



(43) International Publication Date
17 November 2016 (17.11.2016)

(10) International Publication Number
WO 2016/182980 A1

- (51) **International Patent Classification:**
C09K 8/528 (2006.01) *E21B 37/06* (2006.01)
C02F 5/10 (2006.01)
- (21) **International Application Number:**
PCT/US2016/031402
- (22) **International Filing Date:**
9 May 2016 (09.05.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/160,686 13 May 2015 (13.05.2015) US
- (71) **Applicant:** DOW GLOBAL TECHNOLOGIES LLC
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).
- (72) **Inventor:** PADILLA-ACEVEDO, Angela I.; 2301 N.
Brazosport Blvd, Freeport, TX 77541 (US).
- (74) **Agent:** CHRISTY, M. Robert; The Dow Chemical Com-
pany, Intellectual Property, PO Box 1967, Midland,
Michigan 48641-1967 (US).

- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** THERMALLY STABLE SCALE INHIBITOR COMPOSITIONS

(57) **Abstract:** The present invention relates to a thermally stable polymeric scale inhibitor compositions and use thereof. Preferably, the polymeric scale inhibitor is a polycarboxylic acid copolymer comprising a styrene sulfonic acid group. The polymeric scale inhibitor compositions of the present invention are particularly suitable for high pressure/high temperature scale inhibition treatment of oil and gas production wells and/or subterranean formations.



WO 2016/182980 A1

THERMALLY STABLE SCALE INHIBITOR COMPOSITIONS

FIELD OF THE INVENTION

5 The present invention relates to thermally stable polymeric scale inhibitor compositions, and use thereof. The polymeric scale inhibitor compositions of the present invention are particularly suitable for high pressure/high temperature applications.

BACKGROUND OF THE INVENTION

10 Scale inhibiting polymers are often used in water treatment and oil field applications to minimize and/or prevent scale deposition. The deposition of scale can occur in the transport of aqueous mixtures and in subterranean rock formations due to the presence of water bearing alkaline earth metal cations such as calcium, barium, strontium and the like as well as the presence of anions such as phosphate, sulfates, carbonates, silicates and the like. 15 When these ions are in sufficient concentrations, a precipitate can form that builds up on interior surfaces of the conduits used for transport or in the subterranean rock formations, which restrict flow of the media of interest, e.g., water or oil.

20 In oilfield applications, scales that are commonly formed include calcium sulfate, barium sulfate, and/or calcium carbonate scales that are generally formed in the fresh waters or brines used in well stimulation as a result of increased concentrations of these particular ions, the water pH, pressures, and temperatures. In addition, calcium phosphate can form in the presence of phosphates commonly used to treat wells and pipes for corrosion. The buildup of these mineral precipitates can reduce or block flow in the conduits and rock 25 formations as well as cause other problems. In many cases, the first warning of the existence of a significant scale deposit may be a decline in well performance. In these instances, scale removal techniques may become necessary. As a result, a potentially substantial cost including downtime is required to affect repair as a result of scaling.

30 Scale inhibiting materials are commonly applied to rock formations by means of a squeeze treatment prior to production. In these applications, a relatively concentrated form of the scale inhibitor is added. Using the method, the scale inhibitor is pumped into a water-producing zone and attaches to the formation by chemical adsorption or by temperature-

activated precipitation. When the well is put back into production, the scale inhibitor leaches out of the formation rock to provide scale inhibition.

Capillary injection is another method for delivering scale inhibiting materials. In capillary injection, a relatively concentrated form of the scale inhibitor composition is
5 continuously pumped into the well during production.

Due to changing patterns of energy usage and availability, exploration and production is occurring at increasing depths. As a result, the chemicals used to enhance oil and gas production are subjected to increasing temperatures (i.e., 150°C to 230°C) and pressures (i.e., 25,000 to 30,000 psi), which are generally known to both increase as a
10 function of well depth. Many of the compositions commonly used as scale inhibitors have an acidic pH and are unstable under high temperature and pressure conditions. Under such conditions, these compositions degrade and do not perform their desired function as a scale inhibitor.

US Publications 2012/0118575 and 2005/0096233 relate to a process for preventing
15 scale in an aqueous system by introducing a water soluble polymer comprising a non-ionizable unsaturated monomer, a vinyl sulfonic acid, and a styrene sulfonic acid. While water soluble polymeric scale inhibitors comprising in their backbone an aliphatic sulfonic acid (i.e., vinyl sulfonate) demonstrate good inhibition to forming calcite, upon thermal aging at moderate to high temperatures said inhibitors demonstrate a dramatic reduction in
20 effectiveness.

There is a need for a scale inhibitor composition having good thermal stability useful for high pressure/high temperature applications.

BRIEF SUMMARY OF THE INVENTION

25

A method for scale inhibition treatment of an operation comprising a water system comprising the step of introducing an aqueous scale inhibiting composition into the water system wherein the aqueous scale inhibiting composition comprises, consists essentially of, or consists of a polycarboxylic acid copolymer comprising, consisting essentially of, or
30 consisting of the following monomers i) one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts, preferably acrylic acid, methacrylic acid, or

mixtures thereof and ii) a styrene sulfonic acid and/or one of its salts, preferably 4-styrene sulphonic acid.

In one embodiment of the present method disclosed herein above, i) the one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts is present in an amount of 50 to 98 weight percent of the polymerized monomers and ii) styrene sulfonic acid and/or one of its salts is present in an amount of 2 to 50 weight percent wherein weight percent is based on the total weight of the polymerized monomers.

In one embodiment of the present method disclosed herein above, the polycarboxylic acid copolymer is a copolymer consisting of acrylic acid and 4-styrene sulphonic acid having a weight average molecular weight of from 1,000 to 50,000 Daltons.

In one embodiment of the present method disclosed herein above, the aqueous scale inhibiting composition is introduced by a squeeze treatment.

In another embodiment of the present method disclosed herein above, the aqueous scale inhibiting composition is introduced by a capillary injection treatment.

In another embodiment of the present method disclosed herein above, the operation comprising a water system is a boiler, an oil and gas production well, or a geothermal well, preferably the operation comprising a water system is steam assisted gravity drainage (SAGD) or steam flooding.

DETAILED DESCRIPTION OF THE INVENTION

The scale inhibitor composition according to the present invention comprises a polycarboxylic acid copolymer which comprises, consists essentially of, or consists of the reaction product of the following monomers i) one or more monoethylenically unsaturated acids and/or anhydrides and/or its salts and ii) a styrene sulfonic acid and/or one of its salt. Polycarboxylic acid polymers and methods to polymerize them are well known; see USP 5,294,686 and USP 6,001,940, both of which are incorporated by reference in their entirety. Any suitable polymerization method can be used to prepare the polycarboxylic acid copolymers of the present invention, such as free-radical polymerization method, aqueous bulk/dispersion polymerization, solution polymerization, or emulsion polymerization.

The copolymerization of the comonomers can be carried out in the presence of polymerization initiators including, without limitation, ammonium persulfate, sodium

persulfate, potassium persulfate, azo initiators, azobisisobutyronitrile (AIBN), organic or inorganic peroxides, cerium ammonium nitrate, perchlorates, and the like. The polymerization initiators are generally in an amount of about 0.01 to about 10 weight percent based on the total weight of the monomers as is appreciated by those skilled in the art.

In some embodiments, the polycarboxylic acid copolymer of the present invention has only two comonomers (i.e., a monoethylenically unsaturated acid and styrene sulfonic acid), in other embodiments a copolymer may have, in addition to a monoethylenically unsaturated acid and styrene sulfonic acid, one or more additional comonomers.

Suitable monoethylenically unsaturated acids can be mono-acids, di-acids or polyacids and the acids may be carboxylic acids, phosphonic acids, salts or combinations thereof. Suitable monoethylenically unsaturated acids are, for example, acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, acid and the alkali metal and ammonium salts thereof. Suitable monoethylenically unsaturated dicarboxylic acids and the anhydrides of the cis-dicarboxylic acids are, for example, maleic acid, maleic anhydride, 1,2,3,6-tetrahydrophthalic anhydride, 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, 5-norbornene-2,3-dicarboxylic anhydride, bicyclo[2.2.2]-5-octene-2,3-dicarboxylic anhydride, 3-methyl-1,2,6-tetrahydrophthalic anhydride, 2-methyl-1,3,6-tetrahydrophthalic anhydride, itaconic acid, mesaconic acid, fumaric acid, citraconic acid and the alkali metal and ammonium salts thereof. Other suitable monoethylenically unsaturated acids include allylphosphonic acid, isopropenylphosphonic acid, vinylphosphonic acid, and the alkali metal and ammonium salts thereof. Most preferably, the one or more monoethylenically unsaturated carboxylic acids are acrylic acid and methacrylic acid.

Suitable polycarboxylic acid copolymers may comprise one or more monoethylenically unsaturated acid monomer copolymerized with one or more monoethylenically unsaturated acid-free monomers.

Suitable monoethylenically unsaturated acid-free monomers include C₁ to C₄ alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate. Other monoethylenically unsaturated acid-free monomers are acrylamides and alkyl-substituted

acrylamides including acrylamide, methacrylamide, N-tertiarybutylacrylamide, N-methylacrylamide, and N,N-dimethylacrylamide. Other examples of monoethylenically unsaturated acid-free monomers include acrylonitrile, methacrylonitrile, allyl alcohol, phosphoethyl methacrylate, 2-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, N-vinylformamide, N-vinylimidazole, vinyl acetate, and styrene.

Preferred comonomers are a maleic acid and vinyl acetate, acrylic acid and vinyl acetate, acrylic acid and N-tertiarybutylacrylamide, methacrylic acid and vinyl acetate, methacrylic acid and N-tertiarybutylacrylamide, more preferably acrylic acid and methacrylic acid, wherein the resulting polymers may consist of only the two monomers described herein above or comprise the two monomers described and one or more additional monomers.

The monoethylenically unsaturated acid is present in the copolymer in an amount equal to or greater than 50 weight percent, preferably equal to or greater than 60 weight percent, and more preferably equal to or greater than 70 weight percent based on the total weight of the polymerized monomers. The monoethylenically unsaturated acid is present in the copolymer in an amount equal to or less than 98 weight percent, preferably equal to or less than 90 weight percent, and more preferably equal to or less than 80 weight percent based on the total weight of the polymerized monomers.

The one or more monoethylenically unsaturated acid is polymerized with a styrene sulfonic acid or its salt. Among the styrene sulphonic acids (and their salts), 4-styrene sulphonic acid is preferably used.

The styrene sulfonic acid is present in the polycarboxylic acid copolymer in an amount equal to or greater than 2 weight percent, preferably equal to or greater than 10 weight percent, and more preferably equal to or greater than 20 weight percent based on the total weight of the polymerized monomers. The styrene sulfonic acid is present in the polycarboxylic acid copolymer in an amount equal to or less than 50 weight percent, preferably equal to or less than 40 weight percent, and more preferably equal to or less than 30 weight percent based on the total weight of the of polymerized monomers.

When the polycarboxylic acid copolymer comprises units derived from unsaturated polycarboxylic acids (and/or their salts) and/or styrene sulfonic acid (and/or its salts), sodium, potassium, or ammonium salts of said acids are preferably used. When one or more salt is present, each salt is preferably equal to or less than 30 weight percent, more

preferably equal to or less than 20 weight percent, more preferably equal to or less than 15 weight percent, more preferably equal to or less than 10 weight percent, more preferably equal to or less than 5 weight percent, more preferably equal to or less than 1 weight percent based on the total weight of the polymerized monomers.

5 The aqueous solution of the present invention comprises from 1 weight percent to 50 weight percent polycarboxylate copolymer based on the total weight of the aqueous solution. Preferably, the polycarboxylic acid copolymer is present in the aqueous solution of the present invention in an amount equal to or greater than 1 weight percent, more preferably equal to or greater than 5 weight percent, and even more preferably equal to or
10 greater than 10 weight percent based on the total weight of the aqueous solution. Preferably, the polycarboxylic acid copolymer is present in the aqueous solution of the present invention in an amount equal to or less than 60 weight percent, more preferably equal to or less than 50 weight percent, and even more preferably equal to or less than 20 weight percent based on the total weight of the aqueous solution.

15 Preferably the polycarboxylic acid copolymer is a low molecular weight polymer having a weight average molecular weight equal to or less than 50,000. Preferably, the weight average molecular weight of the polycarboxylic acid copolymer is equal to or greater than 1,000 Daltons, more preferably equal to or greater than 1,000 Daltons, and even more preferably equal to or greater than 5,000 Daltons. Preferably, the weight average molecular
20 weight of the polycarboxylic acid copolymer is equal to or less than 50,000 Daltons weight percent, more preferably equal to or less than 40,000 Daltons, and even more preferably equal to or less than 30,000 Daltons.

 Experiments can be conducted in a laboratory to determine an effective minimum inhibitor concentration (MIC) which just inhibits inorganic scale formation under simulated
25 production conditions. The ability of the operator to quickly and accurately determine the amount of scale inhibitor in the produced fluids and compare this to the MIC values generated allows him to decide when it is necessary or desirable to retreat the reservoir or increase the topside addition rate to ensure that no damage occurs to his reservoir or equipment due to inorganic scale deposition.

30 The effective MIC for a non-thermally aged scale inhibitor of the present invention is equal to or less than 30 ppm, more preferably equal to or less than 25 ppm, and most preferably equal to or less than 10 ppm. The effective minimum inhibitor concentration

(MIC) for a 200°C thermally aged scale inhibitor of the present invention is equal to or less than 20 ppm, more preferably equal to or less than 15 ppm, and most preferably equal to or less than 10 ppm. Preferably the scale inhibitor of the present invention has a % difference in MIC (MIC_{Δ}) between $MIC_{non-aged}$ and $MIC_{aged @ 200^{\circ}C}$ of equal to or less than 50%,
 5 preferably equal to or less than 25%, preferably equal to or less than 20%, and most preferably equal to or less than 15% where

$$MIC_{\Delta} = \frac{MIC_{aged @ 200^{\circ}C} - MIC_{non-aged}}{MIC_{non-aged}} \times 100$$

10

wherein MIC_{Δ} may be a negative number, for example a value of $MIC_{\Delta} = -20\%$ denotes a MIC_{Δ} value less than zero.

According to some embodiments, the scale inhibiting polymer compositions of the present invention may be used treat scale in the water system of an operation comprising a
 15 water system in which scale may be likely to form. Exemplary operations comprising water systems, include, without limitation, cooling tower water systems (including open recirculating, closed and once-through systems); oil and gas recovery operations for petroleum wells, gas wells, downhole formations, and oil sands, including thermal recovery operations, for example steam assisted gravity drainage (SAGD), steam flooding, cyclic
 20 steam stimulation (CSS), and *in situ* combustion; geothermal wells; boilers and boiler water systems; mineral process waters including mineral washing, flotation and benefaction; paper mill digesters, washers, bleach plants and white water systems; black liquor evaporators in the pulp industry; gas scrubbers and air washers; continuous casting processes in the metallurgical industry; air conditioning and refrigeration systems; industrial and petroleum
 25 process water; indirect contact cooling and heating water, such as pasteurization water; water reclamation and purification systems; membrane filtration water systems; food processing streams (meat, vegetable, sugar beets, sugar cane, grain, poultry, fruit and soybean); and waste treatment systems as well as in clarifiers, liquid-solid applications, municipal sewage treatment and industrial or municipal water systems.

30 A preferred embodiment of the present invention is a method for scale inhibition treatment of an oil or gas production well and/or subterranean formation. The scale

inhibition composition of the present invention may be introduced to the water system by capillary injection and/or by a squeeze treatment.

Capillary injection of scale inhibitor can be carried out topside or downhole via chemical injection lines. Capillary injection at the wellhead or downhole may be needed in injector wells, especially for produced water reinjection, or in producing well streams. Capillary injection in the injector wells has also been carried out to prevent scaling in producing wells. Capillary injection into produced waters is usually carried out topside at the wellhead, where other production chemicals, such as corrosion inhibitors, may be injected. In fact, many scale inhibitors are not compatible with certain corrosion inhibitors. Scale inhibitors can also be injected downhole if a capillary string is available or via the gas lift injection system. In gas lift injection, it is important to add a low-vapor-pressure solvent (vapor pressure depressant, VPD) such as a glycol to the aqueous scale inhibitor solution to avoid excessive solvent evaporation and “gunking” of the scale inhibitor. In addition, glycol or some other hydrate inhibitor may be needed to suppress gas hydrate formation. A scale dissolver blended with a scale inhibitor has also been deployed in a gas lift system.

For capillary injection applications, the concentration of polycarboxylic acid copolymer in the aqueous scale inhibitor composition of the present invention is equal to or greater than 1 weight percent, preferably equal to or greater than 5 weight percent, more preferably equal to or greater than 10 weight percent, more preferably equal to or greater than 15 weight percent, more preferably equal to or greater than 20 weight percent, and more preferably equal to or greater than 25 weight percent based on the total weight of the aqueous scale inhibitor composition. For capillary injection applications, the concentration of polycarboxylic acid copolymer in the aqueous scale inhibitor composition of the present invention is equal to or less than 90 weight percent, preferably equal to or less than 80 weight percent, more preferably equal to or less than 70 weight percent, more preferably equal to or less than 60 weight percent, more preferably equal to or less than 50 weight percent, more preferably equal to or less than 40 weight percent, more preferably equal to or less than 35 weight percent, and more preferably equal to or less than 30 weight percent based on the total weight of the aqueous scale inhibitor composition.

Downhole injection of some scale inhibitors can lead to increased downhole corrosion rates.

The basic idea in a scale inhibition squeeze treatment is to protect the well downhole from scale deposition and formation damage. The inhibitor will, of course, continue to work above the wellhead, protecting the pipeline from scaling, but a further dose of a scale inhibitor may be needed topside. In a squeeze treatment, a solution of the scale inhibitor is
5 injected into the well above the formation pressure whereby the inhibitor solution will be pushed into the near-well formation rock pores. The well is then usually shut in for a period of hours to allow the inhibitor to be retained, by various mechanisms, in the rock matrix. When the well is put back on stream again, produced water will pass the pores where the chemical has been retained, dissolving some of it. In this way, the produced water should
10 contain enough scale inhibitor to prevent scale deposition. When the concentration of the inhibitor falls below the MIC (minimum inhibitor concentration that prevents scale deposition), the well should be resqueezed. Naturally, long squeeze lifetimes will keep the overall downhole scale treatment costs to a minimum.

In one embodiment, the scale inhibiting polymer composition used in a squeeze
15 application may be diluted in a carrier solvent (usually brine) and propagated out to an optimized radial distance into the oil producing formation, where it is retained and then released slowly back into the aqueous phase during normal well production. In one embodiment, the squeeze process generally includes applying a dilute solution of the scale inhibiting polymer with surfactant (0.1 weight percent) to clean and cool the near wellbore.
20 Once cleaned, a high concentration solution of the scale inhibiting polymer at between 5 and 20 weight percent is introduced, followed by a low concentration solution of the scale inhibiting polymer. The solutions are left in contact with the reservoir for a period of time effective to allow for adsorption equilibration, after which the well is returned to production. Adhesion to the formation allows the scale inhibiting polymer to remain within the near-
25 wellbore area without being pumped up in the oil/water emulsion

Although squeeze application of the chemical is one of the most common method of treating downhole scale, the product could also be applied by other techniques commonly used offshore, which include gas-lift injection, downhole annulus injection, encapsulation or soluble matrix techniques, sub-sea wellhead injection via umbilical or indeed secondary
30 topside treatments to enhance inhibitor performance as process conditions vary scaling tendency.

In a preferred embodiment, the scale inhibiting composition of the present invention is used in treating scale under high temperature and/or high pressure conditions, for example in oil or gas production wells. The scale inhibiting compositions may be used to treat scale in conditions wherein the temperature is at least about 100°C or in the range of about 120°C to about 230°C. The scale inhibiting compositions also may be used to treat scale in conditions wherein the pressure is at least about 5,000 psi or in the range of about 5,000 psi to about 35,000 psi. In a particular embodiment, the scale inhibition treatment is at a temperature of about 120°C to about 230°C and a pressure of about 5,000 to 35,000 psi.

The scale inhibitor polymer and/or composition may be used in an amount effective to produce any necessary or desired effect. In one embodiment, an effective amount of the scale inhibitor composition of the embodiments may be dependent on one or more conditions present in the particular system to be treated and scale inhibiting moieties in the scale inhibiting polymer, as would be understood to one of skill in the art. The effective amount may be influenced, for example, by factors such as the area subject to deposition, temperature, water quantity, and the respective concentration in the water of the potential scale and deposit forming species.

For squeeze applications, the concentration of polycarboxylic acid copolymer in the aqueous scale inhibitor composition of the present invention is equal to or greater than 1 weight percent, preferably equal to or greater than 5 weight percent, more preferably equal to or greater than 10 weight percent, more preferably equal to or greater than 20 weight percent, and more preferably equal to or greater than 30 weight percent based on the total weight of the aqueous scale inhibitor composition. For squeeze applications, the concentration of polycarboxylic acid copolymer in the aqueous scale inhibitor composition of the present invention is equal to or less than 60 weight percent, preferably equal to or less than 50 weight percent, and more preferably equal to or less than 40 weight percent, based on the total weight of the aqueous scale inhibitor composition.

In one embodiment of the present invention, the aqueous scale inhibitor compositions of the present invention comprise 10 weight percent, more preferably 15, more preferably 16, more preferably 17, more preferably 18, more preferably 19, more preferably 20, more preferably 21, more preferably 22, more preferably 23, more preferably 24, more preferably 25, more preferably 26, more preferably 27, more preferably 28, more preferably 29, more preferably 30, more preferably 31, more preferably 32, more preferably 33, more

preferably 34 or more preferably 35 weight percent of the polymer by weight of the total aqueous scale inhibitor composition.

According to various embodiments, the treatment composition according to the present disclosure will be effective when the scale inhibitor polymer is used at levels equal to or less than 500 parts per million (ppm). In some embodiments, the composition is effective at concentrations of at least 1 ppm, preferably from 1 ppm to 100 ppm; and in still other embodiments; the effective concentration is 1 to about 50 ppm. In certain embodiments, the effective concentration of the polymer is equal to or less than 10 ppm, preferably equal to or less than 20 ppm, more preferably equal to or less than 30 ppm, more preferably equal to or less than 40 ppm or even more preferably equal to or less than 50 ppm. In various embodiments, the treatment composition can be added directly into the desired aqueous system to be treated in a fixed quantity provided the pH is subsequently adjusted to neutralize the polymer as noted above or can be provided as an aqueous solution and added continuously or intermittently to the aqueous system as can be desired for some applications.

EXAMPLES

Aqueous solutions of scale inhibitor comprising a polycarboxylic acid copolymer of the present invention (Example 1) and a polycarboxylic acid copolymer not of the present invention (Comparative Example A) are evaluated in a test brine solution for inhibition effectiveness. The evaluations are done for samples prepared under ambient conditions and for samples that have been aged under pressure at in a Parr reactor for five days at 200°C. For each Comparative Example A and Example 1, five different samples comprising varying concentrations of the scale inhibitor are evaluated: 2, 4, 6, 10, and 20 parts per million (ppm) scale inhibitor.

The scale inhibitor evaluated in Example 1 is a low molecular weight polyacrylic acid copolymer comprising 75 weight percent acrylic acid and 25 weight percent styrene sulfonic acid) having a weight average Mw of about 27,000 Daltons.

The scale inhibitor evaluated in Comparative Example A is a low molecular weight polyacrylic acid copolymer comprising 77 weight percent acrylic acid and 23 weight percent

2-acryloamido-2-methyl propane sulfonic acid (AMPS) having a weight average Mw of about 7,600 Daltons available as ACCENT™ 1120 from The Dow Chemical Company.

Thermal aging of scale inhibitors is carried out primarily under squeeze application type conditions. The scale inhibitors are tested as 20 wt% solutions in sulfate-free sea water
5 in a Teflon-lined Parr acid digestion bomb placed in a vented oven.

Preparation of aqueous scale inhibitor solutions

The scale inhibitor is dissolved in synthetic sulfate-free sea water. The composition of the sulfate-free sea water is described in Table 1. The appropriate amount of scale
10 inhibitor is added to a 6 oz. glass bottle and diluted with the appropriate amount sulfate-free sea water to prepare a 20 wt% active solution. Next the bottle is capped and shaken manually to mix thoroughly.

Table 1

Ion	Ion in solution (ppm)	Salt	Mass of salt (g) in 1 L deionized water
Na	10890.00	NaCl	27.682
K	460.00	KCl	0.877
Mg	1368.00	MgCl ₂ 6H ₂ O	11.443
Ca	428.00	CaCl ₂ 2H ₂ O	1.570
Ba	0.00	BaCl ₂ 2H ₂ O	0.000
Sr	0.00	SrCl ₂ 6H ₂ O	0.000
SO ₄	0.00	Na ₂ SO ₄	0.000
Cl	21957.00		
		Total Mass	41.572

15

Preparation of non-aged scale inhibitor aqueous solutions.

For both Comparative Example A and Example 1, a 1000 ppm aqueous solution of the scale inhibitor is made in a 250 mL plastic bottle using deionized water.

Preparation of aged scale inhibitor aqueous solutions.

Parr vessel PTFE liners are weighed and then filled with inhibitor solution (Note: the amount of inhibitor solution added is equal to or less than 60% of the PTFE cup capacity).

The PTFE liners and solutions are weighed and weights recorded. Said samples of

5 Comparative Example A and Example 1 are placed in a Parr vessel equipped with a PTFE liner. Prior to sealing the vessels, nitrogen gas is bubbled through the solution for 30 minutes and then the solution is degassed under vacuum. Once degassed, the vessels are sealed and heated at 200°C for five days. After five days, the vessels are removed from the Parr reactor and allowed to cool to ambient temperature for 24 hours. After aging, visually,
10 Comparative Example A turns black with precipitate and Example 1 has a slight change in color with no precipitate.

Preparation of test brine solution.

The composition of the test brine solution for evaluating scale inhibition
15 effectiveness for Comparative Example A and Example 1 is made up in accordance with to NACE TM0374 method and is a combination of a calcium-containing brine solution and a bicarbonate-containing brine solution. A 1,000 mL calcium-containing brine solution is prepared by adding 12.15 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 3.68 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 33 g NaCl and dissolving to 1,000 mL with deionized water. A 1,000 mL bicarbonate-containing brine is prepared by
20 adding 7.36 g NaHCO_3 and 33 g NaCl and dissolving to 1,000 mL with deionized water. Prior to evaluating the scale inhibition effectiveness for Comparative Example A and Example 1 the test brine solution is prepared by combining in a 1:1 ratio the calcium-containing brine and the bicarbonate-containing brine stock solutions. Immediately prior to combining the brine solutions, each brine solution independently is saturated at room
25 temperature with CO_2 gas by bubbling CO_2 gas through a fritted-glass dispersion tube at a rate of 250 mL for 30 minutes.

Scale inhibitor sample preparation for scale inhibition evaluation.

Into a 125 mL glass bottle is added 50 mL of each CO_2 saturated calcium-
30 containing; brine and the bicarbonate-containing brine stock solutions. To the 100 mL test brine solution is added the appropriate amount from the non-aged 1,000 ppm solutions or the 200°C aged 20 percent solutions of Comparative Example A and Example 1 to provide

non-aged and 200°C aged brine solutions comprising scale inhibitor at 2, 4, 6, 10, and 20 ppm. After addition of the scale inhibitor the bottles are sealed with septa caps and immediately agitated to mix the contents. Duplicate test solutions are prepared for each sample. A blank solution of brine (50 mL of each CO₂ saturated brine solution) with no
5 scale inhibitor is also prepared, sealed, and agitated. The test bottles are placed in an oven at about 71 °C for 24 hours. Then removed and cooled to ambient temperature for a time not to exceed two hours.

Inductively Coupled Plasma (ICP) testing.

10 Scale inhibition is determined by ICP using a JY 2 ICP ULTIMA™ 2 from Horiba. The following procedure is followed to prepare the samples for ICP analysis:

- add approximately 1 g of inhibitor solution via a filtered syringe into a 50 mL ICP vial,
- dilute the sample to approximately 40 g with a solution of 0.25 N HCl,
- 15 - add approximately 0.5 g of the calcium-containing brine stock solution (non-heated with no CO₂ bubbling) to 40 g with 0.25 N HCl for use as blank reference samples,
- cap each ICP vial and mix the contents well,
- record the weights of each sample,
- and
- 20 - determine calcium ion concentration.

A calcium ion concentration calibration curve is prepared from control samples with known concentrations of calcium and other ions present in the brines. The standards are prepared by selecting the inorganic salts, weighing accurately the desired amounts, and dissolving them with deionized water. Each standard is filtered prior to use employing
25 Whatman filter paper. The compositions of the standards are shown in Table 2.

Table 2

Salt	Ion	Standard #1, ppm	Standard #2, ppm	Standard #3, ppm	Standard #4, ppm	Standard #5, ppm
CaCl ₂ ·2H ₂ O	Calcium	400	800	1200	1600	2000
MgCl ₂ ·6H ₂ O	Magnesium	220	220	220	220	220
NaCl	Sodium	14000	14000	14000	14000	14000

The calcium ion concentration for each sample is determined by ICP. According to the NACE TM0374 method calcium ion concentration values for duplicate samples often differ by 2 percent or more. A 5 percent difference in calcium ion concentration is considered unacceptable and this result is discarded and the test repeated.

Percent Inhibition is calculated according to the following formula:

$$\% \text{ Inhibition} = \frac{[\text{Ca Sample}] - [\text{Ca "0 ppm"}]}{[\text{Ca Blank}]/2 - [\text{Ca "0 ppm"}]}$$

$$[\text{Ca Blank}]/2 - [\text{Ca "0 ppm"}]$$

wherein:

[Ca Sample] = calcium ion concentration in the sample comprising scale inhibitor after precipitation,

[Ca "0 ppm"] = calcium ion concentration in the blank without scale inhibitor after precipitation,

and

[Ca Blank] = calcium ion concentration in the blank without scale inhibitor before precipitation.

The scale inhibition (% Inhibition) results for aged and non-aged Comparative Example A and Example 1 are shown in Table 3.

Table 3

	% Inhibition				
Scale Inhibitor	2 ppm	4ppm	6ppm	10ppm	20ppm
Com Ex A					
not aged, %	90	92	92	95	94
aged 200°C, %	57	90	91	97	97
Ex 1					
not aged, %	71	94	93	95	97
aged 200°C, %	68	92	93	92	96

5 Calcium carbonate dynamic “Tube Blocking” performance testing.

Dynamic “tube blocking” testing is conducted using a PSL Systemtechnik Automated Scale Rig, model number 4025. Test Brine that is prepared by mixing Brine 1 and Brine 2, brine compositions are listed in Table 4.

10

Table 4

Ion	Test Brine, mg/l	Brine 1, mg/l	Brine 2, mg/l
Na	68000	47600	88400
Ca	18960	37920	0
Mg	680	1360	0
K	4960	9920	0
Ba	2340	4680	0
Sr	1625	3250	0
SO ₄	0	0	0
Fe	0	0	0
HCO ₃	560	0	1120

The dynamic tests are conducted using the following conditions:

- Brine = 100% Test Brine (Table 4)
- System Temperature = 100 °C
- System Pressure = 250 psi
- 5 - Coil: 1/16" OD SS316, L = 1,000 mm
- Flow Rate = 10 ml/min total (5 mL from each pump)
- pH: 6.2
- Blank Scaling Time = 5 to 6 min
- Pass criterion = > 1 psi increase in 30 min

10 Brine Preparation = Brine 1 and Brine 2 are prepared separately in order to keep scaling cations (Brine 1) and scaling anions (Brine 2) separate, such that on mixing Brine 1 and Brine 2 in a 50:50 ratio would give the required Test Brine composition. Brine 1 and Brine 2 are filtered before use using a 0.45 µm filter. The pH of a 50:50 mix of Brine 1 and Brine 2 is targeted to be pH 6.2.

15 Testing = Brine 1 and Brine 2 are separately injected into the rig. Once at temperature and pressure they are mixed through a microbore scaling coil. The differential pressure is recorded across the coil to establish the extent of scaling recorded as a function of time.

Blank Testing = Fit a 1 m SS316 coil, start the pumps to flow distilled water through
20 the coil in Test mode and adjust the system pressure to the required 250 psi. Next, prime the pumps in Test Outlet mode with the required brines and put the system back in Test mode. Heat the oven to 100°C. Next, start the blank test with pump 1 injecting Brine 1, pump 2 injecting Brine 2. Record the base line increase in differential pressure as the brine flows through the coil. Measure the time taken to scale to 1 psi increase in differential
25 pressure above the brine base line previously determined across the coil. Allow to scale completely (10 psi is the differential pressure threshold) difference in differential pressure then record the differential pressure and time.

Coil Cleaning = Rinse the coil with 10 % citric acid for 2 to 3 hours at 2 ml/min. Rinse the coil with distilled water for 2 to 3 hours at 2 ml/min to 5 ml/min. Check the
30 differential pressure to make sure it returns to the original value to make sure that the coil is clean to start the next experiment.

MIC (Minimum Inhibitor Concentration) Experiment = A solution of the scale inhibitor to be tested is prepared in Brine 2. Prime pump 3 with the inhibitor in Brine 2 stock solution at 5 ml/min. Prime pumps 1 and 2 with the required brines. Start the appropriate chemical MIC testing profile. An example of a MIC testing profile of a scale inhibitor is: 40 ppm (scale inhibitor in Brine 2) for 30 minutes, next 30 ppm for 30 min, next 25 ppm for 30 min, next 20 ppm for 30 min, next 15 ppm for 30 min, next 10 ppm for 30 min. Allow to scale completely and record the differential pressure, the final scale inhibitor concentration and the time of the experiment. The results for Example 1 and Comparative Example A before and after aging are shown in Table 5.

Table 5

	MIC before aging, ppm	MIC after aging @ 200°C, ppm
Comparative Example A	14 to 15	>50
Example 1	20	20

What is claimed is:

1. A method for scale inhibition treatment of an operation comprising a water system comprising the step of introducing an aqueous scale inhibiting composition into the water system wherein the aqueous scale inhibiting composition comprises a polycarboxylic acid copolymer comprising the following monomers:
 - i) one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts
and
 - ii) styrene sulfonic acid and/or one of its salts.
2. The method of Claim 1 wherein
 - i) the one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts is acrylic acid, methacrylic acid, or mixtures thereof
and
 - ii) the styrene sulfonic acid and/or one of its salts is 4-styrene sulphonic acid.
3. The method of Claim 1 wherein
 - i) the one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts is present in an amount of 50 to 98 weight percent
and
 - ii) styrene sulfonic acid and/or one of its salts is present in an amount of 2 to 50 weight percent,
wherein weight percent is based on the total weight of the polymerized monomers.
4. The method of Claim 1 wherein the polycarboxylic acid copolymer is a copolymer consisting of acrylic acid and 4-styrene sulphonc acid having a weight average weightctular weight of from 1,000 to 50,000 Daltons.
5. The method of Claim 1 wherein the aqueous scale inhibiting composition is introduced by a squeeze treatment.
6. The method of Claim 1 wherein the aqueous scale inhibiting composition is introduced by a capillary injection treatment.
7. The method of Claim 1 wherein the operation comprising a water system is a boiler, an oil and gas production well, or a geothermal well.
8. The method of Claim 1 wherein the operation comprising a water system is steam assisted gravity drainage (SAGD) or steam flooding.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/031402

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/528 C02F5/10 E21B37/06
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 C02F E21B

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	EP 0 792 998 A1 (ROHM & HAAS [US]) 3 September 1997 (1997-09-03) * page 2, line 47 through page 3, line 8, page 4, lines 2-7, lines 17-57, page 6, Table 1, polymer 17, page 8, Table 6B, Examples, claims *	1-8
X	US 4 952 327 A (AMJAD ZAHID [US] ET AL) 28 August 1990 (1990-08-28) * column 2, line 39 through column 3, line 26, column 3, line 63 through column 4, line 55, Table 1, column 7, line 32 through column 8, line 3, claims * ----- -/--	1-8

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 July 2016

Date of mailing of the international search report

25/07/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/031402

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/176419 A1 (KEMIRA OYJ [FI]; MOORE LUCAS [US]; SANDERS LAURA [US]) 30 October 2014 (2014-10-30) * page 3, paragraph [0009], page 4, paragraph [0004], page 6, paragraph [0021] through page 7, paragraph [0025], page 7, paragraphs [0028] and [0029], page 13, paragraphs [0050], [0051] and [0053], claims * -----	1-8
X	FR 2 803 304 A1 (CECA SA [FR]) 6 July 2001 (2001-07-06) * page 2, lines 32-36, page 3, lines 7-12, 18-22 and 29-35, page 4, lines 13-29, page 5, line 31 through page 6, line 4, claim 5 * -----	1-8
X	US 4 288 327 A (GODLEWSKI IRENE T ET AL) 8 September 1981 (1981-09-08) * column 2, line 44 through column 3, line 21, column 14, lines 29-63, claims * -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/031402

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0792998	A1	03-09-1997	AR 005997 A1	21-07-1999
			AU 706503 B2	17-06-1999
			AU 1474997 A	11-09-1997
			BR 9701118 A	25-08-1998
			CA 2198841 A1	01-09-1997
			CN 1174817 A	04-03-1998
			CO 4560448 A1	10-02-1998
			EP 0792998 A1	03-09-1997
			ID 16097 A	04-09-1997
			MX 198823 B	27-09-2000
			NO 970854 A	02-09-1997
			SG 52918 A1	28-09-1998
			US 5755972 A	26-05-1998
			ZA 9701767 A	04-09-1997

US 4952327	A	28-08-1990	NONE	

WO 2014176419	A1	30-10-2014	EP 2989176 A1	02-03-2016
			US 2016060147 A1	03-03-2016
			WO 2014176419 A1	30-10-2014

FR 2803304	A1	06-07-2001	AT 305015 T	15-10-2005
			AU 2861101 A	16-07-2001
			DE 60022784 T2	13-07-2006
			EP 1261652 A1	04-12-2002
			FR 2803304 A1	06-07-2001
			NO 20023093 A	26-08-2002
			US 2003149210 A1	07-08-2003
			US 2005096233 A1	05-05-2005
			WO 0149756 A1	12-07-2001

US 4288327	A	08-09-1981	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/US2016/031402

International filing date (day/month/year)
09.05.2016

Priority date (day/month/year)
13.05.2015

International Patent Classification (IPC) or both national classification and IPC
INV. C09K8/528 C02F5/10 E21B37/06

Applicant
DOW GLOBAL TECHNOLOGIES LLC

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0
Fax: +49 89 2399 - 4465

Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Nemes, Csaba A.

Telephone No. +49 89 2399-0



Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed.
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:
 - a. ☐ forming part of the international application as filed:
 - ☐ in the form of an Annex C/ST.25 text file.
 - ☐ on paper or in the form of an image file.
 - b. ☐ furnished together with the international application under PCT Rule 13ter.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.
 - c. ☐ furnished subsequent to the international filing date for the purposes of international search only:
 - ☐ in the form of an Annex C/ST.25 text file (Rule 13ter.1(a)).
 - ☐ on paper or in the form of an image file (Rule 13ter.1(b) and Administrative Instructions, Section 713).
4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>2-8</u>
	No: Claims	<u>1</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-8</u>
Industrial applicability (IA)	Yes: Claims	<u>1-8</u>
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

- D1** EP 0 792 998 A1 (ROHM & HAAS [US]) 3 September 1997 (1997-09-03)
- D2** US 4 952 327 A (AMJAD ZAHID [US] ET AL) 28 August 1990 (1990-08-28)
- D3** WO 2014/176419 A1 (KEMIRA OYJ [FI]; MOORE LUCAS [US]; SANDERS LAURA [US]) 30 October 2014 (2014-10-30)
- D4** FR 2 803 304 A1 (CECA SA [FR]) 6 July 2001 (2001-07-06)
- D5** US 4 288 327 A (GODLEWSKI IRENE T ET AL) 8 September 1981 (1981-09-08)

2 The present application does not meet the criteria of Article 33(2) PCT, because the subject-matter of claims 1 is not new.

Documents D1 to D5 disclose (cf. D1: page 2, line 47 through page 3, line 8, page 4, lines 2-7, lines 17-57, page 6, Table 1, polymer 17, page 8, Table 6B, Examples, claims; D2: column 2, line 39 through column 3, line 26, column 3, line 63 through column 4, line 55, Table 1, column 7, line 32 through column 8, line 3, claims; D3: page 3, paragraph [0009], page 4, paragraph [0004], page 6, paragraph [0021] through page 7, paragraph [0025], page 7, paragraphs [0028] and [0029], page 13, paragraphs [0050], [0051] and [0053], claims; D4: page 2, lines 32-36, page 3, lines 7-12, 18-22 and 29-35, page 4, lines 13-29, page 5, line 31 through page 6, line 4, claim 5; D5: column 2, line 44 through column 3, line 21, column 14, lines 29-63, claims) a method for scale inhibition treatment of an operation comprising a water system comprising the step of introducing an aqueous scale inhibiting composition into the water system wherein the aqueous scale inhibiting composition comprises a polycarboxylic acid copolymer comprising the following monomers:

- i) one or more monoethylenically unsaturated acid and/or anhydride and/or one of its salts and
- ii) styrene sulfonic acid and/or one of its salts.

Dependent claims 2-8 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, since these features are either known from the prior art or they constitute the general knowledge of the person skilled in the art.

In particular:

D1 foresees the combination of acrylic acid and 4-styrene sulphonic acid according to present claim 2. D1 also discloses the amounts of the monomeric components as defined in claim 3.

The weight average molecular weight of the copolymer can be adequately selected by the skilled person for the particular needs (cf. present claim 4).

Squeeze treatment (cf. present claim 5) and capillary injection treatment (cf. present claim 6) as well SAGD or steam flooding (cf. present claim 8) are routine techniques in oilfield applications.

According to D1, the copolymers can be used in oilfield operations (cf. present claim 7).