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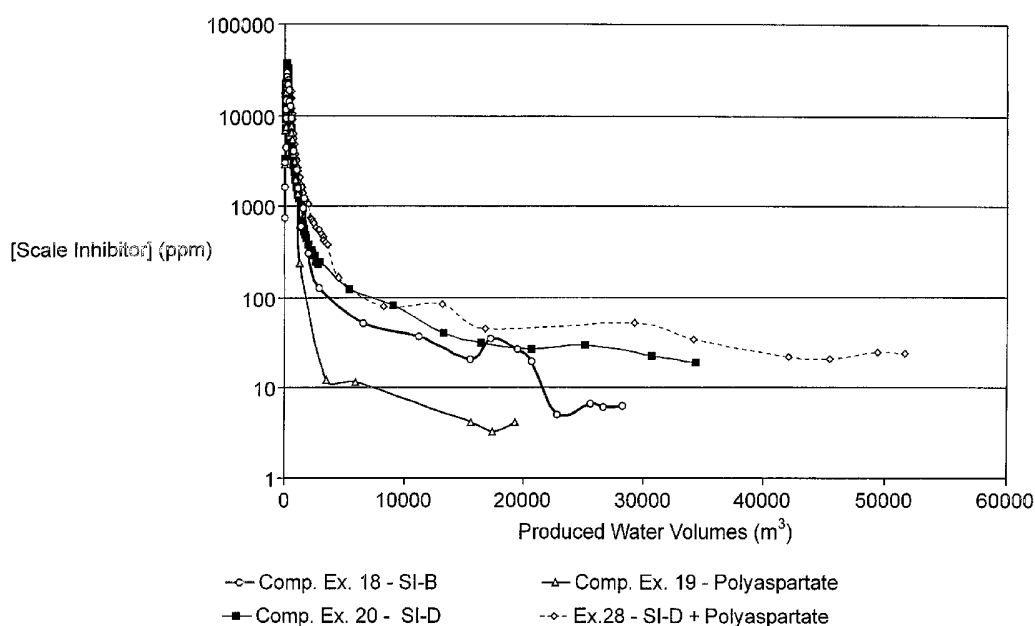
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(54) Title: METHOD OF CONTROLLING SCALE FORMATION



(57) Abstract: The invention provides a method of increasing the retention of a scale inhibitor on a rock material comprising pre-conditioning the rock material with a positively charged bridging agent and contacting the rock material with said scale inhibitor.

WO 2004/011772 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD OF CONTROLLING SCALE FORMATION

The present invention relates to a method of controlling scale formation. More particularly, the present invention relates to increasing the retention of scale inhibitors in rock formations from which oil is being extracted.

- 5 When a well bore is initially drilled in an oil field, the oil extracted is usually "dry", being substantially free of aqueous impurities. However, as the oil reserves dwindle, a progressively greater quantity of aqueous impurities becomes mixed with the oil. Changes in physical conditions during the production cycle as well as mixing of incompatible waters (i.e. sea water and barium or strontium containing formation waters) can cause
- 10 scaling in any part of the production system. Scale arises from the precipitation of inorganic minerals contained in water passing through an oil well, such as flush water or water which has seeped into the rock formation. Compounds such as carbonates and sulphates of calcium, barium and strontium may then precipitate in an oil well or in production equipment as a result of changes in pressure, temperature or ionic strength.
- 15 Scale that occurs in the production system can result in a significant loss in production and associated revenue.

A particular problem with scale formation in large industrial wells is the formation of scale on the equipment used to extract oil from the field, particularly on the interior surfaces of conduits and in the perforations in the wall of the well pipe itself. At the well head, the sub-

20 surface safety valve is also susceptible to damage caused by scale formation. The build-up of scale is therefore an economic burden on oil production. In order to avoid costly losses in production or post-scale treatments, it is desirable to avoid deposition of scale in the oil well as far as possible.

There are several conventional techniques to counter the problem of oil field scale formation,

25 all of which bear significant disadvantages. The technique of "downhole squeezing" is commonly used, wherein inhibitor chemicals in aqueous solution are injected into the near-wellbore area. Usually, a treatment involves injecting a scale inhibitor at a concentration of 5 to 20 % w/v into the rock formation. A number of scale inhibitors are well known in the art. Phosphonates and phosphate esters are two commonly used scale inhibitors in the oil

30 industry. The scale inhibitor is then expected to flow back to the surface at a suitable concentration and protect the well from scale precipitation. Such treatments are generally referred to in the art as 'squeeze' treatments.

A typical squeeze in a vertical well will comprise a preflush, a squeeze pill and an overflush treatment, before the well is returned to normal function. The preflush, typically comprising a mixture of surfactant/demulsifier solution, stops the formation of emulsions that would block the perforation pores and often water-wets the formation rock surface. The squeeze pill itself
5 typically involves injection of scale inhibitor as a solution in water, causing saturation of the matrix in a radial area around the well. The overflush comprises a displacement of the squeeze pill that propels the chemical front in a wider circumference around the well bore so that a significant surface of rock matrix is exposed to the inhibitor compound.

When the pressure applied down the well is reversed, about 30% of inhibitor chemical is often
10 immediately flushed from the rock. The inhibitor chemical that remains adsorbed to the rock surface acts to inhibit scale formation by constant treatment as fluid passes through the rock into the well conduit. However, over time the inhibitor is gradually washed from the rock surface as oil and water production continues until a further descaling treatment is required.

Various techniques have been used to try to increase the proportion of chemical that adsorbs
15 to the rock. For example, the chemical can be "shut in" for a period of time with the expectation that the greater period of exposure to the rock surface might increase the degree of adsorption of the inhibitor. However, this leads to an increase in the time for which a well is not in production and therefore is not considered to be particularly effective.

Treatment with scale inhibitors is thus an economic burden in itself. Usually oil production
20 needs to be stopped for about a day to allow the scale inhibition treatment. Moreover, with conventional scale inhibitors, the treatment needs to be repeated regularly. A typical treatment is effective for between one month and two years, depending on the inhibitor retention and release properties in the formation. Accordingly, there is a need for improved scale inhibitor treatments, which are long-lasting and do not require regular repeat
25 treatments.

US 5,893,416 describes one approach to providing long term scale inhibition. In this approach, a bed of porous ceramic spheres impregnated with a scale inhibitor is installed in the oil well. The inhibitor material gradually dissolves in the well's fluids during operation and inhibits scale formation.

30 It is an object of the present invention to provide a method of inhibiting scale in oil wells. It is a further object of the present invention to provide a method of increasing the retention of scale inhibitors in rock formations. Hence, it is a further object of the present invention

to provide a method of inhibiting scale in oil wells which is long-lasting and does not require repeat treatments at regular intervals.

Accordingly, the present invention provides a method of increasing the retention of a scale inhibitor on a rock material comprising preconditioning the rock material with a positively charged bridging agent and contacting the rock material with said scale inhibitor.
5 charged bridging agent and contacting the rock material with said scale inhibitor. Preferably, the positively charged bridging agent is a positively charged polymer. Even more preferably, the positively charged bridging agent is a positively charged polymer selected from polyaminoacids or diallyldimethylammonium chloride.

As used herein, the term "positively charged bridging agent" means any positively charged compound that increases the retention of a scale inhibitor on a rock material when said rock material is preconditioned with said positively charged compound.
10 compound that increases the retention of a scale inhibitor on a rock material when said rock material is preconditioned with said positively charged compound.

As used herein, the term "polyaminoacid" means any polymeric substance comprised of repeating amino acid units. A preferred example of a polyaminoacid used in the present invention is polyaspartate (or polyaspartic acid). Polyaminoacids, such as polyaspartate,
15 are biodegradable materials and are used advantageously in the present invention.

As used herein, the term "scale inhibitor" means any substance which inhibits the formation of scale. Such substances will be well known to the skilled person and include, for example, phosphonates, phosphate esters, and polymers, such as (co)polymers comprising phosphonate and/or carboxylate groups. Examples of specific inhibitors that
20 are suitable for use in the present invention include, but are not limited to: hexamethylene diamine tetrakis (methylene phosphonic acid); diethylene triamine tetra (methylene phosphonic acid); diethylene triamine penta (methylene phosphonic acid); bis-hexamethylene triamine pentakis (methylene phosphonic acid); polyacrylic acid (PAA); phosphino carboxylic acid (PPCA); diglycol amine phosphonate (DGA phosphonate); 1-
25 hydroxyethylidene 1,1-diphosphonate (HEDP phosphonate); bisaminoethylether phosphonate (BAEE phosphonate); polymers of sulphonic acid on a polycarboxylic acid backbone; phosphate esters; polyvinylsulphonic acid; copolymers including phosphonic acid and/or carboxylic acid moieties (e.g. polymers comprising vinyl-phosphonate and/or vinyl-diphosphonate); polymaleic acid (e.g. terpolymers comprising maleate) and 2-
30 acrylamido-2-methyl-1-propanesulphonic acid (AMPS).

It will be appreciated that certain polyaminoacids, such as polyaspartate, have been used previously as scale inhibitors (see, for example, US 5,152,902). However, in the context of this invention, the term scale inhibitor does not include polyaminoacids, such as polyaspartate. Nevertheless, the inherent scale inhibiting properties of polyaminoacids are a further advantage of the present invention. Thus, the polyaminoacids used in the present invention have the dual advantages of improving the retention of scale inhibitors by rock materials, and providing a further scale inhibiting effect.

Most scale inhibitors are retained, at least to some extent, on rock materials. It is understood that the scale inhibitors are adsorbed onto the surface of rock materials via Van der Waals forces and hydrogen bonding. The extent of retention is governed by a number of factors including solution pH, salinity, temperature, nature of the rock surface and nature of the scale inhibitor.

The adsorption of scale inhibitors onto rock materials means that they may be released slowly into a liquid in contact with the rock material. Generally, a greater degree of adsorption means a longer period in which an effective concentration of scale inhibitor may be delivered to a liquid in contact with the rock material. The present invention provides a method of increasing the retention of scale inhibitors on rock materials and, hence, provides a method of controlling scale in wells used for extracting oil from rock formations over a prolonged period of time.

A problem with most scale inhibitors is that they are small, negatively charged molecules, which are readily soluble in water. This means they may be readily washed away from the surface of rock materials. Moreover, many types of rock material have a negatively charged surface, meaning that Coulombic repulsion forces between the rock material and the scale inhibitor decrease further the extent of retention.

Without wishing to be bound by theory, it is believed that the bridging agent preconditioning used in the present invention provides a bridge between the rock material and the scale inhibitor, which facilitates retention of the scale inhibitor. For example, polyaminoacids are generally adsorbed more strongly onto rock materials than scale inhibitors. Polyaminoacids are large molecules, which benefit from increased Van der Waals interaction with the rock surface. Furthermore, polyaminoacids contain a number of N-H bonds that may hydrogen bond with the rock surface. Therefore, polyaminoacids are generally adsorbed more strongly onto rock surfaces than typical scale inhibitor

compounds. Similarly, diallyldimethylammonium chloride is a positively charged polymer that offers a strong adsorption property to a negatively charged rock surface.

It is believed that the adsorbed bridging agents provide a bridge for the scale inhibitors to adsorb to rock materials. The adsorbed bridging agents present a less negatively charged surface than the rock itself, with which the scale inhibitor compounds can interact. Thus, the Coulombic repulsion forces between the rock material and the scale inhibitor may be reduced. Furthermore, adsorbed bridging agents such as polyaminoacids may form hydrogen bonds with the scale inhibitor as well as with the rock surface. Thus, the bridging agents provide a bridge between the rock material and the scale inhibitor which increases the retention of the scale inhibitor.

The method of the present invention may be performed by contacting a dispersion of the bridging agent with the rock material in a first preconditioning step and then contacting a dispersion of the scale inhibitor with the rock material in a second step. The period between the preconditioning step and the second step may be varied. For example, the dispersion of the bridging agent may be left in contact with the rock material for up to 24 hours. Preferably, the preconditioning dispersion is left in contact with the rock material for 1 to 12 hours, more preferably 2 to 12 hours, and more preferably about 4 hours.

Alternatively, the method of the present invention may be practised by contacting a dispersion comprising the bridging agent compound and the scale inhibitor compound with the rock material in a single step. In this alternative embodiment, the preconditioning of the rock material occurs simultaneously with contacting the rock material with the scale inhibitor. This may have the disadvantage of less effective adsorption of the bridging agent and, hence, less retention of the scale inhibitor. However, simultaneous delivery of the bridging agent and the scale inhibitor to the rock material has the advantage of being more convenient. A convenient method for increasing retention of scale inhibitors is particularly useful in large scale applications of the present invention, for example, when used in oil wells.

The dispersions of the bridging agent and/or the scale inhibitor may be aqueous or non-aqueous. Non-aqueous dispersions of scale inhibitors are disclosed in European Patent Publication Number EP0976911. In preferred embodiments, where the bridging agent is polyaminoacid, it is further preferred that the dispersions of polyaminoacid and/or a scale inhibitor are aqueous dispersions. In other preferred embodiments, where the bridging

agent is diallyldimethylammonium chloride, it is further preferred that the dispersions of diallyldimethylammonium chloride and/or a scale inhibitor are non-aqueous dispersions. However, the dispersions of diallyldimethylammonium chloride and/or a scale inhibitor may also be aqueous. Further, the dispersions of the bridging agent and/or the scale
5 inhibitor may comprise sodium chloride. In many applications of the present invention, the dispersions of the bridging agent and/or the scale inhibitor are solutions made up from seawater. Seawater is obviously available in abundance at off-shore oil wells and provides an economical medium for delivering the bridging agent and the scale inhibitor to a formation. It is a feature of the present invention that it achieves excellent retention of
10 scale inhibitors on rock materials when the bridging agent and the scale inhibitor are dispersed in seawater.

In the method of the present invention, the dispersion of bridging agent preferably has a pH in the range of 1 to 7. In preferred embodiments, where the bridging agent is polyaminoacid, a pH in the range of 1 to 7 means the polyaminoacid will normally be
15 positively charged by protonation of amino or amido groups in the polyaminoacid. A positively charged polyaminoacid is preferable for enhancing the bridging effect described hereinabove. Thus, the negatively charged scale inhibitor compounds and rock surface (which is usually negatively charged) will be attracted to the polyaminoacid by Coulombic attraction forces. The result is that the scale inhibitors will usually be more tightly
20 adsorbed to the rock material. In preferred embodiments, where the bridging agent is polyaminoacid, it is further preferred that the dispersion of polyaminoacid has a low pH, such as a pH in the range of 2 to 4, or a pH of less than 3. In other preferred embodiments, where the bridging agent is diallyldimethylammonium chloride, it is further preferred that the dispersion of diallyldimethylammonium chloride has a pH of less than 7.

25 It will be readily apparent to the skilled person that the method of the present invention may be used in the oil industry for prolonging the lifetime of scale inhibitor treatments. Thus, the method of the present invention is preferably used for controlling scale formation in an oil-producing well. The term "well" as used herein refers not only to the bore through which extracted oil passes, but also to any auxiliary machinery or equipment associated
30 with the bore which is in contact with mineral-containing water and which, therefore, is liable to scale formation.

In accordance with the present invention, there is also provided a method of controlling scale formation in a well used for extracting oil from a rock formation comprising the steps of:

- (a) contacting the rock formation with a dispersion of a bridging agent;
- 5 (b) allowing the bridging agent to adsorb to the rock formation; and
- (c) contacting the rock formation with a dispersion of a scale inhibitor.

Typically, an aqueous dispersion of bridging agent is injected into the rock formation. The solution is preferably acidic, although the exact pH will depend on factors such as the nature of the scale inhibitor and rock type. The dispersion is then left in contact with the
10 rock formation for a period of time to allow adsorption of the bridging agent to the rock surface. The time allowed for adsorption will vary depending on the rock type and the degree of scale inhibitor retention required. Typically, the dispersion of bridging agent is left in contact with the rock formation for 1 to 24 hours. Following adsorption of the
15 dispersion of bridging agent may be flushed away before introduction of the scale inhibitor. Alternatively, the scale inhibitor dispersion may be introduced in addition to the bridging agent dispersion.

In an alternative embodiment, the present invention provides a method of controlling scale formation in a well used for extracting oil from a rock formation comprising contacting the
20 rock formation with a dispersion comprising a bridging agent and a scale inhibitor. Thus, in this alternative embodiment, the bridging agent and the scale inhibitor are delivered simultaneously to the rock formation.

Once the rock formation has been treated in either manner described above, the well will receive an effective concentration of scale inhibitor for a prolonged period of time, due to
25 the increased retention of the scale inhibitor by the rock formation. Thus, the method of the present invention allows longer intervals between successive scale inhibitor treatments in oil wells.

Brief Description of the Figures.

- 30 Figure 1. Comparison of inhibitor return profiles of maleate terpolymer (acid form) in the presence or absence of a polyaspartate preflush in core flood tests.

Figure 2. Comparison of scale inhibitor concentration in the production water from the Heidrun well A28 following treatment with *bis*-hexamethylene triamine pentakis(methylene phosphonic acid), polyaspartate, a polymer containing vinyl-phosphonate or a polymer containing vinyl-phosphonate preceded by a preflush with polyaspartate.

Figure 3. *Squeeze V* model curve for inhibitor return in production water from the Heidrun well A28 following treatment with a polymer containing vinyl-phosphonate .

Figure 4. *Squeeze V* model curve for inhibitor return in production water from the Heidrun well A28 following treatment a polymer containing vinyl-phosphonate preceded by a preflush with polyaspartate.

The present invention will now be explained in more detail with reference to the following Examples.

15 Beaker Tests.

Representative Procedure:

- (i) Polyaspartate was dissolved in 500 ml of 6% w/w NaCl solution to provide a polyaspartate concentration of 5000 ppm. Likewise, a 5000 ppm scale inhibitor solution was made up from 500 ml of 6% NaCl solution.
- 20 (ii) The pH of each solution was adjusted to a desired level using HCl.
- (iii) Disintegrated rock material (8 g) from the A53 Heidrun oil well was placed in a 60 ml HDPE bottle.
- (iv) Polyaspartate solution (16 ml), as prepared above, was added to the HDPE bottle containing the crushed rock material and placed in an oven at 90°C.
- 25 (v) After 4h, 10 ml of supernatant was replaced by 10 ml of scale inhibitor solution.
- (vi) The concentration of scale inhibitor in the supernatant was analysed after 20 hours.

As control experiments, the effect of preconditioning with either phosphonate solution or 6% w/w NaCl solution in step (iv) was also tested at various pHs.

Table 1 shows the results of 6 experiments in which the preconditioning solution was varied. A lower concentration of scale inhibitor in the supernatant indicates greater adsorption of the scale inhibitor to the rock material. The phosphonate scale inhibitor used was *bis*-hexamethylene triamine pentakis(methylene phosphonic acid).

5

Table 1

Experiment	Preconditioning Solution	Scale Inhibitor Solution	Conc. of scale inhibitor after 20h, ppm
Comparative Example 1	6% NaCl, pH 5.5	polyaspartate, pH 7.15	375
Comparative Example 2	phosphonate, pH 3.85	polyaspartate, pH 7.15	402
Comparative Example 3	6% NaCl, pH 5.5	phosphonate, pH 3.85	2598
Example 1	polyaspartate, pH 7.15	phosphonate, pH 3.85	2664
Example 2	polyaspartate, pH 2.5	phosphonate, pH 3.85	2294
Comparative Example 4	6% NaCl, pH 2.5	phosphonate, pH 3.85	2574

Comparative Examples 1 and 2 both used a scale inhibitor solution of polyaspartate at pH 10 7.15. Polyaspartate has high adsorption to the rock material. However, the degree of adsorption is relatively unaffected by the nature of the preconditioning solution.

Comparative Example 3 and Example 1 both used a scale inhibitor solution of phosphonate at pH 3.85. The amount adsorbed was about the same for a preconditioning step of 6% NaCl at pH 5.5 and a preconditioning step of polyaspartate at pH 7.15.

Example 2 and Comparative Example 4 both used a scale inhibitor solution of phosphonate at pH 3.85. The amount adsorbed was greater in Example 2, which used a preconditioning step of polyaspartate at pH 2.5. Less adsorption was observed in Comparative Example 4, which employed a preconditioning step of 6% NaCl at pH 2.5.

- 5 Thus, preconditioning using a polyaspartate solution at low pH advantageously enhances the adsorption of a phosphonate scale inhibitor to a rock material.

Using the same general procedure as above, the scope of the present invention was investigated with respect to different scale inhibitors. The effect of changing the pH of the scale inhibitor solution, the pH of the preconditioning solution and the concentration of
10 preconditioning solution was also investigated.

Table 2 shows the applicability of the present invention on three different scale inhibitors. The rock material is preconditioned with either 6% NaCl solution or polyaspartate at pH 3. After preconditioning, a scale inhibitor solution is contacted with the rock material and the degree of adsorption measured after 20h. The scale inhibitor solutions were at either pH 3
15 or pH 5. The scale inhibitors used were:

SI-B: *bis*-hexamethylene triamine pentakis(methylene phosphonic acid);

SI-C: triethanolamine phosphate ester; and

SI-D: polymer containing vinyl-phosphonate.

Table 2

Experiment	Preconditioning at pH 3	Scale Inhibitor	Adsorption mg/g	% of adsorption increase
Comparative Example 5	6% NaCl	SI-D, pH 3	3.17	
Example 3	polyaspartate	SI-D, pH 3	3.39	7.07
Comparative Example 6	6% NaCl	SI-D, pH 5	2.87	
Example 4	polyaspartate	SI-D, pH 5	3.16	10.09

Comparative Example 7	6% NaCl	SI-C, pH 3	1.68	
Example 5	polyaspartate	SI-C, pH 3	1.85	9.87
Comparative Example 8	6% NaCl	SI-C, pH 5	1.59	
Example 6	polyaspartate	SI-C, pH 5	2.01	26.61
Comparative Example 9	6% NaCl	SI-D, pH 3	4.53	
Example 7	polyaspartate	SI-D, pH 3	4.91	8.44
Comparative Example 10	6% NaCl	SI-D, pH 5	3.82	
Example 8	polyaspartate	SI-D, pH 5	4.04	5.87

In all cases, preconditioning with polyaspartate provided greater adsorption of the scale inhibitor than preconditioning with 6% NaCl solution. It is readily apparent that other scale inhibitors would also benefit from preconditioning with a polyaspartate solution.

- 5 Table 3 shows the effect of varying the concentration and pH of the polyaspartate preconditioning solution. The pH is set at 3, 4.5 or 6, while the concentration is set at 1000, 5000 or 10000ppm. The scale inhibitor is a phosphate ester at either pH 3 or pH 5.

Table 3

10

Experiment	Preconditioning	Ads. mg/g, pH3 SI-C	% increase	Ads. mg/g, pH5 SI-C	% increase
Comparative Example 11	NaCl pH3	2.65		1.96	
Example 9	polyaspartate, 1000 ppm pH3	2.65	0.00	2.04	4.08

Example 10	polyaspartate, 5000ppm pH3	3.03	14.34	2.53	29.08
Example 11	polyaspartate, 10,000ppm pH3	2.97	12.08	2.66	35.71
Comparative Example 12	NaCl pH4.5	2.77		1.82	
Example 12	polyaspartate, 1000ppm pH4.5	2.72	0.00	1.97	8.24
Example 13	polyaspartate, 5000ppm pH4.5	2.88	3.97	2.51	37.91
Example 14	polyaspartate, 10,000ppm pH4.5	2.84	2.53	2.4	31.87
Comparative Example 13	NaCl pH6	2.72		1.79	
Example 15	polyaspartate, 1000ppm pH6	2.66	0.00	1.93	7.82
Example 16	polyaspartate, 5000ppm pH6	2.85	4.78	2.21	23.46
Example 17	polyaspartate, 10,000 pH6	2.87	5.51	2.3	30.17

Table 4 shows identical experiments to Table 3, with the exception that the scale inhibitor is a polymer containing vinyl-phosphonate at either pH 3 or pH 5.

Table 4

Experiment	Preconditioning	Ads. mg/g, pH3 SI-D	% increase	Ads. mg/g, pH5 SI-D	% increase
Comparative Example 14	NaCl pH3	6.244		6.476	
Example 18	polyaspartate, 1000ppm pH3	6.144	0.00	6.684	3.21
Example 19	polyaspartate, 5000ppm pH3	6.13	0.00	6.744	4.14
Example 20	polyaspartate, 10,000ppm pH3	6.2	0.00	6.764	4.45
Comparative Example 15	NaCl pH4.5	6.218		6.742	
Example 21	polyaspartate, 1000ppm pH4.5	6.306	1.42	6.782	0.62
Example 22	polyaspartate, 5000ppm pH4.5	6.446	3.67	6.766	0.37
Example 23	polyaspartate, 10,000ppm pH4.5	6.492	4.41	6.708	0.00
Comparative Example 16	NaCl pH6	6.188		6.714	
Example 24	polyaspartate, 1000ppm pH6	6.164	0.00	6.69	0.00
Example 25	polyaspartate, 5000ppm pH6	6.456	4.33	6.778	0.95
Example 26	polyaspartate, 10,000ppm pH6	6.538	5.66	6.8	1.28

Tables 3 and 4 show that there is an optimum preconditioning concentration and pH, which is dependent on the nature and pH of the scale inhibitor.

5 Similar studies were carried out with diallyldimethylammonium chloride.

Representative Procedure:

- (i) Diallyldimethylammonium chloride was prepared at 10% in 6% w/w NaCl and a 10,000 ppm scale inhibitor solution made up from 500 ml of 6% NaCl solution.
- (ii) The pH of each solution was adjusted to a desired level using HCl.
- 10 (iii) Disintegrated rock material (16 g) from the A53 Heidrun oil well was placed in a 60 ml HDPE bottle.
- (iv) Diallyldimethylammonium chloride solution (32 ml), as prepared above, was added to the HDPE bottle containing the crushed rock material.
- (v) After 5h, 25 ml of supernatant was replaced by 25 ml of scale inhibitor solution
- 15 (SI-D).
- (vi) The concentration of scale inhibitor in the supernatant was analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy after 24 hours.

As a control experiment, the effect of preconditioning with 6% w/w NaCl solution in step (iv) was also tested. The test results are given in Table 5.

20

Table 5

Experiment	Pre-conditioning	Ads. mg/g pH 5 SI- D
Comparative Example 17	pH 3, 6% NaCl brine	3.85
Example 27	pH 3, 10% diallyldimethylammonium chloride in 6% NaCl	5.04

Table 5 indicates that in the absence of pre-conditioning diallyldimethylammonium chloride, the inhibitor adsorption level was 3.85 mg per gram of crushed sandstone particles. However, in the presence of preconditioning diallyldimethylammonium chloride, the inhibitor adsorption level increased to 5.04 mg per gram of crushed sandstone particles.

- 5 This shows that preconditioning diallyldimethylammonium chloride enhances inhibitor adsorption.

Thus, it has been shown that a preconditioning step using a positively charged bridging agent, exemplified by polyaminoacid and diallyldimethylammonium chloride, enhances the adsorption of a scale inhibitor to rock materials. The skilled person will readily
10 understand that the present invention may be used advantageously in oil wells for increasing the lifetime of scale inhibitor treatments.

Core Flood Tests

Standard core flood tests were carried out to evaluate the effect of polyaspartate on the
15 scale inhibitor return profile of maleate terpolymer (acid form) (hereinafter referred to as SI-E).

Core flood tests are often performed on reservoir or outcrop core. They are used to determine chemical injectivity and initial/return effective permeability to oil and/or water (formation damage); and also to provide samples for the determination of scale inhibitor
20 adsorption/desorption isotherms.

General aspects of core analysis, core handling and preservation procedures are described in detail in the *American Petroleum Institute (API) Work Group Report Sub-committee on Core Analysis (RP27/40) Core Handling Procedures (Wellsite)* and the *American Petroleum Institute (API) Recommended Practice for Core Analysis Procedure (API RP*
25 *40)*, both of which are incorporated herein by reference. The importance of wettability and its effect on relative permeability and other coreflood procedures is described in *Anderson, W.G. 'Wettability Literature Survey – Parts 1-6'. Journal of Petroleum Technology (JPT) (1986-1987)*, incorporated herein by reference.

In the present study, the core material was a highly quartzitic "Clashach" outcrop
30 sandstone. The Clashach sandstone material originates from a quarry near Elgin in Scotland. This substrate is often used as an analogue core material for comparative

inhibitor adsorption/desorption core floods. For the brine, Heidrun formation water was adopted. Sulphate ions were omitted for the purposes of this core flood study. The brines were filtered through a 0.45 µm membrane filter prior to use. The brine was adjusted to pH 6.5 prior to injection.

5 Outline Procedures:

Core floods 1 and 2 were performed in the presence and absence of polyaspartate pre-flush respectively.

Core flood 1:

- 10 Brine (100% FW) Saturation at room temperature (20°C) following which the temperature was raised to 85°C.

Brine Permeability and Porosity (Lithium tracer) at 85°C.

Preflush (i): 5 pore volumes of 6% NaCl injected at 85°C.

Preflush (ii): 5 pore volumes of 6% NaCl plus 50ppm Lithium injected at 85°C.

- 15 Preflush (iii): 5 pore volumes of pre-flush solution of Additive A (polyaspartate) injected at 85°C.

Main treatment: 10 pore volumes (10% as supplied scale inhibitor E plus 50 ppm Li in NaCl) injected at 85°C.

Shut In, 16 hours at 85°C.

- 20 Inhibitor Release Profile over approx. 1000 pore volumes of post flush with brine (100% FW) at 85°C.

Core flood 2:

- 25 All conditions were identical to core flood 1, although the pre-flush with polyaspartate was omitted.

The inhibitor return profiles for core floods 1 and 2 are presented in Figure 1. The data indicates that the concentration of SI-E in core flood 1 fell below 1ppm after 180 pore volumes. In core flood 2, the concentration of SI-E fell below 1ppm after the elution of 100

pore volumes. This data suggests that the presence of a positively charged bridging agent, such as polyaminoacid, in a squeeze treatment package will increase squeeze life.

Field Study

- 5 A number of scale inhibitors were squeezed on Heidrun well A28 to evaluate the potential of the bridging agent treatment to increase squeeze life. All treatments were performed using similar treatment designs to allow a representative comparison of squeeze duration. A representative pumping sequence is given below. The scale inhibitors and bridging agent (polyaspartate) were dissolved in 6% w/w NaCl brine. Pumping rates were
- 10 maintained as high as possible without exceeding the fracture pressure. The shut in time was 24 hours.

Pumping sequence:

Stage	Pumping Step	Volume (m ³)	Composition
Main pill I:	1	20	10% polyaspartate (pH 2.5 - 3)
Main pill II:	2	190	10% scale inhibitor (pH 4 - 5)
Overflush I:	3	20	2% polyaspartate (pH 2.5 - 3)
Overflush II:	4	50	Diesel
Overflush I:	5	30	2% polyaspartate (pH 2.5 - 3)
Overflush II:	6	50	Diesel
Overflush I:	7	30	2% polyaspartate (pH 2.5 - 3)
Overflush II:	8	50	Diesel
Overflush I:	9	30	2% polyaspartate (pH 2.5 - 3)
Overflush II:	10	50	Diesel
Tubing volume	11	52	Tubing displacement, gas
Diesel*	12	52	Diesel

(* One tubing volume of diesel was pumped after the 24 hour shut in time).

Comparative Example 18 represents a squeeze undertaken with *bis*-hexamethylene triamine pentakis(methylene phosphonic acid) (SI-B) scale inhibitor. Comparative Example 19 represents a squeeze undertaken with polyaspartate alone. Comparative Example 20 represents a squeeze undertaken with the polymer containing vinyl-phosphonate (SI-D). Example 28 represents a squeeze undertaken with SI-D deployed in conjunction with polyaspartate.

The scale inhibitor returns concentration as a function of the produced water volumes from these four sequential squeeze treatments is presented in Figure 2. The minimum inhibitor concentration (MIC) requirements steadily increased as the seawater fraction in the produced water increased towards 25% over the course of these squeezes (from 10 ppm to 24 ppm, see Table 6).

The SI-B inhibitor deployed in Comparative Example 18 protected the production of approximately 30,000m³ of brine before the inhibitor return dropped below the laboratory determined minimum inhibitor concentration (MIC) at the seawater fraction present in the well at that time. This was determined to be 10ppm (Figure 2, Table 6). Comparative Example 19, performed with polyaspartate, was less effective, protecting the production of just 20,000m³ of brine before the inhibitor return dropped below the laboratory determined MIC at the higher seawater fraction present in the well at that time. This was 10ppm (Figure 2, Table 6). Comparative Example 20 was performed with SI-D. The application of this inhibitor protected the production of approximately 35,000m³ of brine before the inhibitor return dropped below the MIC at the seawater fraction present in the well at that time. This was 20ppm (Figure 2, Table 6). In contrast, in Example 28, where polyaspartate was deployed as part of a pre-treatment prior to squeezing with SI-D, the same volume and concentration of scale inhibitor and overflush fluids protected the production of approximately 52,000m³ of brine before the inhibitor return dropped below the MIC determined in the well for the current seawater breakthrough level. This was 24ppm (Figure 2, Table 6).

Table 6

Experiment	Comparative Example 18	Comparative Example 19	Comparative Example 20	Example 28
Scale Inhibitor	SI-B	polyaspartate	SI-D	SI-D with polyaspartate preflush
MIC (ppm)	10	10	20	24
Treatment Water Volume (m ³)	30,000	20,000	35,000	52,000

In Silico Modelling

- 5 To further understand the effect of polyaspartate on inhibitor retention and release properties, the software package *Squeeze V* was used (in accordance with the instructions in Zhang, H.R and Sorbie, K.S. , *Squeeze V User Manual*, Dept of Petroleum Engineering, Heriot-Watt University, Edinburgh, 1997, incorporated herein by reference) to simulate the results from Comparative Example 20 and Example 28. The simulation data generated for
- 10 Comparative Example 20 and Example 28 are presented in Figures 3 and 4.

To match the field returns data from the two experiments, a different set of isotherm parameters was required, (Figures 3 and 4 and Table 7). The Freundlich isotherm was found to give the best match to the two treatments. The Freundlich parameters K and n indicate the inhibitor adsorption property. A larger K and n value indicate higher levels of

15 adsorption of the scale inhibitor onto the rock surface. The Freundlich parameter r_2 defines the inhibitor adsorption/desorption rate constant. A larger r_2 value indicates a faster rate of inhibitor adsorption/desorption from the rock surface whilst a smaller r_2 indicates a slow rate of inhibitor adsorption/desorption from the rock surface.

Table 7

Freundlich Parameter	Comparative Example 20	Example 28
K	800	1200
n	0.16	0.4
r_2	0.29	0.11

5 The Freundlich parameters identified for Comparative Example 20 were insufficient to describe the return curve obtained from Example 28. A larger K, n and r_2 value than that required to fit Comparative Example 20 (800, 0.16 and 0.29 respectively) was necessary to match Example 28 (1200, 0.4 and 0.11 respectively). This further indicates that the polyaspartate alters the rate and extent of inhibitor retention and release. Thus, it is
10 thought that the polyaspartate presents a new surface onto which the scale inhibitor can adsorb.

The above data shows that the deployment of a positively charged bridging agent, such as polyaminoacid, as part of a pre-flush treatment before the main scale inhibitor pill can result in an averaged increase in squeeze treatment life of 50%. This will reduce the
15 number of squeeze treatments that need to be performed per year. Furthermore, this will increase the net availability of the well, which reduces chemical and operational costs.

It will, of course, be understood that the present invention has been described by way of example, and that modifications of detail may be made within the scope of the invention.

CLAIMS

1. A method of increasing the retention of a scale inhibitor on a rock material comprising preconditioning the rock material with a positively charged bridging agent and contacting the rock material with said scale inhibitor.
- 5 2. A method as claimed in claim 1, wherein a dispersion of the positively charged bridging agent is contacted with the rock material in a first preconditioning step and a dispersion of the scale inhibitor is contacted with the rock material in a second step.
3. A method as claimed in claim 1, wherein a dispersion of the positively charged bridging agent and scale inhibitor is contacted with the rock material in a single step.
- 10 4. A method as claimed in claims 2 or 3, wherein the dispersion of positively charged bridging agent and/or scale inhibitor further comprises sodium chloride.
5. A method as claimed in any one of claims 2 to 4, wherein the dispersion of positively charged bridging agent is at a pH in the range of 1 to 7.
6. A method as claimed in any one of the preceding claims, wherein the scale inhibitor
15 comprises at least one substance selected from phosphonates, phosphate esters or (co)polymers comprising phosphonate and/or carboxylate groups.
7. A method as claimed in any one of the preceding claims, wherein said method is used for controlling scale formation in an oil-producing well.
8. A method of controlling scale formation in a well used for extracting oil from a rock
20 formation comprising the steps of:
 - a) contacting the rock formation with a dispersion of a positively charged bridging agent;
 - b) allowing the positively charged bridging agent to adsorb to the rock formation; and
 - 25 c) contacting the rock formation with a dispersion of a scale inhibitor.
9. A method as claimed in claim 8, wherein in step (b) the positively charged bridging agent is left in contact with the rock formation for a period ranging from 1 hour to 24 hours.

10. A method of controlling scale formation in a well used for extracting oil from a rock formation comprising contacting the rock formation with a dispersion comprising a positively charged bridging agent and a scale inhibitor.
11. A method as claimed in any one of claims 1-10, wherein the positively charged
5 bridging agent is a positively charged polymer.
12. A method as claimed in claim 11, wherein the positively charged polymer is a polyaminoacid.
13. A method as claimed in claim 12, wherein the polyaminoacid is polyaspartate.
14. A method as claimed in claims 11, wherein the positively charged polymer is
10 diallyldimethylammonium chloride.
15. A method as claimed in any one of claims 1-10, wherein the positively charged bridging agent is as defined in claims 13 or 14 and the scale inhibitor is as defined in claim 6.

Fig. 1

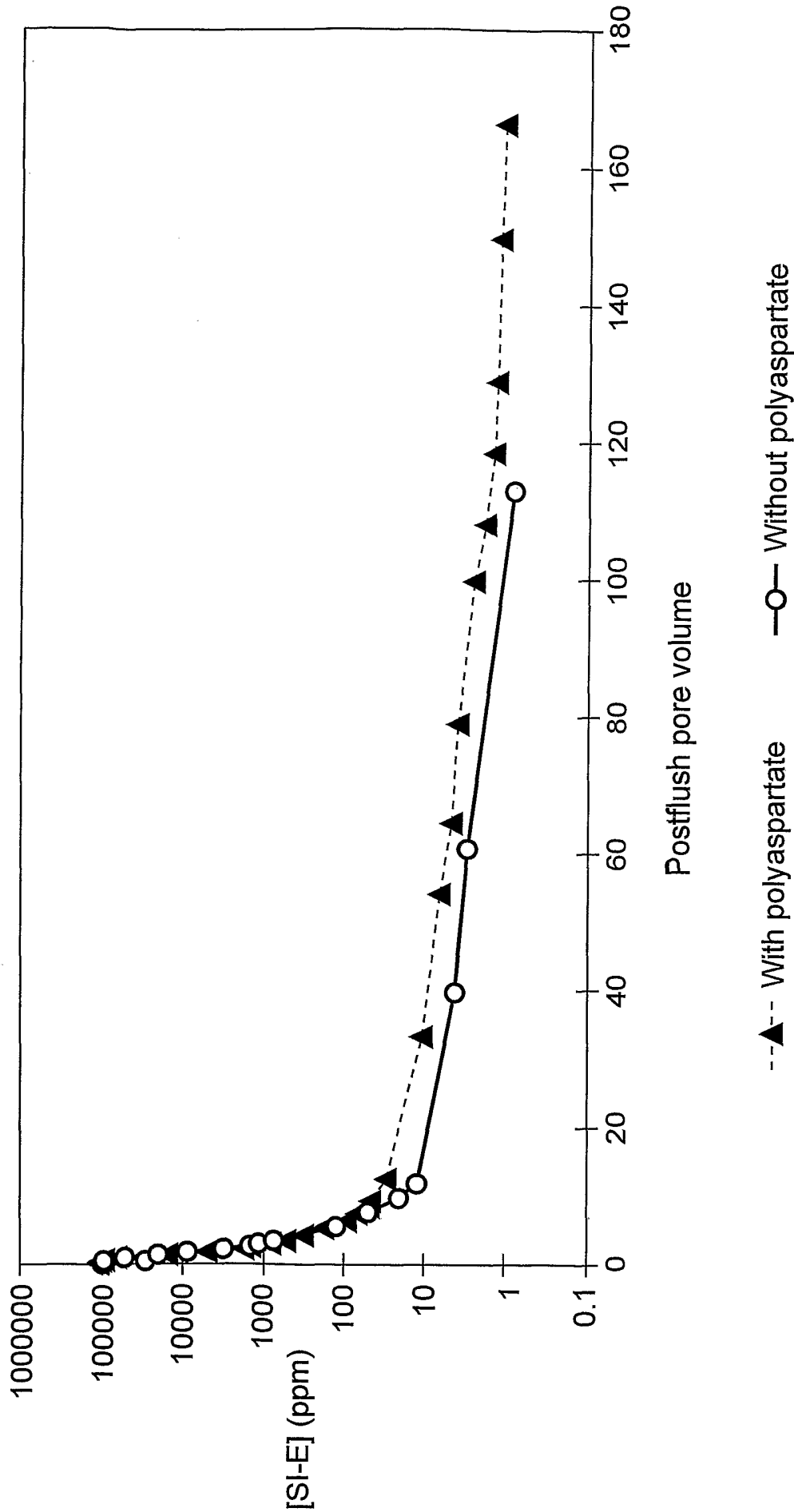


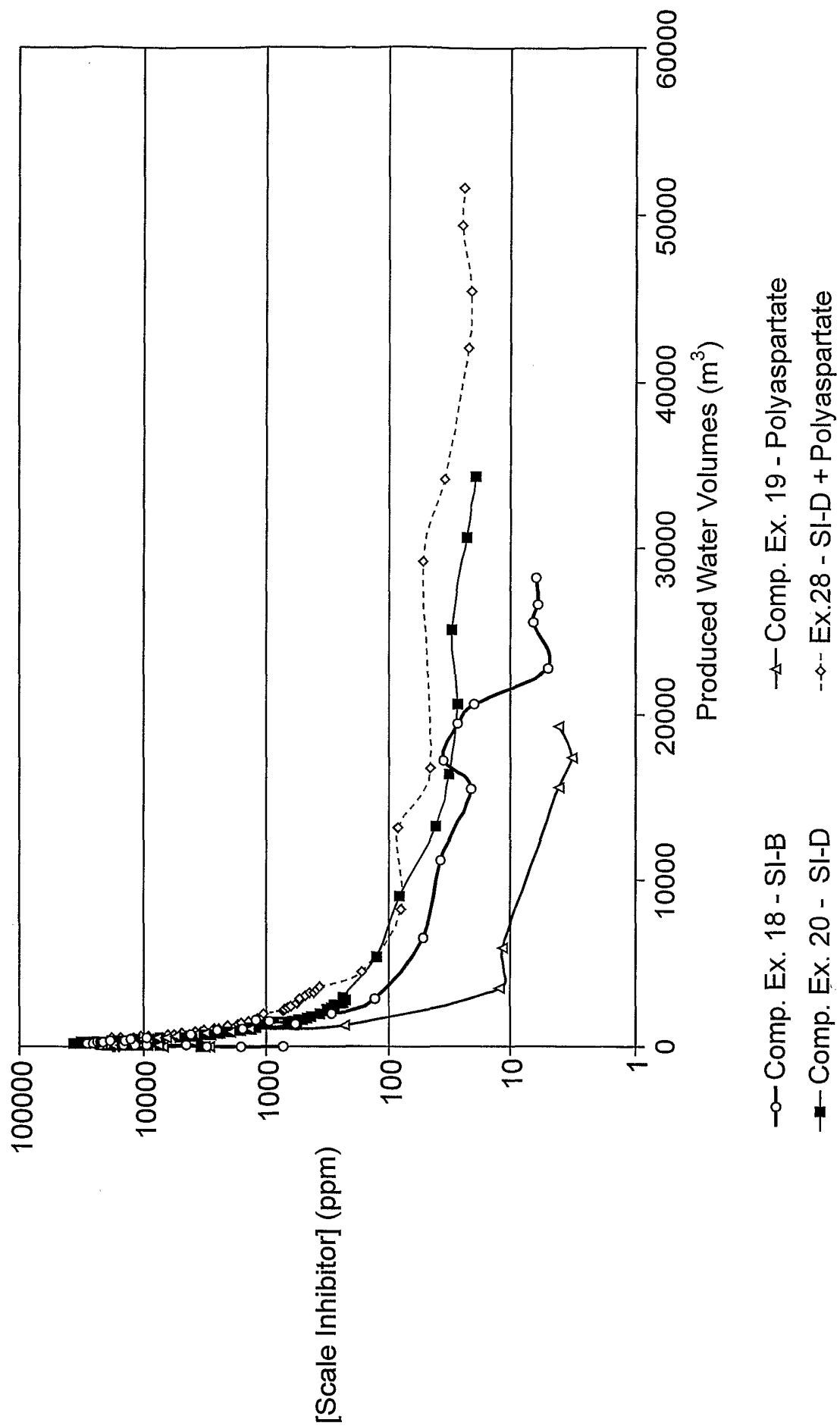
Fig. 2

Fig. 3

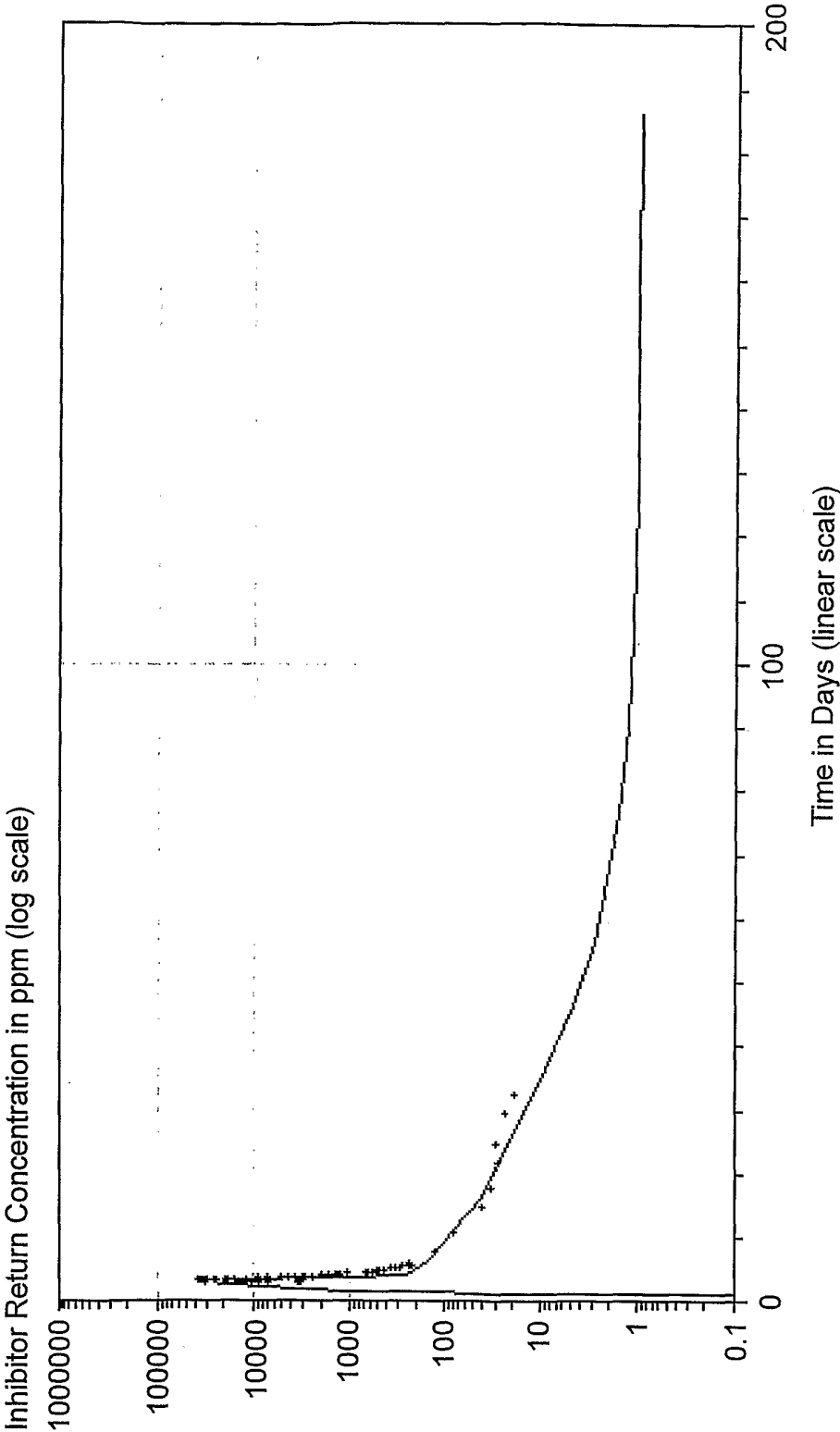
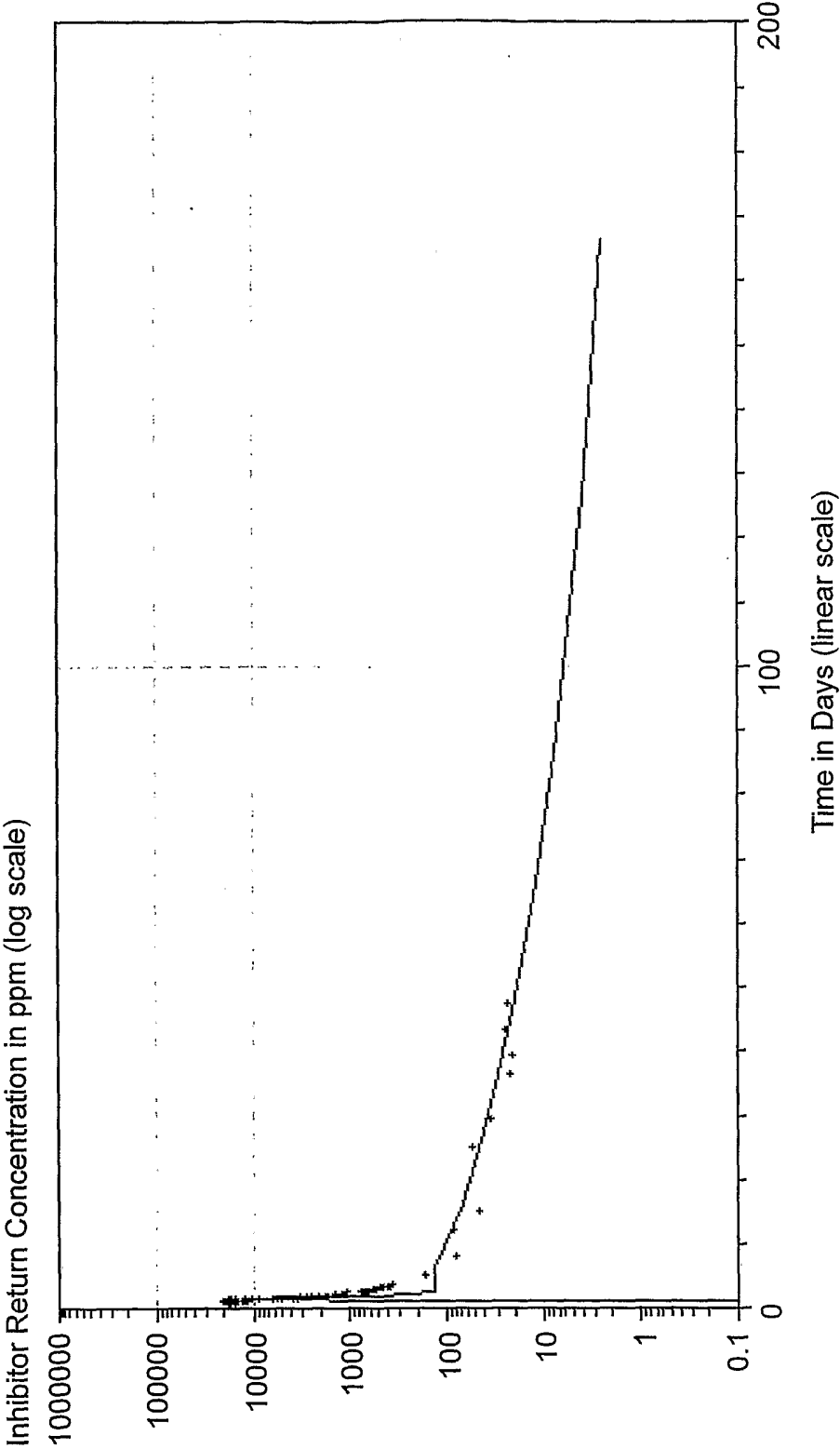


Fig. 4



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 03/03339

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 E21B41/02 E21B37/06

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)
IPC 7 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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	paragraph '0012! - paragraph '0029! ---	4
X	US 5 939 362 A (BLUTH MATTHEW J ET AL) 17 August 1999 (1999-08-17)	1-3, 5-11, 14, 15
Y	column 3, line 44 -column 4, line 23 ---	4
X	US 5 181 567 A (SHULER PATRICK J) 26 January 1993 (1993-01-26)	1-3, 5-11, 14, 15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- * & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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Y	page 5, line 13 -page 8, line 2 -----	4
X	WO 95 20617 A (DONLAR CORP) 3 August 1995 (1995-08-03) page 2 -page 18 -----	1-13,15
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Internati

Application No

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