymethyl glutamic acid, diamino cyclohexane-N,N,N',N'-tetraacetic acid, ethylenediaminoxyethyleneamine-N,N',N',N'-tetraacetic acid, hydroxyethyliminodiacetic acid, hydroxyethylethylenediaminetetraacetic acid, salts of these acids, partial salts of these acids, and combinations thereof.

14. The method of claim 1, wherein the processing aid is a carbohydrate.

15. The method of claim 1, wherein the processing aid is an organic alcohol.

16. The method of claim 1, wherein the processing aid is an organic amine, a derivative of an organic amine, or a combination thereof.

17. The method of claim 16, wherein the organic amine is from a hydroxy amine, an aromatic amines, derivatives or salts of the amines, and combinations thereof.

18. The method of claim 16, wherein the organic amine is selected from ethylene diamine, benzotriazole, triethanolamine, 2,2'-dipyridyl, or combinations thereof.

19. The method of claim 1, wherein the processing aid is an organic acid selected from acetic acid, malonic acid, citric acid, isocitric acid, humic acid, vulinic acid, salts of these acids, partial salts of these acids, and combinations thereof.

20. The method of claim 1, wherein the processing aid is a hydroxy organic acid selected from glycolic acid, malic acid, glucaric acid, glucoheptonic acid, tartaric acid, malic acid, folic acid, salicylic acid, salts of these acids, partial salts of these acids, and combinations thereof.

21. The method of claim 1, wherein the processing aid is a polymeric acid selected from polycrylic acid, polymethacrylic acid, salts of these acids, partial salts of these acids, and combinations thereof.

22. The method of claim 1, wherein the processing aid is a polymer based on monomers of maleic anhydride.

23. The method of claim 1, wherein the processing aid is a salt of a carboxylic acid having cations selected from sodium, potassium, and combinations thereof.

24. The method of claim 1, wherein the processing aid is a phosphoric acid derivative selected from sodium tripolyphosphate, potassium tripolyphosphate, sodium polyphosphate, disodium hydrogenphosphate, and combinations thereof.

25. The method of claim 1, wherein the processing aid is an organophosphonate selected from methylphosphonic acid, hydroxyethylidyne diphosphoric acid, any of the salts or partial salts of these acids, and combinations thereof.

26. The method of claim 1, wherein the processing aid is an organophosphonate based on a nitrogen containing organic compound selected from aminomethanephosphonic acid, nitrotris(methylene)triphosphonic acid, ethylenediaminetetra(methylene)phosphonic acid, and combinations thereof.

27. The method of claim 1, wherein the processing aid is an organic compound containing both carboxylic and phosphonic functional groups, the organic compound selected from 2-phosphonobutane 1,2,4-tricarboxylic acid, any of the salts or partial salts of these acids, and combinations thereof.

28. The method of claim 1, wherein the processing aid is a polymer selected from a homo polymer, a co-polymer, a salt or partial salt of these polymers, and combinations thereof, wherein the polymer includes a functional group selected from hydroxyl, carboxylic, amine, or combinations thereof.

29. The method of claim 1, wherein the processing aid is a sulfur-containing organic acid selected from 2,3-dicarbapto-1-propanal, sulfosalicylic acid, lignosulfonate, a salt or partial salt thereof, and combinations thereof.

30. The method of claim 1, wherein the processing aid is an oxyalkylate derivative of an amine.

31. The method of claim 1, wherein the processing aid is used to control the amount of hydrocarbons in the tailings portion.

32. The method of claim 1, wherein the processing aid is suitable for sequestering cations selected from calcium, magnesium, iron, alumina, silica, titanium, zinc, and combinations thereof.

33. The method of claim 2, wherein the step of separating includes a mechanical separation.

34. The method of claim 33, wherein the step of separating includes centrifuging.

35. A method, comprising:

   contacting a hydrocarbon-containing source selected from tar sand, oil shale, petroleum residues and combinations thereof with water, a transfer agent and a chelating agent during a primary separation of the hydrocarbon-containing source into a hydrocarbon-containing froth portion and a tailings portion.

36. The method of claim 35, further comprising:

   determining an amount of hydrocarbons in the tailings portion; and
   varying the amount of the chelating agent added to the hydrocarbon-containing source to reduce the amount of hydrocarbons in the tailings portion.

37. The method of claim 35, wherein the tailings portion comprises silica, clay and heavy minerals.

38. The method of claim 35, characterized in that a greater percentage of hydrocarbons in the hydrocarbon-containing source is separated into the froth portion than under the same conditions without the chelating agent.
39. The method of claim 35, further comprising: varying the amount of processing aid to control the amount of hydrocarbons in the tailings portion.

40. A method, comprising:
separating a hydrocarbon-containing source into a hydrocarbon-containing froth portion and a tailings portion; and
contacting the tailings portion with water, a transfer agent and a processing aid to produce a second hydrocarbon-containing froth portion and a second tailings portion.

41. The method of claim 40, wherein the tailings portion comprises silica, clay and heavy minerals.

42. The method of claim 40, further comprising:
contacting the hydrocarbon-containing froth portion with water, a transfer agent and a processing aid to produce a substantially solids-free froth portion and a substantially hydrocarbon-free tailings portion.

43. The method of claim 40, wherein the processing aid sequesters cations in the tailings portion.

44. The method of claim 1, wherein the processing aid is a polymeric processing aid.

45. The method of claim 44, wherein the polymeric processing aid is provided in an amount that is effective to increase the liberation of the hydrocarbons.

46. The method of claim 45, wherein the hydrocarbons and inorganic solids are obtained from a poor processing ore.

47. The method of claim 44, wherein the hydrocarbons and inorganic solids are obtained from oil sand, oil shale, petroleum residue, or a combination thereof.

48. The method of claim 44, further comprising:
recovering liberated hydrocarbons from the mixture.

49. The method of claim 48, wherein the recovering liberated hydrocarbons includes forming froth with the hydrocarbons attached to air bubbles.

50. The method of claim 48, further comprising:
separating the inorganic solids into a tailings portion.

51. The method of claim 50, further comprising:
providing an additional amount of a polymeric processing aid to the tailings portion to flocculate solids.

52. The method of claim 51, wherein the polymeric processing aid provided to the tailings is the same polymeric processing aid provided to the aqueous mixture.

53. The method of claim 50, wherein the polymeric processing aid separates along with the tailing portion to flocculate solids.

54. The method of claim 44, wherein the aqueous mixture is provided with between 1 and 150 ppm of the polymeric processing aid.

55. The method of claim 44, wherein the aqueous mixture is provided with between 10 and 100 ppm of the polymeric processing aid.

56. The method of claim 44, wherein the aqueous mixture is provided with between 15 and 60 ppm of the polymeric processing aid.

57. The method of claim 56, wherein the addition of the polymeric processing aid increases the bitumen recovery by at least 5 percent.

58. The method of claim 56, wherein the addition of the polymeric processing aid increases the bitumen recovery by at least 10 percent.

59. The method of claim 44, wherein the hydrocarbons comprise bitumen and the inorganic solids comprise clay.

60. The method of claim 59, characterized in that the bitumen and clay have a zeta potential distribution that exhibits a common bitumen/clay peak before providing the polymeric processing aid and exhibits separate bitumen and clay peaks after providing the polymeric processing aid.

61. The method of claim 44, wherein the cations include multivalent ions selected from calcium, magnesium, iron and combinations thereof.

62. The method of claim 44, wherein the processing aid is suitable for sequestering cations selected from calcium, magnesium, iron, alumina, silica, titanium, zirconium, and combinations thereof.

63. The method of claim 44, wherein the aqueous mixture includes greater than 10 parts-per-million of multivalent ions selected from calcium, magnesium, iron and combinations thereof.

64. The method of claim 44, wherein the aqueous mixture includes greater than 30 parts-per-million of multivalent ions selected from calcium, magnesium, iron and combinations thereof.

65. The method of claim 44, wherein the aqueous mixture has a combined concentration of calcium ions, magnesium ions and iron ions that is greater than 40 parts per million.

66. The method of claim 65, further comprising:
reducing the concentration of unsequestered multivalent ions in the aqueous mixture to less than 30 parts-per-million.

67. The method of claim 44, wherein the polymeric processing aid is oil soluble.

68. The method of claim 44, wherein the polymeric processing aid is water soluble.

69. The method of claim 44, wherein the polymeric processing aid is a hydrolysis product or salt capable of sequestering calcium.

70. The method of claim 44, wherein the polymeric processing aid comprises an acrylic acid-based polymer or a polymer based on a substituted polyacrylic acid.

71. The method of claim 70, wherein the polymeric processing aid comprises polyacrylic acid or poly(meth)acrylic acid.

72. The method of claim 44, wherein the polymeric processing aid comprises an acrylamide-based polymer or a polymer based on a substituted acrylamide.

73. The method of claim 72, wherein the polymeric processing aid comprises polyacrylamide or polymethacrylamide.

74. The method of claim 44, wherein the polymeric processing aid comprises a polymer, copolymer or terpolymer based on monomers selected from acrylic acid, acrylamide, acrylonitrile, or substituted derivatives of these monomers.

75. The method of claim 44, wherein the polymeric processing aid hydrolyzes under conditions of the aqueous mixture.

76. The method of claim 74, wherein the polymeric processing aid is a derivative selected from sulfonates, phosphates, phosphonates, betaines, sulfobetaines, and combinations thereof.

77. The method of claim 74, wherein the polymeric processing aid is a salt selected from amine salts, ammonium salts, phosphonium salts, thiourea salts, and combinations thereof.
78. The method of claim 73, wherein the polymeric processing aid has a hypophosphate in the polymer backbone.

79. The method of claim 78, wherein the hypophosphate backbone is formed by reacting the polyacrylic acid or the polymethacrylic acid with hypophosphorous acid.

80. The method of claim 44, wherein the polymeric processing aid comprises a methylene sulfonate modified polyacrylamide, a methylene sulfonate modified polymethacrylamide, a hydroxamic acid modified polyacrylamide, or a hydroxamic acid modified polymethacrylamide.

81. The method of claim 44, wherein the polymeric processing aid is a polyacrylamide.

82. The method of claim 81, wherein the polyacrylamide is prepared by the reaction of polyacrylonitrile with water.

83. The method of claim 81, wherein the polyacrylamide has a molecular weight between 1 and 50 million with between 20 and 30 percent ionic character.

84. The method of claim 81, wherein the polyacrylamide forms a polycarboxylic acid at alkaline pH.

85. The method of claim 44, wherein the polymeric processing aid is a hydrolysed polyacrylamide polymer characterized by an ability to sequester cations and an ability to flocculate solids.

86. The method of claim 44, wherein the polymeric processing aid is a polymer with a nitrogen functionality.

87. The method of claim 86, wherein the polymeric processing aid is a polyetheramine that has been reacted with methylchloride or salted with a polyacid.

88. The method of claim 44, wherein the polymeric processing aid is a triethanolamine-based polymer having a molecular weight up to 150,000.

89. The method of claim 44, wherein the polymeric processing aid is a polymeric acid selected from polyacrylic acid, polymethacrylic acid, salts of these acids, partial salts of these acids, and combinations thereof.

90. The method of claim 44, wherein the polymeric processing aid is a polymer based on monomers of maleic anhydride.

91. The method of claim 44, wherein the polymeric processing aid is a polymer selected from a homo polymer, a co-polymer, a salt or partial salt of these polymers, and combinations thereof, wherein the polymer includes a functional group selected from hydroxyl, carboxylic, amine, or combinations thereof.

92. The method of claim 44, wherein the polymeric processing aid is added into a pipeline transporting the aqueous mixture.

93. The method of claim 44, wherein the polymeric processing aid is added into a separation vessel.

94. The method of claim 44, wherein the liberation is performed at a pH between about 7 and about 10.

95. The method of claim 44, wherein the liberation is performed at a pH between about 8 and about 9.

96. The method of claim 44, wherein the liberation is performed at a pH between about 8.2 and about 8.7.

97. The method of claim 44, wherein the liberation is performed at a pH between about 8.2 and about 8.5.

98. The method of claim 52, further comprising:

99. The method of claim 44, wherein the liberation is performed at a pH between about 8 and about 9.

100. The method of claim 99, wherein the transfer agent is selected from a caustic, a phosphate, a silicate, a carbonate, and combinations thereof.

101. The method of claim 99, wherein the transfer agent is a caustic.

102. The method of claim 99, wherein the transfer agent is a caustic selected from sodium hydroxide, potassium hydroxide, and combinations thereof.

103. The method of claim 99, wherein the transfer agent is sodium hydroxide.

104. The method of claim 44, wherein the polymeric processing aid is provided as an aqueous solution.

105. The method of claim 44, characterized in that a reduction in the multivalent ion concentration allows greater bubble attachment of the hydrocarbons.

106. The method of claim 48, further comprising:

107. The method of claim 49, characterized in that a reduction in the multivalent ion concentration allows greater bubble attachment of the hydrocarbons.

108. A formulation for liberating hydrocarbons from an aqueous mixture of hydrocarbons and inorganic solids, comprising:

109. The formulation of claim 108, wherein the citric acid comprises at least 50 weight percent of the solution.

110. The formulation of claim 109, wherein the antifreeze comprises between 1 and 25 weight percent methanol.

111. The method of claim 81, wherein the polyacrylamide has between 60 and 85 percent anionic character.

112. The method of claim 81, wherein the polyacrylamide is cationic.

113. The method of claim 50, wherein the polymeric processing aid flocculates solids in the tailings portion.

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