

Process, Method, and System for Removing Heavy Metals from Fluids

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application is a continuation-in-part of US Patent Application Serial Nos.
5 12/950,060; 12/950,170; and 12/950,637, all with a filing date of November 19, 2010. This application claims priority to and benefits from the foregoing, the disclosures of which are incorporated herein by reference.

TECHNICAL FIELD

10 [002] The invention relates generally to a process, method, and system for removing heavy metals such as mercury, arsenic, and the like from hydrocarbon fluids such as crude oil.

BACKGROUND

15 [003] Heavy metals such as lead, zinc, mercury, silver, arsenic and the like can be present in trace amounts in all types of hydrocarbon streams such as crude oils. In some crude oils, amounts of a heavy metal such as arsenic are associated with the mercury level. The amount can range from below the analytical detection limit (0.5 µg/kg) to several thousand ppb depending on the feed source. It is desirable to remove the trace amounts of these metals from crude oils.

20 [004] Various methods to remove trace metal contaminants in liquid hydrocarbon feed prior to fractional distillation have been developed. With respect to arsenic, filtration has been employed. However, filtering crude oil and / or condensate to remove arsenic is cumbersome and not cost effective. U.S. Pat. No. 4,474,896 claims the use of absorbent compositions, mainly polysulfide based, for removal of elemental mercury from gaseous and liquid
25 hydrocarbon streams. Absorbent beds tend to get clogged by solid particulates in the crude, thus impeding the flow of the feed. Absorbents can also be very costly due to the large quantity needed.

[005] US Patent Application No. 2010/0078358 discloses the use of NaOCl as the oxidizing agent for converting at least a portion of Hg(0) to Hg(II). However, there is still a
30 need to extract or convert the free mercury ions into a form that can be easily recovered and disposed. US Patent Publication No. 2010/0051553 discloses the removal of mercury from

liquid streams such as non-aqueous liquid hydrocarbonaceous streams upon contact with a Hg-complexing agent for mercury to form insoluble complexes for subsequent removal.

[006] There is still a need for improved methods to extract trace amounts of heavy metals such as mercury and arsenic, wherein the heavy metals form water-soluble metal complexes for subsequent removal from the crude by water-oil phase separation. .

SUMMARY OF THE INVENTION

[007] In one aspect, the invention relates to an improved method to treat a crude oil to reduce its heavy metal concentration. In the method, a water stream consisting essentially of an oxidizing agent is added to the crude oil to extract at least a portion of the heavy metals into the water stream forming a waste stream. The improvement comprises adding a complexing agent, facilitating the formation of soluble compounds in the water stream, prior to separating the wastewater from the crude oil, leaving a treated crude oil having a reduced heavy metal level.

[008] In another aspect, the invention relates to a method for reducing a trace amount of heavy metals, e.g., mercury, arsenic, etc., in a crude oil. The method comprises mixing into the crude oil an amount of an oxygen-containing compound selected from the group of oxyhalites, hydroperoxides, and organic peroxides, inorganic peracids, organic peracids, molecular halogens such as iodine (I₂), bromine (Br₂), and ozone to extract the heavy metals into a water-oil emulsion; adding an amount of a complexing agent to the water-oil emulsion to facilitate the formation of soluble heavy metal complexes in the water phase; and separating the water containing the soluble heavy metal complexes from the crude oil, leaving a treated crude oil having a reduced concentration of heavy metals such as arsenic and or mercury.

[009] In yet another aspect, the invention relates to a method for reducing a trace amount of arsenic in a crude oil. The method comprises: mixing into the crude oil an effective amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, molecular halogens, ozone and combinations thereof to extract at least a portion of arsenic into a water-oil emulsion as arsenic cations, forming a mixture; adding an effective amount of a complexing agent to the water-oil emulsion mixture to convert the extracted arsenic cations to water-soluble arsenic compounds in a water phase; and

separating the water phase containing the water-soluble arsenic compounds from the crude oil to obtain a treated crude oil having a reduced concentration of arsenic.

DETAILED DESCRIPTION

5 [010] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[011] “Crude oil” refers to a liquid hydrocarbon material. “Hydrocarbon material” refers to a pure compound or mixtures of compounds containing hydrogen and carbon and optionally sulfur, nitrogen, oxygen, and other elements. Examples include crude oils, synthetic
10 crude oils, petroleum products such as gasoline, jet fuel, diesel fuel, lubricant base oil, solvents, and alcohols such as methanol and ethanol. In one embodiment, crude oil has a specific gravity of at least 0.75 at a temperature of 60°F. In another embodiment, the specific gravity is at least 0.85. In a third embodiment, the specific gravity is at least 0.90.

[012] “Heavy metals” refers to gold, silver, mercury, osmium, ruthenium, uranium,
15 cadmium, tin, lead, and arsenic. In one embodiment, “heavy metals” refers to mercury.

[013] “Trace amount” refers to the amount of heavy metals in the crude oil. The amount varies depending on the crude oil source and the type of heavy metal, for example, ranging from a few ppb to up to 30,000 ppb for mercury and arsenic.

[014] “Mercury sulfide” may be used interchangeably with HgS, referring to mercurous
20 sulfide, mercuric sulfide, or mixtures thereof. Normally, mercury sulfide is present as mercuric sulfide with a stoichiometric equivalent of one mole of sulfide ion per mole of mercury ion.

[015] “Mercury salt” or “mercury complex” means a chemical compound formed by replacing all or part of hydrogen ions of an acid with one or more mercury ions.

[016] “Arsenic salt” or “arsenic complex” means a chemical compound formed by
25 replacing all or part of hydrogen ions of an acid with one or more arsenic ions, e.g., As³⁺ or As⁵⁺.

[017] “Oil-water” or “oil-water emulsion” or “emulsion” or “emulsions” in the context of oil-water (or water-oil) emulsion refers to an admixture containing a crude oil with water, inclusive of both oil-in-water emulsions and water-in-oil emulsions. In one embodiment, emulsion includes locations within an oil-water mixture in which heavy metal concentrates,
30 including interfaces and interface layers. In one embodiment, emulsion is present in the initial product of oil and produced water from the reservoir. In another embodiment, it is formed

during the mixing of the crude oil with the oxidizing agent and / or the complexing agent.

“Emulsion” can be stable or unstable, such as in dispersions of oil and water which can subsequently separate; e.g., an oil-water mixture left standing for 10 minutes at room temperature, where at least a portion (e.g., 10 vol %.) will resolve into separate phases. In one embodiment, the oil-water emulsion particles are of droplet sizes. In another embodiment, the emulsion particles are the size of micron or nano particles. In one embodiment of oil-water emulsion, oil is present as fine droplets contained in water in the form of an emulsion, e.g., emulsified hydrocarbons, or in the form of undissolved, yet non-emulsified hydrocarbons. In another embodiment, oil-water emulsion refers to a mixture which after mixing and allowed to stand undisturbed, a portion of the mixture is resolved into separate phases in 10 seconds. In yet another embodiment, less than 50% of the mixture is resolved in separate phases in 10 seconds.

[018] “Interphase,” or “interphase layer,” or “interface layer,” or “emulsion layer” may be used interchangeably, referring to the layer between the oil and water phases, having characteristics and properties different from the oil and water phases. In one embodiment, the interface layer is a cloudy layer between the water and oil phases. In another embodiment, the interface layer comprises a plurality of aggregates of coalescence (or droplets), with the aggregates being randomly dispersed in either the water phase or the oil phase.

[019] “Complexing agent” or “chelating agent” refers to a compound that is capable of reacting with a heavy metal compound, e.g., mercury or arsenic compounds.

[020] “Oxidant” may be used interchangeably with “oxidizing agent,” referring to compound that oxidizes heavy metals such as mercury to form mercury cations.

[021] “Soluble” refers to materials that dissolve in water, in conjunction with heavy metal removal, meaning materials that are able to dissolve in water at concentrations comparable to the original concentration of the heavy metals in the crude oil (e.g., 1 ppb or greater).

[022] “Halogens” refers to diatomic species from the column of the periodic table headed by fluorine, for example F₂, Cl₂, Br₂, I₂, etc.

[023] “Halogen oxides” refers to molecules which combine one or more halogen atoms and oxygen, for example NaClO, ClO₂, NaClO₄.

[024] “Organic peracids” refers to multiple-carbon organic compounds where the –OH in an acid group has been replaced with a –OOH group, e.g. a compound of the general formula

RCO-OOH. Examples include but are not limited to peracetic acid, perbenzoic acid, meta-chloroperoxybenzoic acid and combinations thereof.

[025] "Inorganic peracids" refers to compounds of sulfur, phosphorous, or carbon where the -OH in an acid group has been replaced with a -OOH group. Examples include but are not limited to peroxydiphosphoric acid, $H_4P_2O_8$ and peroxydisulfuric acid, $H_2S_2O_8$, sodium percarbonate $Na_2CO_3 \cdot 1.5H_2O_2$, sodium peroxydisulfate $Na_2S_2O_8$, potassium peroxydisulfate $K_2S_2O_8$, ammonium peroxydisulfate $(NH_4)_2S_2O_8$, and combination thereof.

[026] Crude, crude oil, crudes and crude blends are used interchangeably and each is intended to include both a single crude and blends of crudes. In one embodiment, the crude oil to be treated is in the form of a mixture of crude oil and produced water. The water-to-oil ratio increases with the age of the crude oil source, as the production of oil declines with the age of the well. For some sources, the crude stream to be treated may contain little if any produced water. For some other sources, the amount of produced water can be as much as 98% of the crude stream to be treated. As used herein, the crude oil or crude oil feed to be treated refers to both crude oil by itself as well as crude oil-water mixtures.

[027] Crudes may contain small amounts of heavy metals such as mercury and / or arsenic. In one embodiment, mercury may be present as elemental mercury Hg^0 , ionic Hg, inorganic mercury compounds, and / or organic mercury compounds. Examples include but are not limited to: mercuric halides (e.g., $HgXY$, X and Y could be halides, oxygen, or halogen-oxides), mercurous halides (e.g., Hg_2XY , X and Y could be halides, oxygen, or halogen-oxides), mercuric oxides (e.g., HgO), mercuric sulfide (e.g., HgS , meta-cinnabar and/or cinnabar), mercuric sulfate ($HgSO_4$), mercurous sulfate (Hg_2SO_4), mercury selenide (e.g., $HgSe_2$, $HgSe_8$, $HgSe$), mercury hydroxides, and organo-mercury compounds (e.g., alkyl mercury compounds) and mixtures of thereof. Mercury can be present in various forms, e.g., in dissolved form, as particles, and / or adsorbed onto the surfaces such as clay minerals, inorganic mineral scale, sand, and asphaltenes.

[028] In one embodiment for a crude containing a heavy metal such as arsenic, the arsenic species present can be in any of the forms triphenylarsine (Ph_3As), triphenylarsine oxide (Ph_3AsO), arsenic sulfide minerals (e.g., As_4S_4 or AsS or As_2S_3), metal arsenic sulfide minerals (e.g., $FeAsS$; $(Co, Ni, Fe)AsS$; $(Fe, Co)AsS$), arsenic selenide (e.g., As_2Se_5 , As_2Se_3), arsenic-

reactive sulfur species, organo-arsenic species, and inorganic arsenic held in small water droplets.

[029] In the invention, crude oil is effectively treated to decrease trace levels of heavy metals such as mercury, lead, arsenic, etc. In one embodiment, the crude oil is brought into contact with an oxidant. In another embodiment, a complexing agent is added to the crude oil / oxidant mixture to extract at least a portion of the oxidized heavy metal complexes from the interphase to the water phase.

[030] In one embodiment for the removal of mercury, the crude oil is brought into contact with a composition containing both the oxidizing agent and the complexing agent to form a soluble mercury compound. Mercury in the water phase is subsequently recovered. In one embodiment for the removal of arsenic, when sufficient amount of oxidizing agent is added in the crude oil, the arsenic species become arsenate, which is negatively charged. In the next step, complexing agents for the creation of strong complexes with arsenic species are injected into the hydrocarbon or water mixtures to form highly water-soluble complexes that can be subsequently removed from the crude oil. By-products of arsenic complexes will preferentially partition into the water phase. The water containing mercury / arsenic in one embodiment can be injected back into the reservoir for water flooding, or reservoir pressure support, as a mean to dispose of the heavy metals that were originally present in the crude oil.

[031] Oxidizing Agent: In one embodiment, the crude oil is brought into contact with an excess amount of oxidant under suitable conditions to oxidize at least a portion of the heavy metals to cations. An organic oxidizing agent or an oxidant in an aqueous form can be used.

[032] In one embodiment of a crude oil feed containing arsenic with produced water at a water to oil ratio of at least 1:1, as produced water pH typically is typically in the range of 6.5 to 8, the charge of the arsenic species present is neutral (H_3AsO_3^0) or anions (H_2AsO_4^- , or HAsO_4^{2-}). In one embodiment for the removal of arsenic, the oxidizing agent oxidizes reduced forms of arsenic, e.g., arsine or other organic arsenic forms (soluble in hydrocarbons), or arsenite (soluble in water) to the 5+ oxidation state. In one embodiment, arsenic compounds are oxidized into inorganic arsenic species such as arsenite (As^{3+}) or arsenate (As^{5+}). In an embodiment for the removal of mercury, the oxidant reacts with elemental Hg droplets, elemental Hg adsorbed on formation minerals, elemental Hg dissolved in the crude oil, as well as mercury compounds

including but not limited to HgS, HgSe, HgO, converting at least a portion of elemental mercury (Hg^0) to cations, having an oxidation state equal to or greater than 1 (e.g., Hg^{2+}).

[033] The amount of oxidants used should be at least equal to the amount of heavy metal to be removed on a molar basis, if not in an excess amount. In one embodiment, an amount of oxidants (and the water stream containing oxidants) is added for a molar ratio of oxidant to heavy metals ranging from 1.5:1 to 30,000:1. In another embodiment, an amount of water containing oxidants is provided for a molar ratio of oxidant to heavy metals ranging from 5:1 to 20,000:1. In a third embodiment, the amount is a molar ratio of oxidants to heavy metals ranging from 50:1 to 10,000:1. In a fourth embodiment, the amount is molar ratio ranging from 100:1 to 5,000:1. In a fifth embodiment, the ratio ranges from 150:1 to 500:1. The contact can be carried out at room temperature or at an elevated temperature (e.g., 30 – 80°C) for a period of time, generally ranging from seconds to 1 day. In one embodiment, the contact is between 20 seconds to 5 hours. In another embodiment, from 1 minute to 1 hour.

[034] The volume ratio of water containing oxidants to crude oil ranges from 0.05:1 to 5:1 in one embodiment; from 1:1 to 2:1 in a second embodiment; from 0.1:1 to 1:1 in a third embodiment; and at least 0.5:1 in a fourth embodiment. The amount of oxidants added can be adjusted to control the type and amount of heavy metal complexes formed. For example, in one embodiment for the removal of arsenic from a crude oil, excess oxidants can be added to for the conversion of as much of the arsenic into As^{5+} as possible, e.g., at least 90%, instead of a mixture of As^{3+} and As^{5+} .

[035] In one embodiment, the pH of the water stream or treatment solution containing the oxidizing is adjusted to a pre-selected pH depending on the heavy metals contained in the crude oil to be treated. The pre-select pH is less than 6 in one embodiment; less than 5.5 in a second embodiment; less than 4 in a third embodiment; and less than 3 in a fourth embodiment.

[036] In one embodiment, a sufficient amount of oxidant is employed to convert at least 75% of the heavy metals, e.g., elemental mercury, to mercury cations. In another embodiment, an amount is used for a conversion of at least 95%. In a third embodiment at least 99%. In a fourth embodiment, an amount for at least 50% of heavy metals to be extracted from the crude oil. In a fifth embodiment, an amount for at least 25% of heavy metal extraction from the crude oil. In one embodiment for the removal of mercury, the oxidant generates non-complexed ionic mercury ions from elemental mercury and complexed mercury.

[037] In one embodiment, the oxidant is selected from the group of halogens, halogen oxides, molecular halogens, peroxides and mixed oxides, including oxyhalites, their acids and salts thereof. In another embodiment, the oxidant is selected from the group of peroxides (including organic peroxides) such as hydrogen peroxide (H_2O_2), sodium peroxide, urea peroxide, alkylperoxides, cumene hydroperoxide, t-butyl hydroperoxide, benzoyl peroxide, cyclohexanone peroxide, dicumyl peroxide. In yet another embodiment, the oxidant is selected from the group of inorganic peracids such as Caro's acid (H_2SO_5) or salts thereof, organic peracids, such as aliphatic C_1 -to C_4 -peracids and, optionally substituted, aromatic percarboxylic acids, peroxy salts, persulfates, peroxoborates, or sulphur peroxy-compounds substituted by fluorine, such as $\text{S}_2\text{O}_6\text{F}_2$, and alkali metal peroxomonosulfate salts. Suitable oxygen-containing oxidizing agents also include other active oxygen-containing compounds, for example ozone. In one embodiment, the oxidant is selected from the group of monopersulfate, alkali salts of peroxide like calcium peroxide, and peroxidases that are capable of oxidizing iodide.

[038] In one embodiment, the oxidizing agent is selected from the group of sodium perborate, potassium perborate, potassium peroxymonosulfate, sodium peroxocarbonate, sodium peroxodicarbonate, and mixtures thereof. In another embodiment, the oxidizing agent is hydrogen peroxide in the form of an aqueous solution containing 1 % to 60 % hydrogen peroxide (which can be subsequently diluted as needed). In another embodiment, the oxidizing agent is H_2O_2 in the form of a stable aqueous solution having a concentration of 16 to 50 %. In a third embodiment, the oxidizing agent H_2O_2 is used as a solution of 1 – 3 % concentration.

[039] In one embodiment the oxidant selected is a hypochlorite, e.g., sodium hypochlorite, which is commercially produced in significant quantities. The hypochlorite solution in one embodiment is acidic with a pH value of less than 4 for at least 80% removal of mercury. In another embodiment, the solution has a pH between 2 and 3. In a third embodiment, the sodium hypochlorite solution has a pH of less than 2. A low pH favors the decomposition to produce OCl^- ions.

[040] In one embodiment, the oxidant is selected from the group of elemental halogens or halogen containing compounds, e.g., chlorine, iodine, fluorine or bromine, alkali metal salts of halogens, e.g., halides, chlorine dioxide, etc. In yet another embodiment, the compound is an iodide of a heavy metal cation. In yet another embodiment, the oxidant is selected from ammonium iodide, an alkaline metal iodide, and ethylenediamine dihydroiodide. In one

embodiment, the oxidant is selected from the group of hypochlorite ions (OCl^- such as NaOCl , NaOCl_2 , NaOCl_3 , NaOCl_4 , $\text{Ca}(\text{OCl})_2$, NaClO_3 , NaClO_2 , etc.), vanadium oxytrichloride, Fenton's reagent, hypobromite ions, chlorine dioxide, iodate IO_3^- (such as potassium iodate KIO_3 and sodium iodate NaIO_3), and mixtures thereof. In one embodiment, the oxidant is selected from

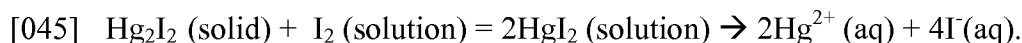
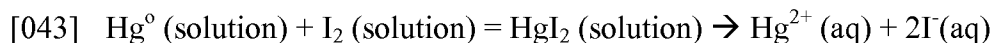
5 KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$, K_2CrO_7 , and Cl_2 .

[041] In one embodiment, iodine is employed as the oxidizing agent. In this embodiment, the crude oil is first brought into contact with iodine or a compound containing iodine such as alkali metal salts of iodine, e.g., halides or iodide of a cation. In one embodiment, the iodide is selected from ammonium iodide, alkali metal iodide, an alkaline earth metal iodide, and ethylenediamine dihydroiodide. In one embodiment, the mercury is converted into soluble by-products upon reaction with molecular iodine (I_2), metallic mercury (Hg^0) being converted into mercury ions (Hg^{2+}), subsequently forming aqueous soluble Hg^{2+} complexes. The water soluble complexes would partition into the aqueous phase for subsequent separation and convenient disposal by methods including but not limited to re-injection, or disposed back into

15 the reservoir.

[042] In one embodiment with iodine as the oxidizing agent, the amount of the iodine is chosen to result in an atomic ratio of iodine to mercury of at least 1:1. In a second embodiment, a ratio ranging from 1.5:1 to 10:1. In a third embodiment, a ratio of 2:1 to 4:1. In one embodiment, the crude oil is brought into contact with solid iodine. In another embodiment, an iodine solution in petroleum distillate is injected into the liquid hydrocarbon, e.g., gas condensate or crude oil. Upon contact with the crude oil, molecular iodine (I_2) reacts with elemental Hg droplets, elemental Hg adsorbed on formation minerals, elemental Hg dissolved in the crude oil, as well as mercury compounds including but not limited to HgS , HgSe , and HgO . In the reactions, Hg^0 is oxidized to Hg^{2+} , and I_2 is reduced to 2I^- . In one embodiment, a slight excess of

20 iodine is employed to prevent the formation of water insoluble Hg_2I_2 . Mercuric iodide is highly soluble in water and not very soluble in hydrocarbons.



[046] With respect to solids such as HgS, the solids are dissolved by I₂, wherein I₂ oxidizes the solids to form Hg²⁺ and elemental S or SO₄²⁻. The reactions proceed very fast at room temperature (e.g., 25°C), and even faster at elevated temperatures.

[047] Complexing Agent: Depending on the selection of the oxidizing agents, some agents easily transform insoluble heavy metals, e.g., Hg⁰ or arsenic, to water soluble heavy metal cations, e.g., Hg²⁺, As³⁺ or As⁵⁺, for greater than 50% removal with portions of the water-oil emulsion resolved into separate phases after a short period of time, e.g., less than 10 minutes. For some other oxidizing agents, the separation of the water and oil phases to remove the heavy metal cations happens with the use of separation devices, e.g., mechanical / rotating means such as a centrifuge or a hydrocyclone, for a long period of time, e.g., more than 10 minutes or 20 minutes, etc.

[048] In one embodiment, the removal of heavy metals can be enhanced with the addition of a complexing agent to the oil-water emulsion mixture, thus alleviating the need for an oil-water separation device, e.g., a device using mechanical or rotating means. Heavy metals such as arsenic, mercury, and the like form coordination complexes with compounds including but not limited to oxygen, sulfur, phosphorous and nitrogen-containing compounds. In treating the oil-water emulsion, the complexing agent forms strong complexes with the heavy metal cations, e.g., Hg²⁺, As³⁺ or As⁵⁺, extracting heavy metal complexes from the oil phase and / or the interface phase of the oil-water emulsion into the water phase by forming water soluble complexes. In one embodiment, the addition of a complexing agent essentially eliminates or reduces the volume of the oil-water emulsion layer, and replaces the emulsion layer with separate oil and water layers.

[049] The addition of the complexing agent can occur either before, simultaneously with, or after the addition of the oxidizing agent to the crude oil. Different complexing agents can be added at the same time, or in succession, for the extraction of different heavy metal cations into the water phase. In one embodiment for the removal of arsenic, an inorganic sulfur compound such as sodium polysulfide is employed as the complexing agent for the extraction of As³⁺ into the water phase, and a transition metal halide such as ferric chloride or zinc chloride is employed for the extraction of As⁵⁺ into the water phase.

[050] In one embodiment, the formation of a water layer containing heavy metal cations occurs within 15 minutes after the addition of the complexing agent. In a second embodiment, a

separate water layer is formed after 10 minutes. In a third embodiment, the formation of a water layer containing soluble heavy metal cations occurs within 20 minutes of the addition of the oxidizing agent to the crude oil. In a fourth embodiment, the formation of a water layer occurs within 15 minutes of the addition of the oxidizing agent to the crude oil. In a fifth embodiment, the formation is within 5 minutes.

[051] The complexing agents are employed in an amount sufficient to effectively stabilize (form complexes with) the soluble heavy metals in the oil-water mixture. In one embodiment, the sufficient amount is expressed as molar ratio of complexing agent to soluble mercury in the ranges of 1:1 to 5,000:1. In a second embodiment from 2:1 to about 3,000:1. In a third embodiment from 5:1 to about 1,000:1. In a fourth embodiment, from 20:1 to 500:1.

[052] In one embodiment for the removal of mercury or arsenic, a selective complexing agent has a large equilibrium binding constant for non-complexed mercury or arsenic ions and is resistant to oxidation by the oxidizing agent added to the oil-water emulsion layer (if it can be isolated), or the crude oil / oxidizing agent mixture. In one embodiment, the addition of the complexing agent allows at least 50% of the cations to react with the complexing agent, forming a water-soluble compound, e.g., mercury or arsenic complexes, when it comes into contact with the heavy metal ions. In another embodiment, at least 75% of the heavy metal ions in the oil phase and / or interface phase are converted into water-soluble complexes. In a third embodiment, at least 90% conversion into water-soluble complexes. In a fourth embodiment, at least 95% of the heavy metal ions are converted / extracted from the oil phase and / or interface phase into the water phase as water-soluble compounds. In yet another embodiment with the selection of a complexing agent which also functions as a reducing agent, it neutralizes excess oxidant that could make the crude oil corrosive.

[053] Examples of chelating groups that are selective toward mercury and / or arsenic include thiol groups, dithiocarbamic acid, thiocarbamic acid, thiocarbazon, cryptate, thiophene groups, thioether groups, thiazole groups, thiourenium groups, amino groups, polyethyleneimine groups, N-thiocarbamoyl-polyalkylene polyamino groups, derivatives thereof, and mixtures thereof.

[054] Examples of complexing agents as reducing agents include but are not limited to sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and thiourea.

[055] In one embodiment, the complexing agent is an inorganic sulfur compound selected from the group of sulfides, thiosulfates and dithionites. Examples include but are not limited to ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, and alkaline earth metal dithionites, and mixtures thereof.

5 Examples of sulfides include but are not limited to potassium sulfide, sodium sulfide, alkaline earth metal sulfides, sulfides of transition elements number 25-30, aluminum sulfides, cadmium sulfides, antimony sulfides, Group IV sulfides, and mixtures thereof. Suitable alkali metal thiosulfate includes ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, and lithium thiosulfate. Examples of alkaline earth metal thiosulfates include calcium thiosulfate and
10 magnesium thiosulfate. Ferric thiosulfate exemplifies an iron thiosulfate which may be employed. Alkali metal dithionites include sodium dithionite and potassium dithionite. Calcium dithionite is particularly suitable as an alkaline earth metal dithionite complexing agent for the removal of arsenic and mercury.

[056] In another embodiment, the complexing agent is a polyamine for forming stable
15 cationic complexes with the ions of heavy metals. Exemplary polyamines include ethylenediamine, propylenediamine, triaminotriethylamine, diethylenetriamine, triethylenetetramine (TRIEN), tetraethylenepentamine and tetra-2-aminoethylethylenediamine. In one embodiment, the polyamine may include carboxyl groups, hydroxyl groups and / other substituents, as long as they do not weaken the complex forming effect of the polyamine. In one
20 embodiment, the complexing agent is tetraethylenepentamine (TETREN), which forms a stable complex with mercury at a pH around 4.

[057] In one embodiment, the complexing agent is selected from the group of DEDCA (diethyl dithiocarbamic acid) in a concentration of 0.1 to 0.5M, DMPS (sodium 2,3-dimercaptopropane-1-sulfonate), DMSA (meso-2, 3-dimercaptosuccinic acid), BAL (2,3-dimercapto-propanol), CDTA (1,2-cyclohexylene-dinitrilo-tetraacetic acid), DTPA (diethylene triamine pentaacetic acid), NAC (N-acetyl L-cystiene), sodium 4,5-dihydroxybenzene-1,3-disulfonate, polyaspartates; hydroxyaminocarboxylic acid (HACA); hydroxyethyliminodiacetic (HEIDA); iminodisuccinic acid (IDS); nitrilotriacetic acid (NTA), aminopolycarboxylic acids (such as ethylenediaminetetraacetic acid or EDTA), amino carboxylic acids
25 (ethylenediaminetetraacetate, diethylenetriaminopentaacetate, nitriloacetate, hydroxyethylethylenediaminotriacetate), oxycarboxylic acids (citrate, tartrate, gluconate), and

other carboxylic acids and their salt forms, phosphonates, acrylates, and acrylamides, and mixtures thereof.

[058] In one embodiment, the complexing agent is a metal halide, for example, halides selected from the group Li, Na, K, Ca, Ni, Fe, Zn, Ba, Sr, Ag and combinations thereof. In
5 another embodiment, the complexing agent is selected from nickel and ferric ions, e.g., salts such as FeCl_3 or NiCl_2 , forming compounds encompassing the heavy metal ions, e.g., ferric arsenate and ferric hydroxide. Another example of a complexing agent is KI, which combines with mercuric iodide to form a water soluble compound having the formula K_2HgI_4 .

[059] In one embodiment with the use of inorganic sulfur compounds as complexing
10 agents, a sufficient amount of inorganic sulfur compounds is employed that correlates to the solubility of the inorganic sulfur compounds in water. For example, complexing agents which are relatively soluble in water include alkali metal sulfides, nitrogen sulfides, alkali metal thiosulfates, ammonium thiosulfate, alkaline earth metal thiosulfates, iron thiosulfate, and alkali metal dithionites. Less soluble inorganic sulfur compounds include alkaline earth metal
15 sulfides, transition metal sulfides of elements 25 to 30, and Group IV sulfides. The sufficient amount ranges from 5:1 to 1,000:1 as molar ratio of the inorganic sulfur compound to heavy metals in the crude oil.

[060] In one embodiment for the removal of arsenic and conversion to water soluble
cations, the complexing agent is selected from the group of metal halides (particularly for As^{5+}
20 conversion) and sulfide compounds (particularly for As^{3+} conversion). In one embodiment, the metal halides are selected from halides of Fe, Cu, Co, Zn, Sr, Ag, which oxidize arsenic species (e.g., arsenate) to form water soluble complexes such as FeHAsO_4^+ , CoHAsO_4^0 , ZnHAsO_4^0 , $\text{SrH}_2\text{AsO}_4^+$, and $\text{Ag}_2\text{H}_2\text{AsO}_4^+$. Examples of inorganic sulfide compounds include but are not limited to sodium polysulfide, sodium thiosulfate, potassium peroxomonosulfate, and mixtures
25 thereof.

[061] In some embodiments for the removal of heavy metals such as arsenic and / or mercury, an acidic complexing agent is employed with the addition of an acid such as HCl, for the complexing agent to have a pH of 5.5 or less in one embodiment, 5 or less in a second
embodiment, and 3 or less in a third embodiment. In one example with the use of KI as the
30 complexing agent, a solution mixture of KI and HCl having a pH in the range of 1.5 to 3 is employed. In another embodiment, a solution mixture of KBr and HCl having a pH of less than

4 is used. In a third embodiment, an HCl-thiourea solution mixture is used, with the acid concentration of less than 5M and thioureas concentration from 0.3 to 1.4M.

[062] In yet another embodiment due to the high produced water to oil ratio in the crude oil to be treated, instead of or in addition to adding an acidic complexing agent, at least an acid is added to the crude oil / water mixture to adjust the pH to an acidic level of 5.5 or less. The pH adjustment can be done prior to the addition of the oxidizing agent, simultaneously with the addition of the oxidizing agent, prior to the addition of the complexing agent, or simultaneously with the addition of the complexing agent. In one embodiment, the pH adjustment is after the addition of the oxidizing agent and prior to the addition of the complexing agent. The acid for the pH adjustment can be any mineral acid known in the art.

[063] Optional Reagent Treatments: In one embodiment, at least a demulsifier is added to the mixture to further chemically separate the crude oil and the water containing the heavy metal compounds. In one embodiment, at least a demulsifier is added at a concentration from 100 to 5,000 ppm. In another embodiment, a demulsifier is added at a concentration from 100 to 1,500 ppm. In a third embodiment, the demulsifier is added along with pH adjustment with caustic or acid. In addition to the demulsifier treatments, surfactants are sometimes required for resolution of solids, viscous oil-water interfaces and sludging if any.

[064] In one embodiment, the demulsifier is a commercially available demulsifier selected from polyamines, polyamidoamines, polyimines, condensates of o-toluidine and formaldehyde, quaternary ammonium compounds and ionic surfactants. In another embodiment, the demulsifier is selected from the group of polyoxyethylene alkyl phenols, their sulphonates and sodium sulphonates thereof. In another embodiment, the demulsifier is a polynuclear, aromatic sulfonic acid additive.

[065] Method for Removing / Decreasing Levels of Heavy Metals in Crude Oil: The trace amount removal rate depends on the type of heavy metal to be removed, the oxidant and complexing reagents employed, and in one embodiment, the pH of the reagents. In one embodiment, an oxidant is first prepared or obtained. The oxidant is brought in contact with the crude oil containing heavy metals by means known in the art. In the next step, at least a complexing agent is added to the crude oil-oxidant mixture, forming soluble metal complexes, thus extracting the heavy metal complexes into the aqueous phase.

[066] Depending on the selected oxidant and / or the subsequent complexing reagent to be used, the pH of the solution can first be adjusted or maintained by the use of a buffer to improve the removal rate. Exemplary buffers, such as phosphate and citrate, are serviceable for a prescribed pH range. The pH can be adjusted to the alkaline range using ammonium hydroxide, ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, and mixtures thereof. Additionally, nitriloacetic acids can be used as buffers. The pH can be adjusted to the acidic range using acids such as HCl. Other exemplary acids include phosphoric acid and acetic acid. In one embodiment, the pH of the solution is maintained in a neutral range of 6-8. In another embodiment, the pH of the solution is kept acidic at a pH of less than 3.

[067] The contact between the crude oil and the reagents can be at any temperature that is sufficiently high enough for the crude oil to be completely liquid. In one embodiment, the contact is at room temperature. In another embodiment, the contact is at a sufficiently elevated temperature, e.g., at least 50°C. In one embodiment, the process is carried out about 20°C to 65°C.

[068] The contact time between the reagents and the crude oil is for a sufficient amount of time for a portion of the heavy metals to be extracted from the crude oil into the water-oil emulsion, and subsequently into the water phase. In one embodiment, the contact time is sufficient for at least 50% of the heavy metals to be extracted from the crude oil into the water phase. In a second embodiment, at least 75% extraction. In a third embodiment, at least 90% extraction. The sufficient amount of time is dependent on the mixing of the crude oil with the reagents. If vigorous mixing is provided, the contact time can be as little as 20 seconds. In one embodiment, the contact time is at least 5 minutes. In another embodiment, the contact time is at least 30 minutes. In a third embodiment, at least 1 hr. In a fourth embodiment, the contact is continuous for at least 2 hrs.

[069] The oxidant and complexing reagents can be introduced continuously, e.g., in a water stream being brought into contact continuously with a crude oil stream, or intermittently, e.g., injection of a water stream batch-wise into operating gas or fluid pipelines. Alternatively, batch introduction is effective for offline pipelines.

[070] In one embodiment instead of separate or sequential feeding steps, the oxidant and complexing reagents are added to the crude oil in one single step, as separate compositions

or as a single composition, for the oxidation of elemental dissolved heavy metals to be immediately followed by or almost simultaneously with the extraction of the oxidized heavy metals, e.g., Hg^{2+} , into the water phase.

[071] In one embodiment, the reagents are injected into the crude oil / water stream to
5 form highly soluble mercury or arsenic complexes in the water phase, and away from the crude oil. After the heavy metal complexes are extracted into the water phase, the water containing the complexes is separated from the crude oil in a phase separation device known in the art, resulting in a crude oil with a significantly reduced level of heavy metals. The soluble heavy metal complexes can be isolated / extracted out of the effluent and subsequently disposed. In one
10 embodiment, the water phase after separation can be injected back into the reservoir for water flooring, or reservoir pressure support as a mean of disposing the mercury that was originally in the crude oil. In one embodiment, the water phase is disposed into or injected back to the reservoir which produced the crude oil.

[072] In one embodiment, instead of or in addition to the addition of at least a
15 complexing agent, other means are employed to enhance the resolution of the water-oil emulsions, including but not limited to heating the crude oil mixture to over 50°C , and up to 85°C , adding further mixing time, further quiescent time (8 to 24 hours), adjusting pH of the oil-water emulsion, or adding at least a demulsifier. In another embodiment, a continuous electrostatic dehydrator is used to help with the water / oil separation. In yet another
20 embodiment, resolution of the water-oil emulsions is enhanced with the aid of ionic liquids and / or microwave treatment.

[073] The contact between the crude oil and the oxidizing agent / complexing agent can be either via a non-dispersive or dispersive method. The dispersive contacting method can be via mixing valves, static mixers or mixing tanks or vessels. In one embodiment, the non-
25 dispersive method is via either packed inert particle beds or fiber film contactors.

[074] In one embodiment, the heavy metal removal is carried out in a unit operation with two separate zones, a contact zone and a separation zone. The contact zone is for the contact between the crude oil and the oxidizing agent / complexing agent, which contact zone can be in any form of packed tower, bubble tray, stirred mixing tank, fiber contacting, rotating
30 disc contactor or other contacting devices known in the art. In one embodiment, the liquid-liquid contact is via fiber contacting, which is also called mass transfer contacting, wherein large

surface areas are provided for mass transfer in a non-dispersive manner as described in US Patent Nos. 3,997,829; 3,992,156; and 4,753,722. The separation zone can be at least a separation device selected from settling tanks or drums, coalescers, electrostatic precipitators, or other similar devices.

5 [075] In one embodiment, the heavy metal removal treatment is via an integrated unit, e.g., a single vessel having a contact zone for crude containing heavy metals to be in intimate contact with the oxidizing agent (and / or complexing agent), and a settling zone for the separation of the treated crude from water phase containing soluble heavy metal complexes. The oxidizing agent can be mixed with the crude oil prior to entering the contact zone, or
10 injected as a separate stream into the contacting zone. The flow of the oxidizing agent and the crude oil in the unit can be counter-current or concurrent.

 [076] In one embodiment, the heavy metal removal is via a single tower with a top section for the mixing of the crude oil with the oxidizing agent / complexing agent and a bottom section for the separation of the treated crude from the water phase. In one embodiment, the top
15 section comprises at least a contactor characterized by large surface areas, e.g., a plurality of fibers or bundles of fibers, allowing mass transfer in a non-dispersive manner. The fibers for use in the contactors are constructed from materials consisting of but not limited to metals, glass, polymers, graphite, and carbon, which allow for the wetting of the fibers and which would not contaminate the process or be quickly corroded in the process. The fibers can be porous or non-
20 porous, or a mixture of both.

 [077] In one embodiment, the oxidizing section contains at least two contactors comprising fibers in series. The fibers in each contactor are wetted by the oxidizing agent to form a thin film on the surface of fibers, and present a large surface area to the crude oil to be treated. In one embodiment, the admixture of the treated crude oil and the oxidizing agent exits
25 the bottom of the first contactor and flows into the next contactor in series, wherein the complexing agent is introduced. The admixture with the addition of the complexing agent exits the bottom contactor and is directed to a bottom separation section. In one embodiment with at least two contactors in series, the oxidizing agent feed and / or complexing agent feed can be split and added to any of the contactors in series for the treatment of the crude. In yet another
30 embodiment, crude oil feed may be split with additional crude being injected into any of the

contactors in series for enhanced surface contact between the crude and the oxidizing agent, while oxidizing agent feed flows through the fibers from one contactor to the next one in series.

[078] In the water-oil separation section, the treated crude is allowed to separate from the aqueous phase containing the extracted heavy metals via gravity settling. In one
5 embodiment, the bottom section also comprises fibers to aid with the separation, wherein the mixture of treated crude oil and the aqueous phase flows through the fibers to form two distinct liquid layers, an upper layer of treated crude and a lower aqueous phase layer containing oxidized heavy metals.

[079] In yet another embodiment, the heavy metal removal is carried out in an
10 integrated unit having multiple sections, e.g., an extractor section for oxidizing the heavy metals in crude oil upon contact with the oxidizing agent; a pre-mixing section for the preparation of a complexing agent to be added to the admixture of crude oil and oxidizing agent, with the pre-mixing section in direction communication with the extractor section; and a coalescer / separation section in communication with the extractor section for the separation of treated crude
15 from the aqueous phase containing extracted heavy metals.

[080] Further details regarding the description of the different integrated units and the interface control structure are described in US Patent Publication Nos. US20100200477, US20100320124, US20110163008, US20100122950, and US20110142747; and US Patent Nos. 7326333 and 7381309, and the relevant disclosures are included herein by reference.

[081] In one embodiment, after the oil / water separation, the heavy metal complexes
20 are removed from water through the use of a selective adsorbent material, e.g., a porous resin having mercury selective chelating groups bound thereto. In another embodiment, the heavy metal complexes are subsequently removed through techniques such as filtration, coagulation, flotation, co-precipitation, ion exchange, reverse osmosis, ultra-filtration using membranes and
25 other treatment processes known in the art.

[082] Depending on the source, the crude oil feed can have an initial heavy metal level such as mercury of at least 50 ppb. In one embodiment, the initial level is at least 5,000 ppb. Some crude oil feed may contain from about 2,000 to about 100,000 ppb of heavy metals such as mercury. In one embodiment with the trace amount removal or reduction of heavy metals
30 including mercury, the heavy metal level in the crude oil is reduced to 100 ppb or less. In another embodiment, the level is brought down to 50 ppb or less. In a third embodiment, the

level is 20 ppb or less. In a fourth embodiment, the level is 10 ppb or less. In a fifth embodiment, the level is 5 ppb or less. In yet another embodiment, the removal or reduction is at least 50% from the original level of heavy metals such as mercury or arsenic. In a fifth embodiment, at least 75% of a heavy metal is removed. In a seventh embodiment, the removal or the reduction is at least 90%.

[083] Heavy metal levels, e.g., mercury or arsenic, can be measured by conventional techniques known in the art, including but not limited to cold vapor atomic absorption spectroscopy (CV-AAS), cold vapor atomic fluorescence spectroscopy (CV-AFS), Gas Chromatography Combined with Inductively Coupled Plasma Mass Spectrometry (or GC-ICP-MS with 0.1ppb detection limit), Flam Atomic Absorption Spectroscopy (FAAS), etc.

[084] EXAMPLES: The following examples are given to illustrate the present invention. It should be understood, however, that the invention is not limited to the specific conditions or details described in these examples. In examples calling for mercury vapor feed, a sufficient amount of mercury (e.g., one or two drops of elemental mercury in a bottle) was sparged by using nitrogen (N₂) gas into another bottle containing white mineral oil overnight. The ppm and ppb concentrations in the tables are by weight. % Hg removal indicates the removal as a percent of the amount of Hg initially present.

[085] Examples 1 - 11: A series of experiments are carried out, each for a different oxidant. Example 1 is a control experiment without any oxidant being used (complexing agent TETREN only at a final concentration of 30μM). For each of experiments 2-11, 5mL of mercury vapor feed was placed into a 10mL Teflon-capped centrifuge tube. Oxidant was added to make a final concentration as shown in Table 1. The tube was shaken vigorously for about 2 minutes. 5 mL of distilled water was added to tube. A pre-determined volume of TETREN was added for a final concentration of 30μM. Tube was again shaken by hand vigorously for about 2 minutes, then centrifuged for 1 minute to separate oil from water. Aliquots of the oil and water were measured for Hg using a Lumex Hg analyzer equipped with Pyro-915+. Results of the experiments are shown in Table 1.

[086] Table 1

No.	Oxidant	Dosage ppm	Hg in oil ppb	Hg in water ppb	Hg removal %
1	None – control	-	1027 ± 41	39	3.7
2	Iodine	1000	25 ± 15	944	98

3	Sodium polysulfide	29,000	58 ± 8	1000	94
4	Sodium polysulfide	2,900	884 ± 19	234	13.9
5	Na persulfate Na ₂ S ₂ O ₈	940	540 ± 15	580	47.4
6	Dimethylsulfoxide	310	1050 ± 0	58	0
7	Na perborate, NaBO ₃	610	978 ± 123	-	4.8
8	Na percarbonate, Na ₂ CO ₃ ·1.5H ₂ O ₂	620	1065 ± 14	74	0
9	Na periodate, NaIO ₄	840	980 ± 15	116	4.6
10	2-Iodobenzoic acid	980	892 ± 103	92	13.1
11	2-Iodobenzoic acid	1960	449 ± 111	780	56.3

[087] Examples 12 – 14: The same procedures in Examples 1-11 are repeated, but with Oxone™ (2KHSO₅·KHSO₄·K₂SO₄) as the oxidant at different dosage levels, and with different complexing agents (or none) as indicated in Table 2. The results are listed in Table 2.

5 [088] Table 2

No.	Oxidant / Complexing Agent	Dosage ppm	Hg in oil ppb	Hg in water ppb	Hg removal %
12	Oxone™ / None	2420	305 ± 21	800	70.3
13	Oxone™ / None	2420	246 ± 3	877	76.0
14	Oxone™ / TETREN	7260	127±8	829	87.6

[089] Examples 15- 25: The same procedures were repeated but with different oxidants at different concentrations as shown in the table, and with TETREN as the complexing agent added for a final concentration at 1,500 ppm. Results are shown in Table 3:

10 [090] Table 3

No.	Oxidant	Dosage ppm	Hg in oil ppb	Hg in water ppb	Hg removal %
15	None - control		1150	-	5.7
16	Iodine	50	114	955	90.1
17	KBrO ₃	540	972 ± 83	196	15.5
18	KIO ₃	690	1083 ± 25	112	5.8
19	NaClO ₃	340	974 ± 33	166	15.3
20	NaClO ₂	290	1107 ± 23	44	3.7
21	Fe ₂ (SO ₄) ₃	1290	1111 ± 10	36	3.4
22	FeCl ₃	1060	906 ± 24	179	21.2
23	CuSO ₄	520	1160 ± 140	41	0
24	KMnO ₄	510	49 ± 5	1120	96
25	HNO ₃	200	1142 ± 103	21	0.1

[091] Examples 26 – 50: The same procedures in Examples 2-11 are repeated, but with different oxidants at different dosage levels, as well as different complexing agents at different final concentrations. Results are as indicated in Table 4.

[092] Table 4

No.	Oxidant	dosage ppm in oil	Complexing agent ppm in water	Hg in oil ppb	Hg removal %
26	None - control		Tetren / 1500	1150	5.7
27	Iodine	50	NONE	1060	7.8
28	benzoyl peroxide	50	NONE	1190	-
29	benzoyl peroxide	50	Na thiosulfate / 124	1020	11.3
30	benzoyl peroxide	50	Na thiosulfate / 248	931	19.0
31	benzoyl peroxide	50	Na thiosulfate / 496	922	19.8
32	benzoyl peroxide	100	Tetren / 500	1200	0
33	benzoyl peroxide	100	Tetren / 1500	1130	1.7
34	benzoyl peroxide	100	KI / 5000	679	41.0
35	benzoyl peroxide	800	KI / 2000	213	81.5
36	benzoyl peroxide	800	KI / 4000	29	97.5
37	benzoyl peroxide	200	KI / 5000	600	47.8
38	benzoyl peroxide	300	KI / 5000	454	60.5
39	benzoyl peroxide	400	KI / 5000	354	69.2
40	benzoyl peroxide	500	KI / 5000	214	81.4
42	benzoyl peroxide	600	KI / 5000	142	87.7
42	benzoyl peroxide	700	KI / 5000	62	94.6
43	<i>t</i> -butyl hydroperoxide	25	KI / 5000	410	64.3
44	<i>t</i> -butyl hydroperoxide	50	KI / 5000	88 ± 6	92.3
45	<i>t</i> -butyl hydroperoxide	100	KI / 5000	79	93.1
46	<i>t</i> -butyl hydroperoxide	200	KI / 5000	40	96.5
47	<i>t</i> -butyl hydroperoxide	250	KI / 5000	45	96.1
48	Hydrogen peroxide	25	KI / 5000	77	93.3
49	Hydrogen peroxide	50	KI / 5000	32	97.2
50	Hydrogen peroxide	75	KI / 5000	15	98.7

5

[093] Examples 51-53: 50 mL of mercury vapor feed preparation containing approximately 1,100 ppb Hg was added to a number of 100 mL glass tubes, then mercury level was measured using LUMEX mercury analyzer equipped with PYRO-915+. 50 mL of distilled water was placed in the tubes, and the mercury level was measured using LUMEX mercury
 10 analyzer equipped with PYRO-915+. A pre-determined volume of 3 different oxidants (hydrogen peroxide (H₂O₂), *t*-butyl hydroperoxide, and cumene hydroperoxide) was added to each reactor for a final oxidant concentration of 50 ppm. The oil-water mixture was stirred up

for 1 minute. In the next step, different complexing reagents (potassium iodide (KI), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), TETREN, and Na_4EDTA) were added to each reactor to make a final concentration of: 50, 500 and 5,000 ppm KI; 470 and 4,700 ppm $\text{Na}_2\text{S}_2\text{O}_3$; 570 and 5,700 ppm TETREN; 1,200 and 12,000 ppm Na_4EDTA . The tubes were shaken vigorously for 1 minute.

5 Aliquots of both oil and water from each were analyzed for mercury. Results are presented in Table 5 showing mercury removal rate for each combination of oxidants and reagents.

[094] Table 5

No.	Oxidant	KI (in ppm)			$\text{Na}_2\text{S}_2\text{O}_3$		Tetren		EDTA	
		5,000	500	50	4,700	470	5,700	570	1,200	12,000
51	50 ppm H_2O_2	99%	88%	30%	-	24%	17%	19%	na	2%
52	50ppm tBHP*	40%	11%	-	10%	-	16%	14%	15%	12%
53	50ppm CHP**	35%	-	-	16%	-	-	-	-	-

* tBHP: t-butyl hydroperoxide

** CHP: cumene hydroperoxide

10 [095] Example 54: 50 mL of mercury vapor feed preparation (i.e., mineral oil) containing approximately 1,100 ppb Hg is added to a number of 100 mL glass tubes, then mercury level is measured using LUMEX mercury analyzer equipped with PYRO-915+. Four different samples of pre-determined volume of 5 mmol/L sodium chlorite at different pH (3, 6, 9, and 11) is added to each tube for a final oxidant concentration of 50 ppm. The pH of the sodium

15 chlorite solution is adjusted by the addition of HCl. The mixture is stirred up for at least 10 minutes. It is expected that high pH values weakens the rate of Hg^0 oxidation, e.g., from greater than 80% mercury removal at a pH of 3 to less than 10% at a pH of 11.

[096] Example 55: 50 mL of crude oil containing approximately 1,000 ppb Hg was added to a 100 mL glass tube, then mercury level was measured using LUMEX mercury

20 analyzer equipped with PYRO-915+. A pre-determined volume of 5 wt.% sodium hypochlorite solution was added to the glass tube for a final oxidant concentration of 50 ppm. The mixture was stirred for at least 10 minutes. A cloudy oil-water emulsion was formed in the test tube, indicating that oxidation took place but it would be difficult to separate the emulsion from the crude oil.

[097] Example 56: 50 mL of crude oil containing approximately 1,000 ppb Hg is added to a 100 mL glass tube, then mercury level is measured using LUMEX mercury analyzer equipped with PYRO-915+. A pre-determined volume of 5 wt. % aqueous solution of FeCl_2 is added to the glass tube for a final concentration of 50 ppm. It is expected that oxidation is to take place, but the mercury cations will remain trapped in a cloudy oil-water emulsion and that it will be difficult to separate the emulsion layer from the crude oil.

[098] Example 57: Example 56 is repeated, except that a complexing agent, e.g., KI solution at different pH (7, 5, and 3) is added to the oil-water emulsion, and the mixture is stirred up for at least 10 minutes. It is expected that the acidic KI enhances the mercury removal with the formation of soluble mercury compounds which minimizes the volume of the emulsion, resulting in separate water / crude oil layers with reduced mercury level of at least 50% in the treated crude oil, or for at least 50% of the mercuric compounds to be removed from the emulsion into the water phase. It is expected that an acidic pH of 3 or less allows at least 80% of the mercuric compounds from the interface layer into the water layer.

[099] Example 58: 50 mL of mercury vapor feed preparation containing approximately 1,100 ppb Hg is added to a number of 100 mL glass tubes, then mercury level is measured using LUMEX mercury analyzer equipped with PYRO-915+. A pre-determined volume of hydrogen peroxide (H_2O_2) is added to each tube for a final oxidant concentration of 50 ppm. The oil-water mixture is stirred up for 1 minute. Thiourea is added to 200 cm³ of HCl 2M to produce a concentration of 110 g/l. The mixture is added to the glass tube and stirred up for at least 60 minutes. Mercury extraction into the water phase is expected to be as comparable to using KI as a complexing agent, of up to 99 %, with the advantage that thioureas as a complexing agent is more economical than KI.

[0100] Example 59. To four glass bottles, the following is added: 1) a control sample of 40 g crude oil containing approximately 20,000 ppb Hg, 2) 40 g crude oil and 40 g deionized water, 3) 40 g crude oil and 40 g of 5.6-6.0 % sodium hypochlorite (bleach) solution; 4) 40 g crude oil and 40 g of 5.6-6.0 % sodium hypochlorite (bleach) solution. The samples are shaken for 2 minutes, forming oil-water emulsion in samples 2 – 4. Samples 1 – 3 are centrifuged at 90°C and 3500 RPM for 20 minutes, effecting a water – oil separation. Sample 4 is not centrifuged and left as is – still showing oil-water emulsion even after 20 minutes.

[0101] The oil and water phases from the samples 1- 3 are analyzed for mercury. It is expected that samples 1 – 2 show no mercury removal with the mercury still remaining in the crude oil. Sample 3 (using centrifuge to facilitate oil water separation) is expected to show a mercury removal rate of at least 70%. Sample 4 cannot be easily analyzed due to the oil-water emulsion.

[0102] Example 60: Sample 4 with oil-water emulsion is stirred up for 1 minute. Potassium iodide (KI) is added to the sample for a final concentration of 5,000 ppm KI. The glass bottle is shaken vigorously for 1 minute. Aliquots of both oil and water are analyzed for mercury. The sample is expected to show a mercury removal rate of at least 70% (as with sample 3), and without the need for centrifuge.

[0103] Example 61: To two 100 mL glass reactors, the following were added: a) 70 mL of crude oil containing approximately 5,000 ppb Hg and 30 mL of distilled water were added, then mercury levels in both crude oil and water samples were measured using a LUMEX mercury analyzer equipped with PYRO-915+; b) a pre-determined volume of oxidant 1% w/v gold chloride ($\text{HAuCl}_3 \cdot \text{H}_2\text{O}$) for a final oxidant concentration of $\text{HAuCl}_3 \cdot \text{H}_2\text{O}$ to mercury Hg of 20 and 50 respectively (on a mole basis). The agitators were stirred for about 4 minutes at 600 rpm. A sufficient volume of 30% sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ as a complexing agent was added to each reactor for a final concentration of $\text{Na}_2\text{S}_2\text{O}_3$ to mercury Hg of 200 and 500 respectively (on a mole basis). The agitators were stirred again. Aliquots of both oil and water samples were taken at 1.5, 3, 6, 15, and 60 minute intervals. The aliquot samples were centrifuged with mini-centrifuge for 1 min. prior to Hg analysis by LUMEX mercury analyzer. Results indicated that mercury shows up in water almost immediately (after 1.5 minutes) indicating excellent mercury removal.

[0104] Example 62: 70mL of crude oil containing 130 ppb arsenic and 30 mL of produced water were added into a Waring blender. The initial arsenic concentrations in crude oil and produced water were measured by ICP-MS. A pre-determined volume of 10% iodine (I_2) was added to oil-water mixture for a final oxidant concentration of 26 and 2 ppm respectively. The blender was started for 4 minutes. A pre-determined volume of 30% sodium thiosulfate was added to the blender cup for a final concentration complexing agent of 350 ppm. The blender was started again for 15 minutes. The oil-water mixture was poured into a glass

container and kept at 60°C for 30 minutes prior to analysis. Test results showed at least 30 – 40% of arsenic was extracted from crude oil to water.

[0105] Example 63: Example 62 was repeated, also with 30% sodium thiosulfate as the complexing agent but with a final concentration of 150 ppm. Test results also showed at least 30 – 40% of arsenic was extracted from crude oil to water.

[0106] Example 64: In a number of 100 mL glass tubes, add 50 mL of crude oil containing approximately 6,000 ppb As and 50 mL distilled water, measure arsenic level using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Add a pre-determined volume of hydrogen peroxide (H₂O₂) to each tube for a final oxidant concentration of 100 ppm. Stir the oil-water mixture for at least 5 minutes. Prepare 4 complexing agent samples including FeCl₃, AgCl, ZnCl, and SrCl₂, each with a concentration of 1.0 N are prepared. Adjust the pH of the complexing agent samples to about 4 by the addition of an acid such as HCl. Add the samples to 4 of the glass tubes and stir each for at least 60 minutes. It is expected that at up to 99% of the arsenic is removed from the crude oil and extracted into the water phase.

[0107] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention. It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural references unless expressly and unequivocally limited to one referent. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0108] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they

include equivalent structural elements with insubstantial differences from the literal languages of the claims. All citations referred herein are expressly incorporated herein by reference.

CLAIMS

1. A method for reducing a trace amount of heavy metals in a crude oil, comprising:
mixing into the crude oil an effective amount of at least an oxidizing agent selected from the group of hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, molecular halogens, ozone and combinations thereof to extract at least a portion of the heavy metals in a water oil emulsion;

separating the extracted heavy metals from the crude oil to obtain a treated crude oil having a reduced concentration of heavy metals.

2. A method for reducing a trace amount of heavy metals in a crude oil, comprising:
mixing into the crude oil an effective amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, molecular halogens, ozone and combinations thereof to extract at least a portion of the heavy metals into a water-oil emulsion;

adding an effective amount of a complexing agent to convert at least a portion of the extracted heavy metals in the water oil emulsion to soluble heavy metal compounds in a water phase; and

separating the water phase containing the soluble heavy metal compounds from the crude oil to obtain a treated crude oil having a reduced concentration of heavy metals.

3. In a method for treating a crude oil to reduce its mercury level, comprising mixing into the crude oil a water stream consisting essentially of an oxidizing agent to convert at least a portion of the mercury to mercury cations, and extracting at least a portion of the mercury cations into the water stream forming a mercury-rich wastewater, and separating the wastewater from the crude oil, leaving a treated crude oil having a reduced concentration of mercury, the improvement comprising:

adding an effective amount of a complexing agent to convert at least a portion of the mercury cations to soluble mercury compounds in a water phase prior to separating the water phase containing soluble mercury compounds from the crude oil to obtain a treated crude oil having a reduced mercury level.

4. A method for reducing a trace amount of arsenic in a crude oil, comprising:
mixing into the crude oil an effective amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, molecular halogens, ozone and combinations thereof to extract at least a portion of arsenic into a water-oil emulsion as arsenic cations, forming a mixture;

adding an effective amount of a complexing agent to the water-oil emulsion mixture to convert the extracted arsenic cations to water-soluble arsenic compounds in a water phase; and

separating the water phase containing the water-soluble arsenic compounds from the crude oil to obtain a treated crude oil having a reduced concentration of arsenic.

5. The method of any of claims 1 - 3, wherein the heavy metals comprise mercury.

6. The method of any of claims 1 - 4, wherein the effective amount of oxidizing agent for mixing into the crude oil is in a molar ratio of oxidizing agent to heavy metals of 5:1 to 20,000:1.

7. The method of any of claims 1 - 4, wherein the effective amount of oxidizing agent for mixing into the crude oil is in a molar ratio of oxidizing agent to heavy metals of 50:1 to 500:1.

8. The method any of claims 1 - 4, wherein the oxidizing agent is selected from the group of inorganic peracids and salts thereof, organic peracids and salts thereof, and mixtures thereof.

9. The method of claim 8, wherein the oxidizing agent is selected from the group of sodium perborate, potassium perborate, sodium carbonate perhydrate, potassium peroxymonosulfate, sodium peroxocarbonate, sodium peroxodicarbonate, and mixtures thereof.

10. The method of claim 9, wherein the oxidizing agent is potassium peroxymonosulfate.
11. The method of any of claims 1 - 3, wherein the treated crude oil contains less than 100 ppb heavy metals as mercury.
12. The method of any of claims 1 - 3, wherein the treated crude oil contains less than 10 ppb heavy metals as mercury.
13. The method of any of claims 1 - 4, wherein the treated crude oil contains less than 50 ppb arsenic.
14. The method of claim 13, wherein the treated crude oil contains less than 10 ppb arsenic.
15. The method of any of claims 1 - 4, for treating a crude oil having a specific gravity of at least 0.75 at 60°F.
16. The method of any of claims 1 - 2, wherein the oxidizing agent extracts heavy metals by converting the heavy metals to heavy metal cations in a water-oil emulsion.
17. The method of claim 2, wherein the water phase containing the soluble heavy metal compounds is formed by settling of oil phase and water phase in the water-oil emulsion.
18. The method of claim 2, wherein the water phase containing the soluble heavy metal compounds is formed within 20 minutes of adding the complexing agent.
19. The method of any of claims 17 - 18, wherein the water phase containing the soluble heavy metal compounds is formed without using mechanical or rotating means.

20. The method of claim 1, further comprising adding a complexing agent to the water-oil emulsion.
21. The method of any of claims 2-4 and 20, wherein the complexing agent is a metal halide.
22. The method of claim 21, wherein the complexing agent is KI.
23. The method of claim 2, wherein the addition of the complexing agent results in at least 50 mole % of the heavy metals being extracted from the water-oil emulsion into the water phase as soluble heavy metal compounds.
24. The method of claim 2, wherein the addition of the complexing agent results in at least 80% of the heavy metal being extracted into the water phase as soluble heavy metal compounds.
25. The method of claim 2, wherein the formation of soluble heavy metal compounds in the water phase occurs within 15 minutes of adding the complexing agent.
26. The method of any of claims 2, 3, 4, and 20, wherein the complexing agent is selected from the group of ethylenediamine, propylenediamine, triaminotriethylamine, diethylenetriamine, triethylenetetramine (TRIEN), tetra-2-aminoethylethlenediamine, tetraethylenepentamine (TETREN), sulfides, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, and alkaline earth metal dithionites, and mixtures thereof.
27. A method for reducing a trace amount of mercury in a crude oil, comprising:
mixing into the crude oil an effective amount of an oxidizing agent selected from the group of sodium perborate, potassium perborate, sodium carbonate perhydrate, potassium peroxymonosulfate, sodium peroxocarbonate, sodium peroxodicarbonate, and mixtures thereof to extract at least a portion of the mercury into a water-oil emulsion;

separating a water phase containing the extracted mercury from the crude oil to obtain a treated crude oil having a reduced concentration of mercury.

28. The method of claim 27, wherein the oxidizing agent is potassium peroxymonosulfate.

29. The method of any of claims 27 - 28, wherein the water phase containing the extracted mercury is formed by settling of oil phase and water phase in the water-oil emulsion.

30. The method of claim 27, wherein the effective amount of oxidizing agent is in a molar ratio of oxidizing agent to mercury of 5:1 to 20,000:1.

31. The method of claim 27, wherein the effective amount of oxidizing agent is in a molar ratio of oxidizing agent to mercury of 50:1 to 500:1.

32. The method of claim 27, wherein the effective amount of oxidizing agent is mixed to the crude oil in an amount of water, with a volume ratio of water to crude oil ranging from 0.1:1 to 1:1.

33. The method of claim 27, wherein the water phase containing the extracted mercury from the crude oil is injected back to a reservoir.

34. A method for reducing a trace amount of mercury in a crude oil, comprising:
mixing into the crude oil an amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, ozone and combinations thereof to extract at least a portion of the mercury into a water-oil emulsion;

adding an amount of a complexing agent to convert the extracted mercury to soluble mercury compounds in a water phase; and

separating the water phase containing the soluble mercury compounds from the crude oil, leaving a treated crude oil having a reduced concentration of mercury.

35. The method of claim 34, for treating a crude oil having a specific gravity of at least 0.75 at 60°F.

36. The method of any of claims 34 - 35, wherein the complexing agent is a metal halide.

37. The method of any of claims 34 - 35, wherein the oxidizing agent is an oxygen containing compound selected from the group of oxyhalites, hydroperoxides, and organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, ozone, and combinations thereof.

38. The method of any of claims 34 - 35, wherein the oxidizing agent is selected from the group of sodium perborate, potassium perborate, sodium carbonate perhydrate, potassium peroxymonosulfate, sodium peroxocarbonate, sodium peroxodicarbonate, and mixtures thereof.

39. The method of any of claims 34 - 35, wherein the oxidizing agent is an oxyhalite.

40. The method of any of claims 34 - 35, wherein the oxidizing agent is NaOCl.

41. The method of any of claims 34 - 35, wherein the oxidizing agent is a ferrous halide.

42. The method of any of claims 34 - 35, wherein the oxidizing agent is FeCl₂.

43. The method of any of claims 34 - 35, wherein the oxidizing agent is potassium peroxymonosulfate.

44. The method of any of claims 34 - 35, wherein the addition of the complexing agent converts at least 50 mole % of the extracted mercury to soluble mercury compounds.

45. The method of any of claims 34 - 35, wherein the addition of the complexing agent converts at least 80 mole % of the extracted mercury to soluble mercury compounds.

46. The method of any of claims 34 - 35, wherein the complexing agent is a metal halide selected from the group of K, Li, Na, Ca, Fe, Ni, and Zn.

47. The method of any of claims 34 - 35, wherein the complexing agent is selected from the group of sulfides, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, alkaline earth metal dithionites, alkali metal peroxomonosulfate compounds, and mixtures thereof.

48. The method of any of claims 34 - 35, wherein the complexing agent is selected from the group of ethylenediamine, propylenediamine, triaminotriethylamine, diethylenetriamine, triethylenetetramine (TRIEN), tetra-2-aminoethylethylenediamine, tetraethylenepentamine (TETREN), sulfides, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, and alkaline earth metal dithionites, and mixtures thereof.

49. The method of any of claims 34 - 35, wherein the complexing agent is KI.

50. The method of any of claims 34 - 35, wherein the treated crude oil contains less than 50 ppb heavy metals.

51. The method of any of claims 34 - 35, wherein the separation of the water phase containing soluble heavy metal compounds from the crude oil is without using mechanical or rotating means.

52. The method of any of claims 34 - 35, wherein the formation of soluble metal compounds in the water phase occurs 15 minutes after the addition of the complexing agent.

53. The method of any of claims 34 - 35, wherein at least 50% of the heavy metal are extracted and converted to soluble heavy metal compounds in the water phase.

54. In a method for treating a crude oil to reduce its mercury level, comprising adding to the crude oil a water stream consisting essentially of an oxidizing agent selected from the group of elemental halogens, halogen containing compounds, ozone, oxyhalites, hydroperoxides, and organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, to convert at least a portion of the mercury to mercury cations, and extracting at least a portion of the mercury cations into the water stream forming a mercury-rich wastewater, and separating the wastewater from the crude oil, leaving a treated crude oil having a reduced concentration of mercury, the improvement comprising:

adding a complexing agent to convert at least a portion of the mercury cations to soluble mercury compounds in a water phase prior to separating the water phase containing soluble mercury compounds from the crude oil, leaving a treated crude oil having a reduced mercury level.

55. The method of claim 54, wherein the oxidizing agent is an oxyhalite.

56. The method of claim 55, wherein the oxidizing agent is selected from NaOCl and $\text{Ca}(\text{OCl})_2$ and mixtures thereof.

57. The method of claim 56, wherein the oxidizing agent is NaOCl.

58. The method of claim 54, wherein the oxidizing agent is ferrous halide.

59. The method of claim 54, wherein the oxidizing agent is sodium hypochlorite and the water stream comprising sodium hypochlorite has a pH of less than 6.

60. The method of claim 54, wherein the water stream has a pH of less than 5.

61. The method of claim 54, wherein the water stream has a pH of less than 3.

62. The method of claim 54, wherein the addition of the complexing agent results in at least 50 mole % of the mercury cations being converted to soluble mercury compounds.

63. The method of claim 54, wherein the addition of the complexing agent results in at least 80% of the mercury cations being converted to soluble mercury compounds.

64. The method of claim 54, wherein the complexing agent is a metal halide selected from the group of K, Na, Li, Ca, Fe, Ni, and Zn.

65. The method of claim 54, wherein the complexing agent is selected from the group of sulfides, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, alkaline earth metal dithionites, alkali metal peroxomonosulfate compounds, and mixtures thereof.

66. The method of claim 54, wherein the complexing agent is selected from the group of ethylenediamine, propylenediamine, triaminotriethylamine, diethylenetriamine, triethylenetetramine (TRIEN), tetra-2-aminoethylethlenediamine, tetraethylenepentamine (TETREN), and mixtures thereof.

67. The method of claim 54, wherein the complexing agent is an inorganic sulfur compound selected from the group of sulfides, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, and alkaline earth metal dithionites, and mixtures thereof.

68. The method of claim 54, wherein the treated crude oil contains less than 50 ppb mercury.

69. The method of claim 54, wherein the formation of a water phase containing soluble mercury compounds is carried out in a contact zone comprising at least one of a packed

tower, a bubble tray column, a stirred mixing tank, a fiber contactor, and a rotating disc contactor.

70. The method of claim 54, wherein the formation of a water phase containing soluble mercury compounds occurs within 15 minutes of the addition of water stream consisting essentially of an oxidizing agent to the crude oil.

71. The method of claim 54, wherein at least 50% of the mercury cations are converted to soluble mercury compounds.

72. The method of claim 54, wherein the crude oil is contacted with the water stream consisting essentially of an oxidizing agent in a contact zone comprising fibers, forming an admixture of mercury-rich wastewater that flows over and along the fibers.

73. A method for reducing a trace amount of arsenic in a crude oil, comprising:
mixing into the crude oil an amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, ozone and combinations thereof to extract at least a portion of arsenic into a water-oil emulsion as arsenic cations, forming a mixture;

adding a sufficient amount of acid to the water-oil emulsion mixture for a pH of 5.5 or less

adding an effective amount of a complexing agent to the water-oil emulsion mixture to convert the arsenic cations to soluble arsenic compounds in a water phase; and

separating the water phase containing the soluble arsenic compounds from the crude oil, leaving a treated crude oil having a reduced concentration of arsenic.

74. The method of claim 73, wherein the acid is added to the crude oil at any time prior to the addition of the oxidizing agent, concurrent with the addition of the oxidizing agent, prior to the addition of the complexing agent, or concurrent with the addition of the complexing agent.

75. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding a complexing agent selected from metal halides, sulfur compounds, and mixtures thereof.

76. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding at least a metal halide.

77. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding at least a metal halide selected from halides of Li, Na, K, Ca, Cu, Ni, Fe, Zn, Ba, Sr, Ag, and combinations thereof.

78. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding ferric chloride or cupric chloride.

79. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding at least a sulfur compound selected from the group of sulfides, thiosulfates, dithionites, and mixtures thereof.

80. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding at least a complexing agent selected from the group of sodium polysulfide, ammonium thiosulfate, alkali metal thiosulfates, alkaline earth metal thiosulfates, iron thiosulfates, alkali metal dithionites, alkaline earth metal dithionites, and mixtures thereof.

81. The method of any of claims 73 - 74, wherein adding an amount of a complexing agent comprises adding at least a complexing agent selected from the group of potassium sulfide, sodium polysulfide, sodium thiosulfate, potassium peroxomonosulfate, and mixtures thereof.

82. The method of any of claims 73 - 74, wherein mixing into the crude oil an amount of at least an oxidizing agent comprises adding at least an oxidizing agent selected from the group of molecular halogen, iodine (I₂), oxyhalites, hypochlorites, and mixtures thereof.

83. The method of any of claims 73 - 74, wherein the addition of the complexing agent occurs either before, simultaneously with, or after the addition of the oxidizing agent to the crude oil.

84. The method of any of claims 73 - 74, wherein the addition of the complexing agent results in at least 50 mole % of the arsenic cations being converted to soluble arsenic compounds.

85. The method of any of claims 73 - 74, wherein the addition of the complexing agent results in at least 80% of the arsenic cations being converted to soluble mercury compounds.

86. The method of claim 1, wherein the crude oil feed is mixed with the oxidizing agent in a contact zone comprising at least one of a packed tower, a bubble tray column, a stirred mixing tank, a fiber contactor, and a rotating disc contactor.

87. The method of claim 1, wherein the treated crude oil contains less than 50 ppb arsenic.

88. The method of claim 1, wherein the formation of a water phase containing soluble arsenic compounds occurs within 15 minutes of the addition of the oxidizing agent to the crude oil.

89. A method for reducing a trace amount of arsenic in a crude oil, comprising:
mixing into the crude oil an amount of at least an oxidizing agent selected from the group of oxyhalites, hydroperoxides, organic peroxides, inorganic peracids and salts thereof, organic peracids and salts thereof, ozone and combinations thereof to extract at least a portion of arsenic into a water-oil emulsion as arsenic cations, forming a mixture;
adding a sufficient amount of acid for the water-oil emulsion to have a pH of 5.5 or less;

adding an amount of a complexing agent selected from the group of metal halides and sulfur compounds to the water-oil emulsion mixture to convert the arsenic cations as As^{5+} and As^{3+} to soluble arsenic compounds in a water phase; and

separating the water phase containing the soluble arsenic compounds from the crude oil, leaving a treated crude oil having a reduced concentration of arsenic.

90. A method for reducing a trace amount of arsenic in a crude oil, comprising:
contacting the crude oil with a water stream containing an oxidizing agent to form a water-oil emulsion, the water stream has a pH of 6 or less;
adding an amount of a complexing agent to the water-oil emulsion to form soluble arsenic compounds in a water phase; and
separating the water phase containing the soluble arsenic compounds from the crude oil, leaving a treated crude oil having a reduced concentration of arsenic.

91. The method of claim 20, wherein the crude oil is contacted with the treatment solution in a contact zone comprising fibers and wherein the contact of the crude oil with the treatment solution forms an admixture containing a crude oil and water that flows over and along the fibers.