An improved composition for recovering bitumen from oil sands is used in the traditional "hot water" extraction process. An aliquot of a solvent mixture is mixed with bitumen ore and water. A pH builder is added and following mixing primary and secondary froths are recovered. The solvent mixture contains a monoterpene, nonionic surfactant, a short chain alcohol and a short chain ketone. Primary and secondary froth recovery is at least 80% at temperatures of about 35°C. Only very small amounts of solvent are used, and all solvents are biodegradable.
Recovery in BEU

Fig. 1
COMPOSITION FOR RECOVERING BITUMEN FROM OIL SANDS

CROSS-REFERENCE TO PRIOR APPLICATIONS

[0001] Not applicable.

U.S. GOVERNMENT SUPPORT

[0002] Not applicable.

BACKGROUND


[0004] [AREA OF ART]

[0005] 2. Description of the Background

[0006] Almost all of the energy used on our planet comes ultimately from the Sun. Fossil fuels represent the photosynthetic products of long-dead photosynthetic organisms. Generally, fossils of macroscopic terrestrial organisms yield materials that range from peats to coals. Generally, microscopic marine and freshwater aquatic photosynthetic organisms have left us with "oil" or, more properly, petroleum. When aquatic photosynthetic organisms ("algae" and "zooplankton") die and are entrapped in sediments, the organic matter is modified by heat and pressure and the resulting organic fluids migrate and become trapped by overlying geological structures to form "oil reservoirs" which can be tapped to form oil wells. However, large amounts of aquatic organic matter become deposited with clay minerals or with sand grains to form organically rich sandstone or shale. When the conditions are such that the organic matter is unable to migrate one is left with oil sand, tar sand or even oil shale. The organic matter can be extracted from these materials as "unconventional" petroleum.

[0007] Many of the largest unconventional petroleum deposits actually contain a carbon-rich substance known as "bitumen" or tar. The term "bitumen" includes a variety of viscous or solid mixtures of hydrocarbons that occur naturally as asphalt, tar, mineral waxes, and the like. Bitumen can be thought of as petroleum from which most of the volatile components have been driven off over time. Bitumen deposits can be found in many parts of the world and, where they occur in admixture with sand or clay, such deposits are often referred to as bituminous sands, oil sands or tar sands (hereinafter referred to as "oil sands"). The majority of all the known oil in the world is contained in oil sands.

Large deposits of bituminous sands are present in Canada, the USA, Venezuela and Africa. Canada's oil sands are currently being exploited commercially on a large scale. Because the deposits lie at or close to the surface of the ground in the major Canadian locations (Athabasca oil sands), the bituminous ore can be strip-mined and transported to a central facility for treatment. Although modern refinery processes allow bitumen to be converted into mixtures of more fluid hydrocarbons (and other petrochemicals), the bitumen, which is extremely dense and viscous, must first be separated from the solid portions of the ore (primarily sand and clay) as well as from water added during the mining and transportation processes. The environmental problems currently attributed to oil sand mining are largely related to these removed byproducts.

[0008] Oil sand, as mined commercially, contains an average of 10-12% bitumen, 83-85% mineral matter and 4-6% water. Today, all of the producers doing surface mining, such as Syncrude Canada, Suncor Energy and Albion Sands Energy etc., use a variation of the Clark Hot Water Extraction (CHWE) process. It is possible to think of this process as involving Heat, Air and High pH to remove bitumen from the solids (sand, etc.). The application of heat lowers the viscosity (i.e. melts) of the bitumen so that some of it can detach from the solids. The addition of air provides bubbles that help float the dense bitumen to form a froth. Not only do the air bubbles act as "life jackets" to float the bitumen, the bubbles represent hydrophobic surfaces so that the bitumen is able to transfer from the solid (sand) surface to the bubble surface. Increasing the pH improves the flotation and separation process. To some extent this effect is believed to result from the neutralization and saponification of organic acids, etc., in the bitumen to form natural surfactants.

[0009] In the CHWE process, the ores are mined using open-pit mining technology. The mined ore is then crushed for size reduction. A film of water coats most of the mineral matter, and this property permits extraction by the hot-water process. The oil sand is put into massive rotating drums and slurried with hot water at 50-80 °C. water and some steam. The formed slurry is often transported using a "hydro transport" pipeline which includes mixing the ore with warm water at high pH at the mine and pumping it by pipeline to the extraction plant. During the transport to the plant, the bituminous ore is conditioned, causing complex physical and chemical changes to occur that break the surface tension between hydrocarbon and water components. Bitumen itself contains naturally occurring water-soluble organic acids and surfactants, but these do not become fully active until the pH and temperature conditions are sufficiently high. Sodium hydroxide (NaOH or caustic soda) or other basic chemicals such as potassium hydroxide are added to raise the pH. Under these conditions, the bitumen begins to liquefy and detach from the mineral particles. Conditioned slurry is passed through a screen to remove rocks and large pebbles. At the extraction plant a primary separation vessel (PSV), a large, conical separation vessel, is used to recover bitumen by flotation as bitumen froth which floats to the top while coarse sand settles and is pumped to disposal sites. The froth of bitumen is skimmed from the top of the PSV and generally consists of about 60-65% bitumen, 25-30% water and about 10% solids by weight.

[0010] The initial separation is known as primary extraction and the froth is known as "primary froth." After the primary froth is harvested, additional mixing and addition of air (secondary extraction) produces a "secondary froth" from the bitumen still suspended in the water (known as "middlings"). The primary and secondary extraction yield at least 80% of the bitumen in the ore. The remaining bitumen remains suspended in the water or adheres to the solids. A portion of that bitumen can be recovered by various secondary treatments. Generally, 88-95% (in some cases as much as 100%) of the bitumen in the mined ore is recovered.

[0011] Coarse sand from the primary separators is used to build dikes, forming the large tailings ponds needed to contain the effluent. In these ponds the fine particles settle slowly, producing clarified water that is reused in the extraction process. The fine particles do not consolidate to their original density, so every cubic meter of oil sand mined creates about 1.4 cubic meters of material for disposal. Removal of the contaminants from the froth stream is achieved through dilution with naptha followed by two stages of centrifugation. The industry has recently installed inclined-plate gravity settlers in series with the centrifuges. About 98% of the bitumen in the froth is recovered. The water needs of a large project...
like that of Syncrude are substantial, amounting to about 0.4% of the average flow of the Athabasca River. After removal of residual water and fine solids, the bitumen is mixed with lighter petroleum-based solvents or chemically "cracked" so that it can be transported by pipeline as "synthetic crude oil" for subsequent refining into a variety of hydrocarbon products. After oil extraction, the spent sand and other materials are then returned to the mine, which is eventually reclaimed.

A main disadvantage of this conventional extraction procedure is the large amounts of energy that are required for heating the hot water used for bitumen separation from the ore. A further disadvantage is that the caustic soda employed in the process is toxic and corrosive and requires careful and expensive regeneration or disposal procedures. The energy required for the hot water process is produced by burning hydrocarbons and results in the production of large amounts of carbon dioxide. This greatly increases the amount of greenhouse gases attributable to oil sands even before refining and use as conventional motor fuels. In addition, the large volume of water used for processing becomes contaminated by the added sodium hydroxide and soluble organic and inorganic components extracted from the bitumen. This necessitates complex processing to reclaim the water and isolate the local environment from harm.

There is consequently a great need for improved processes that overcome or at least reduce these problems. Up until now these attempts at improved processes have generally involved the addition of solvents and surfactants. Because bitumen is heavy (i.e., dense) and extremely viscous, it is generally known that added solvents can decrease the viscosity and density of the bitumen so that it can flow and float on water with or without an "air bubble assist." Hopefully, additional solvents would achieve this without requiring high temperatures. Similarly, surfactants ("wetting agents") help detach the bitumen from the mineral particles and suspend the bitumen as an emulsion until the mineral particles settle out gravitationally. An example of this approach is found in U.S. Patent Application 2008/0169222 which discloses an improved tar sand process invented by Kevin Ophus.

The Ophus process uses an emulsion of the organic solvent d-limonene to separate the bitumen from the sand particles. The emulsion is prepared by mixing about 40% D-limonene and about 60% water (in the form of a weak sodium bicarbonate solution) with about 0.2% anionic surfactant and a trace amount of an anti-foaming agent. Vigorous mixing produces an emulsion having the color and consistency of dairy cream. A quantity of this emulsion is added to an aqueous slurry of tar sand where is helps the bitumen separate from the sand. Charts and tables in this application show that for the process to obtain an 80% bitumen recovery, the solvent content of the slurry must be at least about 5% and the temperature must be at least 30°C. At higher temperatures and/or higher solvent concentrations recovery is above 80%, and at lower temperatures and lower solvent concentrations recovery is below 80%. The Ophus process partially solves the disadvantages of the prior art Clark process by lowering the amount of energy used to heat the water and by largely eliminating the use of sodium hydroxide. However, this comes as the expense of introducing a considerable amount of organic solvent (d-limonene) and into the process. To the extent that this solvent dissolves into the bitumen, it can be recovered and recycled by distillation; however, there is a considerable energy cost in such recovery. To the extent that the solvent enters the waste stream, it is considered to be of low toxicity although it has some potential as an irritant. D-limonene is slowly biodegradable. Surfactants used are also biodegradable. Apart from the cost of the d-limonene, the main cost of the Ophus process seems to be that of the energy to heat the water.

The conventional process has not yet been superseded by improved technology and continues to be plagued by a number of environmental problems. First is energy usage. Conventional procedures require large amounts of energy for heating the hot water used for bitumen separation. This is currently provided primarily by natural gas. Obviously, this natural gas is not free. The requirement to heat the extraction water significantly increases the cost of the recovered bitumen.

Second is the problem of environmental pollution; the current extraction process requires huge amounts of natural gas for the heating water. As of 2007, the Canadian oil sands industry used about 4% of the Western Canada Sedimentary Basin natural gas production. By 2015, this may increase 2.5 fold particularly if key pipelines are brought on line. This burning of natural gas generates large amounts of carbon dioxide and diverts natural gas from electric power generation and other uses where it could actually moderate overall carbon dioxide production. The serious "greenhouse" effects of gases such as carbon dioxide on the world climate is well recognized.

An additional environmental problem is produced by the processing of smaller bitumen and mineral particles remaining in an intermediate water layer, called middlings which are pumped onto a separation vessel similar to the one mentioned above. The middlings are ultimately pumped to settling or tailing ponds and ultimately return to the local rivers. Pollutants enter the ecosystem creating numerous hazards for the wildlife as well as humans. Studies have shown that thousands to hundreds of thousands of birds each year die due to the effects of tailing ponds. Many birds migrating across the country landing in waters to rest, and toxic components in the water can lead to an 80-90% death rate. There has also been a large impact on the fish that live and spawn in the area. As toxins accumulate in the rivers due to the refining process, bizarre mutations, tumors and deformed fish species have begun to appear. A study commissioned by the regions health authority, found that several known toxins and carcinogens were elevated. Aboriginal communities that live around the river are becoming increasingly worried about how the animals they eat and their drinking water are being affected.

SUMMARY OF THE INVENTION

An exemplary embodiment of the invention relates to a two part composition useful for extracting bitumen from bituminous sand ores (oil sands). This combination is particularly useful for extracting bitumen from high grade 10% to 14% bituminous sand ores as a full or partial replacement for the conventional hot water/caustic soda process. Typically, the combination recovers 80% of the bitumen using a small amount of the composition and at temperatures no greater than 35°C. The basic rate of recovery can be increased by increasing the temperature and/or the amount of composition employed. Cost benefit analysis can be used to select the optimum combination of temperature and volume of composition. The composition can be used directly in existing
extraction equipment. It is likely that specially designed equipment could yield even better recoveries.

[0019] When used directly in existing PSVs the two part composition particularly enhances the secondary froth recovery rate. Another use for the invention relates to a process of extracting bitumen from lower grade 6% to 8% bituminous sand ores. Another embodiment of the present invention relates to the extraction of residual concentrations of Total Petroleum Hydrocarbons (TPH) from the tailing ponds. The inventive compositions are unique in that they release the bitumen from the sand and keep it in an emulsified state for ease in transport. Thereafter, an additional stage is applied to float the bitumen for ease in recovery. The composition can be easily manipulated to a range sufficient to extract bitumen from a variety of ore.

[0020] The two part composition comprises in the first part a solvent mixture containing an environmentally safe monoterpene solvent, a non-ionic surfactant, a short chain alcohol and a short chain ketone. The preferred monoterpene solvent is a biodegradable cyclic terpene such as D-limonene. The second part of the combination is an aqueous solution of a pH builder such as sodium or potassium carbonate, sodium or potassium hydroxide or sodium or potassium silicate. In use in existing equipment for primary bitumen recovery a small quantity of the solvent mixture is added to the ore and mixed thoroughly. Following that a larger volume of the aqueous pH builder is added and mixing is continued. Finally, a large volume of water is added with continued mixing in a PSV. When mixing stops, the primary froth separates from the ore and water and is harvested. Mixing then is continued along with addition of air and the secondary froth separates and is harvested. Unlike the traditional caustic soda process, the pH of the middlings is below pH 9.0. The middlings and the tailing are then subjected to enhanced secondary recovery processing which may include use of an embodiment of the present invention to release additional bitumen from the ore and middlings.

[0021] Depending on the precise application the various ingredients of the solvent mixture are included in different amounts. Preferably, these ingredients are present in the following proportions (by volume) selected to make 100%:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terpene</td>
<td>7% to 40%</td>
</tr>
<tr>
<td>Non-Ionic Surfactant</td>
<td>15% to 45%</td>
</tr>
<tr>
<td>Short Chain Ketone</td>
<td>5% to 15%</td>
</tr>
<tr>
<td>Short Chain Alcohol</td>
<td>25% to 45%</td>
</tr>
</tbody>
</table>

[0022] The solvent mixture may also contain one or more other solvents or diluents, but the primary ingredients listed above should preferably comprise at least 90% by volume of the composition.

[0023] The solvent mixture is a combination of surfactants and solvents designed to affect the surface tension of the bitumen in bituminous sand ores to facilitate the separation of the bitumen from the other materials present. The composition also helps to liquify the bitumen and to maintain the bitumen in a suspended form to facilitate the separation process. Following an initial interaction of the mixture with bitumen ore a pH builder such as sodium carbonate is added. The pH builder enhances the emulsification of bitumen and promotes frothing and flotation of the bitumen.

[0024] The composition can be used to extract bitumen from its ore at essentially ambient temperature (e.g. 10 to 35° C), but it can be heated to higher temperatures, but still generally below those used for the conventional hot water process. Energy requirements can therefore be reduced considerably without substantial reduction of extraction yields. Under certain conditions, the exemplary forms of the composition may increase the yield of extracted bitumen as compared to conventional processes.

[0025] The main ingredients of the composition are compounds that are known to be safe and non-toxic and so that the spent composition can be disposed of without procedures required for the disposal of hazardous chemicals.

[0026] The composition may be used in much the same way as the conventional process for extraction of bitumen. That is to say, the mined oil sands ore is mixed and agitated with the composition to form an aqueous phase and a hydrocarbon phase, the hydrocarbon phase is allowed to rise to the top of the mixture, and the hydrocarbon phase is then harvested.

[0027] The composition, at least in its preferred forms, can therefore have the following advantages:

[0028] 1) It can improve the recovery yield of bitumen and saleable synthetic crude oil equal to or above the present level;
[0029] 2) It can improve thermodynamic efficiency and reduce the amount of heat required in bitumen extraction operations; and
[0030] 3) It can reduce, or remove and eliminate, environmental impact.
[0031] 4) The composition does not affect the total petroleum hydrocarbon (TPH) concentrations of the bitumen.

DESCRIPTION OF THE FIGURES

[0032] FIG. 1 shows Bitumen Recovery Units comparing the invention with prior art methods.

DETAILED DESCRIPTION OF THE INVENTION

[0033] The following description is provided to enable any person skilled in the art to make and use the invention and sets forth the best modes contemplated by the inventor of carrying out his invention. Various modifications, however, will remain readily apparent to those skilled in the art, since the general principles of the present invention have been defined herein specifically to provide an improved and environmentally safe composition for recovering bitumen from oil sands.

[0034] As used herein, the term "about" means "approximately," and, in any event, may indicate as much as a 10% deviation from the number being modified.

[0035] Process

[0036] As explained in more detail below the current composition is directly usable in the current CHWE process. However, it somewhat modifies the way in which the process attains its results. The most apparent differences and advantages are the need for much lower amounts of energy because the water temperature is much lower and the use of environmentally safe additives so that the effluents from the process are harmless.

[0037] The process conceptually consists of four phases which are digitized into the CHWE process steps. In the first two phases, Phase I (extraction) and Phase II (separation)—an organic terpenoids solvent such as D-limonene is used to extract the organic compounds. Because the preferred terpenes are non-soluble in water a surfactant is used to
decrease the surface tension of water to emulsify the terpene or even make it soluble both in water and in the organic (bitumen) phase. The large bitumen hydrocarbons are extracted by the terpene and surfactant thus freeing them from their bond to the sand. Also, when the terpene dissolves into the bitumen, it decreases both bitumen viscosity and density. The terpene will not extract/interact with all the organic compounds (particularly the low molecular weight and more hydrophilic compounds) in the bitumen. The alcohol and acetone extract and suspend the rest of the organic compounds that are not extracted by the surfactant/terpene. Alcohol and acetone have a high affinity for small organic compounds therefore they continue to extract and separate the smaller organic hydrocarbons from the sand. The addition of the sodium carbonate pH builder acts to make the organic compounds more soluble in the organic phase because the amount of base added is not sufficient to saponify them as in the CHWE process. As a result the aqueous phase is not above pH 8 (i.e., fairly close to neutrality).

In the next two phases Phase III (blocking) and Phase IV (suspension) the alcohol and acetone as well as the pH builder keep the smaller molecules in suspension and keep them from reattaching themselves to the solids. The use of acetone and alcohol also decreases the boiling point needed separate the organics thus decreasing the heating requirements during the extraction and separation phase of the bitumen. The final product has a neutral pH and no toxic compounds have been added. The terpene, surfactant, alcohol and acetone are readily biodegradable.

**Ingredients**

As indicated, the present invention is a two component system for low temperature extraction of bitumen from oil sands. The first component is a solvent component and the second component is a pH building component. The solvent component comprises a monoterpene such as citral, citronellal, citronellol, limonene or linalool; the preferred terpene being the cyclic terpene D-limonene; a short chain alcohol, a short chain ketone and a non-ionic surfactant. The purpose of the solvent component is to dissolve into the bitumen and to loosen it from the sand and other solid material and help suspend it in an emulsion. The alcohol and ketone are relatively hydrophilic and interact with the hydrophilic moiety of the surfactant to emulsify and suspend the more organic hydrophobic components and/or to directly solvate them. Isopropyl and propyl alcohol are the preferred short chain alcohols although alcohols having between 2 and 5 carbons and ketones having 3-6 carbons (such as 2-butanone) are within the usable range. Acetone is the preferred ketone. The terpene is relatively hydrophobic and interacts/dissolves into the bitumen and interacts with the hydrophilic moiety of the surfactant.

Surfactants are amphiphilic organic compounds that have both hydrophobic and hydrophilic groups so that one end of the molecule is soluble in hydrophobic compounds such as bitumen and limonene while another part of the molecule is soluble in water and water miscible compounds such as isopropyl alcohol. As such they generally lower the surface tension of water and emulsify hydrophilic and hydrophobic compounds. In a typical oil in water emulsion (where hydrophilic particles are embedded in an aqueous milieu) the hydrophobic ends of the surfactant molecule are dissolved into the oil particles so that the surface of each particle is essentially covered by hydrophilic groups (the other ends of the surfactant molecules) which help the particles interact with and remain suspended in the water. Depending on the type of hydrophilic group present on the surfactant molecule, the surfactant may have a negative charge (an anionic surfactant), a positive charge (a cationic surfactant) or a neutral charge (a nonionic surfactant). The present invention generally employs anionic surfactants. Depending on the nature of the hydrophobic and hydrophilic groups a given surfactant may be generally hydrophobic or generally hydrophilic. This is known as the HL.B or hydrophilic-lipophilic balance of the surfactant. The HL.B scale runs from 0 to 20 with surfactants with an HL.B number below about 10 being so hydrophobic that they are primarily lipid soluble while those with an HL.B of greater than 10 are primarily water soluble. Surfactants having an HL.B value in the range of about 7-11 act as emulsifiers that produce stable water in oil emulsions while those having an HL.B value in the range of about 12-16 act as emulsifiers that produce stable oil in water emulsions. Surfactants having very high HL.B values (e.g. 16-20) act as hydrotropes which are capable of solubilizing hydrophobic materials without forming micelles or small particles of the hydrophobic substance. It will be apparent that the preferred surfactants with be in the HL.B range of 12-16 because bitumen is emulsified into water and then floated free to be recovered as a froth. Currently, ethoxylated/propoxylated alkylphenol polyethoxylated branched alcohols (such as TRITO XL-80N) are preferred. A preferred single surfactant has an HL.B of between 11 and 12. Addition of a quantity of lower HL.B surfactant may encourage the bitumen particles to coalesce and allow separation particularly in a secondary recovery situation. Different surfactants can be combined to obtain an ideal HL.B value. An ideal surfactant blend would create an HL.B value between 12 and 16. In some situations addition of hydrotrropic surfactant may aid in the initial separation of the bitumen from the solid mineral portion of the ore.

The preferred surfactants are nonionic although a small quantity of an anionic hydrotropic may be included in combination with the anionic surfactant(s). The surfactant may include one or more ethoxylated acrylonitrile alcohols, such as, for example, 2.5,8,11-tetramethyl-6-dodecyne-5,8-diol ethoxylate. In most cases, the ethoxylate analog of the ethoxylate can be substituted. Suitable non-ionic surfactants include, for example, DYNOIL® surfactants such as DYNOIL 604, or 607 (Air Products and Chemicals, Inc.); SURFYNOL® surfactants (Air Products and Chemicals, Inc.) such as SURFYNOL 420, 440, 465, and 485; TOMADOL® surfactants (Tomah Products, Inc.) such as TOMADOL 1-3, 1-5, 1-7, 1-9, 1-73B, 2.5, 23-1, 23-3, 23-5, 23-6, 5-25, 25-3, 25-7, 25-5, 25-12, 45-7, 45-13, 91-6 and 91-8, TERGITOL® nonionic surfactants (Dow Chemical Company) such as TERGITOL MinFoam, L-61, L-64, L-81, L-101, NP-4, NP-6, NP-7, NP-8, NP-9, NP-11, NP-12, NP-13, NP-15, NP-30, and NP-40; TRITON® surfactants (Dow Chemical Company), such as TRITON X-15, X-35, X-45, X-100, X-114, X-165, X-305, X-405, X-207, BP and CA; NOVEC® Fluorosurfactant FC-4434 (3M Company); POLYFOX® AT-1118B (Omega Novonovations, Inc.); ZONYL® surfactants (DuPont) such as ZONYL 210, 225, 321, 8740, 8834L, 8857A, 8952, 9027, 9338, 9360, 9361, 9582, 9671, FS-300, FS-500, FS-610, 1031D, FSE, FSK, FSM, FSI, FSA, and FSN-100; LUTENSOL® surfactants (DAF) such as LUTENSOL OP 30-79%, A 3 N, A 9 N, A 12 N, A 65 N, AO 3, AO 4, AO 8, AT 25, AT 55, CF 10 90, DNP 10, NP 4, NP 6, NP 9, NP 10, NP 50,
NP-70-70%, NP-100, ON 40, ON 60, OP-10, TDA 3, TDA 6, TDA 9, TDA 10, XL 40, XL 50, XL 60, XL 69, XL 70, XL 78, XL 80, XL 89, XL 90, XL 99, XL 100, XL 140, XP 100, XP 140, XP 30 XP 40, XP 50, XP 60, XP 69, XP 70, XP 79, XP 80, XP 89, XP 90 and XP 99; MACOL® surfactants (BASF) such as MACOL 16, CSA 20 POLYETHYLAB, LA 4, LA 12, LF 110 and LF 125A; MAPHOS polyphosphate ester nonionic surfactants (BASF) such as MAPHOS 58, 60A, 66H, 8135 and ND80; MAZON® 1651 surfactant (BASF); MAZOX® LDA 1amine oxide (BASF); PLURAFAC® surfactants (BASF) such as PLURAFAC A08A, B-26, B25-5, D25, LF 1200, LF 2210, LF 4030, LF 7000, RA-20, RA 30, RA 40, RCS 43, RCS 48, S025LF, S035LF, S055LF, SLF-18B-45, SLF 37, SL-22, SL-42, SL 62, SL 92, and L1220; PLURONIC® surfactants (BASF) such as PLURONIC 10R5, 17R2, 17R4, 25R2, 25R4, 31R1, F38, F68 LF, F68, F77, F87, F88, F98, F108, F108 NF, F127, F127 NF, F127NF 500BHT, L10, L31, L92, L101, L121, M, N5, P65, P84, P85, P103, P105, P23; TETRONIC® surfactants (BASF) such as TETRONIC 304, 701, 901, 904, 1107, 1301, 1304, 1307, 1501. Mixtures of one or more of these surfactants can be used. Although nonionic surfactants are used almost exclusively, small quantities of ionic hydrophobic agents may be included. Suitable hydrophobic agents may include, for example, one or more of TRITON® products (Dow Chemical Company) such as TRITON H-66, H-55, QS-44 or QXS-20.

[0043] Soluble salts are added as pH builders to increase solubility of organic compounds in the organic phase and to help prevent reattachment of the bitumen. The preferred salts are sodium or potassium carbonate, silicate or hydroxide. The amount of pH builder added brings the extracted bitumen to near neutrality in pH. The “middlings” or effluent water is also near neutrality (e.g., below pH 8.0) unlike the high pH caustic effluents of the CHWE.

[0044] A laboratory test of a preferred embodiment of the present invention was made according to methods routinely used to test extraction of bitumen from oil sands. The method used is based on a paper “Batch Extraction Unit for Tar Sand Processing Studies” by E. C. Sanford and F. A. Seyer of the Syncrude Canada Ltd., Research Department, Edmonton, Alberta, Canada which was a portion of the HENRY H. STORCH AWARD SYMPOSIUM presented in Miami Beach, Fla. in the fall of 1978. The method described in this paper defined the Bitumen Extraction Unit by providing a laboratory simulation of the commercial Clark extraction process. In this method a jacketed extraction cell (stainless steel pot) is maintained at a constant temperature (approximately 80°C. in the traditional process). The cell is square to facilitate slurrying and agitation by air or paddle stirring without need for added baffles. Air is added through the impeller (paddle) shaft, and the container is of sufficient height to provide a quiescent zone for froth accumulation. Impeller speed is controlled by a variable speed motor and tachometer. The cell has a valve at its bottom to remove tailings. In testing with the traditional hot water method, about 1.5 L of distilled water is heated to about 90°C. in a separate container. A quantity of oil sand is homogenized and an aliquot is subjected to a procedure to determine bitumen, solids and water content. A 500 g sample of the oil sand is weighed and 150 ml of the 90°C. water is added to the extraction cell. This water is stirred with the impeller in its lowest position until the water temperature is reduced to the jacket temperature (here 80°C.). The 500 g oil sand sample is added to the cell and the motor assembly and impeller are used to break up lumps with the impeller being left about ¾ of an inch above the bottom. The impeller is then set to 600 rpm and the airflow is adjusted to 465 c/min and stirring is continued for 10 min. The airflow is stopped and 1 L of 80°C. water is added and stirring is continued for 10 min. Mixing is then stopped and the primary froth is skimmed off the top of the cell with a special spatula. The remaining material is mixed at 800 rpm with an airflow of about 232 c/min for 5 min. The secondary froth is then collected. The froth samples are analyzed for bitumen, solid and water content. Finally, solids and remaining water are drained from the cell; the cell is cleaned with solvent and the next sample is analyzed.

[0045] This same procedure (with slight modification described below) is carried out to test the inventive compositions except that test temperatures are lower than 80°C. As explained briefly above, the inventive composition consists of two parts, a solvent mixture and a pH builder. For the following tests a preferred embodiment of the solvent mixture was used and the pH builder was sodium carbonate as a 20% solution. For the tests the temperature was set to 35°C. For the “control” 500 g of tar sand (containing about 9.6% bitumen) was added to the cell along with 150 ml of 35°C. tap water. This mixture was stirred for 10 min (as described above). At that point a liter of 35°C. tap water was added and the stirring continued for another 10 min. The primary froth was collected and stirring (800 rpm) and air addition were started again for 5 min. Thereafter, the secondary froth was collected.

[0046] The solvent composition for this test contained D-limonene (15-25%), nonylphenol ethoxylated surfactant with HLB of 11-12 (25-35%), acetone (5-15%) and isopropanol alcohol (35-45%). For the treatment, the steps were the same except that 1 mL of the solvent component was added along with the 150 ml of water for the initial stirring. The 40 ml of pH builder (20% sodium carbonate) was added along with 960 ml of tap water for the stirring prior to primary froth collection. Following collection of the primary froth, air and stirring were restarted for 5 min. Then the secondary froth was allowed to float up and was collected.

[0047] A preferred solvent mixture for this use is 15%-25% D-limonene, 25-35% surfactant, 5%-15% acetone and 35%-45% isopropanol alcohol. A more preferred solvent mixture for this use is 18%-22% D-limonene, 28-32% surfactant, 8%-12% acetone and 38%-42% isopropanol alcohol. The remarkable thing is that only 1 ml of the solvent mixture was used to treat 500 g of oil sand ore in just over 1 L of water. The most useful range of the solvent mixture appears to be about 0.1 ml to about 5 ml per 100 g of ore. Larger amounts of the mixture can be used, of course. Because the minimum amount of surfactant is 35%, the formula cannot contain more than 65% mixed organic solvents. This comes out to 1.3 ml solvent per kilogram of ore or 1.3 L of solvent per metric ton of ore. This means that the actual concentration of solvents or surfactants released into the environment is extremely low. This also makes the cost of the solvent composition essentially insignificant. Even more important is that the small amounts of biodegradable solvents (and surfactants) that are added to the environment are essentially nontoxic. In terms of added pH builder about 16 g of sodium carbonate are used per kilogram of ore which equals about 1.6 kg of sodium carbonate per metric ton of ore—again a negligible quantity.

[0048] FIG. 1 shows the results of the inventive composition versus the control. Interestingly, the primary froth recovery was essentially identical for the control and the treatment, but the secondary froth recovery was dramatically higher for
the treatment. Therefore, the total bitumen recovered for the control was 60% while that for the treatment was 79% which is essentially the recovery level produced by the traditional hot water system. Thus, the inventive process recovers the same amount of bitumen with a much lower energy burden to heat the water and without using sodium hydroxide and extremely high pH values. In fact, the middlings after the removal of froth and sand had a pH of only 8.6 whereas the control pH was 7.8. Quality measurements of the froths according to the methods developed by Sanford and Seyer showed that the qualities were comparable except that the treatment method produced froths having a lower level of solids (e.g., sand and clay particles). This is good because it reduces the amount of purification that the recovered bitumen must undergo. However, the primary froth from the treatment contained somewhat more water than the control. This appears to be related to the chain length of the surfactant (i.e., the hydrophilic-lipophilic balance (HLB) characteristic). Certain sand particle whose advancing water contact angles (θw) are in the range of 15-60° demonstrate a repulsive hydration force at relatively short separation distances. Appearance of the strong hydrophobic force is due to the likelihood that the double-chain cationic surface can create a higher hydrocarbon chain packing density than the single-chain cationic surfaces, thereby resulting in a significantly lower water inclusion in the froth while still rejecting solids. The ideal surfactant blend would create an HLB value between 12 and 16.

To demonstrate the innocuous characteristics of these ingredients a toxicology test was performed on the minnow Pimephales promelas. The test material was a 2% aqueous solution of the solvent composition. At the preferred use amounts (1 ml per liter) the effluent concentration would be 0.1% rather than 2%. It is assumed that the effluent would be further diluted before reaching the environment. The effluent was tested by treating the minnows with 750 mg/L of the effluent (a further dilution of over 1,000 fold). The diluted effluent showed no effect on the fish indicating that even without natural degradation of the active ingredients, simple dilution is sufficient to render the solvent composition innocuous. In actual practice, all of the solvent ingredients are biodegradable so that even less of the active ingredients will ever reach the environment. In addition, a certified microtox analysis was carried out using Vibrio fischeri as a test organism. Again, a 2% dilution of the material was tested at a dilution of 10 g/L of test solution using 2% NaCl to achieve osmotic balance. A 50% dilution series (50 g/L down to 0.39 g/L) was carried out with a Model 50 benchtop unit following the procedures given in “Microtox Acute Toxicity Basic Test Procedures (1995) Microbics Corporation, Carlsbad, Calif.” and “Biological Test Method: Toxicity Test Using Luminescent Bacteria.” (November 1992). Report EPS 1/RM/24, Environment Canada. This produced an 15-min EC50 (mg/L) of 4.30 with a 95% confidence limit of 3.76-4.91 with a zinc sulfate reference toxicant. This translates to a Cumulative mean EC50 (±SD) for 20 tests of 4.02±0.91. This indicates extremely low toxicity.

The following claims are thus to be understood to include what is specifically illustrated and described above, what is conceptually equivalent, what can be obviously substituted and also what essentially incorporates the essential idea of the invention. Those skilled in the art will appreciate that various adaptations and modifications of the just-described preferred embodiment can be configured without departing from the scope of the invention. The illustrated embodiment has been set forth only for the purposes of example and that should not be taken as limiting the invention. Therefore, it is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described herein.

What is claimed is:

1. A two part composition for extracting bitumen from bituminous sand ore by sequentially mixing a first part and then a second part with the ore, the composition comprising:
   - an organic solvent mixture as the first part, the organic solvent mixture comprising:
     - 7 to 27 percent by volume of a monoterpenne;
     - 15 to 45 percent by volume of a nonionic surfactant;
     - 25 to 45 percent by volume of a short chain alcohol; and
     - 5 to 15 percent by volume of a short chain ketone;
   - and an aqueous pH builder selected from the group consisting of an aqueous solution of sodium carbonate, an aqueous solution of potassium carbonate, an aqueous solution of sodium hydroxide, an aqueous solution of sodium silicate and an aqueous solution of potassium silicate.

2. The two part composition according to claim 1, wherein the nonionic surfactant is selected from the group consisting of alcohol ethoxylates and alcohol ethoxysulfates.

3. The two part composition according to claim 1, wherein the organic solvent mixture comprises:
   - 15 to 25 percent by volume of D-limonene;
   - 25 to 35 percent by volume of a nonionic surfactant;
   - 35 to 45 percent by volume of isopropyl alcohol; and
   - 5 to 15 percent by volume of acetone.

4. The two part composition according to claim 3, wherein the nonionic surfactant is selected from the group consisting of TRITON X-100, TRITON XL-80N, TERGITOL NP-6, TERGITOL NP-7, TERGITOL NP-8, NEXEO 579 and mixtures thereof.

5. The two part composition according to claim 1, wherein the organic solvent mixture comprises:
   - 18 to 22 percent by volume of D-limonene;
   - 28 to 32 percent by volume of a nonionic surfactant;
   - 38 to 42 percent by volume of isopropyl alcohol; and
   - 8 to 12 percent by volume of acetone.

6. The two part composition according to claim 5, wherein the nonionic surfactant is selected from the group consisting of TRITON X-100, TRITON XL-80N, TERGITOL NP-6, TERGITOL NP-7, TERGITOL NP-8, NEXEO 579 and mixtures thereof.

7. The two part composition according to claim 1, wherein the monoterpenes is selected from the group consisting of citral, citronellal, citronellol, D-limonene and linalool.

8. The two part composition according to claim 7, wherein the monoterpenes is D-limonene.

9. The two part composition according to claim 1, wherein the short chain alcohol is selected from the group consisting of propanol, isopropanol, butanol and isobutanol.

10. The two part composition according to claim 9, wherein the short chain alcohol is isopropanol.

11. The two part composition according to claim 1, wherein the short chain ketone is selected from the group consisting of acetone and 2-butane.

12. The two part composition according to claim 11, wherein the short chain ketone is acetone.

13. A process for extracting bitumen from bitumen containing ore comprising the steps of:
adding a solvent mixture to an aliquot of bitumen containing ore, the solvent mixture comprising:
7 to 27 percent by volume of a monoterpenes;
15 to 45 percent by volume of a nonionic surfactant;
25 to 45 percent by volume of a short chain alcohol; and
5 to 15 percent by volume of a short chain ketone;
mixing said ore and aliquot with water to form a mixture;
dispensing an aqueous pH builder selected from the group consisting of an aqueous solution of sodium carbonate, an aqueous solution of potassium carbonate, an aqueous solution of sodium hydroxide, an aqueous solution of potassium hydroxide, an aqueous solution of sodium silicate and an aqueous solution of potassium silicate into the mixture;
mixing;
dispensing air into the mixture;
collecting a primary froth; and
collecting a secondary froth.
14. The process according to claim 13, wherein the organic solvent mixture comprises:
15 to 25 percent by volume of D-limonene;
25 to 35 percent by volume of a nonionic surfactant;
35 to 45 percent by volume of isopropyl alcohol; and
5 to 15 percent by volume of acetone.
15. The process according to claim 14, wherein the nonionic surfactant is selected from the group consisting of TRITON X-100, TRITON XL-80N, TERGITOL NP-6, TERGITOL NP-7, TERGITOL NP-8, NEXEO 579 and mixtures thereof.
16. The process according to claim 13, wherein the organic solvent mixture comprises:
18 to 22 percent by volume of D-limonene;
28 to 32 percent by volume of a nonionic surfactant;
38 to 42 percent by volume of isopropyl alcohol; and
8 to 12 percent by volume of acetone.
17. The process according to claim 16, wherein the nonionic surfactant is selected from the group consisting of TRITON X-100, TRITON XL-80N, TERGITOL NP-6, TERGITOL NP-7, TERGITOL NP-8, NEXEO 579 and mixtures thereof.
18. The process according to claim 13, wherein the nonionic surfactant is selected from the group consisting of alcohol ethoxylates and alcohol ethoxysulfates.
19. The process according to claim 13 carried out at a temperature below 40°C.
20. The process according to claim 13, wherein the monoterpenes is selected from the group consisting of citral, citronellal, citronellol, D-limonene and linalool.
21. The process according to claim 20, wherein the monoterpenes is D-limonene.
22. The process according to claim 13, wherein the nonionic surfactant is selected from the group consisting of alcohol ethoxylates and alcohol ethoxysulfates.
23. The process according to claim 13, wherein the short chain alcohol is selected from the group consisting of propanol, isopropanol, butanol and isobutanol.
24. The process according to claim 23, wherein the short chain alcohol is isopropanol.
25. The process according to claim 13, wherein the short chain ketone is selected from the group consisting of acetone and 2-butanone.
26. The process according to claim 25, wherein the short chain ketone is acetone.
27. The process according to claim 13, wherein the solvent mixture added is between 0.1 mL and 5 mL per 100 g of ore.
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