



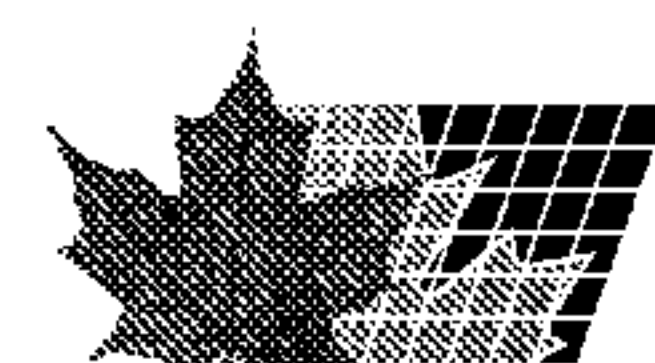
(22) Date de dépôt/Filing Date: 2010/07/02
(41) Mise à la disp. pub./Open to Public Insp.: 2011/01/02
(45) Date de délivrance/Issue Date: 2014/02/04
(30) Priorité/Priority: 2009/07/02 (US12/497,399)

(51) Cl.Int./Int.Cl. *C23F 14/02* (2006.01),
B08B 17/02 (2006.01)
(72) Inventeurs/Inventors:
FALANA, OLUSEGUN MATTHEW, US;
SHAH, KHALID ALI, CA
(73) Propriétaire/Owner:
CLEARWATER INTERNATIONAL LLC, US
(74) Agent: MARKS & CLERK

(54) Titre : COMPOSITIONS ANTI-INCRUSTANTES DANS L'EAU, SANS DANGER POUR L'ENVIRONNEMENT, ET
PROCEDE DE PREPARATION ET METHODE D'UTILISATION
(54) Title: ENVIRONMENTALLY BENIGN WATER SCALE INHIBITOR COMPOSITIONS AND METHOD FOR MAKING
AND USING SAME

(57) **Abrégé/Abstract:**

Scale inhibition compositions and methods for use are disclose, where the composition including one or a plurality chelating agents, one or a plurality dispersing agents, one or a plurality of oxygen scavenging agents including one sugar alcohol or a plurality of sugar alcohols, and pH adjusted to a pH greater than about 9.



ABSTRACT

[0020] Scale inhibition compositions and methods for use are disclose, where the composition including one or a plurality chelating agents, one or a plurality dispersing agents, one or a plurality of oxygen scavenging agents including one sugar alcohol or a plurality of sugar alcohols, and pH adjusted to a pH greater than about 9.

TITLE: ENVIRONMENTALLY BENIGN WATER SCALE INHIBITOR COMPOSITIONS AND METHOD FOR MAKING AND USING SAME

INVENTOR: Olusegun Matthew Falana and Ali Shah

ASSIGNEE: CLEARWATER INTERNATIONAL, LLC, a Delaware Corporation

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] Embodiments of the present invention relate to composition for use in drilling, completing and fracturing formations including an environmentally benign scale inhibitor.

[0002] More particularly, embodiments of the present invention relate to composition for use in drilling, completing and fracturing formations, where the composition includes an effective of an environmentally benign water scale inhibitor.

2. Description of the Related Art

[0003] Historically, several scale inhibitors have been developed for water boilers, heat exchangers and similar systems. Generally, the choice of controlling scale is dependent on water chemistry and equipment. Thus, in some systems use of chemicals (antiscalants) might be combined with mechanical means to control scale formation. While mechanical control means include filtration, sedimentation filtration and clarification (coagulation and flocculation); scales can also be controlled chemically using dispersants such as polyphosphates, phosphonates, synthetic polymers and their blends. See, e.g., U.S. Pat. Nos 7,087,189 and 5,024,783. Though polyphosphates have low toxicity to the environment (Zahid Amjhad, NACE-96-230), orthophosphates that are toxic to algae are easily formed at proper pH, temperature, polyphosphate concentration and water chemistry.

[0004] Although scale inhibitors, either alone or in combination with mechanical scale reduction means are known in the art, there is still a need in the art of scale inhibitors operable in aqueous environments that are environmentally benign and yet effective and do not suffer from the negative environmental problems associated with the use of polyphosphates and phosphonates based scale inhibitors or antiscalants.

SUMMARY OF THE INVENTION

[0005]Embodiments of the present invention provide an environmentally benign and economical

scale inhibiting composition for boilers or other equipment in contact with water containing scale forming contaminants. The composition comprises a blend of one or a plurality chelating agents, one or a plurality dispersing agents, and one or a plurality of oxygen scavenging agents, pH adjusted to a pH greater than about 9. The blend can be diluted in water. Thus, the blend can be used neat or in an aqueous dilution down to about 20 wt.%. In certain embodiments, the blend is diluted in water at a concentration between about 60 wt.% to about 20 wt.%. In certain embodiments, the blend is diluted in water at a concentration between about 50 wt.% to about 20 wt.%. In certain embodiments, the blend is diluted in water at a concentration between about 40 wt.% to about 20 wt.%. In certain embodiments, the blend is diluted in water at a concentration between about 50 wt.% to about 30 wt.%. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 1500 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 1250 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 1000 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 750 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 500 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration less than or equal to 250 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 50 ppm and 5000 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 100 ppm and 2500 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 150 ppm and 2000 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 200 ppm and 2000 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 200 ppm and 1000 ppm. In certain embodiment, the blend is present in a solution to be treated in concentration is between about 100 ppm and 500 ppm.

[0006] Embodiments of the present invention provide methods for treating a fluid including scale forming contaminants in contact with a surface upon which a scale deposit can form including adding to the fluid an effective amount of a scale inhibiting composition of this invention, where the amount is sufficient to reduce or prevent scale deposits on the surfaces.

[0007] Embodiments of the present invention provide methods for treating a fluid including scale forming contaminants in contact with a surface upon which a scale deposit can form including

continuously, semi-continuously, periodically and/or intermittently adding to the fluid an effective amount of a scale inhibiting composition of this invention, where the amount is sufficient to reduce or prevent scale deposits on the surfaces.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The inventors have found that an environmental benign antiscalant or scale inhibiting composition can be formulated for use in aqueous environments contaminated with scale forming salts such as calcium sulfate, calcium carbonate, iron and magnesium oxides or hydroxides or the like. The scale inhibiting composition includes a chelating agent, a dispersant, an oxygen scavenger and a base, where the base is used to adjust the pH of the composition, but no additional base is required during the use of the composition. Each component of the composition is biodegradable and benign to the environment. Not only is the composition effective and efficient at low concentrations, like polyphosphate inhibitors, it is uniquely more economical than the phosphate or phosphonate inhibitors or other competitive products in the market. A water solution of this composition was found to be stable to temperature up to -15°F without use of any pour point depressants. Unlike most known water scale inhibitors, this novel formulation precludes use of inorganic bases for pH adjustment during use, thereby eliminating handling of hazardous astringents and reducing chemical consumption and the need for additional equipment.

[0009] The inventors have found that a composition of this invention designated S11, when added to a fluid including calcium and magnesium scale forming contaminants at 0.5 wt.% of a 35.1 wt.% solution of the composition corresponding to a 17.55 ppm treatment offered complete inhibition of calcium or magnesium scale deposit, where the calcium and magnesium concentrations were ≤ 250 ppm, which is higher than the concentration commonly found in boilers, which is generally < 200 ppm. S11 comprises sodium ethylenedimaine tetraacetate (EDTA), a metal chelating agent, FLOSPERSE™ 1000 A and sodium lignosulfonate, polyelectrolytes dispersing agents and d-sorbitol, an oxygen inhibiting agent. S11 is essentially an environmentally benign product, eliminates the need and cost of chemicals for pH adjustment during use, and is recommended as scale inhibitor in boilers. However, this product inhibits higher than 250 ppm concentrations of multi-cations (see Example 2) and might find uses in other markets including water treatment.

SUITABLE REAGENTS OF THE INVENTION

[0010] Suitable chelating agents include, without limitation, alkaline earth salt of ethylene diamine tetraacetic acid (EDTA), such as sodium EDTA salt, potassium EDTA salt; ethylenediamine

tetrakis(alkoxylate) tetrols, nitrilotriacetonitrile or its derivatives or mixtures or combinations thereof.

[0011] Suitable polyelectrolytes or dispersants include, without limitation, polycarboxylate dispersants such as the FLOSPERSE™ including FLOSPERSE™ 1000 A, sodium lignosulfonates, potassium lignosulfonates, cesium lignosulfonates, BELCLENÉ® 200 (BC), polymaleic acid (PMA), lignosulphonate sodium salt (LGS), 2-acrylamido-2-methylpropane sulfonic acid homopolymers such as AMPS® products (a registered trademark of Lubrizol Corporation, and mixtures or combinations thereof.

[0012] Suitable oxygen scavengers include, without limitation, sugar alcohols like D-Sorbitol, D-Mannitol, Xylitol; ascorbic acid or erythorbic acid and their salts or mixtures or combinations thereof.

[0013] Suitable base include, without limitation, such as sodium hydroxide, potassium hydroxide, cesium hydroxide, sodium carbonate, potassium carbonate, sodium oxide, cesium oxide, potassium oxide or mixtures or combinations thereof. This invention is illustrated by the following examples.

EXPERIMENTS OF THE INVENTION

EXAMPLE 1

General Procedure

[0014] A formulation (Formula Y) with constituents presented in **Table 1** was prepared by adding each component beginning with the addition of sodium hydroxide to measured amount of distilled water. To this solution was added the indicated amount of EDTA or other chelating agent. The resulting solution was then stirred for 30 minutes. To the resulting solution was added the indicated amount of lignosulfonate or similar polyelectrolyte, in four portions with a 30 minute stir time between each addition. After the last 30 minute stir time, the indicated amount of D-Sorbitol or other O₂ inhibitor was added and the resulting solution is stirred for 10 minutes. To this solution was added the indicated amount of FLOSPERSE™ 1000A, or other comparable polyelectrolyte, all at once and stirred for 10 minutes. The solution was then tested for pH, usually between pH 10 and pH 11.5. The specific gravity of the final product should be between 1.16 and 1.20.

TABLE 1
Example 1 Formula Y Components and Amounts

Component	Amount (wt.%)
FLOSPERSE 1000A	12.00
EDTA	10.00
Sodium Lignosulfonate	12.00
D-Sorbitol	2.00
Sodium Hydroxide (50%)	15.00
Distilled Water	49.00
Total	100.000

Testing

[0015] Formula Y (FY) was used in two boilers at 250°F on a drilling site. The results of the trial with the composition was quite impressive. Water analysis (see Table 2) showed that calcium carbonate and iron levels stayed below detectable levels indicating minimal scaling.

TABLE 2
Water Analysis

Results	
pH	10
Calcium	0.0
Hardness	100 ppm
Iron	0
Magnesium	0
Chloride	100 ppm

[0016] Once the pH was properly set, there was no need to add caustic to the composition during use, unlike many other scale inhibitors. For the field trials only 18 gallons of product in example 1 (FY) were used for 190 barrels of water compared to 35 gallons of phosphate based inhibitor without accounting for additional usual caustic consumption.

EXAMPLE 2

[0017] Using NACE Standard TM 0197-2002, a sample of Formula Y (example 1) was tested against WFT commercial product Alpha 2867 at 208°F. Thus, to an untreated brine (**Blank, 6**) and 2 jars were added 350 ppm brine. The 2 jars (**3**, containing FY; and **5**, **WFT A2867**) were treated with 0.5 % of corresponding scale inhibitors, see Table 3. Similar treatments was carried out at 1.0

% concentration with FY scale inhibitor (**Table 3**). Results show that FY inhibits satisfactorily at both 0.5 (or 17.6 ppm) and 1.0 % whereas WFT A2867 failed. Essentially, complete inhibition is suggestive of overtreatment at 0.5 % inhibitor (FY) concentration in 350 ppm brine containing 522 ppm Ca^{2+} and 21 ppm Mg^{2+} .

TABLE 3
Jar Test Treatment of Brines with Scale Inhibitors

Brine Concentration (ppm)	Bottle #	Scale Inhibitor	Scale Inhibitor (wt.%)	Scale Inhibitor (mL)	Observation
350	1	Brine A	NA	NA	NA
	2	Brine B	NA	NA	NA
350	3	Formula Y	0.50	0.5	No Scale
	4	Formula Y	1.00	1.0	No Scale
350	5	WFT A2867	0.50	0.5	Scaled
350	6	Blank (A+B)	NA	NA	Scaled
350	7	Control (A+C)	NA	NA	NA

Temperature Stability

[0018] In North America and some cold regions of the globe, pourability of the inhibitor in cold temperatures is critical. Therefore, pour point of FY was determined. FY remains fluid up to -10°C (14°F) or have a freezing point of -15°C (5°F). A formulation containing 10 wt.% ethylene glycol (EG) has a pour point below -45°C (-49°F) and therefore suitable for use when environmental temperature is expected to be below -10°C while unmodified FY is desirable at or above 10°C .

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An environmentally benign scale inhibiting composition for boilers or other equipment in contact with water containing scale forming contaminants comprising:
one or a plurality chelating agents,
one or a plurality dispersing agents, wherein the dispersing agents comprise sodium lignosulfonates, potassium lignosulfonates, cesium lignosulfonates, lignosulfonate sodium salt (LGS), or 2-acrylamido-2-methylpropane sulfonic acid homopolymers, or any mixture or combination thereof, and
one or a plurality of oxygen scavenging agents including one sugar alcohol or a plurality of sugar alcohols, and
pH adjusted to a pH greater than about 9.
2. The composition of claim 1, wherein the alcohol sugar comprises D-Sorbitol, D-Mannitol, Xylitol, ascorbic acid or erythorbic acid, or any salt, mixture or combination thereof.
3. The composition of claim 1, wherein the alcohol sugar comprises D-Sorbitol.
4. The composition of claim 1, wherein the composition is diluted in water.
5. The composition of claim 2, wherein the composition includes 80 wt.% water.
6. The composition of claim 2, wherein the composition is diluted in water at a concentration between about 60 wt.% to about 20 wt.%.
7. The composition of claim 2, wherein the composition is diluted in water at a concentration between about 50 wt.% to about 20 wt.%.
8. The composition of claim 2, wherein the composition is diluted in water at a concentration between about 40 wt.% to about 20 wt.%.

9. The composition of claim 2, wherein the composition is diluted in water at a concentration between about 50 wt.% to about 30 wt.%.
10. A method for treating a fluid including scale forming contaminants in contact with a surface comprising:
adding, to the fluid to be treated, a scale inhibiting composition comprising:
one or a plurality chelating agents,
one or a plurality dispersing agents, wherein the dispersing agents comprise sodium lignosulfonates, potassium lignosulfonates, cesium lignosulfonates, lignosulfonate sodium salt (LGS), or 2-acrylamido-2-methylpropane sulfonic acid homopolymers, or any mixture or combination thereof, and
one or a plurality of oxygen scavenging agents including one sugar alcohol or a plurality of sugar alcohols, and
pH adjusted to a pH greater than about 9,
where the amount of the scale inhibiting composition is sufficient to reduce or prevent scale deposits on surfaces in contact with the fluid.
11. The method of claim 10, wherein the alcohol sugar comprises D-Sorbitol, D-Mannitol, Xylitol, ascorbic acid or erythorbic acid, or any salt, mixture or combination thereof.
12. The method of claim 10, wherein the alcohol sugar comprises D-Sorbitol.
13. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1500 ppm.
14. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1250 ppm.
15. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1000 ppm.

16. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 250 ppm.
17. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration between about 50 ppm and 5000 ppm.
18. The method of claim 10, wherein the effective amount of the scale-inhibiting composition is a concentration between about 100 ppm and 500 ppm.
19. A method comprising:
adding a scale inhibiting composition to a fluid including scale forming contaminants on a continuously, semi-continuously, periodically and/or intermittently basis,
where the composition comprises:
one or a plurality chelating agents,
one or a plurality dispersing agents, wherein the dispersing agents comprise sodium lignosulfonates, potassium lignosulfonates, cesium lignosulfonates, lignosulfonate sodium salt (LGS), or 2-acrylamido-2-methylpropane sulfonic acid homopolymers, or any mixture or combination thereof, and
one or a plurality of oxygen scavenging agents including one sugar alcohol or a plurality of sugar alcohols, and
pH adjusted to a pH greater than about 9, and
where the fluid is in contact with a surface or surfaces, and
where the amount of the scale inhibiting composition is sufficient to reduce or prevent scale deposits on the surfaces.
20. The method of claim 19, wherein the alcohol sugar comprises D-Sorbitol, D-Mannitol, Xylitol, ascorbic acid or erythorbic acid, or any salt, mixture or combination thereof.
21. The method of claim 19, wherein the alcohol sugar comprises D-Sorbitol.

22. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1500 ppm.
23. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1250 ppm.
24. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 1000 ppm.
25. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration less than or equal to 250 ppm.
26. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration between about 50 ppm and 5000 ppm.
27. The method of claim 19, wherein the effective amount of the scale-inhibiting composition is a concentration between about 100 ppm and 500 ppm.