

SPECIFICATION

Aqueous compositions

The invention relates to a process for cleaning a well penetrating an underground formation and optionally cleaning formation parts in the vicinity of the said well.

5 In particular, the invention relates to a cleaning process wherein the well and optionally the formation parts in the vicinity of the well are contacted with an aqueous composition suitable for dissolving barium sulphate scale. The invention relates further to an aqueous composition suitable to be used in such cleaning process.

10 One of the factors that may contribute to uneconomically and therefore undesirable low production rates of oil that is being recovered from an oil containing subterranean formation via a well penetrating the formation, is the fouling of the tubular equipment in the well with barium sulphate scale. Another one of such factors is the permeability decrease in the formation pore space of the formation parts surrounding the well by barium sulphate that is being precipitated on the walls of the pore space during the oil-recovery operations.

15 Generally, the barium sulphate scale is deposited or formed from a pressure or temperature change in the flow of oil flowing from the oil-containing subterranean formation into and through the well communicating with the pore space of said formation. Barium sulphate scale deposits on the surface of the passage ways through which the oil and other fluids (such as water) flow that are being recovered, inhibit the flow of these fluids and if left unchecked will result in a complete blockage of these passageways such as the tubular goods in the well and/or the pore space of the formation parts in the vicinity of the well. Inert materials such as silicate grains may be deposited on the scale and become entrapped therein. In wells and formations suffering from barium sulphate scale deposits, repeated cleaning will have to take place, which adds considerably to the recovery cost of the oil.

20 Another mechanism whereby barium scale can be formed in the well-bore is the co-mingling of individually stable waters, of which one is rich in sulphate ions and the other is rich in barium ions. Such a situation develops when sulphate containing seawater that is being injected into the formation for oil-displacement purposes reaches the production well via highly permeable streaks of formation and mixes with barium-ion containing reservoir water produced together with the oil. It is believed that such mechanism may cause barium sulphate scale in some of the northern North Sea fields.

30 Further, it is often required to clean the formation parts in the vicinity of a production well from fine barite particles that have been included in the drilling mud applied in drilling the well and that have invaded the pay-zone of the formation, thereby causing a permanent impairment of the well productivity. Such barium sulphate particles should be removed preferably therefrom already in the early life of a well.

35 Various cleaning methods have been described in the past, wherein use is made of aqueous compositions containing active ingredients, which compositions are brought into contact with the equipment present in a well, and optionally with the surface of the pore space parts of the formation in the vicinity of the well, for cleaning the well and the formation parts by dissolving barium sulphate that has been precipitated therein.

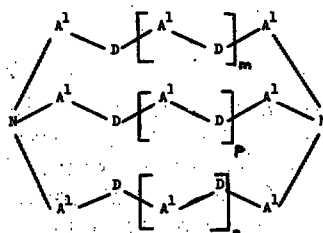
40 For such treatments to be commercially attractive, the down time — i.e. the time during which an oil well is being cleaned and out of operation — should be as short as possible. This means that the barium sulphate scale should dissolve rapidly into the aqueous composition and that the barium complex formed should be highly soluble in water. In addition, a high loading of the active ingredient is desirable.

45 It is known from "Tetrahedron Letters" No. 34 (1969) 2889—2892 — that barium sulphate can be dissolved by contacting this solid with an aqueous solution of 4, 7, 13, 16, 21, 24-hexaoxa-1,10-diazabicyclo[8,8,ε]hexacosane, also referred to as "Compound A" (see formula page). Although compound A can be loaded up highly and the barium complex formed has a high solubility in water, but it appears that the complex is formed rather slowly which would mean a substantial drawback in using Compound A as the active ingredient for cleaning wells penetrating underground functions.

50 It is further known from U.S. patent specification 4,030,548 that subterranean scale can be removed by flowing an aqueous composition containing a dissolved aminopolyacetic acid salt as the active ingredient through the well into the subterranean location. Although the complex between barium sulphate and this salt is initially formed rapidly, it appears that only a very low loading of this salt can be reached, which mean that the complex possesses a very low saturation value.

55 It has now been found that the down time can be reduced considerably as compared with known processes for dissolving barium sulphate solid by using a special aqueous composition which combines several highly attractive features: The solvent does not only dissolve barium sulphate solid rapidly, but the barium complex formed has also a high solubility in water and the active ingredient can be loaded up to a high degree.

60 Accordingly, the invention provides a process for cleaning a well penetrating an underground formation and optionally formation parts in the vicinity of the said well by contacting the well and optionally the said formation parts with an aqueous composition comprising (1) a bicyclic macrocyclic polyether of the general formula:



(I)

wherein each A¹ which may be the same or different represents a hydrocarbon radical having up to 12 carbon atoms and each D which may be the same or different represents an oxygen or a sulphur atom or a hydrocarbon radical having up to 12 carbon atoms or a group N—R², R² represents a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbonsulphonyl radical having up to 12 carbon atoms, an alkoxy carbonyl radical of up to 4 carbon atoms, an alkoxy carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical, at least two of the said D members representing an oxygen or a sulphur atom or a group N—R², and m, n and p are integers from 0 to 5 inclusive, the bicyclic macrocyclic polyether of the general formula I being compatible with a barium ion, as hereinafter defined, and (2) a salt of an organic acid.

The expression "the bicyclic macrocyclic polyether of the general formula I being compatible with a barium ion" is used to denote that the bicyclic macrocyclic polyether of the general formula I is capable of accommodating a barium ion in the three-dimensional intramolecular cavity of the polyether molecule.

Compounds according to formula I which can be consequently used are those wherein A¹ represents a hydrocarbon radical having in the range of from 2 to 8 carbon atoms or a 1,2-phenylene radical; D represents an oxygen atom or a group N—R² wherein R² represents an alkyl group of up to 8 carbon atoms, a hydrocarbonsulphonyl radical of up to 8 carbon atoms or an alkoxy carbonyl radical of up to 4 carbon atoms at least 4 of the said D numbers representing an oxygen atom; and m, n and p are 1 or 2.

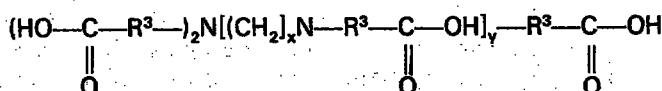
Preferred compounds according to formula I are those wherein A¹ represents an acetylene ethylene, diethylene, triethylene or tetraethylene radical, particularly an ethylene radical; D represents an oxygen atom or a group N—R² wherein R² represents an alkyl group of up to 4 carbon atoms, particularly a methyl group, a hydrocarbonsulphonyl radical with up to 4 carbon atoms or a methoxy- or ethoxycarbonyl radical, at least four of the said D members representing an oxygen atom and two further members each representing an oxygen or a nitrogen atom; and m, n and p are 1 or 2.

Examples of suitable compounds according to formula I are those in which A¹ represents an ethylene group and D, m, n and p are:

D	m	p	n	
oxygen	1	1	1	(Compound A), or
oxygen	2	1	2,	or
oxygen	2	2	2	

A particularly preferred compound according to formula I is 4, 7, 13, 16, 21, 24-hexaoxa-1, 10-diazabicyclo[8,8,8] hexacosane (compound A). Further examples of compounds of formula I are: 16-methyl-4,7,13,21,24-pentaoxa-1,10,16-triaza-bicyclo[8,8,8]hexacosane and 13,16-dimethyl-4,7,21,24-tetraoxa-1,10,13,16-tetraaza-bicyclo[8,8,8]hexacosane.

A preferred class A organic acids whose salts can be used in the process according to the present invention comprises polycarboxylic acids, particularly aminopolycarboxylic acids. Salts of monoaminopolycarboxylic acids and especially polyaminopolycarboxylic acids such as the alkylene polyaminopolycarboxylic acids are preferred. The alkylene polyaminopolycarboxylic acids can be represented by the general formula:



wherein each of the subscripts x and y is an integer of from 1 to 4 and R³ represents an alkylene group with one to three carbon atoms and wherein up to x of the carboxyalkyl groups can be replaced by beta-hydroxyethyl groups. Examples of suitable alkylene polyaminopolycarboxylic acids are:

ethylenediaminetetraacetic acid (R³ is —CH₂—; x=2; y=1),

ethylenetriaminepentaacetic acid (R³ is —CH₂—; x=2; y=2),

propylene-1,3-diaminetetraacetic acid (R³ is —CH₂—; x=3; y=2),

and the isomeric butylenediaminetetraacetic acids.

Ethylenediaminetetraacetic acid (hereinafter also named "EDTA") is particularly preferred.

Other examples of aminopolycarboxylic acids whose salts can be used conveniently are:

N-hydroxyethyliminodiacetic acid, monoethanolthylenediaminetriacetic acid, diethanolthylenediaminediacetic acid, 2,2',2''-nitrilotriacetic acid, tri(carboxymethyl)amine, and propylene-1,2-diaminetetraacetic acid.

In another preferred embodiment of the process according to the present invention the polyaminopolycarboxylic acid whose salts can be used conveniently is 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (see formula page: compound B). Further classes of organic acids whose salts may be used comprise aromatic (poly)carboxylic acids such as:

benzenecarboxylic acids, for example, benzenecarboxylic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid and salicylic acid and pyridine(poly)carboxylic acids, such as 2-pyridinecarboxylic acid, 3-pyridinecarboxylic acid, 4-pyridinecarboxylic acid, 2,3-pyridinedicarboxylic acid, 2,4-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid and 2,6-pyridinedicarboxylic acid; alkane(poly)carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid, 2,3,5-hexanetricarboxylic acid, 1,2,3-butanetricarboxylic acid and 2-(3-carboxypropyl)-1,1,5,6-heptanetetracarboxylic acid; hydroxy acids, for example, citric acid, glycolic acid, lactic acid, glyceric acid and tartronic acid; phenols, for example, phenol, o-cresol, m-cresol, p-cresol, 2,3-xylenyl, pyrocatechol and pyrogallol;

Also salts of benzenephosphonic acids, for example, benzenephosphonic acid, 1,2-benzenediphosphonic acid, 1,3-benzenediphosphonic acid and 1,4-benzenediphosphonic acid as well as sulphonic acids, for example, methanesulphonic acid, methanedisulphonic acid, 1,2-ethanedisulphonic acid and propanesulphonic acid and carboxyamino compounds, for example, 1,2-di(dicarboxyamino)benzene and 1,2-di(dicarboxyamino)cyclohexane can be used.

The molar ratio of salt of organic acid to the bicyclic macrocyclic polyether of formula I in the aqueous composition used according to the invention is not critical and may vary within wide limits. It has been found that commercially attractive features of the invention, listed hereinbefore, already become apparent when using very low, molar ratios, for example between 0.0001 and 0.001, in other words, when the salt of the organic acid is present in a so-called "catalytic amount". A molar ratio in the range of from 0.001 to 1, preferably of from 0.01 to 0.5. Can be suitably applied if desired, this molar ratio may be higher than 1, but high molar ratios will not be necessary.

The concentration in which the bicyclic macrocyclic polyether of formula I is present in the aqueous composition is not critical. This concentration is suitably taken substantially equivalent to the saturation concentration of the complex of barium with this polyether in the aqueous composition under the prevailing conditions. Suitably, the concentration of the bicyclic macrocyclic polyether is at least 0.01 mol/l and preferably higher than 0.05 mol/l, for example, 0.3 mol/l.

The aqueous composition will normally be of alkaline nature due to the presence of the nitrogen-bridging atoms in the bicyclic macrocyclic polyether. Protonation of the free bicyclic macrocyclic polyether should be avoided as it reduces its tendency to form barium complexes. Therefore, a pH value of at least 8 is preferred since the higher the pH value the higher the unprotected portion of the macrocyclic polyether will be and, consequently, the higher the extent to which this macrocyclic polyether can be loaded up with barium ions. In view of this the aqueous composition preferably has a pH of at least 10.0, and particularly a pH in the range of from 10.0 to 11.5. The unprotonated portion of the macrocyclic polyether can be increased by incorporating a base into the aqueous composition, preferably a base whose cation is hardly compatible, if at all, with the bicyclic macrocyclic polyether of the general formula I; an example of a base that is not compatible with compound A is lithium hydroxide.

The cation of the salt of the organic acid present in the aqueous composition is preferably lithium or potassium, but may be sodium or any other cation, for example, an ammonium-ion or alkyl-substituted ammonium-ions, for example a tetraalkyl-substituted ammonium-ion. It will be understood that this cation is preferably incompatible with the bicyclic macrocyclic polyether of formula I.

Alternatively, the cation may be an ammonium ion derived from this bicyclic macrocyclic polyether in which case the aqueous composition may be prepared by taking up in water this polyether and the selected organic acid, preferably ethylene tetraacetic acid, provided that the organic acid is used in a sub-stoichiometric amount.

The aqueous composition used in the process according to the present invention may contain well-treating or cleaning solution additives which are compatible with the composition. Such additives include, for example, surfactant materials. These surfactant materials may be ionic or non-ionic. Examples are alkali metal salts of alkyl aryl sulphonates such as sodium dodecylbenzene sulphonate, alkali metal salts of sulphates of fatty alcohols such as sodium lauryl sulphate and materials having a polyoxyethylene chain. The surfactant material may be present in the composition in a concentration in the range of from, for example, 1 to 3 percent by weight.

The contact time for dissolving a barium sulphate solid with the aqueous composition will vary not only with the conditions but also with the relative proportions of the constituents in the composition and will generally be in the range of from 1 minute to three hours; for example from 15 minutes to 1.5 hours.

In general, when using an aqueous composition according to the present invention for dissolving a barium sulphate solid, there is no need to adopt temperatures substantially above ambient temperature.

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Temperatures as low as 10 to 20°C have been found satisfactory. However, the relatively high temperature (say 30—70°C or higher) prevailing in an oil producing formation into which a production well penetrates, greatly enhances the dissolution of the solid.

It will be appreciated that the aqueous solution according to the present invention can also be applied when the other types of scale and/or compounds whose ions can be accommodated by the bicyclic macrocyclic polyether of the general formula I are present in wells and/or formation parts in the vicinity of said wells. The aqueous solution can be suitably applied when for instance, calcium sulphate solid is also present in the well and/or the formation parts in the vicinity of said well.

Compound B (1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadiene) may be prepared in a manner known per se, e.g. by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadiene with a salt of 2-chloroacetic acid in the presence of a base. Very good results have been obtained using alkali metal salts of 2-chloroacetic acid. Suitable bases are alkali metal hydroxides, for example lithium hydroxide, sodium hydroxide and potassium hydroxide.

The invention further provides an aqueous composition for dissolving barium sulphate solid, which composition comprises a bicyclic macrocyclic polyether of the general formula I and a salt of an organic acid.

The barium sulphate scale-dissolving capacities of several aqueous compositions have been demonstrated in the laboratory tests described in the following Examples.

The experiments described below were carried out in a cylindrical glass vessel having a height of 2.5 cm and an internal diameter of 0.8 cm. The vessel was charged with the starting materials and then fixed lengthwise to a horizontal shaft parallel to its central axis. The shaft was rotating at a speed of 180 revolutions per minute. The temperature of the vessel was 20°C, unless otherwise indicated.

Examples I and II and Comparative Experiments A, B and C

The vessel was charged with barium sulphate (0.3 mmol), an aqueous liquid (1 ml) and five stainless-steel balls having a diameter of 0.32 cm. Five experiments were carried out, each with another aqueous liquid. Table I states the compositions of the aqueous liquids.

TABLE I

	Starting concentration, mol/l		
	Compound A	EDTA	KOH
Comparative Experiment A	0.1	0	0
Comparative Experiment B	0.1	0	0.1
Comparative Experiment C	0	0.005	0.05
Example I	0.1	0.005	0
Example II	0.1	0.005	pH=11 ^{x)}

x) so much KOH was added that the pH reached a value of 11.

At various intervals the rotating shaft was brought to a standstill, the suspension was allowed to separate by settling, a sample was drawn from the aqueous layer and the amount of barium sulphate dissolved therein was determined. Table II presents these amounts for the five experiments.

TABLE II

Time h	BaSO ₄ dissolved in the aqueous liquid, g/l				
	A	Comparative Experiment B	C	I	Example II
0.5	8.7	8.5	0.	16.0	20.4
1	10.9	11	0.9	18.9	21.1
3	18.2	18.5	0.9	19.7	21.8
5	20.4	20.5	0.9	19.7	21.8
7	21.1	21	0.9	19.7	21.8
16	21.1	21	0.9	19.7	21.1

From the amounts of 0.9 and 21.1 g BaSO₄/l, dissolved in Comparative Experiment C and Example II, respectively, it can be calculated that the loadings of EDTA in Comparative Experiment C and of Compound A in Example II are 77% and 90%, respectively.

5 In Figure 1 the content of barium sulphate, in g/l, of the aqueous liquid and the time, in hours, at which these contents were measured have been set out along the vertical and horizontal axes, respectively. The values for the time and contents of barium sulphate presented in Table II have been plotted and are indicated with five different marks, each of which relates to one experiment, as indicated in the figure with A, B, C, I and II.

10 A curve has been drawn through each set of marks thus obtained for one particular aqueous liquid. The curves for Comparative Experiments A and B coincide. The position of curves I and II shows that barium sulphate has dissolved very rapidly in the compositions according to the invention.

EXAMPLES III—XVII

15 The vessel was charged with barium sulphate (0.15 mmol), Compound A (0.1 mmol), an organic acid (0.005 mmol) and water (1 ml) to which so much lithium hydroxide had been added that the pH reached a value of 11. After one hour's rotation the amount of barium sulphate dissolved in the aqueous liquid was determined. Then, the quotient

$$Q = \frac{[\text{BaSO}_4]_{t=1}}{[\text{BaSO}_4]_{t=\infty} - [\text{BaSO}_4]_{t=1}}$$

20 was calculated. In this quotient $[\text{BaSO}_4]_{t=1}$ is the content of dissolved barium sulphate in the aqueous liquid after one hour and $[\text{BaSO}_4]_{t=\infty}$ is the stoichiometric content of dissolved barium sulphate, being 23.3 g/l.

Fifteen organic acids were tested in this manner. Table III states the organic acids tested and presents the values found for Q.

TABLE III

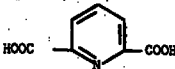
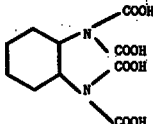
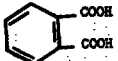
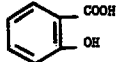
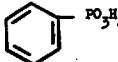
Example	Organic acid Name	Formula	Q
III	Ethylenediaminetetraacetic acid	$(\text{HOOC}-\text{CH}_2)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-$ $(\text{CH}_2-\text{COOH})_2$	19.9
IV	2,6-pyridinedicarboxylic acid		2.7
V	tri(carboxymethyl)amine	$\text{N}(\text{CH}_2\text{COOH})_3$	1.5
VI	1,2-di(dicarboxyamino)cyclohexane		1.3

TABLE III (continued)

Example	Name	Organic acid	
VII	1,2-benzenedicarboxylic acid		1.3
VIII	citric acid	$\text{HOOC}(\text{OH})(\text{CH}_2\text{COOH})_2$	1.3
IX	di(carboxymethyl)amine	$\text{HN}(\text{CH}_2\text{COOH})_2$	1.2
X	malonic acid	$\text{HOOCCH}_2\text{COOH}$	1.2
XI	succinic acid	$\text{HOOCCH}_2\text{CH}_2\text{COOH}$	1.2
XII	salicylic acid		1.2
XIII	benzenephosphonic acid		1.2
XIV	methanesulphonic acid	$\text{CH}_3\text{SO}_3\text{H}$	1.0
XV	methanedisulphonic acid	$\text{CH}_2(\text{SO}_3\text{H})_2$	0.8
XVI	1,2-ethanedisulphonic acid	$\text{HO}_3\text{SCH}_2\text{CH}_2\text{SO}_3\text{H}$	0.8
XVIII	1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane	compound B	7.9

EXAMPLE XVIII

The experiment of Example III was repeated with 0.00125 instead of 0.005 mmol of EDTA. The value found for Q was 2.4 after one hour's rotation.

5 COMPARATIVE EXPERIMENT D

The vessel was charged with water (1 ml), barium sulphate (0.15 mmol), compound A (0.1 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane. After one hour's rotation the value for Q was 0.5.

COMPARATIVE EXPERIMENT E

10 The vessel was charged with water (1 ml), barium sulphate (0.15 mmol) and Compound A (0.1 mmol). After one hour's rotation the value for Q was 0.5.

EXAMPLE XIX

15 The vessel was charged with water (1 ml), natural barite (430 mg, grain size 4 mm) and EDTA (0.018 mmol). Then, so much potassium hydroxide was added that the pH of the aqueous liquid reached a value of 11 and compound A (0.37 mmol) was added. The natural barite contained the following compounds:

Compound	%w	Compound	%w
BaSO_4	80	Fe_2O_3	3
SiO_2	13	SrSO_4	2

20 Hence, 1.5 mmol of barium sulphate was present in the flask. After 90 hours' rotation the aqueous liquid contained dissolved barium sulphate in a concentration of 0.116 M. Hence, compound A had been used with an efficiency of 20

$$\frac{0.116}{0.37} \times 100 = 31\%$$

25 The experiment was repeated at a temperature of 70°C. After 6 hours' rotation an efficiency of 57% had been reached which increased to 71% after a further 42 hours' rotation. The favourable effect of the higher temperature is clearly demonstrated by the above-given data.

COMPARATIVE EXPERIMENT F

The first experiment described in Example XIX was repeated in the absence of EDTA. Compound A was used with an efficiency of 14%.

EXAMPLE XX

5 Preparation of compound B

A solution of sodium hydroxide (80 mmol) in water (12 ml) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (20 mmol) were consecutively added to a solution of 2-chloroacetic acid (40 mmol) in water (8 ml). The mixture formed was stirred for 4 hours at 60°C, cooled to 25°C and acidified with a concentrated solution of hydrochloric acid (specific gravity 1.19) until a pH of 1 was reached. The water was evaporated from the acidified mixture at a pressure of 2 kPa, leaving a residue to which methanol (40 ml) was added. The suspended sodium chloride was filtered off, the methanol was evaporated from the filtrate and the residue formed was taken up in a mixture of methanol (6 ml) and chloroform (18 ml) at reflux temperature. The solution formed was cooled to 20°C and the precipitated 2HCl salt of compound B (4.9 g, yield 55%) was filtered off. This salt had a melting point of 106—107°C. Its PMR spectrum showed the following absorptions (60 MHz, D₂O)

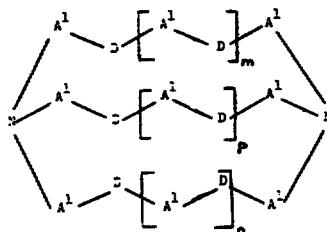
	δ, ppm
4 H singlet	0.58
8 H triplet, broad	0.88
16 H multiplet	1.10

The 2 HCl salt of compound B (201.7 mg) was dissolved in water (7 ml), 1 drop of phenolphthalein was added and the solution was titrated with a 0.09 N aqueous solution of sodium hydroxide (10.95 ml) until the colour changed; in this way a solution of compound B was obtained.

In the cleaning method according to the invention, the aqueous cleaning composition adapted for dissolving barium sulphate is contacted with the surfaces to be cleaned for a period of time sufficiently long to remove at least a portion of the barium sulphate scale on said surfaces. Hereby, the composition may be circulated over the surfaces to be cleaned. Thus, when cleaning equipment in a well, the composition may be circulated through the tubular goods in the well, such as by being pumped down through the production tube and being returned to the surface through the annular space between the production tube and the casing (or vice versa). Also, the composition may be pumped down through the production tubing and into the formation, thereby cleaning the well and the formation pore space by dissolving barium sulphate present therein whilst flowing along the surfaces that need cleaning. The spent composition of such once-through-dynamic wash procedure is later on returned to the surface by the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning composition may be applied batchwise. The composition is then pumped down in the well and optionally in the pore space of the formation parts to be cleaned and kept in contact in non-flowing condition with the surfaces that are covered with barium sulphate scale, over a period of time sufficiently long to dissolve at least a considerable part of said scale. If desired, the cleaning composition, or portions thereof in which barium sulphate has been dissolved can be acidified to protonate the bicyclic macrocyclic polyether so that it can be recovered and reused.

40 CLAIMS

1. Process for cleaning a well penetrating an underground formation and optionally formation parts in the vicinity of the said well by contacting the well and optionally the said formation parts with an aqueous composition characterised in that it comprises (1) a bicyclic macrocyclic polyether of the general formula:



wherein each A¹ which may be the same or different represents a hydrocarbon radical having up to 12 carbon atoms and each D which may be the same or different represents an oxygen or a sulphur atom or a hydrocarbon radical having up to 12 carbon atoms or a group N—R², R² represents a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbonsulphonyl radical having up



COMPARATIVE EXPERIMENT F

The first experiment described in Example XIX was repeated in the absence of EDTA. Compound A was used with an efficiency of 14%.

EXAMPLE XX

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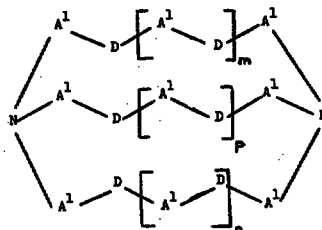
	δ, ppm
4 H singlet	0.58
8 H triplet, broad	0.88
16 H multiplet	1.10

- The 2 HCl salt of compound B (201.7 mg) was dissolved in water (7 ml), 1 drop of phenolphthalein was added and the solution was titrated with a 0.09 N aqueous solution of sodium hydroxide (10.95 ml) until the colour changed; in this way a solution of compound B was obtained.

- In the cleaning method according to the invention, the aqueous cleaning composition adapted for dissolving barium sulphate is contacted with the surfaces to be cleaned for a period of time sufficiently long to remove at least a portion of the barium sulphate scale on said surfaces. Hereby, the composition may be circulated over the surfaces to be cleaned. Thus, when cleaning equipment in a well, the composition may be circulated through the tubular goods in the well, such as by being pumped down through the production tube and being returned to the surface through the annular space between the production tube and the casing (or vice versa). Also, the composition may be pumped down through the production tubing and into the formation, thereby cleaning the well and the formation pore space by dissolving barium sulphate present therein whilst flowing along the surfaces that need cleaning. The spent composition of such once-through-dynamic wash procedure is later on returned to the surface by the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning composition may be applied batchwise. The composition is then pumped down in the well and optionally in the pore space of the formation parts to be cleaned and kept in contact in non-flowing condition with the surfaces that are covered with barium sulphate scale, over a period of time sufficiently long to dissolve at least a considerable part of said scale. If desired, the cleaning composition, or portions thereof in which barium sulphate has been dissolved can be acidified to protonate the bicyclic macrocyclic polyether so that it can be recovered and reused.

40 CLAIMS

1. Process for cleaning a well penetrating an underground formation and optionally formation parts in the vicinity of the said well by contacting the well and optionally the said formation parts with an aqueous composition characterised in that it comprises (1) a bicyclic macrocyclic polyether of the general formula:



wherein each A¹ which may be the same or different represents a hydrocarbon radical having up to 12 carbon atoms and each D which may be the same or different represents an oxygen or a sulphur atom or a hydrocarbon radical having up to 12 carbon atoms or a group N—R², R² represents a hydrogen atom or a hydrocarbonsulphonyl radical having up to 12 carbon atoms,



to 12 carbon atoms, an alkoxy carbonyl radical of up to 4 carbon atoms, an alkoxy carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical, at least two of said D members representing an oxygen or a sulphur atom or a group $N-R^2$, and m, n and p are integers from 0 to 5 inclusive, the bicyclic macrocyclic polyether of the general formula I being compatible with a barium ion, as hereinbefore defined, and (2) a salt of an organic acid.

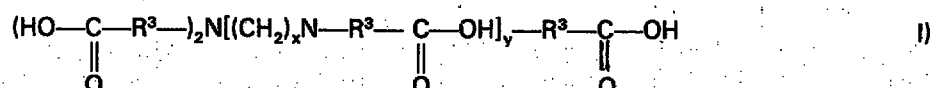
2. Process as claimed in claim 1, wherein a bicyclic macrocyclic polyether of formula 1 is used in which A^1 represents a hydrocarbon radical having in the range of from 2 to 8 carbon atoms or a 1,2-phenylene radical, D represents an oxygen atom or a group $N-R^2$, wherein R^2 represents an alkyl group of up to 8 carbon atoms, a hydrocarbon sulphonyl radical of up to 8 carbon atoms or an alkoxy carbonyl radical of up to 4 carbon atoms, at least 4 of the said D members representing an oxygen atom, and m, n, and p are 1 or 2.

3. Process as claimed in claim 2, wherein a bicyclic macrocyclic polyether of formula I is used in which A' represents an acetylene, ethylene, diethylene, triethylene or tetraethylene radical, D represents an oxygen atom or a group $N-R^2$ wherein R^2 represents an alkyl group of up to 4 carbon atoms, a hydrocarbon sulphonyl radical with up to 4 carbon atoms or a methoxy- or ethoxycarbonyl radical at least 4 of the said D members representing an oxygen atom and two further members each representing an oxygen or a nitrogen atom, and m, n and p are 1 or 2.

4. Process as claimed in claim 3, wherein the bicyclic macrocyclic polyether of formula I is 4, 7, 13, 16, 21, 24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane.

5. Process as claimed in any of the preceding claims, in which the salt of the organic acid is a salt of a (poly)aminopolycarboxylic acid.

6. Process as claimed in claim 5, in which the salt of the aminopolycarboxylic acid is a salt of an alkylene polyaminocarboxylic acid having the general formula:



wherein each of the subscripts x and y is an integer of from 1 to 4 and R^3 represents an alkylene group with one to three carbon atoms and wherein up to x of the carboxyalkyl groups can be replaced by beta-hydroxyethyl groups.

7. Process as claimed in claim 6, in which the alkylene polyaminopolycarboxylic acid according to formula II is ethylene diaminetetraacetic acid.

8. Process as claimed in claim 5, in which the polyaminocarboxylic acid is 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

9. Process as claimed in any one of the preceding claims, in which the salt of the organic acid and the bicyclic macrocyclic polyether of the general formula I are used in a molar ratio of from 0.001 to 1.

10. Process as claimed in any one of the preceding claims, in which the aqueous composition has a pH of at least 10.0, preferably in the range of from 10.0 to 11.5.

11. Process as claimed in any one of the preceding claims, in which the aqueous composition contains a base, whose cation is hardly compatible, if at all, with the bicyclic macrocyclic polyether of the general formula I.

12. An aqueous composition for dissolving barium sulphate solid comprising a bicyclic macrocyclic polyether of the general formula I in claim 1 and a salt of an organic acid.

13. An aqueous composition as claimed in claim 12, comprising 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane and ethylenediaminetetraacetic acid, preferably also containing a base.

14. An aqueous composition as claimed in claim 12, comprising 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane and 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, preferably also containing a base.

15. An aqueous composition as claimed in claim 12, substantially as hereinbefore described with reference to Examples I—XIX.