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SALT OF MONOCHLOROACETIC ACID WITH CHELATING AGENT FOR DELAYED ACIDIFICATION IN THE OIL FIELD INDUSTRY

5 Field

The present invention is directed to a process for treating a subterranean earth formation and an aqueous acidizing treatment fluid therefor.

Background

10 Acidification fluids are commonly used in the oil industry to create wormholes and to connect the wellbore with the formation. Typically, hydrochloric acid (HCl) has been used for decades. However, HCl has a main disadvantage related to its high reactivity with the calcium carbonate (CaCO_3) present in the limestone reservoirs. The reactivity of the HCl is highly affected by the
15 temperature in the reservoir. The higher the temperature, the faster the HCl reacts, thus forming wormholes with unstable structures that may subsequently collapse and block the access to the formation. For the previous reasons, when using HCl containing acidification fluid at higher temperatures specific measures need to be taken. This evidently increases costs and limits application freedom.
20 Another disadvantage is the high corrosivity and this makes the acidizing treatment expensive. As a rule of thumb, up to 200 °F (93 °C) the treatment can be performed with HCl and a corrosion inhibitor, but above 200 °F (93°C) a corrosion inhibitor intensifier is also needed. The use of corrosion inhibitor intensifiers add to the costs of acidifying fluids. They can be up to 60% of the
25 total costs of the treatment.

There is a need to access deeper wells as many of the recently discovered reservoirs are categorized as High Pressure High Temperature (HPHT). In that sense, it is of interest to find an alternative option to the HCl, which is not as
30 reactive when exposed to high temperatures and offers an acidification feature which can be released in a controlled fashion.

Several publications have been published trying to address these issues:

US 2014/0296113 discloses a method of servicing a wellbore in a subterranean formation comprising preparing a wellbore servicing fluid comprising an amino multicarboxylic acid chelating agent, a pH adjusting compound, and an aqueous
5 base fluid, and contacting the wellbore servicing fluid with scale deposits on a surface in fluid communication with the wellbore and/or subterranean formation.

GB 2519388 discloses a process for treating formation damage in an underground formation comprising the use of a cyclodextrin comprising treatment
10 fluid which may also comprise an acid, an organic acid precursor, a chelating agent and a chelating agent precursor.

WO 2015/030801 relates to acidizing fluids for use in subterranean applications, and more specifically, to complexing-acidizing self-diverting treatment fluids and
15 methods relating thereto for use in subterranean formations comprising carbonates.

US 2009/0042748 relates to stimulation of wells penetrating subterranean formations. More particularly it relates to matrix acidizing of sandstone; most
20 particularly it relates methods of injecting matrix acidizing fluids that include polymeric additives into a sandstone formation without the use of acid preflush.

US 2016/0115376 relates to a process to treat a subterranean formation by introducing into the formation a composition containing between 1 and 40 wt %
25 on total weight of the composition of a chelating agent selected from the group of glutamic acid N,N-diacetic acid or a salt thereof (GLDA), aspartic acid N,N-diacetic acid or a salt thereof (ASDA), and methylglycine N,N-diacetic acid or a salt thereof (MGDA), wherein the process contains a soaking step.

30 US 3885630 is directed to a method wherein acid-reactive material in or around a bore hole or well is acidized by contacting water-soluble weak acid and water-soluble weak acid salt such as acetic acid and sodium acetate.

US 4122896 is directed to a method wherein subterranean reservoirs are acidized by injecting into the reservoir a substantially acid-free aqueous solution of a chloro carboxylic acid salt, such as mono or di-chloro acetic acid salt or 2 chloro propionic acid salt.

5

The latter two publications describe delayed acidification using the hydrolysatation of chlorocarboxylic acid salts. During the hydrolyzation glycolic acid and HCl are formed. It was however found that the glycolic acid formed may react with the calcium carbonate being present in the lime stone reservoirs forming calcium glycolate. The calcium glycolate may cause plugging in the piping if a sufficient amount of precipitate is formed. Calcium glycolate has low solubility and precipitates easily. Precipitation of calcium glycolate during acidation in the oil wells (also referred to as scaling), is undesirable. It was further found that solutions with calcium glycolate in solution form a gel upon cooling to room temperature. This gelation may cause plugging of the pipes.

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The present disclosure aims to find solutions to the above- identified problems.

Summary of the disclosure

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The disclosure is directed to a process for treating a subterranean earth formation by introducing a monovalent salt of monochloroacetic acid into said subterranean earth formation in the presence of a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.

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In the present invention, only a monovalent salt of monochloroacetic acid is used. "Monovalent salt of monochloroacetic acid" means that the cation in the monochloroacetate salt has a valency of one. Preferably the cation, (also denoted as the monovalent counterion) of the salt of monochloroacetic acid is selected from the group consisting of lithium, potassium, sodium, and ammonium.

30

The cation of the salt of monochloroacetic acid is most preferably sodium (the sodium salt of monochloroacetic acid is hereinafter also denoted as SMCA).

5 The number of carboxylate groups of the chelating agent (n) is between 1 and 5 (or in other words, the chelating agent comprises 1, 2, 3, 4, or 5 carboxylate groups). Preferred chelating agents are selected from the group consisting of monovalent salts of glucaric acid, monovalent salts of gluconic acid, monovalent salts of glucoheptonic acid and other stereoisomers of 2,3,4,5,6-pentahydroxyhexanoic acid and 2,3,4,5,6,7-hexahydroxyheptanoic acid
10 (wherein "monovalent salt" means that the carboxylate group(s) of the chelating agent has/have monovalent cation(s)). Specific examples are sodium gluconate, sodium glucoheptonate, other stereoisomers of sodium 2,3,4,5,6-pentahydroxyhexanoate and sodium 2,3,4,5,6,7-hexahydroxyheptanoate.

15 Usually more than 2 wt% of chelating agent is present and the molar ratio between the salt of monochloroacetic acid (e.g. sodium monochloroacetate) and the chelating agent lies between 1: 0.5/n and 1: 10/n, n being the number of carboxylate groups of the chelating agent.

20 In the process according to the disclosure the monovalent salt of the monochloroacetic acid and the chelating agent may be introduced into the subterranean formation in the form of an aqueous acidizing treatment fluid comprising the monochloroacetate salt and the chelating agent.

25 In the process according to the disclosure the temperature of the earth formation into which the monochloroacetate salt according to the invention and the chelating agent are introduced may be between 80 and 200 °C, preferably between 85 and 180 °C, more preferably between 90 and 160 °C.

30 The disclosure is directed to an aqueous acidizing treatment fluid comprising
(i) a monovalent salt of monochloroacetic acid, and

(ii) a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.

5 The disclosure is further directed to an aqueous acidizing treatment fluid wherein the monochloroacetate salt according to the present invention is present in an amount of at least 3 wt%, preferably at least 5 wt%, and most preferably at least 10 wt% (based on the total amount of the aqueous acidizing treatment fluid). The aqueous acidizing treatment fluid preferably comprises at most 20 wt% of the
10 monochloroacetate salt, preferably at most 18 wt% of the monochloroacetate salt, and most preferably, at most 14 wt% of the monochloroacetate salt (based on the total amount of the aqueous acidizing treatment fluid). In general, the salt of monochloroacetic acid is present in an amount of between 3 and 20 wt%, preferably between 4 and 18 wt% and most preferably between 5 and 14 wt%,
15 based on the total weight of the aqueous acidizing treatment fluid. The concentration of the monochloroacetate salt may be adjusted to the desired dissolution power of the treatment fluid. It will be clear to the person skilled in the art that the solubility of the total formulation is also dependent on the temperature at which the treatment fluid is used.

20 In general the molar ratio between the monovalent salt of the monochloroacetic acid (preferably being sodium monochloroacetate) and the chelating agent according to the present invention in the aqueous acidizing treatment fluid lies between $1 : 0.5/n$ and $1 : 10/n$, preferably between $1 : 0.5/n$ and $1 : 5/n$ and most
25 preferably between $1 : 0.8/n$ and $1 : 2/n$, n being the number of carboxylate groups in the chelating agent (being 1, 2, 3, 4, or 5).

The aqueous acidizing treatment fluid according to the disclosure may further comprise one or more conventional additives from the group of mutual solvents,
30 anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitors, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives,

friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives such as further acids and/or bases, bactericides/biocides, particulates, crosslinkers, salt substitutes (such as tetramethyl ammonium chloride), relative permeability modifiers, sulfide
5 scavengers, fibres, nanoparticles, combinations thereof, or the like.

Detailed description

The various aspects of the present invention will be elucidated further below.

10

As indicated above, the invention is directed to a process for treating a subterranean earth formation by introducing a monovalent salt of monochloroacetic acid into said subterranean earth formation in the presence of a chelating agent which comprises at least one carboxylate group having a
15 monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.

In the present invention, only a monovalent salt of monochloroacetic acid is used. "Monovalent salt of monochloroacetic acid" means that the cation in the
20 monochloroacetate salt has a valency of one. Preferably the cation, (also denoted as the monovalent counterion) of the salt of monochloroacetic acid is selected from the group consisting of lithium, potassium, sodium, and ammonium. The cation of the salt of monochloroacetic acid is most preferably sodium (the sodium salt of monochloroacetic acid is hereinafter also denoted as SMCA).

25

The monovalent salt of monochloroacetic acid can hydrolyse into Glycolic Acid (GA) and hydrochloric Acid (HCl). The hydrolysis rate depends on the temperature, concentration and pH. With the use of a salt of monochloroacetic acid, a well-controlled delayed acidification could be established.

30

It was found that with the addition of a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore

comprises a carbon chain carrying at least five hydroxyl groups, the formation of calcium glycolate is inhibited, so that scaling and plugging may be avoided.

5 Further, with the process according to the disclosure face dissolution at the injection site may be inhibited or avoided altogether, so that nicely formed wormholes are created, the stability of the earth formation is ensured and the acidizing treatment fluid is effectively used.

10 The chelating agent comprises at least one carboxylate group having a monovalent counterion. "Monovalent counterion" denotes a cation of which the valency is one. Examples of suitable cations are sodium, ammonium, lithium, and potassium.

15 Depending on the type of rock to be treated the most preferred cation can be chosen. In the case of carbonate-based rock the cation of the salt of monochloroacetic acid preferably is sodium, potassium and/or lithium. In the case of sandstone ammonium is the preferred cation.

20 The number of carboxylate groups of the chelating agent n is between 1 and 5, with n preferably being 1. Preferred chelating agents are selected from the group consisting of monovalent salts of glucaric acid, monovalent salts of gluconic acid, monovalent salts of glucoheptonic acid, uronic acids such as galacturonic acids, aldonic acids and other stereoisomers of 2,3,4,5,6-pentahydroxyhexanoic acid and 2,3,4,5,6,7-hexahydroxyheptanoic acid (wherein "monovalent salt" means
25 that the carboxylate group(s) of the chelating agent has/have monovalent cation(s)). Specific examples are sodium gluconate, sodium glucoheptonate, other stereoisomers of sodium 2,3,4,5,6-pentahydroxyhexanoate and sodium 2,3,4,5,6,7-hexahydroxyheptanoate.

30 In the process according to the disclosure, the monovalent salt of the monochloroacetic acid and the chelating agent are introduced into the

subterranean formation in the form of an aqueous acidizing treatment fluid comprising the monovalent salt of monochloroacetic acid and the chelating agent.

5 Usually more than 2 wt% of chelating agent is used (based on the total weight of the treatment fluid) and the molar ratio between the salt of monochloroacetic acid and the chelating agent lies between 1: 0.5/n and 1: 10/n, n being the number of carboxylate groups of the chelating agent.

10 In the process according to the disclosure the temperature of the earth formation into which the monochloroacetate salt and the chelating agent are introduced is preferably between 85 and 180 °C, more preferably between 90 and 160 °C.

The disclosure is directed to an aqueous acidizing treatment fluid comprising

- (i) a monovalent salt of monochloroacetic acid, and
- 15 (ii) a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.

20 As is shown in the examples, a mixture of monochloroacetic acid salt in a concentration of above 4 wt% will form a precipitation with calcium carbonate. However, with the addition of a chelating agent according to the disclosure, this precipitation can be avoided and monochloroacetic acid salts may be used in concentrations above 8 wt%, or even higher (e.g. 10 wt%). From the experimental data it is clear that this effect could not be reached with other conventional multi-

25 carboxylate chelating agents such as EDTA and trisodiumcitrate.

Therefore, the disclosure is further directed to an aqueous acidizing treatment fluid wherein the monochloroacetate salt according to the present invention is present in an amount of at least 3 wt%, preferably at least 5 wt% and most preferably at

30 least 10 wt%, based on the total amount of treatment fluid. The aqueous acidizing treatment fluid preferably comprises at most 20 wt% of the monochloroacetate salt, preferably at most 18 wt% of the monochloroacetate salt and most

preferably, at most 14 wt% of the monochloroacetate salt (based on the total amount of the aqueous acidizing treatment fluid). The concentration of the monochloroacetate salt may be adjusted to the desired dissolution power of the treatment fluid. It will be clear to the person skilled in the art that the solubility of the total formulation is also dependent from the temperature at which the treatment fluid is used.

In general, the monochloroacetate salt according to the present invention is present in an amount of between 3 and 20 wt%, preferably between 4 and 18 wt% and most preferably between 5 and 14 wt%, based on the total weight of the aqueous acidizing treatment fluid.

In general, the molar ratio between monochloroacetate salt according to the present invention and the chelating agent of the aqueous acidizing treatment fluid lies between 1 : 0.5/n and 1 : 10/n, preferably between 1 : 0.5/n and 1 : 5/n and most preferably between 1 : 0.8/n and 1 : 2/n, n being the number of carboxylate groups in the chelating agent.

The aqueous acidizing treatment fluid according to the disclosure contains water as a solvent for the other ingredients wherein water can be e.g. fresh water, produced water or seawater. Other solvents may be added as well for instance to create emulsions. Suitable other solvents are ketones, alcohols or esters.

The aqueous acidizing treatment fluid according to the disclosure may further comprise one or more conventional additives from the group of mutual solvents, anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitors, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives such as further acids and/or bases, bactericides/biocides, particulates, crosslinkers, salt substitutes (such as

tetramethyl ammonium chloride), relative permeability modifiers, sulfide scavengers, fibres, nanoparticles, combinations thereof, or the like.

5 A mutual solvent is a chemical additive that is soluble in oil, water, acids (often HCl based), and other well treatment fluids. Mutual solvents are routinely used in a range of applications, controlling the wettability of contact surfaces before, during and/or after a treatment, and preventing or breaking emulsions. Suitable mutual solvents are ketones, alcohols or esters.

10 The surfactant can be any surfactant known to the person skilled in the art for use in oil and gas wells. Preferably, the surfactant is a nonionic or cationic surfactant, even more preferably a cationic surfactant.

15 Anti-sludge agents stabilize the acid-oil emulsion and include alkyl phenols, fatty acids, and anionic surfactants. Frequently used as the surfactant is a blend of a sulfonic acid derivative and a dispersing surfactant in a solvent. Such a blend generally has dodecyl benzene sulfonic acid (DDBSA) or a salt thereof as the major dispersant, i.e. anti-sludge, component.

20 Corrosion inhibitors may be selected from the group of amine and quaternary ammonium compounds and sulfur compounds. Examples are diethyl thiourea (DETU), which is suitable up to 185°F (about 85°C), alkyl pyridinium or quinolinium salt, such as dodecyl pyridinium bromide (DDPB), and sulfur compounds, such as thiourea or ammonium thiocyanate, which are suitable for
25 the range 203-302°F (about 95-150°C), benzotriazole (BZT), benzimidazole (BZI), dibutyl thiourea, a proprietary inhibitor called TIA, and alkyl pyridines.

One or more corrosion inhibitor intensifiers may be added, such as for example formic acid, potassium iodide, antimony chloride, or copper iodide.

30

In general, the most successful inhibitor formulations for organic acids and chelating agents contain amines, reduced sulfur compounds or combinations of

a nitrogen compound (amines, quats or polyfunctional compounds) and a sulfur compound. The amount of corrosion inhibitor is preferably between 0.1 and 5.0 volume%, more preferably between 0.1 and 2.0 volume% on total fluid.

- 5 One or more salts may be used as rheology modifiers to modify the rheological properties (e.g., viscosity and elastic properties) of the treatment fluids. These salts may be organic or inorganic. When adding salts care should be taken not to detrimentally affect the pH and therewith detrimentally affect the hydrolyzation rate.

10

Wetting agents that may be suitable for use in this invention include crude tall oil, oxidized crude tall oil, surfactants, organic phosphate esters, modified imidazolines and amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or derivatives of these and similar such compounds that
15 should be well known to one of skill in the art.

20

Gelling agents in a preferred embodiment are polymeric gelling agents. Examples of commonly used polymeric gelling agents include, but are not limited to, biopolymers, polysaccharides such as guar gums and derivatives thereof, cellulose derivatives, synthetic polymers like polyacrylamides and viscoelastic surfactants, and the like. These gelling agents, when hydrated and at a sufficient concentration, are capable of forming a viscous solution.

25

When used to make an aqueous-based treatment fluid, a gelling agent is combined with an aqueous fluid and the soluble portions of the gelling agent are dissolved in the aqueous fluid, thereby increasing the viscosity of the fluid.

30

Viscosifiers may include natural polymers and derivatives such as xanthan gum and hydroxyethyl cellulose (HEC) or synthetic polymers and oligomers such as poly(ethylene glycol) [PEG], poly(diallyl amine), poly(acrylamide), poly(aminomethyl propyl sulfonate) [AMPS polymer], poly(acrylonitrile), polyvinyl acetate), polyvinyl alcohol), polyvinyl amine), polyvinyl sulfonate),

poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), polyvinyl pyrrolidone), polyvinyl lactam), and co-, ter-, and quaterpolymers of the following (co-)monomers: ethylene, butadiene, isoprene, styrene, divinyl benzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6- heptadiene-4-one (diallyl ketone), diallyl amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinyl pyrrolidone, and vinyl lactam. Yet other viscosifiers include clay-based viscosifiers, especially laponite and other small fibrous clays such as the polygorskites (attapulgite and sepiolite). When using polymer-containing viscosifiers, the viscosifiers may be used in an amount of up to 5% by weight of the fluid.

The use of brines is known in the art and needs no further elucidation here. Any brine chosen should be compatible with the formation and should have a sufficient density to provide the appropriate degree of well control.

Additional salts may be added to a water source, e.g., to provide a brine, and a resulting treatment fluid, in order to have a desired density. The amount of salt to be added should be the amount necessary for formation compatibility, such as the amount necessary for the stability of clay minerals, taking into consideration the crystallization temperature of the brine, e.g., the temperature at which the salt precipitates from the brine as the temperature drops. Preferred suitable brines may include seawater and/or formation brines.

It is noted that various elements of the present invention, including but not limited to preferred ranges for the various parameters, can be combined unless they are mutually exclusive.

The invention will be elucidated by the following examples without being limited thereto or thereby.

Examples

Example 1: Dissolution of CaCO_3 in the presence of SMCA

5 To study the forming of a precipitate, 750 g of 10 wt% SMCA (pH about 8-9) solution was added to a stirred 1 L reactor. 32.2 g of calcium carbonate powder was added to the mixture via a funnel. The reactor was closed and the headspace was filled with 3 barg nitrogen gas. A temperature probe was continuously measuring the temperature of the solution. This solution was then
10 heated with an oil bath to 120 °C for about 5 h. A first sample was taken from the reactor using a dip tube and the chloride concentration was measured by titration using silver nitrate to check if SMCA was completely reacted to acid. After 5 h the heating was stopped and the temperature of the reaction mixture was lowered to 80 °C at ambient pressure. A second sample of 25 mL was
15 drained from the reactor and transferred to a glass vial. This sample was kept at a constant temperature of 40 °C in an oil bath. After 24 h it was noticed that the sample had become completely solid (see Figure 2a). This experiment was repeated using different solutions of SMCA varying between 2 and 8 wt% SMCA in an aqueous solution. Also the calcium carbonate was equimolar added
20 to these solutions. As can be seen in Table 1 only the mixture containing 2 wt% SMCA gave a clear solution after reaction.

25

30

Table 1: Results of SMCA solutions of different concentrations with added calcium carbonate

wt% SMCA used (based on total weight of the solution in the reactor)	Amount of SMCA (g)	Amount of calcium carbonate (g)	Precipitation of calcium salts (Y/N)
2	15	6.4	N
4	30	12.9	Y
5	37.5	16.1	Y
6	45	19.2	Y
8	60	25.6	Y
10	75	32.2	Y

5 **Example 2: Dissolution of CaCO_3 in the presence of SMCA and sodium gluconate**

Example 1 was repeated but now 10 wt% of SMCA was used in the presence of sodium gluconate. The experiment was performed using the same conditions as applied in Example 1. Only in this experiment 750 g of an aqueous solution comprising 75 g (10 wt%) of SMCA and 142.5 g (19 wt%) of D-gluconic acid sodium salt (purity 99% from Sigma Aldrich) was loaded to the reactor. Also 32.2 g of calcium carbonate was added to the reactor via a funnel. The reactor was subsequently closed and the headspace was filled with 3 barg nitrogen gas. A temperature probe was continuously measuring the temperature of the solution. This solution was then heated with an oil bath to 120 °C for about 5 h. A first sample was taken from the reactor using a dip tube and the chloride concentration was measured by titration to check if SMCA was completely converted to acid. After 5 h the heating was stopped and the temperature of the reaction mixture was lowered to 80 °C at ambient pressure. A sample of 25 mL

was drained from the reactor and transferred to a glass vial. This sample was kept at a constant temperature of 40 °C in an oil bath. After 24 h it was noticed that the sample was still completely clear and did not contain any precipitates (see Figure 2b). Thus, by the addition of a chelating agent according to the present disclosure, high amounts of SMCA can be used without the forming of precipitates.

Example 3: Core-flood test with 10 wt% SMCA solution and 18 wt% sodium gluconate at 150°C

Figure 1 shows a schematic diagram for the core flooding apparatus. For the core flooding test a new piece of core with a diameter of 1.5 inches (3.81 cm) and a length of 6 inches (15.24 cm) was used. The core was placed in the coreholder and shrinkable seals were used to prevent any leakage between the holder and the core. The coreholder was placed in an oven. The temperature of the heated core was controlled by a Binder ED400 series, with a fluctuation of $\pm 0.3^{\circ}\text{C}$. In the inlet and outlet of the coreholder, a Pt-100 was installed to control the temperature of the injection fluid.

An Isco Syringe double piston pump was used to pump the brine or test fluid through the core and an Enerpac hand hydraulic pump was used to apply the required overburden pressure. A back pressure of 1,000 psi (6.9 MPa) was applied to keep CO_2 in solution. The brine solution was kept into a storage accumulator inside the oven. The test fluid was placed in a second accumulator outside the oven and connected to a pre-heating line with the coreholder.

The back pressure was controlled by a Mity-Mite back pressure regulator model S91W - EQ and kept constant at 300 - 400 psi (2.1 – 2.8 MPa) less than the overburden pressure. The pressure drop across the core was measured with a set of Jumo dTrans p02 differential pressure transducers, and monitored by lab view software. Two gauges were installed with ranges of 0-800 psi (0 - 5.5 MPa) and 0-1500 psi (0 – 10.3 MPa), respectively.

Before running a core flooding test, the core was first dried in an oven at 160°F (71 °C) and weighted. Subsequently the core was saturated with water under

vacuum at room temperature. The pore volume was calculated from the difference in weight of the dried and saturated core.

The core permeability before and after the treatment was calculated from the pressure drop using Darcy's equation for laminar, linear, and steady-state flow of Newtonian fluids in porous media:

$$K = (122.81 \text{ q}\mu\text{L})/(\Delta p D^2)$$

where K is the core permeability in md, q is the flow rate in cm^3/min , μ is the fluid, viscosity in cP, L is the core length in inch, Δp is the pressure drop across the core in psi, and D is the core diameter in inch.

Prior to the core flooding test the core was pre-heated to the required test temperature for at least 12 hours with brine at a low injection speed of $0.01 \text{ cm}^3/\text{min}$.

This procedure was used to prove the concept of creating wormholes by injecting a mixture of 10 wt% SMCA with 19 wt% sodium(D)gluconate and 0.25 wt% corrosion inhibitor at pH=7.5 into an Indiana limestone core with a permeability of 12 mD, flow rate $1.5 \text{ cm}^3/\text{min}$.

Upon inspection of the core, by means of a CT scan, it was shown that with the process according to the disclosure nicely formed wormholes are formed without face dissolution.

Example 4: Dissolution of CaCO_3 in the presence of 10 wt% of SMCA and various chelating agents

To study the performance of various chelating agents, crystalline EDTA-Na_4 tetra hydrate, also known as product Dissolvine Na-X from AkzoNobel, trisodium citrate dihydrate (with a purity of 99% from J.T.Baker) and α -D-glucoheptonic acid sodium salt (with a purity of 99% from Sigma Aldrich) were separately equimolar mixed with 750 g of an aqueous 10 wt% SMCA solution. The same procedure as explained in example 1 was applied for each mixture.

Accordingly, after addition of a solution of SMCA and the respective chelating agent to the reactors, 32.2 g of calcium carbonate was added to each reactor. After a reaction time of 5 h at 120 °C samples were taken from the reaction mixtures to check the complete release of acid and a sample of 25 mL was
5 taken separately and controlled for 24 h at 40 °C.

Table 2 Overview of chelating agents used in Example 4

	Chelating agent	Amount (g)
1	EDTA-Na ₄ tetra hydrate	72.8
2	trisodium citrate dihydrate	93.0
3	α -D-glucoheptonic acid sodium salt	159.8

10 When comparing the reaction product of the mixture of SMCA with respectively Na₄-EDTA, trisodium citrate and sodium glucoheptonate, it was clear that only the sample starting from SMCA with sodium glucoheptonate was still completely clear (see Figure 2d) and did not contain any precipitates. The reaction mixtures starting from respectively SMCA with Na₄-EDTA and SMCA with trisodium
15 citrate were filled with precipitates (see Figure 2c and Figure 2e, respectively). This example demonstrates that formation of a precipitate from the reaction of SMCA and calcium carbonate can be prevented by using a chelate according to the present disclosure.

20 **Example 5: CaCO₃ dissolution rate of SMCA and MCA**

The time required to dissolve a given amount of CaCO₃ with SMCA and MCA is compared in this example. The reaction rate of this process can be controlled by temperature. SMCA hydrolyses with water and by heating into glycolic acid
25 and sodium chloride. Glycolic acid reacts very fast with CaCO₃. The extent of this reaction is followed by measuring the concentration of chloride. 750 g of 10 wt% SMCA (pH about 8-9) solution was added to a stirred 1 L reactor. 32.2 g of

calcium carbonate powder was added to the mixture via a funnel. The reactor was closed, and the headspace is filled with 3 barg nitrogen gas. A temperature probe was continuously measuring the temperature of the solution. This solution was then heated with an oil bath to 100°C. Samples were taken using a dip tube and a pressurized sample system. These samples were analysed on chloride to calculate the hydrolysis rate. Chloride was measured by titration using silver nitrate. The chloride concentration was then compared with the theoretical amount of chloride when all SMCA is converted into glycolic acid and sodium chloride. When full hydrolyzation was reached, it was assumed that CaCO₃ was completely dissolved. This procedure was repeated for temperatures at 140 and 160 °C. The time measured to completely dissolve CaCO₃ with SMCA at various temperatures is depicted in Table 3. For 10 wt% MCA a different procedure was used. Due to its high reactivity, the experiment was carried out at room temperature and atmospheric pressure. 750 g of 10 wt% MCA solution and 39.7 g of calcium carbonate powder were added to a glass vessel. The time to completely dissolve CaCO₃ with MCA was monitored visually and it is shown in Table 3. These results confirm the CaCO₃ dissolution rate of SMCA is much slower than the CaCO₃ dissolution rate of MCA which is advantageous to access deeper wells.

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Table 3 CaCO₃ dissolution rate for SMCA and MCA

	Temperature (°C)	Time needed for complete CaCO ₃ dissolution (min)
10 wt% SMCA	100	540
10 wt% SMCA	140	60
10 wt% SMCA	160	43
10 wt% MCA	25	5

25

CLAIMS

1. A process for treating a subterranean earth formation by introducing a monovalent salt of monochloroacetic acid into said subterranean earth formation in the presence of a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.
2. Process according to claim 1 wherein the subterranean earth formation comprises carbonate-based rock.
3. Process according to claim 2 wherein the cation of the salt of monochloroacetic acid is sodium, potassium and/or lithium.
4. Process according to claim 1 wherein the subterranean earth formation comprises sandstone.
5. Process according to claim 4 wherein the cation of the salt of monochloroacetic acid is ammonium and/or potassium.
6. Process according to any one of claims 1-4 wherein the cation of the salt of monochloroacetic acid is sodium.
7. Process according to any one of the preceding claims wherein the number of carboxylate groups in the chelating agent, n, is between 1 and 5.
8. Process according to any one of the preceding claims wherein the chelating agent is selected from the group consisting of monovalent salts of glucaric acid, monovalent salts of gluconic acid, monovalent salts of glucoheptonic acid, uronic acids such as galacturonic acids, aldonic acids and monovalent salts of other stereoisomers of 2,3,4,5,6-pentahydroxyhexanoic acid and 2,3,4,5,6,7-hexahydroxyheptanoic acid.

9. Process according to any one of the preceding claims wherein the monovalent salt of monochloroacetic acid and the chelating agent are introduced into the subterranean formation in the form of an aqueous acidizing treatment fluid comprising the monovalent salt of monochloroacetic acid and chelating agent.
10. Process according to claim 9 wherein more than 2 wt% of chelating agent is present in the aqueous acidizing treatment fluid (based on the total weight of the aqueous acidizing treatment fluid) and the molar ratio between the monovalent salt of monochloroacetic acid and the chelating agent lies between 1 : 0.5/n and 1 : 10/n, n being the number of carboxylate groups of the chelating agent.
11. Process according to any one of the preceding claims wherein the temperature of the earth formation into which the monovalent salt of monochloroacetic acid and the chelating agent are introduced is between 80 and 200 °C, preferably between 85 and 180 °C, more preferably between 90 and 160 °C.
12. An aqueous acidizing treatment fluid comprising
- (i) a monovalent salt of monochloroacetic acid, and
 - (ii) a chelating agent which comprises at least one carboxylate group having a monovalent counterion and furthermore comprises a carbon chain carrying at least five hydroxyl groups.
13. Aqueous acidizing treatment fluid according to claim 12 wherein the monovalent salt of monochloroacetic acid is present in an amount of at least 3 wt%, preferably at least 5 wt%, more preferably at least 10 wt%, and most preferably at least 14 wt%, based on the total weight of the aqueous acidizing treatment fluid.

14. Aqueous acidizing treatment fluid according to claim 12 or 13 wherein the molar ratio between the monovalent salt of monochloroacetic acid and the chelating agent lies between $1 : 0.5/n$ and $1 : 10/n$, n being the number of carboxylate groups in the chelating agent.
- 5 15. Aqueous acidizing treatment fluid according to any one of claims 12-14, wherein the cation of the monovalent salt of monochloroacetic acid is selected from the group consisting of sodium, potassium, lithium, and ammonium.
- 10 16. Aqueous acidizing treatment fluid according to any one of claims 12-15, wherein the cation of the monovalent salt of monochloroacetic acid is sodium.
- 15 17. Aqueous acidizing treatment fluid according to any one of claims 12 - 16 further comprising one or more compounds selected from the group of mutual solvents, anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitors, corrosion inhibitors intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives such as further acids and/or bases, bactericides/biocides, particulates, crosslinkers, salt substitutes (such as tetramethyl ammonium chloride), relative permeability modifiers, sulfide scavengers, fibres, nanoparticles, combinations thereof, or the like.
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- 25

Figure 1: Schematic view of core flooding set-up.

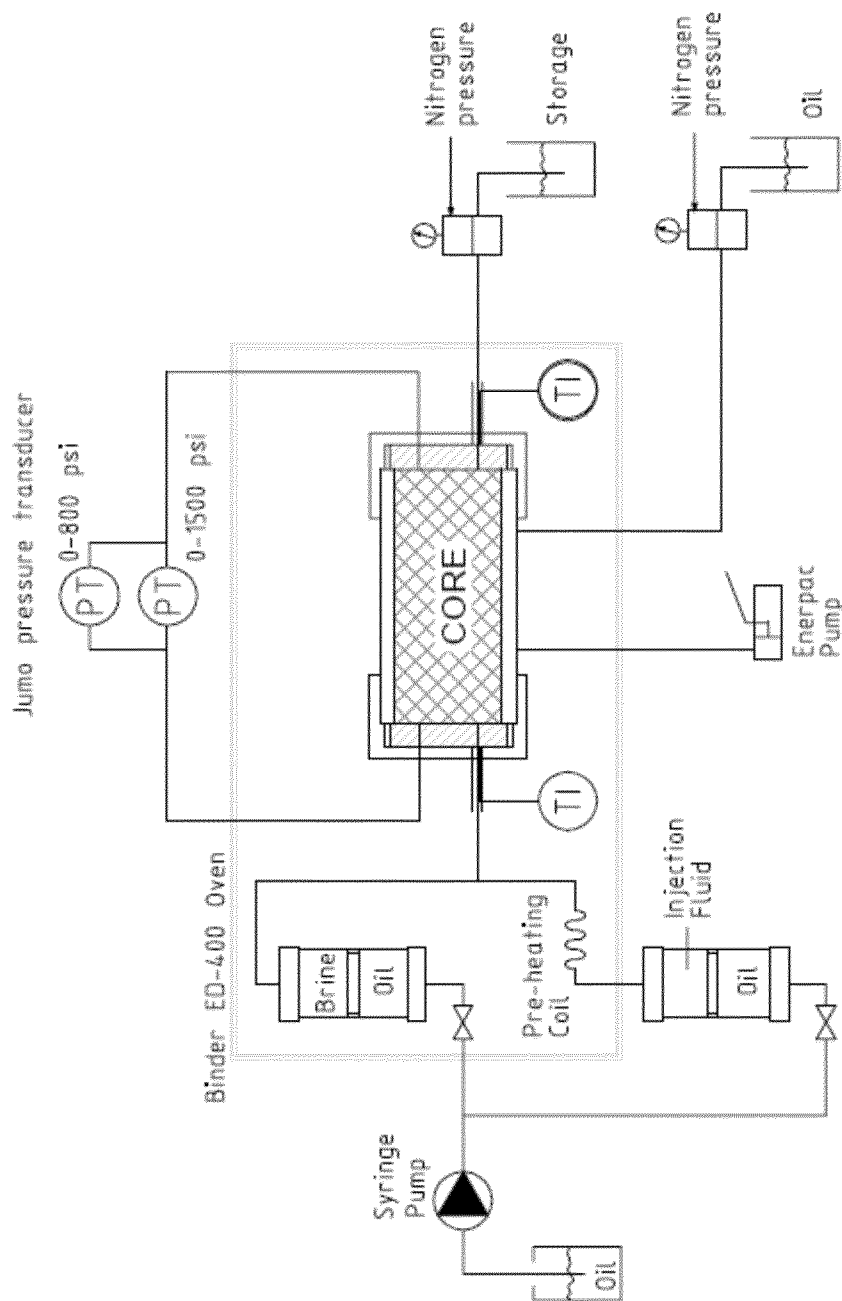
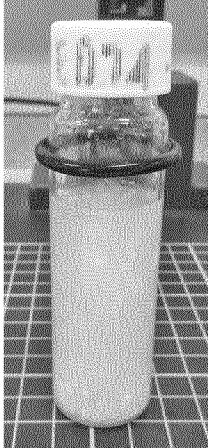
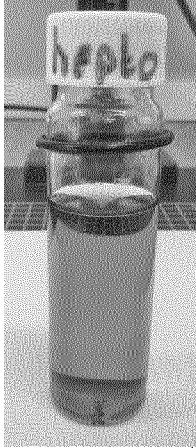


Figure 2a-e: Photos of samples taken in Examples 1, 2 and 4

				
No chelate	19 wt% sodium gluconate	10 wt% EDTA- Na_4 tetrahydrate	21.5 wt% α -D-gluc-heptonic acid sodium salt	12.5 wt% trisodium citrate dihydrate

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/065805

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/74
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/030801 A1 (HALLIBURTON ENERGY SERV INC [US]) 5 March 2015 (2015-03-05) cited in the application claims paragraph [0003] -----	1-17
X	US 2009/042748 A1 (FULLER MICHAEL J [US]) 12 February 2009 (2009-02-12) cited in the application claims -----	1-17
X	US 2014/296113 A1 (REYES ENRIQUE ANTONIO [US] ET AL) 2 October 2014 (2014-10-02) cited in the application claims ----- -/-	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/065805

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/065805

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