

SPECIFICATION

Process and aqueous composition for well cleaning by dissolving barium sulphate scale

The invention relates to a process for cleaning a well penetrating an underground formation and/or cleaning formation parts in the vicinity of the said well, and to an aqueous composition therefor.

In particular, the invention relates to a cleaning process wherein the well and/or 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, to novel compounds, and to a process for the preparation of these novel compounds.

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.

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.

Another mechanism whereby barium sulphate scale can be formed in the well-bore is the comingling 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.

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 already in the early life of a well.

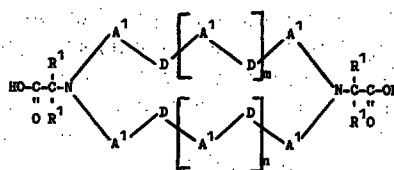
Various cleaning methods have been described in the past, wherein use is made of aqueous compositions containing active ingredients, which compositions are brought into contact with the equipment present in a well, and optionally with the surface of the pore space parts of the formation in the vicinity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

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 must dissolve rapidly into the aqueous composition and that the barium complex formed must have a high solubility in water. In addition, a high loading of the active ingredient is desirable.

A process making use of certain bicyclic macrocyclic polyethers, and having these attractive features is described in British patent applications 1567/78;7913463.

We have now found that a particular class of salts of macrocyclic polyethers can be used advantageously in cleaning wells. The process according to the present invention is not only of great interest in that it requires only one active ingredient having the above-mentioned attractive features, but it also allows a considerably shorter down time than the known processes.

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 or the well and said formation parts with an aqueous composition comprising a salt of a macrocyclic polyether of the general formula:



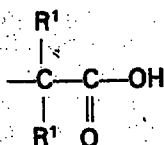
(II)

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 $N-R^2$, R^2 representing a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbonsulphonyl radical having up to 12 carbon atoms, an alkoxycarbonyl or alkoxycarbonyl-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 $N-R^2$; and each R^1 which may be the same or different represents a hydrogen atom or an alkyl group having up to 6 carbon atoms or a carboxy group and m and n are integers from 0 to 5 inclusive, the macrocyclic polyether according to the general formula II being compatible with a barium ion, as hereinafter defined.

The expression "the macrocyclic polyether of the general formula II being compatible with a barium ion" is used to denote that the macrocyclic polyether of the general formula II is capable of accommodating a barium ion in the intramolecular cavity of the polyether molecule. The expression "salt of a macrocyclic polyether of the general formula II" is used to denote a carboxylate salt of this macrocyclic polyether.

It has been found that the presence of just one carbon atom between the macrocyclic ring and the carboxy(ate) groups is essential for the performance of the salts of the macrocyclic polyethers of the general formula II. When a compound according to formula II is modified by replacing the two groups



by two 2-carboxyethyl groups (two carbon atoms being present between each of the two $-C(O)OH$ groups and the macrocyclic ring even when the carbon atom adjacent to the nitrogen atom carries a further carboxy group) or by two hydrogen atoms, two alkyl groups or by two ethoxycarbonyl ($-C(O)OC_2H_5$) groups (the compounds thus formed not being acids), the macrocyclic polyethers thus obtained appear to be loaded up with barium ions to a small extent only (see Comparative Experiments A-D).

Compounds according to formula II which can be used conveniently are those wherein 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 hydrocarbonsulphonyl radical of up to 8 carbon atoms or an alkoxycarbonyl radical of up to 4 carbon atoms; at least 4 of the said D members representing an oxygen atom; and each R^1 represents a hydrogen atom or an alkyl group having up to 4 carbon atoms or a carboxy group and m and n are in the range of from 1 to 3.

Preferred compounds according to formula II are those wherein A^1 represents an ethylene, diethylene, triethylene or tetra ethylene radical, particularly an ethylene 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, particularly a methyl group, a hydrocarbonylsulphonyl radical of up to 4 carbon atoms or a methoxy- or ethoxycarbonyl radical; at least 4 of the said D members representing an oxygen atom, and each R^1 represents a hydrogen atom or a methyl, ethyl or carboxy group and m and n are 1 or 2.

A particularly preferred compound according to formula II is 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane; this compound is also referred to as "compound A" hereinafter.

The concentration in which the salt of the macrocyclic polyether according to formula II is present in the aqueous solution is not critical. This concentration is suitably taken substantially equivalent to the saturation concentration of the complex of barium with the polyether in the aqueous composition under the prevailing conditions. Suitably, the concentration of the salt of the 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 according to the present invention will normally be alkaline. It will be clear that protonation of the nitrogen bridging atoms in the macrocyclic polyether according to formula II will reduce its tendency to form barium complexes. Thus, the higher the pH, the higher the unprotonated portion of the macrocyclic polyether will become 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 8, more preferably of at least 10, and particularly a pH in the range of from 10 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 competitive, if at all, with the barium ion to be complexed by the macrocyclic polyether according to the general formula II; an example of a base that is not, or hardly competitive is lithium hydroxide. It will be appreciated that the aqueous composition according to the present invention can be obtained in various ways. It is possible, for instance, to dissolve the salt of the macrocyclic polyether according to formula II in water, whether or not in the presence of an additional base. It is also possible and quite convenient to obtain an aqueous solution of an acid salt of a macrocyclic polyether according to formula II-e.g. the bis-hydrochloric acid salt of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-

tetraoxacyclooctadecane-, which a solution is then treated with at least an equivalent amount of a base

preferably a base which is hardly compatible, if at all, with the macrocyclic polyether structure. Thus, at least 4 equivalents of base (e.g. lithium hydroxide) should be used to convert the bis-hydrochloric acid salt referred to hereinabove into the salt of the macrocyclic polyether according to the present invention. Good results have been obtained using up to 16, preferably up to 6 equivalents of base.

An other interesting method of obtaining the aqueous composition according to the present invention comprises the in situ production of the salts of the macrocyclic polyethers by reacting the corresponding macrocyclic polyether with an alpha-halocarboxylic acid and a (n excess of a) base (vide infra). This method becomes of even greater interest as the reaction can be carried out suitably at the temperatures prevailing in an oil-producing formation (e.g. temperatures up to 80°C or even higher). In other words, the salt of the macrocyclic polyether according to formula II can be prepared in the presence of the compound to be dissolved by the salt of the macrocyclic polyether under practically optimal conditions. It is also possible to use the crude reaction mixture obtained in the synthesis of the salts of the macrocyclic polyethers according to formula II.

The cation of the salt of the macrocyclic polyether present in the aqueous composition may be any cation, for example, a lithium, sodium, potassium or an ammonium, or alkyl substituted ammonium-ion, for example a tetraalkyl substituted ammonium ion. This cation is preferably not, or hardly competitive with the barium ion to be complexed with the macrocyclic polyether according to formula II. Preference is given to the use of lithium salts.

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 nonionic. 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 5 minutes to 1.5 hours.

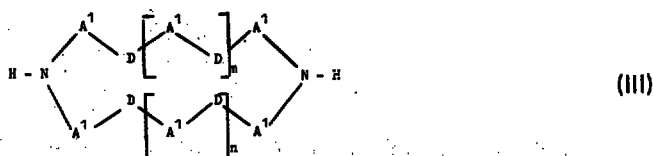
In general, when using an aqueous composition according to the present invention for dissolving a barium sulphate solid, there is no need to adopt temperatures substantially above ambient temperature. Temperatures as low as 10 to 20°C have been found satisfactory. However, the relatively high temperature (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. As discussed hereinbefore, this is of great advantage for the in situ preparation of the salts of the macrocyclic polyethers according to formula II.

It will be appreciated that the aqueous composition according to the present invention can also be applied when other types of scale and/or compounds whose ions can be accommodated by the salts of the macrocyclic polyethers according to formula II are present in wells and/or formation parts in the vicinity of said wells. The aqueous composition 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.

The invention further provides an aqueous composition for dissolving barium sulphate solid which comprises a salt of a macrocyclic polyether according to the general formula II.

Macrocyclic polyethers according to the general formula II 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 representing 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-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 each R¹ which may be the same or different represents a hydrogen atom or an alkyl group having up to 6 carbon atoms or a carboxy group and m and n are integers from 0 to 5 inclusive, the macrocyclic polyether of the general formula II being compatible with a barium ion, as hereinbefore defined, and salts thereof—with the exception of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and salts thereof—are novel compounds.

The salts of the macrocyclic polyethers according to the general formula II may be prepared in a manner known per se by reacting the corresponding macrocyclic polyether of the general formula:



with a salt of an alpha-halocarboxylic acid, such as 2-chloroacetic acid, 2-bromoacetic acid, 2-chloro-

or 2-bromobutyric acid, in the presence of a base. Examples of suitable salts of, for instance, 2-chloroacetic acid and 2-bromoacetic acid are alkali metal salts. Suitable bases comprise alkali metal hydroxides, for example lithium hydroxide, sodium hydroxide and potassium hydroxide. It is also possible to react a macrocyclic polyether according to the general formula III with an alpha-halocarboxylic acid in the presence of a base, and preferably in the presence of an excess of a suitable base. Acidification of an aqueous solution of the salts of the macrocyclic polyethers according to the general formula II yields the macrocyclic polyethers according to the general formula II. Further acidification gives quaternary ammonium salts for the macrocyclic polyethers of formula II, which inner salts are also considered to be within the scope of the present invention. In the event that at least one of the groups R¹ represents a carboxy group, it was found convenient to use a halomalonate ester which after subsequent hydrolysis gives the macrocyclic polyether according to the general formula II.

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 and containing five stainless steel balls with a diameter of 0.32 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.

Example I

The vessel was charged with barium sulphate (0.5 mmol), water (1 ml), compound A (0.1 mmol) and so much lithium hydroxide that the aqueous solution in the vessel had a pH of 11. After 24 hours of rotation the suspension was allowed to separate by settling. A sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, both in amounts of 15.2 g/l, calculated as barium sulphate. Hence, the lithium salt of compound A had been used with an efficiency of

$$\frac{15.2}{233 \times 0.1} \times 100 = 65\%.$$

Comparative Experiment A

This experiment differed from that described in Example I in that compound A was replaced by 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane. The sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, both in amounts of 0.09 g/l, calculated as barium sulphate. Hence, the 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane had been used with an efficiency of

$$\frac{0.09}{233 \times 0.1} \times 100$$

or only 0.4%.

Replacement of compound A by 1,10-dimethyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane gave an efficiency of 1.3% (0.3 g BaSO₄/l).

Comparative Experiment B

This experiment differed from that described in Example I in that compound A was replaced by 1,10-di(2-carboxyethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 mmol). The sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate in amounts of 0.033 and 1.4 g/l, respectively, calculated as barium sulphate, indicating that most of the complexed barium was present in the vessel as an unwanted solid. Hence, the 1,10-di(2-carboxyethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane had been used with an efficiency of

$$\frac{1.43}{233 \times 0.1} \times 100$$

or 6.1% on sulphate and with an efficiency of

$$\frac{0.033}{233 \times 0.1} \times 100$$

or only 0.14% on barium, thus indicating that the presence of an additional carbon atom between the nitrogen atom and any carboxy group of the macrocyclic polyethers according to the general formula II virtually destroys their complexing ability.

Comparative Experiment C

This experiment differed from that described in Example I in that compound A was replaced by 1,10-di(ethoxycarbonyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M) and in that 0.3 M barium sulphate was used. The sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, both in amounts of 0.18 g/l, calculated as barium sulphate. Hence, the 1,10-di(ethoxycarbonyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane has been used with an efficiency of

$$\frac{0.18}{233 \times 0.1} \times 100 = 0.8\%$$

thus indicating that the absence of a carbon atom between the macrocyclic ring structure and the carboxylate function virtually destroys the complexing ability of this macrocyclic polyether.

10 Example II

The vessel was charged with barium sulphate (0.3 mmol), water (1 ml), compound A (0.1 mmol) and so much lithium hydroxide that the aqueous solution the vessel had a pH of 11. After 15 minutes of rotation the suspension was allowed to separate by settling. A sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, both in amounts of 14.5 g/l, calculated as barium sulphate. Hence, the lithium salt of compound A had been used with an efficiency of

$$\frac{14.5}{233 \times 0.1} \times 100$$

or 62%. This efficiency remained constant after prolonged rotation.

Example III

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

Compound	%w	Compound	%w
BaSO ₄	80	Fe ₂ O ₃	3
SiO ₂	13	SrSO ₄	2

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 0.104 M. Hence, compound A had been used with an efficiency of

$$\frac{0.104}{0.37} \times 100 = 28\%$$

When the experiment was repeated at 70°C it was found that an efficiency of 21% had already been reached after 6 hours.

Example IV

a) The vessel was charged with barium sulphate (0.45 mmol), 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M), 2-chloroacetic acid (0.2 M) sodium hydroxide (0.4 M) in water 1.5 ml). The mixture was heated to 70°C under rotation. After 24 hours of rotation the suspension was allowed to separate by settling. A sample drawn from the aqueous layer contained equal amounts of dissolved barium and dissolved sulphate. The efficiency of the insitu prepared sodium salt of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (calculated as the amount of BaSO₄ (mole) dissolved per mole of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged) was 28.3%. It should be noted that the efficiency of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane under the same conditions amounts to 1%.

b) The experiment was repeated this time with the use of 0.8M sodium hydroxide and 0.4 M 2-chloroacetic acid. The efficiency, after 24 hours (in situ production at 70°C) of the sodium salt had increased to 35.3% (calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged).

c) The efficiency could be improved even further when instead of sodium hydroxide the less competitive base lithium hydroxide was used. Under similar conditions as in Example IIb but using up to 1.6 M lithium hydroxide the efficiency—calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged— was 54% (12.5 g BaSO₄/l).

d) An efficient of 51% was found when preformed 1,10-di(carboxymethyl)-4,7,13,16-tetraoxacyclooctadecane was used as the macrocyclic polyether according to formula II, (LiOH as base).

e) Finally a crude reaction mixture of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M) and 2-chloroacetic acid (0.2 M) was used as the "macrocyclic polyether" in the presence of sodium hydroxide (0.4 M). The efficiency on solving solid barium sulphate (0.3 moles per litre) at 20°C after 24 hours under standard conditions as described in Example I was 23% (calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged). It should be noted that this efficiency compares well with that obtained using the in situ prepared macrocyclic polyether described in Example IVa.

10 Example V

a). The novel compound 1,10-di(alpha-ethylcarboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (compound B) was prepared in situ, i.e. in the presence of barium sulphate (3 moles per litre) by reacting, 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M) and 2-chlorobutyric acid (0.2 M) and lithium hydroxide (0.8 M) at 70°C. The compound was characterised by ¹H and ¹³C nuclear magnetic resonance technique in D₂O.

The following signals were assigned:

¹H NMR (H₂O as 0 ppm):

δ: -1.2 (m, 16H; 1,2); -1.8 (t, 2H, 3); -2.1 (t, 8H, 4); -3.2 (m, 4H, 5); -4.0 (t, 6H, 6) ppm.

¹³C NMR (external reference):

δ: 183.4 (7); 73.2 (1,2,3); 54.4 (4); 23.4 (5); 14.6 (6) pm.

Compound B was formed in about 14% yield.

b) The efficiency of the compound B prepared in situ was tested using 3 moles per litre of barium sulphate. After 24 hours at 70°C the efficiency proved to be 2.6% (0.6 g BaSO₄/l), calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged, which means after corrections for the efficiency of unconverted starting material and for the yield of the compound an efficiency of about 11% (calculated on compound B).

Example VI

The novel compound bis(dicarboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (compound C) was prepared by reacting dimethylbromomalonate (1.61 g, 7.2 mmol) with 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (1 g, 3.8 mmol) in dry benzene (26 ml) under reflux for 6 hours. After cooling the reaction mixture was filtered and the filtrate evaporated and purified by column chromatography (Al₂O₃, CH₂Cl₂ as eluent) yielding the tetramethyl ester of compound C (23%, 0.45 g).

The tetramethyl ester (0.35 g, 0.67 mmol) was dissolved in tetrahydrofuran (30 ml) to which lithium hydroxide (67.5 mg, 4 equivalents on ester) and water (2 ml) were added. After 5 days stirring at ambient temperature, the precipitate formed was isolated (0.21 g) as the tetralithium salt of compound C (about 65%).

Upon acidification (excess HCl) and treatment with acetone/ethanol to remove LiCl, compound C was obtained as a hygroscopic HCl salt.

Analysis: for C₁₈H₅₂Cl₄N₂O₂₀ (compound C 4HCl.8H₂O)

Calculated:

C: 28.6%; H: 6.9%; Cl: 18.8%; N: 3.7%.

Found:

C: 24.6%; H: 5.4%; Cl: 20%; N: 3.5%.

P.M.R.-data were in accordance with the expected structure.

The efficient of compound C was determined using the method described in Example II. A sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, in amounts of 8.5, resp. 8.2 g/l, calculated as barium sulphate. Hence, the lithium salt of compound C had been used with an efficiency of about 36%.

Comparative Experiment D

This experiment differed from that described in Example I in that compound A was replaced by 1,10-bis-(2-succinyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (prepared by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane with oxalacetic acid in the presence of sodium cyanoborohydride) and in that 0.3 M barium sulphate was used. The sample drawn from the aqueous layer contained dissolved barium and dissolved sulphate, both in amounts of 0.4 g/l, calculated as barium sulphate. Hence, the succinyl compound had been used with an efficiency of 1.9%, thus indicating that the additional presence of a carbon atom between the nitrogen atom and any carboxy group virtually destroys the complexing ability.

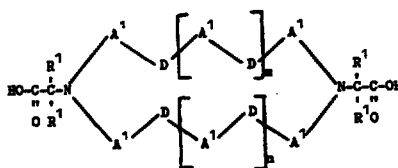
In the cleaning method according to the invention, the aqueous cleaning composition adapted for dissolving barium sulphate is contacted with the surfaces to be cleaned for a period of time sufficiently

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. It is also possible to pump down through the production tubing and into the formation the reactants (the macrocyclic polyether according to formula II, the alpha-halocarboxylic acid and the base, in particular 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, 2-chloroacetic acid and an excess of lithium hydroxide) which cause in situ formation of the salt of the macrocyclic polyether according to formula II which will then exert its cleaning activities under the prevailing conditions. Also crude reaction mixtures can be pumped down through the production tubing and into the formation. If desired, the cleaning composition, or portions thereof, in which barium sulphate has been dissolved can be acidified to obtain the macrocyclic polyether according to formula II so that it can be recovered and reused.

It is noted that our Patent Application No. 82 20996 describes and claims the macrocyclic polyethers of formula II and salts thereof, with the exception of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and salts thereof; and a process for the preparation thereof.

25 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 or the well and said formation parts with an aqueous composition, characterised in that it comprises a salt of a 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 group N—R² R² representing 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 or alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxy-methylene radical, at least two of the said D members representing an oxygen or a sulphur atom or a group N—R², and each R¹ which may be the same or different represents a hydrogen atom or an alkyl group having up to 6 carbon atoms or a carboxy group and m and n are integers from 0 to 5 inclusive, the macrocyclic polyether according to the general formula II being compatible with a barium ion, as hereinbefore defined.

2. Process as claimed in claim 1, wherein a macrocyclic polyether according to formula II is used in which 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 members representing an oxygen atom; and each R¹ represents a hydrogen atom or an alkyl group having up to 4 carbon atoms or a carboxy group and m and n are in the range of from 1 to 3.

3. Process as claimed in claim 2, wherein a macrocyclic polyether according to formula II is used in which A¹ represents an 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 of up to 4 carbon atoms or a methoxy- or ethoxy carbonyl radical; at least 4 of the said D members representing an oxygen atom and each R¹ represents a hydrogen atom or a methyl, ethyl or carboxy group and m and n are 1 or 2.

4. Process as claimed in claim 3, wherein the macrocyclic polyether according to formula II is 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

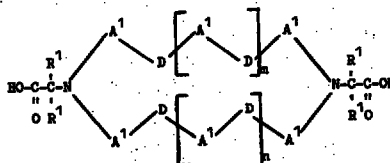


long to remove at least a portion of the barium sulphate scale on said surfaces. Hereby, the composition may be circulated over the surfaces to be cleaned. Thus, when cleaning equipment in a well, the composition may be circulated through the tubular goods in the well, such as by being pumped down through 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. It is also possible to pump down through the production tubing and into the formation the reactants (the macrocyclic polyether according to formula II, the alpha-halocarboxylic acid and the base, in particular 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, 2-chloroacetic acid and an excess of lithium hydroxide) which cause in situ formation of the salt of the macrocyclic polyether according to formula II which will then exert its cleaning activities under the prevailing conditions. Also crude reaction mixtures can be pumped down through the production tubing and into the formation. If desired, the cleaning composition, or portions thereof, in which barium sulphate has been dissolved can be acidified to obtain the macrocyclic polyether according to formula II so that it can be recovered and reused.

It is noted that our Patent Application No. 82 20996 describes and claims the macrocyclic polyethers of formula II and salts thereof, with the exception of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and salts thereof; and a process for the preparation thereof.

25 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 or the well and said formation parts with an aqueous composition, characterised in that it comprises a salt of a 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 group N—R², R² representing 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 or alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxy-methylene radical, at least two of the said D members representing an oxygen or a sulphur atom or a group N—R², and each R¹ which may be the same or different represents a hydrogen atom or an alkyl group having up to 6 carbon atoms or a carboxy group and m and n are integers from 0 to 5 inclusive, the macrocyclic polyether according to the general formula II being compatible with a barium ion, as hereinbefore defined.

2. Process as claimed in claim 1, wherein a macrocyclic polyether according to formula II is used in which 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 members representing an oxygen atom; and each R¹ represents a hydrogen atom or an alkyl group having up to 4 carbon atoms or a carboxy group and m and n are in the range of from 1 to 3.

3. Process as claimed in claim 2, wherein a macrocyclic polyether according to formula II is used in which A¹ represents an 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 of up to 4 carbon atoms or a methoxy- or ethoxy carbonyl radical; at least 4 of the said D members representing an oxygen atom and each R¹ represents a hydrogen atom or a methyl, ethyl or carboxy group and m and n are 1 or 2.

4. Process as claimed in claim 3, wherein the macrocyclic polyether according to formula II is 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.



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

5 6. Process as claimed in any one of the preceding claims, in which the aqueous composition contains a base whose cation has substantially no or only low compatibility with the macrocyclic polyether according to the general formula II.

7. Process as claimed in any one of the preceding claims, in which an aqueous composition is used in which the salts of the macrocyclic polyethers according to the general formula II are produced in situ.

10 8. Process as claimed in claim 7, in which an aqueous composition is used in which a macrocyclic polyether according to the general formula III as defined in the foregoing description, an alpha-halocarboxylic acid and a base or an excess of a base are caused to react.

15 9. Process as claimed in claim 8, in which an aqueous composition is used in which 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, 2-chloroacetic acid and sodium hydroxide or lithium hydroxide, preferably an excess of sodium hydroxide or lithium hydroxide are caused to react at a temperature up to 80°C.

20 10. Process as claimed in any one of claims 1—9, in which macrocyclic polyether according to the general formula II or salt thereof is formed in situ in the well and/or the formation parts by reacting a macrocyclic polyether according to formula III as defined in the foregoing description, an alpha-halocarboxylic acid and a base or an excess of a base the reaction being carried out in the presence of solid barium sulphate.

11. Process as claimed in claim 10, in which 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is reacted with a 2-halo-carboxylic acid and sodium hydroxide or lithium hydroxide, preferably an excess of sodium hydroxide or lithium hydroxide at a temperature up to 80°C.

25 12. An aqueous composition for dissolving barium sulphate solid comprising a salt of a macrocyclic polyether according to the general formula II as defined in claim 1.

30 13. An aqueous composition as claimed in claim 12, wherein a salt of a macrocyclic polyether according to the general formula II is used in which A¹ represents an 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 of up to 4 carbon atoms or a methoxy- or ethoxycarbonyl radical; at least 4 of the said D members representing an oxygen atom and each R¹ represents a hydrogen atom or a methyl, ethyl or carboxy group and m and n are 1 or 2.

35 14. An aqueous composition as claimed in claim 13, wherein the sodium- or lithium salt of 1,10-di(carboxymethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is used.

15. An aqueous composition as claimed in any one of claims 12—14 substantially as hereinbefore described with reference to any of Examples I—V.