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SYSTEMS AND METHODS FOR USING GLYCEROL-BASED SCALE INHIBITORS IN WASTE STREAMS

Abstract

Provided herein is a method for generating a glycerol-based scale inhibitor and utilizing it to generate a glycerol-based scale inhibitor solution. The method includes providing a glycerol feed and a scale-inhibiting precursor to generate the glycerol-based scale inhibitor. Further, the method includes providing one or more additives to the one or more glycerol-based scale inhibitor, thereby generating a glycerol-based scale inhibitor solution.

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Background/Summary

BACKGROUND

[0001] This disclosure relates to a glycerol-based scale inhibitor with one or more functional groups. In particular, the processes may include using a feedstock of glycerol with a scale-inhibiting precursor. The disclosed glycerol-based scale inhibitor is especially useful for anti-scaling applications, such as oil and gas, water treatment, power plants, or geothermal applications.

[0002] Low, moderate, or high temperature processes are performed by many industries, such as oil and gas, water treatment, power plant, or geothermal. Such processes are often impacted by scaling depositions. For example, the process for generating hydrocarbons from subterranean reservoirs subjects downhole equipment to harsh conditions, such as high temperatures, caustic chemicals, and limited space. These harsh operating conditions may promote scaling, resulting in poor performance and function of the downhole equipment and an overall reduction in productivity.

[0003] To this end, anti-scaling chemistry is ubiquitous within the oilfield chemistry for the mitigation of inorganic scale. The materials utilized in the development of the scaling agents may be sourced from petroleum refineries and are further functionalized to generate a desired product. Due to the process by which the base materials for the traditional scaling agents are sourced, certain scaling agents exhibit a significant carbon footprint in their manufacturing process. Therefore, current limitations in the production of scaling agents include finding sustainable, environmentally friendly base materials and methods. Moreover, limitations in sustainable, environmentally friendly base materials and methods for phosphonate-based chemistry are hindering a further decrease in carbon footprint in various fields such as oil and gas, water treatment, power plant, or geothermal. It may be desirable to develop more efficient base materials and methods for accessing sustainable, environmentally friendly scaling agents to facilitate a decrease in carbon footprint while mitigating inorganic scale.

SUMMARY

[0004] A summary of certain embodiments disclosed herein is set forth below. It should be understood that these aspects are presented merely to provide the reader with a brief summary of these certain embodiments and that these aspects are not intended to limit the scope of this disclosure. Indeed, this disclosure may encompass a variety of aspects that may not be set forth below.

[0005] In certain embodiments, the present disclosure relates to a method for generating a glycerol-based scale inhibitor solution. The method includes providing a glycerol feed and a scale-inhibiting precursor feed. The method also includes generating one or more glycerol-based scale inhibitors by contacting the glycerol feed with the scale-inhibiting precursor feed. Further, the method includes providing the glycerol-based scale inhibitor feed and one or more additives to generate a glycerol-based scale inhibitor solution.

[0006] In certain embodiments, a composition includes a glycerol-based scale inhibitor. The glycerol-based scale inhibitor includes a glycerol-analogue core and one or more chelating groups linked to the glycerol-analogue core via one or more ethers of the glycerol-analogue core.

[0007] In certain embodiments, a method includes providing a glycerol-based scale inhibitor solution and providing a liquid volume. The liquid volume includes metal ions. The method also includes sequestering the metal ions using the glycerol-based scale inhibitor to form a metal-ion complex. Further, the method includes separating the metal-ion complex and glycerol-based scale inhibitor solution from the liquid volume.

[0008] Various refinements of the features noted above may exist in relation to various aspects of the present disclosure. Further features may also be incorporated in these various aspects as well. These refinements and additional features may exist individually or in any combination. For instance, various features discussed below in relation to one or more of the illustrated embodiments may be incorporated into any of the above-described aspects of the present disclosure alone or in any combination. The brief summary presented above is intended only to familiarize the reader

with certain aspects and contexts of embodiments of the present disclosure without limitation to the claimed subject matter.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings, wherein:

[0010] FIG. 1 is a flow diagram of a method for generating a glycerol-based scale inhibitor solution, in accordance with present disclosure;

[0011] FIG. 2 illustrates an example of a molecular structure for the glycerol-based scale inhibitor, in accordance with the present disclosure;

[0012] FIG. 3A illustrates an example of a glycerol-based scale inhibitor generated with a 1:1 stoichiometric ratio of glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0013] FIG. 3B illustrate an example of a glycerol-based scale inhibitor generated with a 1:2 stoichiometric ratio glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0014] FIG. 3C illustrate an example of a glycerol-based scale inhibitor generated with a 1:3 stoichiometric ratio glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0015] FIG. 4A illustrates an example of a glycerol-based scale inhibitor generated with a 1:1 stoichiometric ratio of glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0016] FIG. 4B illustrate an example of a glycerol-based scale inhibitor generated with a 1:2 stoichiometric ratio glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0017] FIG. 4C illustrate an example of a glycerol-based scale inhibitor generated with a 1:3 stoichiometric ratio glycerol:scale-inhibiting precursor, in accordance with the present disclosure;

[0018] FIG. 5 is a flow diagram of an example method for using a glycerol-based scale inhibitor solution for sequestering metal ions, in accordance with the present disclosure; and

[0019] FIG. 6 illustrates a schematic view of a subsea system where the glycerol-based scale inhibitor solution may be employed in mitigating inorganic scale in oil and gas production.

DETAILED DESCRIPTION

[0020] One or more specific embodiments of the present disclosure will be described below. In an effort to provide a concise description of these embodiments, all features of an actual implementation may not be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[0021] Furthermore, when introducing elements of various embodiments of the present disclosure, the articles “a,” “an,” and “the” are intended to mean that there are one or more of the elements. The terms “comprising,” “including,” and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements. Additionally, it should be understood that references to “one embodiment,” “an embodiment,” or “some embodiments” of the present disclosure are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features. Furthermore, the phrase A “based on” B is intended to mean that A is at least partially based on B. Moreover, unless expressly stated otherwise, the term “or” is intended to be inclusive (e.g., logical OR) and not exclusive (e.g.,

logical XOR). In other words, the phrase A “or” B is intended to mean A, B, or both A and B. elements. In general, it should be noted that “bind,” “sequester,” and/or “chelate” may be used herein interchangeably. All numerical values within the detailed description herein are modified by “about” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art. For example, “about” or “approximately” may refer to $\pm 0.5\%$, $\pm 1\%$, $\pm 2\%$, $\pm 5\%$, $\pm 10\%$, or $\pm 15\%$.

[0022] As described herein, the term “glycerol” refers to “propane-1,2,3-triol”, also called glycerine, or glycerin. The term “glycerol-based scale inhibitor” refers to a glycerol molecule, but one or more of the hydroxyl functional groups of the original glycerol molecule are functionalized with a scale inhibitor. In general, the “scale inhibitor” may inhibit or prevent scaling by chelating or binding or sequestering positive inorganic cations associated with scale. The term “glycerol-based scale inhibitor solution” refers to a solution that includes the glycerol-based scale inhibitor and additives. The term “glycerol-analogue core” refers to glycerol and its three hydroxyl functional groups that can be functionalized using scale-inhibiting precursors (i.e., thereby forming scale-inhibiting functional groups). The term “carbon backbone” or “main carbon chain” or “backbone” refers to the longest carbon chain in the molecule of the compound or group in question.

[0023] The term “scale-inhibiting precursor” or “chelating precursor” refers to a molecule that includes functional groups that can bind to positively charged metal ions. For example, a molecule including phosphate groups, phosphonate groups, sulfonate groups, sulfate groups, phosphate ester groups, carboxylic acid groups, another other functional group, or a combination thereof, is a scale-inhibiting precursor.

[0024] The term “additive” refers to any other molecule, solvent, or buffer that may be added to the glycerol-based scale inhibitor to generate the glycerol-based scale inhibitor solution. The term “buffer” or “buffering agent” refers to solutions that can resist changes in pH when acidic or basic solutions are added.

[0025] A scale inhibitor solution made with sustainable base materials may provide satisfactory chelating properties to positively charged metal ions in industrial applications in which existing scale inhibitors may be unsuitable due to their significant carbon footprint. However, efficient syntheses for scale inhibitor solutions for anti-scaling applications synthesized with sustainable, environmentally friendly base materials having an acceptable combination of solubility and chelating abilities have yet to be identified.

[0026] This disclosure relates to techniques for generating, producing, or otherwise performing one or more reactions to yield a glycerol-based scale inhibitor as a sustainable, environmentally friendly material that may be used in oil and gas operations that has advantageous chelating and solubility properties. Biodiesel waste streams containing crude glycerol are a suitable source for glycerol, acting as a sustainable base material. As such, crude glycerol containing waste streams can be functionalized with appropriate functional groups to form the glycerol-based scale inhibitor that prevent scale depositions by binding to inorganic cations. In general, the techniques discussed herein include generating the glycerol-based scale inhibitor by reacting glycerol (i.e., propane-1,2,3-triol) with one or more scaling precursors (e.g., different or the same scale-inhibiting precursors). The stoichiometric ratio of the one or more scale-inhibiting precursors to the glycerol may be between approximately 1 to 3, thereby generating a glycerol-based scale inhibitor having between 1 to 3 scale-inhibiting functional groups. In certain embodiments, it may be advantageous to generate the disclosed conditions including one or more of a glycerol feed, a scale-inhibiting precursor feed, a type of scale-inhibiting precursor, a stoichiometric equivalent addition of scale-inhibiting precursor, or a combination thereof, to obtain a glycerol-based scale inhibitor. The disclosed techniques provide a glycerol-based scale inhibitor with tunable activity (e.g., chelating activity, scaling activity) by varying the stoichiometric ratio of the one or more scale-inhibiting precursors, utilizing a type of scale-inhibiting precursor, or utilizing a combination of scale-inhibiting precursors. As referred to herein, “chelating activity” refers to the ability of a scale

inhibitor to bind ions (e.g., positive ions in a solution). For example, the “chelating activity” may refer to the number of ions a single scale inhibitor is capable of binding and/or the binding affinity of the scale inhibitor for binding the ions. In some embodiments, the techniques include generating a glycerol-based scale inhibitor solution using the glycerol-based scale inhibitor. In certain embodiments, generating the glycerol-based scale inhibitor includes providing additives (e.g., other molecules, buffers, or solvents) to the glycerol-based scale inhibitor. It is presently recognized that such additives may provide tuning of the chelating activity of the glycerol-based scale inhibitor in the glycerol-based scale inhibitor solution (e.g., adjusting the pH of the scale-inhibiting functional groups of the glycerol-based scale inhibitor). In any case, the glycerol-based scale inhibitor solution may be provided to a liquid volume (e.g., a subterranean reservoir, conduits in a downhole tool, or fluid volumes where tools operate in the presence of a relatively high concentration of metal ions) to chelate, sequester, bind, or otherwise coordinate to metal ions, thereby forming a metal ion complex and reducing or preventing scaling. In any case, the disclosed glycerol-based scale inhibitor may be used to generate glycerol-based scale inhibitor solutions for use as sustainably-synthesized scale inhibitors in industrial applications, which may be more efficient and sustainable as compared to existing scale inhibitor fluids. Further, the disclosed glycerol-based scale inhibitor, and the glycerol-based scale inhibitor solution, have a chelating activity that is readily tunable by way of the stoichiometric ratio of scale-inhibiting precursors used to generate the glycerol-based scale inhibitor.

[0027] In certain embodiments, a method includes reacting a glycerol feed with a scale-inhibiting precursor feed to generate one or more glycerol-based scale inhibitors by contacting the glycerol feed with the scale-inhibiting precursor. The scale-inhibiting precursor may include phosphates, sulfonates, sulfates, carboxylic acids, alkenyl phosphonic acids, phosphonates, phosphate esters, or any combination thereof. In some embodiments, additives may be added to the glycerol-based scale inhibitor to generate a glycerol-based scale inhibitor solution. The additives may include other molecules, solvents, or buffers. The solvents may include phosphonates, sulfonates, sulfates, phosphate esters, phosphates, alkenyl phosphonic acids, glycols, water, alcohols, carboxylic acids, protic solvents, solvents miscible with water, or a combination thereof. In some embodiments, the buffering agents may include phosphate-based buffers, hydroxide-based buffers, carbonate-based buffers, bicarbonate-based buffers, amine-based buffers, acetate-based buffers, or any combination thereof.

[0028] In certain embodiments, a composition of the glycerol-based scale inhibitor includes a glycerol-analogue core and one or more chelating groups linked to the glycerol analogue core via one or more ethers of the glycerol analogue core. In some embodiments, the glycerol analogue core may include glycerol or analogues of glycerol, such as propane-1,2,3-triamine or 1,2,3-trimercaptopropane. In some embodiments, the glycerol analogue core may include three or less hydroxyl functional groups. In some embodiments, the chelating group may include phosphonates, alkenyl phosphonic acids, phosphates, phosphate esters, or any combination thereof.

[0029] In certain embodiments, a method includes providing a glycerol-based scale inhibitor solution to a liquid volume that includes metal ions. The metal ions are sequestered by the glycerol-based scale inhibitor, forming a metal-ion complex. The metal-ion complex and glycerol-based scale inhibitor are separated from the liquid volume. In general, the glycerol-based scale inhibitor solution may be utilized in mitigating inorganic scaling in industrial applications. In certain embodiments, the metal ions may include metal carbonates, metal sulfates, metal hydroxides, metal sulfides, zinc sulfides, lead sulfides, or any combination thereof. In some embodiments, the glycerol-based scale inhibitor solution is injected via a subsea fluid injection system into a subterranean reservoir to mitigate inorganic scale.

[0030] With the foregoing in mind, FIG. 1 illustrates a flow diagram of a method 10 for generating the glycerol-based scale inhibitor solution 24 in accordance with certain embodiments of the present disclosure. In general, the method 10, at block 14, includes reacting a glycerol 16 (e.g.,

glycerol feed) and a scale-inhibiting precursor **18** (e.g., scale-inhibiting precursor feed) in a reactor, generating a glycerol-based scale inhibitor **12**. Further, the method includes **10**, at block **20**, providing additives **22** to the glycerol-based scale inhibitor **12**, thereby generating a glycerol-based scale inhibitor solution **24**. As described herein, the glycerol-based scale inhibitor solution **24** may include advantageous properties such as tunable chelating abilities and solubility properties. Block **14** and block **20** are discussed in more detail below.

[0031] Referring to the method **10**, at block **14**, the glycerol-based scale inhibitor **12** may be generated by reacting the glycerol **16** and scale-inhibiting precursor **18** in a solvent. In some embodiments, reacting the glycerol **16** and scale-inhibiting precursor **18** may include providing a feed (e.g., glycerol feed and scale-inhibiting precursor feed) including the glycerol **16** and scale-inhibiting precursor **18** in the presence of a solvent into a reaction vessel to generate the glycerol-based scale inhibitor **12**. For example, the solvent may serve as a reaction medium and may include phosphonates, sulfonates, sulfates, phosphate esters, phosphates, alkenyl phosphonic acids, carboxylic acids, glycols, water, alcohols, protic solvents, solvents miscible with water, or a combination thereof.

[0032] The glycerol **16** includes three hydroxyl functional groups. In some embodiments, it may be advantageous to convert all three hydroxyl functional groups into a new scale-inhibiting functional group. In some embodiments, it may be advantageous to convert only one or two of the hydroxyl functional groups into a new scale-inhibiting functional group. To do so, the stoichiometric ratio of the scale-inhibiting precursor **18** to the glycerol **16** may be from one to three. For example, one of the hydroxyl groups in the glycerol **16** can react with one scale-inhibiting precursor **18**, two of the hydroxyl groups in the glycerol **16** can react with two scale-inhibiting precursors **18**, or three of the hydroxyl groups in the glycerol **16** can react with three scale-inhibiting precursor **18**. While the description herein relates to the glycerol **16**, it should be noted that the above described techniques may include glycerol analogues having one or more thiols or amines instead of the one or more hydroxyl groups of glycerol. For example, the above techniques may utilize propane-1,2,3-triamine or 1,2,3-trimercaptopropane.

[0033] In some embodiments, the scale-inhibiting precursor **18** is generally a molecule with a functional group or multiple functional groups that is capable of binding to positively-charged metal ions. In one embodiment, the scale-inhibiting precursor **18** may be a phosphonate (e.g., $\text{C}=\text{PO}(\text{OR})_{\text{sub.2}}$, where R may be an alkenyl group, an aryl group, alkyl group, hydrogen, or any combination thereof), alkenyl phosphonic acid (e.g., vinyl phosphonic acid, alternative phosphonic acids with suitably functionalized double bonds in which the double bond is in conjugation with an electron withdrawing group (e.g., carbonyl ($\text{C}=\text{O}$), forming a suitable Michael acceptor, salts of phosphonic acids (e.g., sodium phosphonates, potassium phosphonates, etc.)). For example, in an embodiment when the scale-inhibiting precursor **18** include alkenyl phosphonic acids, the scale-inhibiting precursor **18** may include one or more types of alkenyl phosphonic acid, such as vinyl phosphonic acids (e.g., a first type of phosphonic acid) or alternative phosphonic acids with suitably functionalized double bonds in which the double bond is in conjugation with an electron withdrawing group, forming a suitable Michael acceptor. In another embodiment, phosphorus oxychloride ($\text{POCl}_{\text{sub.3}}$) may be utilized as the scale-inhibiting precursor **18** for the formation of phosphate esters (e.g., $\text{O}=\text{P}(\text{OR})_{\text{sub.3}}$, where R may be an alkenyl group, an aryl group, alkyl group, hydrogen, or any combination thereof). In some embodiments, the scale-inhibiting precursor **18** may include functional groups that may be phosphates, phosphonates, or alkenyl phosphonic acids that include one or more oxides and/or one or more hydroxides that bind to a positive metal ion.

[0034] In another embodiment, the scale-inhibiting precursor **18** may include functionalized carboxylic acids (e.g., acrylic acid, maleic acid, anhydride, itaconic acid, etc.) as suitable Michael acceptors. In a further embodiment, the scale-inhibiting precursor **18** may be sulfonates (e.g., $(\text{R}=(\text{=S})_{\text{sub.2}}-\text{O}-)$, where R may be an alkenyl group, an aryl group, alkyl group, hydrogen, or any

combination thereof), vinyl sulfonic acid, chlorosulfuric acid, salts of sulfonic acids (e.g., sodium sulfonate, potassium sulfonate, etc.). In general, it should be noted that the scale-inhibiting precursor **18** may include a combination of precursors such as phosphate groups, phosphonate groups, sulfonate groups, sulfate groups, phosphate ester groups, carboxylic acid groups, another other functional group, or a combination thereof.

[0035] As discussed above with respect to block **20**, the resulting glycerol-based scale inhibitor **12** may be combined with one or more additives **22** to generate the glycerol-based scale inhibitor solution **24**. For example, the glycerol-based scale inhibitor **12** may be provided to a reaction vessel (e.g., a glycerol-based scale inhibitor feed) with additives **22** (e.g., additive feed) to generate the glycerol-based scale inhibitor solution **24**. As such, the glycerol-based scale inhibitor solution **24** may include additives **22**, such as other molecules, solvents, or buffers. The buffers adjust the pH of the glycerol-based scale inhibitor solution **24**, freeing up the number of binding groups available within the glycerol-based scale inhibitor **12**, allowing the glycerol-based scale inhibitor **12** to bind to positively charged metal ions. As such, the additives **22** may include buffering agents, such as phosphate-based buffers, hydroxide-based buffers, carbonate-based buffers, bicarbonate-based buffers, amine-based buffers, acetate-based buffers, or any combination thereof. Further, solvents may be provided as an additive **22** during the production of glycerol-based scale inhibitor solution **24**. The solvent may serve as a reaction medium and may include phosphonates, sulfonates, sulfates, phosphate esters, phosphates, alkenyl phosphonic acids, glycols, water, alcohols, carboxylic acids, protic solvents, solvents miscible with water, or a combination thereof.

[0036] As described herein, the glycerol **16** is reacted with the scale-inhibiting precursor **18** to generate the glycerol-based scale inhibitor **12**. Additives **22** are provided to the glycerol-based scale inhibitor **12** to generate the glycerol-based scale inhibitor solution **24**. As such, the glycerol-based scale inhibitor solution can be utilized for anti-scaling applications due to its advantageous synthesis with sustainable base materials, such as glycerol, providing tunable chelating and solubility properties. With the preceding in mind, FIG. 2 illustrates an example of a molecular structure **30** for the glycerol-based scale inhibitor **12** in accordance with certain embodiments of the present disclosure. In general, the glycerol-based scale inhibitor **12** includes the main carbon chain **32** of the glycerol **16**. As such, the main carbon chain **32** serves as the backbone of the glycerol-based scale inhibitor **12** or glycerol analogue.

[0037] The glycerol-based scale inhibitor **12** also includes R groups **34a**, **34b**, and **34c** (e.g., collectively, R groups **34**). The R groups **34a**, **34b**, and **34c** may be any oxygen (O), sulfur (S), or nitrogen (N) atom within glycerol (e.g., O atoms) or glycerol analogues (e.g., S or N atoms) that may be used in certain embodiments. Further, the glycerol-based scale inhibitor **12** includes scale-inhibiting functional groups, which are indicated by X, Y, and Z groups **36**, **38**, and **40**. In general, the scale-inhibiting functional groups or X, Y, and Z groups **36**, **38**, and **40** are the scale-inhibiting precursors **18** that are bonded to the main carbon chain **32** of the glycerol-based scale inhibitor **12**. For example, the scale-inhibiting functional group may be linked to the glycerol-based scale inhibitor **12** via an ether in an embodiment when the R group **34** is an O atom. As referred to herein, “linked” refers to covalently bonded. It should be noted that the scale-inhibiting precursor **18** refers to a molecule that has not formed a bond with glycerol **16**, whereas the scale-inhibiting functional group has formed a bond with glycerol **16**, generating the glycerol-based scale inhibitor **12**. As described herein, the glycerol-based scale inhibitor solution **24** may include advantageous properties, such as tunable chelating ability and solubility properties.

[0038] Referring to FIG. 2, the main carbon chain **32** is the carbon backbone within the glycerol-based scale inhibitor **12**. In certain embodiments, a different base material with a longer backbone including 3 hydroxyl functional groups may be utilized (e.g., pentane-1,3,5-triol, heptane-1,4,7-triol, etc.). As described herein, R groups **34** may be an O atom within the hydroxyl functional group of glycerol. In some embodiments, R groups **34** include an S atom within a glycerol analogue, such as 1,2,3-trimercaptopropane. In some embodiments, R groups **34** may be an N atom

within a glycerol analogue, such as propane-1,2,3-triamine. In some embodiments, R groups **34** may include all O atoms, all S atoms, all N atoms, or any combination thereof.

[0039] In general, it should be noted that X, Y, and Z groups **36**, **38**, and **40** may represent an atom within the scale-inhibiting precursor **18** that is bonded to R group **34** of the glycerol **16** or glycerol analogues. In some embodiments, X, Y, and Z groups **36**, **38**, and **40** may represent the scale-inhibiting functional group in its entirety that is bonded to R group **34** of the glycerol **16** or glycerol analogues. In some embodiments, if a scale-inhibiting precursor **18** does not functionalize with the glycerol **16** or glycerol analogues, X, Y, and Z groups **36**, **38**, and **40** may be a hydrogen (H) atom bonded to O atom. In some embodiments, X, Y, and Z groups **36**, **38**, and **40** may be a phosphonate (e.g., C—PO(OR).sub.2, where R may be an alkenyl group, an aryl group, hydrogen, or any combination thereof) or alkenyl phosphonic acid (e.g., vinyl phosphonic acid, alternative phosphonic acids with suitably functionalized double bonds in which the double bond is in conjugation with an electron withdrawing group, forming a suitable Michael acceptor, salts of phosphonic acids (e.g., sodium phosphonates or potassium phosphonates), or phosphate esters. For example, if the scale-inhibiting precursor **18** is vinyl phosphonic acid or vinyl sulfonic acid, the terminal carbon (C) atom of the alkene within vinyl phosphonic acid will bind to **34** R group of the glycerol **16** or glycerol analogue, generating the X, Y, Z group **36**, **38**, **40** scale-inhibiting functional group. In another embodiment, if the scale-inhibiting precursor is phosphorus oxychloride, the phosphorus (P) atom will bind or react with **34** R group of the glycerol **16** or glycerol analogue, generating a phosphate ester as a part of the X, Y, Z group **36**, **38**, **40** scale inhibiting functional group. In some embodiments, X, Y, Z groups **36**, **38**, **40** may include other functional groups (e.g., phosphates (PO.sub.4.sup.3-), phosphate esters, or carboxylic acids that include one or more oxides and/or one or more hydroxides) that bind to a positive metal ion.

[0040] In some embodiments, X, Y, and Z groups **36**, **38**, and **40** may be the same scale-inhibiting functional group (e.g., all three X, Y, Z groups **36**, **38**, and **40** within the glycerol-based scale inhibitor **12** are bound to a scale-inhibiting precursor **18** such as a phosphonate ligand). In other embodiments, X, Y, and Z groups **36**, **38**, and **40** may include different scale-inhibiting functional groups. For example, X may be an unreacted hydroxide functional group of glycerol **16** and Y and Z may be phosphonate ligands (e.g., vinyl phosphonic acid). In another example, X and Y may be unreacted hydroxide functional groups and Z may be a phosphonate ligand (e.g., vinyl phosphonic acid). In some embodiments, a mixture of ligands may be utilized. For example, a mixture of scale-inhibiting precursor **18** may include alkenyl phosphonic acids, phosphates, and phosphorus oxychloride, leading to a glycerol-based scale inhibitor **12** having X, Y, and Z groups **36**, **38**, and **40** scale-inhibiting functional groups that may be a mixture of ligands, such as alkenyl phosphonic acids, phosphates, phosphate esters. In another example, X, Y, and Z groups **36**, **38**, and **40** scale inhibiting functional groups may be a mixture of ligands such as phosphate esters, phosphonates, and carboxylic acids. In a further example, X, Y, and Z groups **36**, **38**, and **40** scale inhibiting functional groups may be a mixture of ligands (e.g., phosphate groups, phosphonate groups, sulfonate groups, sulfate groups, phosphate ester groups, carboxylic acid groups, another other functional group, or a combination thereof). In general, it should be noted that the examples provided herein are meant to be non-limiting. As such, the glycerol-based scale inhibitor **12** may include advantageous properties such as tunable chelating abilities and solubility properties for use in a glycerol-based scale inhibitor solution **24** for anti-scaling applications.

[0041] As described herein, glycerol **16** is reacted with stoichiometric equivalent amounts of the scale-inhibiting precursor **18** to generate the glycerol-based scale inhibitor **12**. As referred to herein, a “stoichiometric equivalent” is an amount of a first reactant to be reacted with a second reactant such that the desired stoichiometric ratio (e.g., of the first reactant to the second reactant) is obtained. For example, in an embodiment where it is desired to obtain a glycerol-based scale inhibitor with three phosphate scale-inhibiting functional groups, three stoichiometric equivalents of a phosphate are reacted with one stoichiometric equivalent of glycerol **16**. In general, the

glycerol **16** includes three hydroxyl functional groups. As such, FIGS. 3A, 3B, and 3C illustrate examples of different stoichiometric equivalents of functionalization of glycerol **16** with the scale-inhibiting precursor **18** in accordance with certain embodiments of the present disclosure. Through controlled reaction conditions, various stoichiometric additions of the scale-inhibiting precursor **18** can range between one to three equivalents of the scale-inhibiting precursor **18** onto the glycerol **16**.

[0042] In some embodiments, the stoichiometric ratio of the scale-inhibiting precursor **18** to the glycerol **16** may be less than 3. Accordingly, one or more of the hydroxyl functional groups of the glycerol **16** may remain unreacted (i.e., are hydroxyls) after block **14** of the method **10** of FIG. **1**. For example, FIG. **3A** illustrates the glycerol-based scale inhibitor **12a**, where one of the hydroxyl functional groups within the glycerol molecule is functionalized with the scale-inhibiting precursor **18**, as depicted within the dashed circle. The illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:1 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18**. In general, scale-inhibiting precursor **18a** represents the scale-inhibiting precursor (e.g., vinyl phosphonic acid) that is bound to feature **54** (e.g. **54a**, **54b**, and **54c**, or collectively **54**), which is the O atom of the former hydroxyl functional group within glycerol **16**. It should be noted that the O atom now acts as an ether in the glycerol-based scale inhibitor **12**. Further, **52a** and **52b** (e.g., collectively **52**) represent two of the three hydroxyl functional groups within glycerol **16** that remain unreacted.

[0043] Further, FIG. **3B** illustrates another example of the glycerol-based scale inhibitor **12** where two hydroxyl functional groups of glycerol **16** are functionalized with two scale-inhibiting precursor **18** molecules, as illustrated within the dashed circles. The illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:2 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18a** and **18b**. As such, FIG. **3B** shows two vinyl phosphonic acid molecules as the scale-inhibiting precursor **18** functionalized to two of the hydroxyl functional groups within glycerol **16**, while one hydroxyl group remains unreacted.

[0044] Additionally, FIG. **3C** illustrates an example of the glycerol-based scale inhibitor where all three of the hydroxyl functional groups within glycerol **16** are functionalized with the scale-inhibiting precursor **18** (e.g., vinyl phosphonic acid). In particular, the illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:3 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18a**, **18b**, and **18c**. It should be noted that depending on the additives **22** present (e.g., other molecules, solvents, or buffers), the unreacted hydroxyl groups **52** or scale-inhibiting precursor **18** of the glycerol-based scale inhibitor **12** may or may not be protonated depending on the pH of the glycerol-based scale inhibitor solution **24**. As such, the compositions described herein describe the properties of the glycerol-based scale inhibitor **12**. Several non-limiting examples of the composition of the glycerol-based scale inhibitor **12** and glycerol-based scale inhibitor solution **24** are described above.

[0045] In another embodiment, the stoichiometric ratio of the scale-inhibiting precursor **18** to the glycerol **16** may be less than 3. Accordingly, one or more of the hydroxyl functional groups of the glycerol **16** may remain unreacted (i.e., are hydroxyls) after block **14** of the method **10** of FIG. **1**. For example, FIG. **4A** illustrates the glycerol-based scale inhibitor **12**, where one of the hydroxyl functional groups within the glycerol molecule is functionalized with the scale-inhibiting precursor **18**, as depicted within the dashed circle. The illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:1 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18**. In general, scale-inhibiting precursor **18d** represents the scale-inhibiting functional group (e.g., phosphate esters that are formed from a reaction between scale-inhibiting precursor **18** phosphorus oxychloride and glycerol **16**) that is bound to feature **54** (e.g. **54a**, **54b**, and **54c**, or collectively **54**), which is the O atom of the former hydroxyl functional group within glycerol **16**. It should be noted that the O atom (feature **54**) now acts as part of the phosphate ester in the glycerol-based scale inhibitor **12**. Further, **52a** and **52b** (e.g., collectively **52**) represent two of the three hydroxyl

functional groups within glycerol **16** that remain unreacted.

[0046] Further, FIG. **4B** illustrates another example of the glycerol-based scale inhibitor **12** where two hydroxyl functional groups of glycerol **16** are functionalized with two scale-inhibiting precursor **18** molecules, as illustrated within the dashed circles. The illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:2 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18d** and **18e**. As such, FIG. **4B** shows two phosphate ester molecules as the scale-inhibiting precursor **18** functionalized to two of the hydroxyl functional groups within glycerol **16**, while one hydroxyl group remains unreacted.

[0047] Additionally, FIG. **4C** illustrates an example of the glycerol-based scale inhibitor where all three of the hydroxyl functional groups within glycerol **16** are functionalized with the scale-inhibiting precursor **18** (e.g., phosphate ester). In particular, the illustrated example depicts a glycerol-based scale inhibitor **12** generated with a 1:3 stoichiometric ratio of glycerol **16**:scale-inhibiting precursor **18d**, **18e**, and **18f**. It should be noted that depending on the additives **22** present (e.g., other molecules, solvents, or buffers), the unreacted hydroxyl groups **52** or scale-inhibiting precursor **18** of the glycerol-based scale inhibitor **12** may or may not be protonated depending on the pH of the glycerol-based scale inhibitor solution **24**. As such, the compositions described herein describe the properties of the glycerol-based scale inhibitor **12**. Several non-limiting examples of the composition of the glycerol-based scale inhibitor **12** and glycerol-based scale inhibitor solution **24** are described above.

[0048] In general, the glycerol-based scale inhibitor **12** can be utilized to prepare a glycerol-based scale inhibitor solution **24** for subsequent use in mitigating inorganic scale in industrial applications. With the preceding in mind, FIG. **5** illustrates a flow diagram of a method **60** for using the glycerol-based scale inhibitor solution **24** for sequestering metal ions in accordance with certain embodiments of the present disclosure. In general, the glycerol-based scale inhibitor solution **24** may be used in anti-scaling applications. At block **62**, the method **60** includes preparing the glycerol-based scale inhibitor solution **24**. In general, block **62** may be performed in a generally similar manner as described in FIG. **1**. As such, a glycerol-based scale inhibitor solution **24** is provided to a liquid volume that includes metal ions, as described at block **64**. The addition of the glycerol-based scale inhibitor solution **24** sequesters (i.e., chelates) the metal ions, thereby forming a metal-ion complex. The metal-ion complex and the glycerol-based scale inhibitor solution **24** are subsequently separated from the liquid volume. As described herein, the glycerol-based scale inhibitor solution **24** may include advantageous properties, such as tunable chelating ability and solubility properties in liquid volumes for sequestering or chelating to metal ions.

[0049] At block **64**, the method **60** provides a glycerol-based scale inhibitor solution **24** to a liquid volume that includes metal ions. The glycerol-based scale inhibitor solution **24** includes glycerol-based scale inhibitor **12** and additives **22**. It is presently recognized that the additives **22** may include, but are not limited to, other molecules, solvents, or buffers. As such, the additives **22** may include buffering agents, such as phosphate-based buffers, hydroxide-based buffers, carbonate-based buffers, bicarbonate-based buffers, amine-based buffers, acetate-based buffers, or any combination thereof. Further, solvents may be provided as an additive **22** during the production of the glycerol-based scale inhibitor solution **24**. The solvent may serve as a reaction medium and may phosphonates, phosphate esters, sulfonates, sulfates, phosphates, alkenyl phosphonic acids, glycols, water, carboxylic acids, alcohols, protic solvents, solvents miscible with water, or a combination thereof. The glycerol-based scale inhibitor solution **24** may be provided as a liquid to a liquid volume. In another embodiment, the glycerol-based scale inhibitor solution **24** may be provided to a liquid volume containing solids. In general, the glycerol-based scale inhibitor solution **24** may be miscible or immiscible with the liquid volume.

[0050] Referring to the method **60**, at block **66**, after the glycerol-based scale inhibitor solution **24** is provided to a liquid volume including metal ions, the glycerol-based scale inhibitor solution **24** may sequester, bind, or chelate to metal ions in solution, forming a metal-ion complex. For

example, the glycerol-based scale inhibitor may bind to metal carbonates (e.g., wherein the metal may be calcium, iron, or any other metal thereof), metal sulfates (e.g., wherein the metal may be calcium, iron, or any other metal thereof), metal hydroxides (e.g., wherein the metal may be calcium, iron, or any other metal thereof), metal sulfides (e.g., wherein the metal may be calcium, iron, or any other metal thereof), zinc sulfides, lead sulfides, or any combination thereof. At block **68**, the metal-ion complex and the glycerol-based scale inhibitor solution **24** are separated from the liquid volume. Separation techniques include, but are not limited to, acid-base extraction, centrifugation, filtration, etc. As such, this method allows for sequestration and separation of inorganic scale from industrial applications.

[0051] With the foregoing in mind, FIG. **6** illustrate a schematic view of a subsea system **70** where the glycerol-based scale inhibitor solution **24** may be employed in mitigating inorganic scale in oil and gas production. In general, the subsea system **70** includes electrical cables **72** used for transmitting information and primary electrical power for various subsea components (e.g., actuators, sensors, etc.). The subsea system **70** may include a subsea hydrocarbon production system configured to extract oil or gas from a subterranean reservoir, a subsea fluid injection system configured to inject fluid (e.g., liquid or gas) into a subterranean reservoir, or any other subsea system associated with subterranean reservoirs. For example, the subsea fluid injection system may include a subsea gas, water, glycerol-based scale inhibitor solution **24** for mitigating inorganic scale. In certain embodiments, the subsea system **70** may include a subsea tree **74** coupled to a wellhead **76** to form a subsea station **78** configured to extract and/or inject fluids relative to a subterranean reservoir. For example, the subsea station **78** may be configured to extract formation fluid, such as oil and/or natural gas, from the sea floor **80** through the well **82**. By further example, the subsea station **78** may be configured to inject CO₂ into the subterranean reservoir. In some embodiments, the subsea system **70** may include multiple subsea stations **78** that extract and/or inject fluids relative to respective wells **82**.

[0052] In certain embodiments of the subsea system **70** configured for production, after passing through the subsea tree **74**, the formation fluid flows through fluid conduits or pipes **84** to a pipeline manifold **86**. The pipeline manifold **86** may connect to one or more flowlines **88** to enable the formation fluid to flow from the wells **82** to a surface platform **90**. In some embodiments, the surface platform **90** may include a floating production, storage, and offloading unit (FPSO) or a shore-based facility. In addition to flowlines **88** that carry the formation fluid away from the wells **82**, the subsea system **70** may include lines or conduits **92** that supply fluids, as well as carry control and data lines to the subsea equipment. These conduits **92** connect to a distribution module **94**, which in turn couples to the subsea stations **78** via supply lines **96**. In some scenarios, the surface platform **90** may be located a significant distance (e.g., greater than 100 m, greater than 1 km, greater than 10 km, or greater than 60 km) away from the wells **82**. As discussed in further detail below, the subsea system **70** (e.g., the subsea tree **74**, the subsea station **78**, the pipeline manifold **86**, and/or the distribution module **94**) may include a subsea power system (e.g., subsea power bus system) that provides secondary power from energy storage units (e.g., batteries, fuel cells, or super capacitors (for initial actuator movement)) over one or more buses to various subsea components (e.g., actuators, sensors, etc.). For example, the subsea power system may be configured to provide secondary power, such as during a power loss from the primary power from the electrical cables **72**, to operate various valves, sensors, and other subsea components. While the subsea system described above is for extracting hydrocarbons, it should be understood that the present disclosure may also apply to other types of subsea systems **70**, such as subsea injection systems (e.g., subsea gas injection system, subsea water injection system, subsea carbon dioxide injection system).

[0053] Accordingly, the present disclosure is directed to techniques for generating a glycerol-based scale inhibitor using glycerol and a scale-inhibiting precursor and further adding additives to generate a glycerol-based scale inhibitor solution. In this way, a glycerol-based scale inhibitor in

the presence of an additive feed may generate a glycerol-based scale inhibitor solution having certain chemical compositions, such as different stoichiometric degrees of functionalization, type of functional group, length of main chain carbon, and pH-mediated binding availability that are useful for mitigating inorganic scale. For example, the resulting glycerol-based scale inhibitor solution may be provided to a liquid volume including metal ions, forming a metal ion complex to reduce inorganic scale. As described above, the disclosed glycerol-based scale inhibitor solution may be used in direct anti-scaling applications due to the different stoichiometric degrees of functionalization, type of functional group, length of main chain carbon, and pH-mediated binding availability. In any case, the glycerol-based scale inhibitor solution may be utilized in oil and gas, water treatment, power plant, or geothermal applications.

[0054] The technical effect of the disclosed embodiments includes a glycerol-based scale inhibitor with tunable chelating activity by adjusting the stoichiometric ratio of scale-inhibiting precursors. Additionally, or alternatively, the chelating activity of the glycerol-based scale inhibitor may be tuned through the use of different scale-inhibiting precursors. For example, the glycerol-based scale inhibitor may include one or multiple different scale-inhibiting functional groups. The chelating activity of the glycerol-based scale inhibitor solution may also be tuned by the use of additives, such as buffers, corrosive inhibitors, and the like.

[0055] The subject matter described in detail above may be defined by one or more clauses, as set forth below.

[0056] A method includes providing a glycerol feed and providing a scale-inhibiting precursor feed. The method also includes generating one or more glycerol-based scale inhibitors by contacting the glycerol feed with the scale-inhibiting precursor feed. The method also includes providing one or more additives to the glycerol-based scale inhibitor, thereby generating a glycerol-based scale inhibitor solution.

[0057] The method of the preceding clause, wherein the glycerol-based scale inhibitor solution comprises the one or more glycerol-based scale inhibitors and the one or more additives.

[0058] The method of any preceding clause, wherein the scale-inhibiting precursor feed comprises alkenyl phosphonic acids.

[0059] The method of any preceding clause, wherein the scale-inhibiting precursor feed comprises phosphate esters.

[0060] The method of any preceding clause, wherein the scale-inhibiting precursor comprises functionalized carboxylic acids.

[0061] The method of any preceding clause, wherein the scale-inhibiting precursor comprises sulfonates.

[0062] The method of any preceding clause, wherein the scale-inhibiting precursor comprises a combination of alkenyl phosphonic acids, phosphate esters, sulfonates, and carboxylic acids.

[0063] The method of any preceding clause, wherein the one or more additives comprise phosphate-based buffers, hydroxide-based buffers, carbonate-based buffers, bicarbonate-based buffers, amine-based buffers, acetate-based buffers, or any combination thereof.

[0064] A composition includes a glycerol analogue core and one or more scale-inhibiting functional groups linked to the glycerol analogue core via one or more ethers of the glycerol analogue core.

[0065] The composition of the preceding clause, wherein the glycerol analogue core comprises three carbon atoms.

[0066] The composition of any preceding clause, wherein the one or more scale-inhibiting functional groups comprise alkenyl phosphonic acids.

[0067] The composition of any preceding clause, wherein the one or more scale-inhibiting functional groups comprise phosphates.

[0068] The composition of any preceding clause, wherein the one or more scale-inhibiting functional groups comprise sulfonates.

[0069] The composition of any preceding clause, wherein the one or more scale-inhibiting

functional groups comprise a mixture of phosphates and alkenyl phosphonic acids.

[0070] The composition of any preceding clause, wherein the one or more scale-inhibiting functional groups are a combination of two or more of phosphates, alkenyl phosphonic acids, sulfonates, and phosphate esters.

[0071] The composition of any preceding clause, wherein the glycerol analogue core comprises less than three hydroxyl functional groups.

[0072] The composition of any preceding clause, further comprising one or more buffers and one or more solvents.

[0073] A method includes providing a glycerol-based scale inhibitor solution. The method also includes providing a liquid volume, wherein the liquid volume comprises metal ions. The method also includes sequestering the metal ions with the glycerol-based scale inhibitor solution, thereby forming a metal-ion complex. The method also includes separating the metal-ion complex and the glycerol-based scale inhibitor solution from the liquid volume.

[0074] The method of preceding clause, wherein the metal ions comprise metal carbonates, metal sulfates, metal hydroxides, metal sulfides, zinc sulfides, lead sulfides, or any combination thereof.

[0075] The method of any preceding clause, wherein the glycerol-based scale inhibitor solution is injected via a subsea fluid injection system into a subterranean reservoir to mitigate inorganic scale.

[0076] The foregoing description, for purpose of explanation, has been described with reference to specific embodiments. However, the illustrative discussions above are not intended to be exhaustive or to limit the disclosure to the precise forms disclosed. Many modifications and variations are possible in view of the above teachings. Moreover, the order in which the elements of the methods described herein are illustrated and described may be re-arranged, and/or two or more elements may occur simultaneously. The embodiments were chosen and described in order to best explain the principals of the disclosure and its practical applications, to thereby enable others skilled in the art to best utilize the disclosure and various embodiments with various modifications as are suited to the particular use contemplated.

[0077] Finally, the techniques presented and claimed herein are referenced and applied to material objects and concrete examples of a practical nature that demonstrably improve the present technical field and, as such, are not abstract, intangible or purely theoretical. Further, if any claims appended to the end of this specification contain one or more elements designated as “means for [perform]ing [a function] . . . ” or “step for [perform]ing [a function] . . . ”, it is intended that such elements are to be interpreted under 35 U.S.C. 112 (f). However, for any claims containing elements designated in any other manner, it is intended that such elements are not to be interpreted under 35 U.S.C. 112 (f).

Claims

1. A method comprising: providing a glycerol feed; providing a scale-inhibiting precursor; generating one or more glycerol-based scale inhibitors by contacting the glycerol feed with the scale-inhibiting precursor; and providing one or more additives to the one or more glycerol-based scale inhibitors, thereby generating a glycerol-based scale inhibitor solution.
2. The method of claim 1, wherein the glycerol-based scale inhibitor solution comprises the one or more glycerol-based scale inhibitors and the one or more additives.
3. The method of claim 1, wherein the scale-inhibiting precursor comprises alkenyl phosphonic acids.
4. The method of claim 1, wherein the scale-inhibiting precursor comprises phosphate esters.
5. The method of claim 1, wherein the scale-inhibiting precursor comprises functionalized carboxylic acids.
6. The method of claim 1, wherein the scale-inhibiting precursor comprises sulfonates.
7. The method of claim 1, wherein the scale-inhibiting precursor comprises a combination of

alkenyl phosphonic acids, phosphate esters, sulfonates, and carboxylic acids.

8. The method of claim 7, wherein the one or more additives comprise phosphate-based buffers, hydroxide-based buffers, carbonate-based buffers, bicarbonate-based buffers, amine-based buffers, acetate-based buffers, or any combination thereof.

9. A composition comprising: a glycerol analogue core; and one or more scale-inhibiting functional groups linked to the glycerol analogue core via one or more ethers of the glycerol analogue core.

10. The composition of claim 9, wherein the glycerol analogue core comprises three carbon atoms.

11. The composition of claim 9, wherein the one or more scale-inhibiting functional groups comprise alkenyl phosphonic acids.

12. The composition of claim 9, wherein the one or more scale-inhibiting functional groups comprise phosphates.

13. The composition of claim 9, wherein the one or more scale-inhibiting functional groups comprise sulfonates.

14. The composition of claim 9, wherein the one or more scale-inhibiting functional groups comprise a mixture of phosphates and alkenyl phosphonic acids.

15. The composition of claim 9, wherein the one or more scale-inhibiting functional groups are a combination of two or more of phosphates, alkenyl phosphonic acids, sulfonates, and phosphate esters.

16. The composition of claim 9, wherein the glycerol analogue core comprises less than three hydroxyl functional groups.

17. The composition of claim 9, further comprising one or more buffers and one or more solvents.

18. A method comprising: providing a glycerol-based scale inhibitor solution; providing a liquid volume comprising metal ions; sequestering the metal ions with the glycerol-based scale inhibitor solution, thereby forming a metal-ion complex; and separating the metal-ion complex and the glycerol-based scale inhibitor solution from the liquid volume.

19. The method of claim 18, wherein the metal ions comprise metal carbonates, metal sulfates, metal hydroxides, metal sulfides, zinc sulfides, lead sulfides, or any combination thereof.

20. The method of claim 18, wherein the glycerol-based scale inhibitor solution is used to mitigate inorganic scale in oil and gas systems, geothermal applications, and industrial water treatment plants.
