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DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention relates generally to methods of removing scale formation on surfaces, especially in subsea environments.

BACKGROUND OF THE INVENTION

[0002] Scale formation typically involves the precipitation and deposition of dense materials on surfaces made of metal and other materials. Scale formation may occur when inorganic mineral salts (including, for example, calcium carbonates, calcium sulfates, calcium oxalates and barium sulfates) precipitate from liquids and deposit on the surfaces of a system (including, boilers, evaporators, reactors, cooling water systems, heat exchangers, pipes, filter cloths, reverse osmosis membrane surfaces, oil wells, and desalination evaporators, among others).

[0003] Scale formation may cause a number of operation problems, including, but not limited to, plugging of equipment, pressure loss, increased utility costs, reduced heat exchange capacity, corrosion, lost production due to downtime, and downgraded products resulting from insufficient feeds. Scaling equipment may occur in a variety of industries. For example, in the petroleum industry, scale deposition costs millions of dollars every year and is one of the leading causes in production decline worldwide. Scale deposition is recognized as one of the top production problems in regions that are prone to scale, such as the North Sea, the United States and Canada.

[0004] Scale can be deposited in various equipment along various water paths, including, but not limited to, piping, injectors, reservoirs and surface equipment. Scale formation at oil-producing wells also may eventually result in lower oil yields and in well failure. Scale found in oil fields may form by direct precipitation from naturally-occurring water in reservoir rocks, or as a result of water becoming over-saturated with scale-forming species when two incompatible water streams combine. Furthermore, scale may also form when an oil or gas well produces water, or alternatively, when water injection is used to enhance recovery.

[0005] Natural water in oil fields may contain dissolved substances acquired through contact with mineral phases in the natural environment. Deep subsurface water may be enriched in soluble ions through alteration and dissolution of minerals. The water in sandstone reservoirs or geological formation water that have contact with sea water may contain abundant scale-forming ions, including but not limited to Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Na^{+} , K^{+} , CO_3^{2-} , SO_4^{2-} , and Cl^{-} . Sea water is also generally rich in scale-forming ions, including ions that are by-product of

marine life and water evaporation. In off-shore oil production, the formation of sulfate scales may occur when sea water, which may be rich with SO_4^{2-} and formation water containing high concentrations of barium and calcium are mixed.

[0006] Furthermore, oil field scale may form when the state of any natural fluid is altered, such that the solubility limit for one or more components is exceeded. Temperature and/or pressure changes, pH shift, out-gassing, and/or the contact with incompatible water may cause the water to become oversaturated with scale-prone species and lead to the formation of scale.

[0007] Barium and strontium sulfate scales may, for example, be particularly troublesome when sulfate-rich seawater is used as an injection fluid in oil wells whose formation water is rich in barium ions. Barium and strontium sulfate generally form very hard, very insoluble scales that can be difficult to prevent by conventional chemical-based scale inhibition techniques. In some instances, this can be particularly troublesome, as barium and strontium sulfates can co-precipitate with radium sulfate, making the scale mildly radioactive. Dissolution of sulfate scales in piping is generally difficult to remove, possibly requiring one or more of high pH, long contact times, heat, high pressure, and high velocity circulation.

[0008] Barium sulfate, as well as other inorganic supersaturated salts, may precipitate onto the various formations to form a scale, thereby clogging the formations and restricting the recovery of oil from a reservoir. The insoluble salts may also precipitate onto production tubing surfaces and associated extraction equipment that may, for instance, limit productivity, limit production efficiency, and compromise safety. Certain oil-containing formation waters are known to contain high barium concentrations of 400 ppm and higher. Since barium sulfate forms a particularly insoluble salt, the solubility of which declines rapidly with temperature, it can be difficult to inhibit scale formation and to prevent plugging of the oil formation and topside processes and safety equipment.

[0009] Scale inhibitors can be used in production wells to prevent scaling in the formation and/or in the production lines down in the hole and at the surface. Scale buildup decreases permeability of the formation, reduces well productivity and shortens the lifetime of production equipment. Various scale inhibitors are known and include chelating agents, phosphates, phosphonates (organophosphates), polycarbonates, and components of polymers, have been developed to inhibit or reduce the formation of inorganic scales, as described for example in U.S. Pat. No. 7,943,058 to Hills et al., U.S. Pat. No. 7,491,682 to Gupta et al., and U.S. Pat. Pub. No. 2011/0089115 to Lu. These scale inhibitors typically work by one of the following mechanisms: precipitation threshold inhibition, dispersion, and crystal distortion/modification.

[0010] Various methods are also known for introducing these scale inhibitors into production wells. For instance, a liquid inhibitor may be forced into the formation by application of hydraulic pressure from the surface which forces the inhibitor into the targeted zone. Alternatively, the delivery method may consist of placing a solid inhibitor into the producing formation in conjunction with a hydraulic fracturing operation.

[0011] Notwithstanding the use of scale inhibitors, once scale has deposited or formed on surfaces, it is necessary that such scale deposits be removed so that the equipment can continue to operate properly. However, strict environmental regulations for the North Sea, as well as many other areas, have required oil field service companies to formulate their products so that their effect on the marine environment is minimized and the components of the products comprises only approved components.

[0012] Using acids to dissolve calcium and other scale deposits in subsea environments is known. Calcium deposits build up on subsea components and eventually interfere with the operation of the components, including connectors and mechanical external valve components, from functioning. High pressure water jets and mild water jets are commonly used to clean equipment. The strength of the acid is also typically kept low to avoid corrosion and degradation of metallic and elastomeric materials on the subsea equipment and a constant flow of acid is required to maintain an acidic environment around the area being cleaned.

[0013] For use in the North Sea, chemical products are categorized into one of four categories based on the ecotoxicological properties of its components. The four categories, each designated by color, are as follows:

1. (1) Black - forbidden to use or discharge;
2. (2) Red - high priority for phasing out via substitution;
3. (3) Yellow - environmentally acceptable; and
4. (4) Green - only for chemicals listed on the OSPAR Convention for the Protection of the Marine Environment of the North East Atlantic PLONOR (Pose Little Or No Risk) database.

[0014] Thus, for oil and gas drilling operations in the North Sea, companies are required to phase out the use of Black and Red components in their products and to use only chemicals which are entirely comprised of "Green" components in any new products.

[0015] Thus, there remains a need in the art for an improved composition for removing scale deposits from surfaces, especially in subsea environments that contains at least substantially only chemicals listed on the OSPAR Convention for the Protection of the Marine Environment of the North East Atlantic PLONOR (Pose Little Or No Risk) database.

[0016] US-A-2011/0190173 discloses a treatment fluid that comprises a phosphorus component useful for inhibiting metal corrosion in acidic environments, and the treatment fluid comprises an aqueous base fluid, a weak acid or salt thereof, and a phosphorus component, which is introduced into a subterranean formation.

[0017] US-A-2758949 discloses alkali metal phosphate coating solutions for forming phosphate coatings on metal surfaces, the solutions comprising an aqueous acidic solution of

an alkali metal phosphate, an oxidising agent and a metallic ion sequestering agent selected from polyphosphates and acetic amino acids and the alkali metal salts thereof.

[0018] US-A-3400078 discloses a scale inhibitor for sulfate and carbonate scale which comprises water, potassium hydroxide, carboxymethyl cellulose, which has been oxidised in the presence of the potassium hydroxide, and potassium pyrophosphate.

SUMMARY OF THE INVENTION

[0019] It is an object of the present invention to provide an improved method of removing scale deposits containing at least substantially only chemicals listed on the OSPAR Convention for the Protection of the Marine Environment of the North East Atlantic PLONOR database.

[0020] It is still another object of the present invention to provide an improved method that can be used without requiring a shroud.

[0021] It is still another object of the present invention to provide an improved method that uses a composition that is capable of dissolving away in seawater.

[0022] It is yet another object of the present invention to provide an improved method of removing scale on or in subsea equipment.

[0023] The present invention provides a method of removing scale deposits on a surface according to claim 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] The present invention relates generally to a method of removing scale deposits on a surface using an aqueous composition for removing scale deposits, the aqueous composition comprising:

1. a) an alkali metal phosphate compound; and
2. b) acetic acid.

[0025] Scale may form from a scale-forming fluid, or scale may form from the interaction of scaling compounds present in a scale-forming fluid. The scale-forming fluid is seawater in the method of the present invention.

[0026] The scale deposits may include any substance present in the scale-forming fluid that may participate in or cause the formation of scale during the administration of a given process.

In one embodiment, the at least one scaling compound is an inorganic salt. Exemplary inorganic salts include, but are not limited to, calcium carbonate, calcium sulfate, calcium oxalate, magnesium carbonate, and barium sulfate. In another embodiment, the at least one scaling compound is at least one scale-forming ion. Exemplary scale-forming ions include, but are not limited to, Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Na^{+} , K^{+} , OH^{-} , NO_3^{-} , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , HPO_4^{2-} , $\text{H}_2\text{PO}_4^{-}$, $\text{C}_2\text{O}_4^{2-}$, SiO_3^{2-} , F^{-} , and Cl^{-} .

[0027] The acetic acid typically comprises a 50% v/v solution of acetic acid. The acetic acid is present in the aqueous composition at a concentration of between 25 and 500 grams/liter, preferably at a concentration of between 100 and 200 grams/liter.

[0028] The alkali metal phosphate compound is preferably selected from those potassium phosphate compounds that are on the PLONOR list of selected chemicals. For example, the potassium phosphate compounds may be selected from the group consisting of potassium phosphate dibasic, potassium phosphate tribasic, potassium phosphate monobasic, phosphoric acid potassium salt (2:1), and combinations of one or more of the foregoing. In a preferred embodiment the potassium phosphate compound comprises phosphoric acid potassium salt (2:1). One additional advantage of using potassium phosphate compounds in the compositions of the present invention is that the composition becomes essentially self-preserving without the need for additional preservatives, which are typically not on the PLONOR list of selected chemicals. The preferred potassium phosphate compound is potassium dihydrogen phosphate.

[0029] The alkali metal phosphate compound is present in the composition at a concentration of between 100 and 400 grams/liter, preferably at a concentration of between 200 and 350 grams/liter.

[0030] The aqueous composition is thickened by the addition of a cellulosic thickener. The use of a cellulosic thickener enables the material to be pumped into voids or on the surface of a piece of equipment as a shear thinned fluid, which increases in viscosity on location. Once applied, sea currents have a much reduced effect in decreasing contact time without the need for a shroud. The cellulosic thickener is preferably a cellulose ether. More particularly, the cellulosic thickener may comprise a cellulose ether selected from the group consisting of ethyl cellulose, hydroxyethyl cellulose, methyl cellulose hydroxypropyl cellulose, ethyl hydroxyethyl cellulose, methyl hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified ethyl hydroxyethyl cellulose, hydrophobically modified methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, carboxymethyl hydroxyethyl cellulose, and combinations of one or more of the foregoing. In a preferred embodiment, the cellulosic thickener comprises ethyl cellulose, hydroxyethyl cellulose, or a combination thereof, both of which are on the PLONOR list of acceptable chemicals. Hydroxyethyl cellulose is especially preferred.

[0031] The cellulosic thickener is present in the composition at a concentration of between 0.5

and 25 grams/liter, preferably at a concentration of between 1.0 and 10 grams/liter.

[0032] In addition, a water miscible glycol solvent is added to the composition of the invention for lower pour point stability or to adjust the density of the product so that the product can float up into cap areas or down into well areas or remain buoyant around vertical structures. In a preferred embodiment, the solvent comprises monoethylene glycol (MEG), which is also on the PLONOR list of acceptable chemicals. Other similar solvents which are on the PLONOR list of acceptable chemicals, including glycerol may also be used in the practice of the invention. The exact concentrations of the water miscible solvents may depend on the desired thermal conductivities and the type of water miscible solvents.

[0033] The additional solvent is present in the composition at a concentration of between 50 and 500 grams/liter, preferably at a concentration of between 100 and 250 grams/liter.

[0034] The product described herein will also eventually dissolve away into seawater.

[0035] The optimum activity level of the acid and retention time to give good decalcification performing without destroying subsea equipment materials is determined by the degree of contamination, temperature, and the type of product application method chosen. This will vary between applications.

[0036] Other additives including yellow metal inhibitors, surfactants, chelating agents, acids, solvents, leak tracing dye and/or biocide may also be added to the composition of the invention. However, the use of these additives may compromise the PLONOR status of the composition if such additives are not on the PLONOR list of acceptable chemicals. It is preferable for the composition to include acids other than acetic acid. Preferable secondary acids include phosphoric acid (especially if partially neutralized), PEK acid (CAS No. 14887-42-4), formic acid and citric acid.

[0037] Surfactants such as anionic, nonionic, cationic and amphoteric surfactants may also be used. Suitable anionic surfactants include, but are not necessarily limited to, alkyl sulfates, sulfonates, sulfosuccinates, phosphates, alkyl benzene sulfonates and the like. Other suitable anionic surfactants include, but are not necessarily limited to, fatty carboxylates, alkyl sarcosinates, alkyl phosphates, alkyl sulfonates, alkyl sulfates and the like and mixtures thereof. The alkyl chain length on the surfactants may range from 8 to 24 carbon atoms.

[0038] Suitable nonionic surfactants include, but are not necessarily limited to, alkoxyated alcohols or ethers, alkyl ethoxylates, alkylamido ethoxylates, alkylamine ethoxylates, alkyl glucosides, alkoxyated carboxylic acids, sorbitan derivatives, again where the alkyl chain length may range from 8 to 24 carbon atoms. More specific examples include, but are not necessarily limited to nonylphenol ethoxylate-3, alkyl ethoxylates-3, oleyl carboxylic diethylamides, and the like and mixtures thereof.

[0039] Suitable surfactants and mixtures thereof include, but are not necessarily limited to,

cationic surfactants such as, monoalkyl quaternary amines, such as cocotrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, soyatrimethylammonium chloride, behentrimethylammonium chloride, and the like and mixtures thereof. Other suitable cationic surfactants that may be useful include, but are not necessarily limited to, dialkylquarternary amines such as dicetyldimethylammonium chloride, dicocodimethylammonium chloride, distearyldimethylammonium chloride, and the like and mixtures thereof.

[0040] In the method of the present invention, the surface is an area of a well in a seawater environment, such as a cap area or a well area. In addition, by using only ingredients that are on the PLONOR list of selected chemicals, the aqueous composition is capable of dissolving away into seawater and poses little or no risk to the environment.

[0041] The aqueous composition preferably has a viscosity of between 2^{cs} and 5^{cs} at 40°C, as measured in centistokes (cs).

[0042] The aqueous composition has a density of between 1.1 g/cm³ and 1.2 g/cm³.

[0043] The retention time, i.e., the time that the surface is contacted with the aqueous composition, is typically between 20 and 120 minutes, more preferably between 30 and 60 minutes, depending on temperature and the type of application method.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- [US7943058B](#) **[0009]**
- [US7491682B](#) **[0009]**
- [US20110089115A](#) **[0009]**
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Non-patent literature cited in the description

- CHEMICAL ABSTRACTS, 14887-42-4 [0036]

PATENTKRAV

1. Fremgangsmåde til fjernelse af aflejringer af uorganisk materiale på en overflade, hvor overfladen er et område af en brønd i et havvandsmiljø, hvilken
5 fremgangsmåde omfatter trinnene med:
 - a) at bringe overfladen i kontakt med en vandig sammensætning, som er i stand til at opløses i havvand, idet den vandige sammensætning har en densitet på mellem 1,1 g/cm³ og 1,2 g/cm³ og omfatter:
 - i) en alkalimetalphosphatforbindelse, hvor alkalimetalphosphatforbindelsen er
10 til stede i sammensætningen i en koncentration på mellem 100 og 400 gram/liter,
 - ii) eddikesyre, hvor eddikesyren er til stede i sammensætningen i en koncentration på mellem 25 og 500 gram/liter,
 - iii) et celluloseholdigt fortykkelsesmiddel, hvor det celluloseholdige fortykkelsesmiddel er til stede i sammensætningen i en koncentration på mellem
15 0,5 og 25 gram/liter,
 - iv) et vandblandbart glycol-opløsningsmiddel, hvor det vandblandbare glycol-opløsningsmiddel er til stede i sammensætningen i en koncentration på mellem 50 og 500 gram/liter, og
 - b) opretholdelse af kontakt mellem overfladen og den vandige
20 sammensætning i et tidsrum, der er egnet til at forårsage, at aflejringerne af uorganisk materiale på overfladen adskilles fra overfladen.
2. Fremgangsmåde ifølge krav 1, hvor overfladen omfatter et dækselområde, eller hvor overfladen bringes i kontakt med den vandige sammensætning i et tidsrum på 30 til 60 minutter.
- 25 3. Fremgangsmåde ifølge krav 1, hvor den vandige sammensætning har en viskositet på mellem omkring 2 ^{CS} og omkring 5 ^{CS} ved 40 °C.
4. Fremgangsmåde ifølge krav 2, hvor den vandige sammensætning synker ned til den overflade, der bringes i kontakt med den vandige sammensætning.
5. Fremgangsmåde ifølge krav 1, hvor den vandige sammensætning
30 endvidere omfatter en sekundær syre, der er udvalgt fra gruppen bestående af phosphorsyre, delvis neutraliseret phosphorsyre, PEK-syre, myresyre og citronsyre.

6. Fremgangsmåde ifølge krav 1, hvor alkalimetalphosphatforbindelsen er udvalgt fra gruppen bestående af dibasisk kaliumphosphat, tribasisk kaliumphosphat, monobasisk kaliumphosphat, phosphorsyre kaliumsalt (2:1) og kombinationer af en eller flere af de foregående.
- 5 7. Fremgangsmåde ifølge krav 1, hvor alkalimetalphosphatforbindelsen er til stede i sammensætningen i en koncentration på mellem 200 og 350 gram/liter.
8. Fremgangsmåde ifølge krav 1, hvor eddikesyren omfatter en 50 % (v/v) opløsning af eddikesyre.
9. Fremgangsmåde ifølge krav 1, hvor eddikesyren er til stede i
10 sammensætningen i en koncentration på mellem 100 og 200 gram/liter.
10. Fremgangsmåde ifølge krav 1, hvor det celluloseholdige fortykkelsesmiddel er til stede i sammensætningen i en koncentration på mellem 1 og 10 gram/liter.
11. Fremgangsmåde ifølge krav 1, hvor det celluloseholdige
fortykkelsesmiddel er udvalgt fra gruppen bestående af ethylcellulose,
15 hydroxyethylcellulose, methylcellulose hydroxypropylcellulose,
ethylhydroxyethylcellulose, methylhydroxyethylcellulose, hydrofobisk modificeret
hydroxyethylcellulose, hydrofobisk modificeret ethylhydroxyethylcellulose,
hydrofobisk modificeret methylhydroxyethylcellulose,
methylhydroxypropylcellulose, carboxymethylhydroxyethylcellulose og
20 kombinationer af en eller flere af de foregående.
12. Fremgangsmåde ifølge krav 1, hvor det vandblandbare glycol-opløsningsmiddel omfatter monoethylenglycol.
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