



- (51) **International Patent Classification:**
C09K 8/56 (2006.01)
- (21) **International Application Number:**
PCT/GB20 12/0527 12
- (22) **International Filing Date:**
31 October 2012 (31.10.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
1118838.0 31 October 2011 (31.10.2011) GB
- (71) **Applicant:** **CLEANSORB LIMITED** [GB/GB]; 1J Merrow Business Centre, Merrow Lane, Guildford, Surrey GU4 7WA (GB).
- (72) **Inventor:** **HOLDSWORTH, Duncan**; 1J Merrow Business Centre, Merrow Lane, Guildford, Surrey GU4 7WA (GB).
- (74) **Agent:** **KEEN, Celia Mary**; J.A. Kemp, 14 South Square, Gray's Inn, London, Greater London WC1R 5JJ (GB).
- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*



WO 2013/064823 A1

(54) **Title:** PROCESS FOR TREATING AN UNDERGROUND FORMATION

(57) **Abstract:** The present invention relates to processes for consolidating an underground formation with a consolidating mineral. The consolidating material is a carbonate and is produced from an alkaline treatment fluid containing, in at least some embodiments, environmentally friendly and inexpensive components. In one embodiment, the process can be applied to consolidation of an underground formation during or following drilling. The present invention also provides a treatment fluid suitable for use in such processes.

PROCESS FOR TREATING AN UNDERGROUND FORMATION

Field of the Invention

5 The present invention relates to the consolidation of underground formations through the deposition of a carbonate mineral from a treatment fluid as well as other situations where deposition of carbonate mineral from a treatment fluid may be desirable.

Background to the Invention

10 A large proportion of hydrocarbon production worldwide is from underground sandstone formations. These formations often have a high porosity and permeability so have the potential to produce hydrocarbons at high rates. Frequently however, such formations have a tendency to produce sand, due to being unconsolidated or poorly
15 consolidated. Sand producing formations generally are relatively young in the sense of geological time and are often composed of loosely attached sand or sediments that have not yet been converted to solid sandstone by geochemical processes.

Sand as used herein refers to fine particulate materials that may be produced from
20 poorly consolidated sandstones. Normally these will be sand grains.

Poorly consolidated sandstones have been defined in US 3,741,308 (cited herein only for the purpose of illustration and not for limiting the scope of the present invention) as follows: any assemblage of particulate matter provided: 1. Particles in the 50 to 2000
25 micron size range account for at least 10 percent of the weight of the entire assemblage. 2. At least about 20 percent by weight of the entire assemblage consists of minerals or compounds containing the element silicon as part of their chemical composition, and 3. The assemblage is either unconsolidated or so poorly consolidated that it behaves as an unconsolidated particulate system under stresses to which it is exposed.

30 Factors that can cause sand production in weak formations include producing drawdown, pressure depletion, *in situ* rock stresses, changes in flow rate or changes in

-2-

water cut (sand production is often associated with water breakthrough). While a certain amount of sand production can be tolerated, excessive sand production can cause a variety of operational problems including erosion of pumps, tubing, chokes, valves and pipe bends. This can lead to serious safety and environmental consequences (US
5 3,741,308). It can also lead to collapse of formation or casing and significant reduction in or loss of production.

The tendency of the formation to produce sand is indicated by the unconfined compressive strength of the formation. As a general guide, if a formation has an
10 unconfined compressive strength of about 7.6×10^6 Pa (1,100 p.s.i.) or greater, sand production is unlikely, so sand control measures are not likely to be required. At an unconfined compressive strength of between about 2.8×10^6 Pa and 7.6×10^6 Pa (400 and 1,100 p.s.i.) sand production may occur and sand control is normally desirable. Below an unconfined compressive strength of about 2.8×10^6 Pa (400 p.s.i.) sand
15 control is almost certainly required.

There have been a number of approaches to sand control. These include mechanical approaches that physically prevent sand from entering the produced fluids and the use of chemical methods that bind the sand grains together.
20

Common approaches to mechanical sand control include gravel packing and the use of screens including pre-packed screens. Gravel packs use gravel (sized sand) placed in the wellbore and physically prevent sand from entering the production stream. A screen is used to prevent gravel production. Gravel packs may be open hole (external gravel
25 pack) or cased hole (internal gravel pack). "Frac-packs" combine cased hole gravel pack and hydraulic fracturing completions and are generally expected to give higher productivity than straight gravel packing. Pre-packed screens are commonly used in horizontal openhole wells and typically consist of a layer of resin-bonded gravel held between two screens. Other types of screen and expandable screens may also be used
30 for mechanical sand control.

Chemical sand control is based on the introduction into the formation of chemicals that bind the sand together. The chemicals increase the strength of the attachments between the sand grains and therefore the tendency for sand production is reduced.

- 5 The principle disadvantages of current mechanical approaches to sand control are the cost and the fact that the sand control barrier creates an additional pressure barrier that can reduce the productivity of the well to considerably below its potential. The principle disadvantages of existing chemical approaches to sand control are the cost and health and safety and environmental considerations relating to the types of chemicals that are
- 10 currently used, which are generally resins such as phenolic resins, furan, furfuryl alcohol and epoxy resins. Resins are often flammable, toxic or hazardous to handle. In addition, the difficulty of treating sections of wellbore which are more than several metres in length make current chemical approaches based on resins generally unsuitable for use in long wellbores. If too much resin is deposited, the formation may be sealed
- 15 off and not just consolidated. Remedial treatments in a case where too much resin has been deposited are unlikely to be successful.

The use of enzymes in processes to deposit resins or minerals in underground formations has been taught in PCT/GB98/021 17. Deposition of resins or minerals in the

20 formation can result in consolidation. Consolidation using an alkali metal silicate in combination with urea or formamide has been taught in US 5,209,296 and US 5,222,556. Methods for consolidation based on the use of alkaline solutions in very hot wells have also been taught.

- 25 A more recent approach has been to use nanoparticles as a means to deliver consolidating materials into the formation (US 6,513,592). Also, consolidation of a formation using resins while drilling has been taught (US 6,702,044). Current mechanical and chemical approaches to sand control are essentially applied after the well is drilled. GB 2435 169 teaches that minerals may be deposited in underground
- 30 formations through the in-situ generation of phosphate, sulphate or other species in the presence of a metal salt. WO 2006/038016 teaches carbonate mineral deposition

processes based on the use of bicarbonates or urea plus a metal salt in the treatment fluid.

There is a need for further processes for chemical consolidation of a formation that can
5 achieve effective sand control through consolidation of the formation, while allowing
good production or injection rates to be achieved and which are also low cost, low
hazard, easy to apply and may be used on long formation intervals. Particularly
desirable would be a methodology that makes use of simple, cheap and environmentally
friendly components, is easy to prepare and carry out, and which operates over a
10 desirable temperature range such that even consolidation (i.e. uniform consolidation)
can be achieved throughout the target formation. There is also a need for processes for
shutting off of a formation to production or injection which are effective, low cost, low
hazard, easy to apply and may be used on long formation intervals. There is a further
need for effective, low cost, low hazard, easy to apply processes for water or gas shut
15 off, for the grouting of tunnels, or for other consolidation applications.

Summary of the Invention

An object of the present invention is to provide further non-resin, chemical processes
20 for consolidation of a formation and for sand control. Another object of the present
invention is to provide further non-resin, chemical processes for formation shut-off.
Yet another object of the present invention is to provide novel, non-resin chemical
treatment processes whereby long formation intervals, for example horizontal openhole
wells, can be consolidated in a simple treatment. A further object of the present
25 invention is to provide chemical processes of consolidation which use chemicals that
are low hazard and low toxicity and have low environmental impact.

Accordingly, the present invention provides a process for consolidating an underground
formation, which process comprises: (a) introducing a treatment fluid into an
30 underground formation, which treatment fluid comprises (I) cations of a metal having
an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is
soluble in the treatment fluid: (II) an amino acid having at least one deprotonated

carboxylic acid group; (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester; and (VII) an alkylene carbonate; and which treatment fluid is alkaline or becomes alkaline *in situ*; and (b) allowing carbonate mineral to be deposited from the fluid, thereby consolidating the underground formation.

10

The present invention also provides the use of a treatment fluid for consolidating an underground formation with a consolidating material, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (II) an amino acid having at least one deprotonated carboxylic acid group; (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester; and (VII) an alkylene carbonate; and which treatment fluid is alkaline or is capable of becoming alkaline *in situ*.

Still further, the present invention provides a treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (II) an amino acid having at least one deprotonated carboxylic acid group; (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester;

25
30

and (VII) an alkylene carbonate; and which treatment fluid is alkaline or is capable of becoming alkaline *in situ* in an underground formation.

In addition, the present invention provides a process for depositing carbonate material
5 from a fluid, which process comprises: (a) providing a fluid comprising (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (II) an amino acid having at least one deprotonated carboxylic acid group; (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula
10 $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester; and (VII) an alkylene carbonate; and which treatment fluid is alkaline or is capable of becoming alkaline; and (b)
15 allowing carbonate mineral to be deposited from said fluid, if necessary after said fluid has become alkaline.

Detailed Description of the Invention

20 The process of the present invention may be used to consolidate underground formations, including those from which hydrocarbons (oil or gas) or water are extracted or injected. The carbonate mineral that is deposited acts as a consolidant in the underground formation.

25 Cations of a metal (herein also referred to as "metal cations") suitable for use in the process of the present invention are those with an oxidation state of +2 or higher. Suitable metals include group II metals and transition metals, including magnesium, calcium, strontium, barium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminium silver or zirconium. Magnesium and calcium are
30 particularly preferred. Calcium is most preferred.

The cations of a metal may be present in the form of a salt of metal cations. For example, the metal cations may conveniently be provided in the form of any water soluble salts compatible with the other components of the treatment fluid, including, but not being limited to, chlorides, bromides, nitrates, propionates, lactates, acetates and
5 formates. Alternatively, though, the metal cations may be present in any complex or coordination compound provided that the consolidation process is still able to proceed.

References throughout this specification to the metal cations being provided "in the form of a particular salt of course mean that the salt has been incorporated into the
10 treatment fluid, e.g. to thereby produce dissociated metal cations and counterion anions, rather than implying that the cations and anions remain physically bound to one another within the treatment fluid.

The consolidation systems of the present invention are based on the deposition of
15 carbonate materials from the metal cations (I) and at least one of the components/component combinations (II) to (VII). Each or every component in (II) to (VII) is typically soluble in the treatment fluid.

In one embodiment, at least one of the components (II), (III)(a), (III)(b)(i), (IV) or (V) is
20 present and is generated *in-situ* in the treatment fluid from another substance. In other words, these components may be provided as such in the treatment fluid or alternatively another substance may initially be mixed into the treatment fluid, which then transforms (e.g. chemically degrades) *in situ* to produce the relevant component.

25 As is very well known in the art, an amino acid is a compound that comprises at least one amine functional group and at least one carboxylic acid functional group (i.e., a group of formula $-CO_2H$). Thus, an amino acid having at least one deprotonated carboxylic acid group means an amino acid that comprises at least one amine functional group and at least one carboxylate functional group (i.e., a group of formula $-COO^-$). It
30 has been found that deprotonation of at least one of the carboxylic acid groups present in an amino acid is needed for consolidation processes based on amino acids to proceed. The amino acid (II) having at least one deprotonated carboxylic acid may alternatively

and interchangeably be referred to as a "deprotonated amino acid" or as an "amino acid salt". The amino acid may be naturally occurring, synthetic, proteogenic, or nonproteogenic.

- 5 If an amino acid (II) is used that contains multiple carboxylic acid functional groups, then the amino acid having at least one deprotonated carboxylic acid group can be, and typically is, an amino acid on which all of the carboxylic acid groups are deprotonated.

The amino acid (II) having at least one deprotonated carboxylic acid group can be any
10 such compound that is capable of generating a carbonate material in conjunction with the metal cations in a treatment fluid.

There is no particular limitation on the chemical structure of the amino acid (II) having at least one deprotonated carboxylic acid group, beyond of course that it must have at
15 least one amine functional group (typically a primary or secondary amine functional group) and at least one carboxylate functional group. For example, other functional groups can be present provided that they do not prevent deposition of carbonate material when the compound is present in a treatment fluid. A person of ordinary skill in the art would have no difficulty in selecting suitable amino acids for use in the present
20 invention. Furthermore, straightforward and routine field and/or laboratory tests could, if desired, be used to confirm whether a particular amino acid is suitable for use in the present invention.

Some suitable amino acids (II) having at least one deprotonated carboxylic acid group
25 are those derived from α -amino acids, β -amino acids and γ -amino acids. Particularly preferred are amino acids having at least one deprotonated carboxylic acid group that are derived from α -amino acids and β -amino acids, most preferably α -amino acids. The amine group may be a secondary amine or a primary amine. In an embodiment, the amine group is a primary amine group.

30

As is well known, many amino acids have chiral centres. It is not important for the purposes of the invention whether the amino acid having at least one deprotonated

carboxylic acid group is chiral or achiral, or whether it is present in a particular enantiomeric form. If a particular amino acid is commercially available at lower cost in a particular chiral form, it is sometimes preferable to use that lower cost form.

Nonetheless, the process of the present invention can be carried out using amino acids
5 having at least one deprotonated carboxylic acid group in any optically active or non-optically active form whatsoever.

Examples of an amino acid (II) having at least one deprotonated carboxylic acid group are the carboxylic-acid-deprotonated forms of alanine, arginine, asparagine, aspartic
10 acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tyrosine, valine, sarcosine, iminodiacetic acid, 3-aminobutyric acid, GABA (γ -aminobutyric acid), ornithine and β -alanine.

15 If the amino acid contains a secondary amine group which is protonated such as with lysine monohydrochloride and L-arginine monohydrochloride, this group also needs to be deprotonated.

Preferred amino acids (II) having at least one deprotonated carboxylic acid group are
20 the carboxylic-acid-deprotonated forms of glycine (otherwise known as "glycinate"), histidine, β -alanine, alanine, serine, glutamic acid (otherwise known as "glutamate") aspartic acid, threonine, sarcosine, lysine, methionine, arginine, valine, iminodiacetic acid, 3-aminobutyric acid or γ -aminobutyric acid. For example, suitable amino acids having at least one deprotonated carboxylic acid group are the carboxylic-acid-
25 deprotonated forms of glycine and glutamic acid, i.e. glycinate and glutamate. The most preferred amino acids (II) are deprotonated forms of glycine, glutamic acid, sarcosine (n-methylglycine) or lysine.

Typically said amino acid (II) having at least one deprotonated carboxylic acid group
30 does not contain a terminal amide group.

When used in combination with cations of a metal with an oxidation state of +2 or higher, the amino acids having at least one deprotonated carboxylic acid group have been found to be highly effective in processes for depositing a carbonate mineral.

5 The inventor has found that the consolidation processes of the present invention proceeds effectively under alkaline conditions. Typically therefore the pH of the treatment fluid when in place in the underground formation is greater than 7. In an embodiment, the pH is greater than or equal to 8, for example greater than or equal to 9. Further suitable pHs are those greater than or equal to 10, for example greater than or
10 equal to 10.5. These preferred pH conditions apply for all systems of the present invention (i.e., they are not limited to amino-acid-based (II) systems). The preferred upper pH will of course vary according to the specific system and could be readily determined by one of ordinary skill in the art. For example, one of ordinary skill in the art would typically use a pH that does not result in the deposition of precipitates other
15 than carbonate salts (such as precipitates that could be formed at very high pHs between the cations (I) and an enolate species formed via deprotonation of a beta oxocarboxylic acid ester component (III)(b)(iii) or (VI)).

With reference to amino-acid-based systems, the pH of the treatment fluid *in situ* is such
20 that there is enough amino acid having at least one deprotonated carboxylic acid group present in the fluid to achieve effective consolidation. A suitable pH for a particular treatment fluid containing particular components can be readily determined by the skilled person through routine experimentation, if need be.

25 An appropriate pH can be achieved by ensuring that the treatment fluid is alkaline before it is placed in the formation. For instance, this may be achieved by addition of a suitable quantity of base, for example an alkali metal hydroxide. Suitable alkali metal hydroxides include sodium hydroxide and potassium hydroxide.

30 The treatment fluid may alternatively become alkaline *in situ*. For example, the treatment fluid may contain a component that hydrolyses or decomposes over time to generate a base *in situ*. It has previously been taught that compounds able to generate a

-11-

base include the following: amides including formamide, acetamide. urea and urea derivatives (e.g.1-methylurea, 1,1-dimethylurea, 1,3-dimethylurea, 1,1,3-trimethylurea, 1-ethylurea, 1,1-diethylurea, 1,3-diethylurea, n-propylurea, n-butylurea, 1-phenylurea, 1-methyl-3-phenylurea, 1-ethyl-1-phenylurea) organic azides, cyanic acid, cyanic acid
5 amines (e.g. hexamethyltetraamine, hexamethylenetetramine), tetraazatricycloalkanes and acyl azides (e.g. acetyl azide, propionyl azide, malonyl azide, succinyl azide, phthaloyl azide). Preferred are hexamethyltetraamine, hexamethylenetetramine formamide and urea; most preferred is urea. As explained already, the pH of the treatment fluid *in situ* must be such that there is enough amino acid having at least one
10 deprotonated carboxylic acid group present in the fluid to achieve effective consolidation. Suitable bases are those capable of deprotonating an amino acid compound to produce an amino acid having at least one deprotonated carboxylic acid group.

15 Typically the consolidation process proceeds in the presence of hydroxide ions. Thus, in the context of the requirement that the treatment fluid is alkaline or becomes alkaline *in situ*, it is preferable that the treatment fluid thereby contains hydroxide ions. It will be appreciated that hydroxide ions will necessarily be present when the treatment fluid comprises water and it is or becomes alkaline *in situ*.

20 For the avoidance of doubt, references throughout this specification to "*in situ*" mean in the underground formation and in particular in the part of the underground formation where consolidation is to be effected. Alternatively, where the consolidation processes are being effected in situations other than in underground formations, then *in situ* refers,
25 by analogy, to the particular location where deposition of carbonate material is desired.

The deposition of the metal carbonate from the treatment fluids of the present invention may be considered to be precipitation from homogeneous solution. Thus, references herein to "depositing" or "deposited" are interchangeable with "precipitating" or
30 "precipitated".

-12-

For systems based on the use of an amino acid (II) the amino acid having at least one deprotonated carboxylic acid group may be provided by adding a carboxylate salt directly to the treatment fluid. For example a suitable glycinate salt may be sodium glycinate. References throughout this specification to an amino acid having at least one
5 deprotonated carboxylic acid group being provided "in the form of a particular salt of course means that the salt has been incorporated into the treatment fluid, e.g. to thereby produce dissociated carboxylate groups and counterion cations, rather than implying that the amino acid having at least one deprotonated carboxylic acid group and its counterion cations remain physically bound to one another within the treatment fluid.

10

Alternatively the amino acid having at least one deprotonated carboxylic acid group may be produced within the treatment fluid by mixing an amino acid and an amount of a suitable strong base at least equimolar to the amino acid. For example, glycine, histidine, β -alanine, alanine or serine may be mixed with at least an equimolar amount
15 of a suitable strong base. Glutamic acid and aspartic acid, which contain two carboxylic acid groups, may be mixed with at least two molar equivalents of a suitable strong base (i.e., an equimolar amount of base with respect to the total mole number of carboxylic acid groups). A suitable strong base is one capable of deprotonating the carboxylic acid groups present in the amino acid. Typically, an excess of no more than 20 mol% and
20 preferably no more than 10 mol% of base is added with respect to the total mole number of carboxylic acid groups in the amino acid, in order to avoid precipitation of metal hydroxide from the treatment fluid. More preferably, an excess of no more than 7.5 mol%, for example no more than 5 mol%, of base is added with respect to the total mole number of carboxylic acid groups in the amino acid.

25

Particularly preferred treatment fluids of the present invention include aqueous fluids containing calcium chloride plus either sodium glycinate, sodium glutamate, sodium sarcosinate, or the sodium salt of lysine. Thus, the treatment fluid may comprise (I) calcium chloride and (II) glycine, glutamic acid, sarcosine or lysine.

30

When generating sodium glycinate within the treatment fluid, preparing this from a mixture of glycine plus sodium hydroxide is most preferred. When generating sodium

glutamate within the treatment fluid, preparing this from a mixture of glutamic acid plus sodium hydroxide is most preferred. Sodium hydroxide is also most preferred for preparing sodium sarcosinate and the sodium salt of lysine.

- 5 It will be understood by those skilled in the art that in some embodiments of the present invention, the amino acid or amino acid having at least one deprotonated carboxylic acid group may be generated *in situ* from suitable precursors. Such precursors will be readily determined by those skilled in the art and include, but are not limited to, di-, tri-, tetra- or polypeptides, including diglycine, triglycine, tetraglycine and polyglycine,
- 10 polyaspartic acid, oligopeptides, cyclic dipeptides (such as 2,5-diketopiperazine "glycine anhydride"), cyclic oligo peptides or esters or amides of amino acids. Also included are proteins rich in suitable amino acids, for example collagen, which is rich in glycine.
- 15 In addition to the use of deprotonated amino acids (II) in processes for depositing carbonate minerals, as described herein, other chemical systems have been determined to be effective for depositing carbonate minerals in the presence of (I) cations of a metal having an oxidation state of +2 or higher.
- 20 These other chemical systems for depositing carbonate mineral are based on (I) in combination with any of: (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V) an alpha
- 25 ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester; and (VII) an alkylene carbonate.

In the case of processes based on (III), either of, or both of, an amine and ammonia are present. The amine is typically a primary or secondary amine that does not contain any

30 terminal amide functional groups. For the avoidance of doubt, "amine" means a compound (e.g., an alkyl or aryl compound) containing an amine functional group (an amine functional group not being part of an amide group). The primary or secondary

-14-

amine may, for example, be selected from monoethanolamine (MEA), diethanolamine (DEA) diethylenetriamine (DETA), triethylenetetramine (TETA), N-methylethanolamine, 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris), bis(2-hydroxypropyl)amine, 2-amino-2-methyl-1,3-propanediol, and polyethyleneimine (PEI). The amine (III) may be provided in the form of a salt, which salt releases the amine under alkaline conditions. Preferably said salt is ethanolamine hydrochloride, Tris-hydrochloride or diethanolamine hydrochloride.

The ammonia may be provided as such, or alternatively, and preferably, may be generated *in-situ* by any means known to those skilled in the art, preferably from the thermal hydrolysis of urea or from the action of urease enzyme on urea. Provision of ammonia generated *in-situ* may be advantageous in view of avoiding, or mitigating the extent of, calcium hydroxide precipitation.

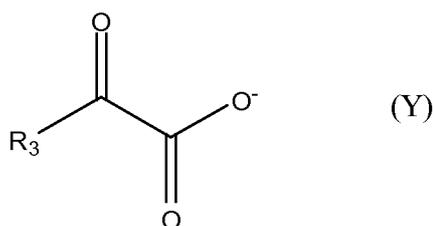
In the case of processes based on (III), the amine and/or ammonia is provided in combination with at least one of: (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (ii) an alkylene carbonate; and (iii) a beta oxocarboxylic acid ester.

There is no particular limitation on the chemical structure of the alpha oxocarboxylic acid, beyond of course that it must have at least one functional group of the formula $-C(=O)-C(=O)-O^-$ (i.e., where the carbonyl group is situated on the alpha carbon with respect to the deprotonated carboxylic acid group). For example, other functional groups can be present provided that they do not prevent deposition of carbonate material when the alpha oxocarboxylic acid is present in a treatment fluid. A person of ordinary skill in the art would have no difficulty in selecting suitable alpha oxocarboxylic acids for use in the present invention. Furthermore, straightforward and routine field and/or laboratory tests could, if desired, be used to confirm whether a particular alpha oxocarboxylic acid is suitable for use in the present invention.

30

The alpha oxocarboxylic acid may, for example, have the formula (Y)

-15-



wherein R_3 is selected from hydrogen, C_{1-6} alkyl, a hydrocarbyl ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10- membered heteroaryl ring and a 5- to 10- membered heterocyclyl ring. Examples of particularly suitable alpha oxocarboxylic acids include glyoxylic acid, pyruvic acid and 2-ketobutyric acid.

In general, an alpha oxocarboxylic acid includes alpha ketocarboxylic acids (where a ketone group is at the alpha position to the carboxylic acid) and alpha aldocarboxylic acids (where an aldehyde group is at the alpha position to the carboxylic acid).

10

There is also no particular limitation on the chemical structure of the alkylene carbonate, beyond of course that contain an alkylene carbonate functional group (otherwise known as an 1,3-dioxolan-2-one group). Thus, "alkylene carbonate" can be used interchangeably with "1,3-dioxolan-2-one compound". Other functional groups can be present provided that they do not prevent deposition of carbonate material when the alkylene carbonate is present in a treatment fluid. A person of ordinary skill in the art would have no difficulty in selecting suitable alkylene carbonates for use in the present invention. Furthermore, straightforward and routine field and/or laboratory tests could, if desired, be used to confirm whether a particular alkylene carbonate is suitable for use in the present invention. Examples of suitable alkylene carbonates include ethylene carbonate, propylene carbonate, butylene carbonate or glycerine carbonate.

Similarly, there is no particular limitation on the chemical structure of the beta oxocarboxylic acid ester, beyond of course that it contains an beta oxocarboxylic acid ester functional group (i.e., a carbonyl group located in the beta position with respect to the carboxylic acid group). Other functional groups can be present provided that they do not prevent deposition of carbonate material when the beta oxocarboxylic acid ester is present in a treatment fluid. A person of ordinary skill in the art would have no

25

-16-

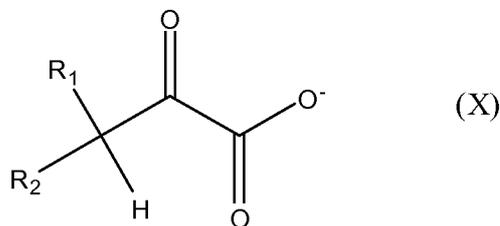
difficulty in selecting suitable beta oxocarboxylic acid esters for use in the present invention. Furthermore, straightforward and routine field and/or laboratory tests could, if desired, be used to confirm whether a particular beta oxocarboxylic acid ester is suitable for use in the present invention. The beta oxocarboxylic acid ester may, for example, have a formula $R_a-C(=O)-CH_2-C(=O)-O-R_b$, where R_a is selected from hydrogen, C_{1-6} alkyl, a hydrocarbyl ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10- membered heteroaryl ring and a 5- to 10- membered heterocyclyl ring and R_b is selected from C_{1-6} alkyl, a hydrocarbyl ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10- membered heteroaryl ring and a 5- to 10- membered heterocyclyl ring. Exemplary beta oxocarboxylic acid esters are ethyl acetoacetate and methyl acetoacetate.

In the case of processes based on (IV), an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group means a compound that contains both an aminoalkyl group and a deprotonated sulphonic acid group ($-SO_3^-$). There is no particular limitation on the chemical structure of this component other than it must contain these functional groups. Other functional groups can be present provided that they do not prevent deposition of carbonate material when this component is present in a treatment fluid. A person of ordinary skill in the art would have no difficulty in selecting suitable amino alkyl sulphonic acids for use in the present invention. Furthermore, straightforward and routine field and/or laboratory tests could, if desired, be used to confirm whether a particular amino alkyl sulphonic acid is suitable for use in the present invention. For example, the amino alkyl sulphonic acid (IV) having at least one deprotonated sulphonic acid group may be a deprotonated form of 2-aminoethane sulphonic acid (commonly known as taurine).

For processes based on (V), the alpha ketocarboxylic acid is a compound that contains a functional group of the formula $-C(=O)-C(=O)-O^-$ and wherein the carbonyl group at the alpha-position to the carboxylate functional group is part of a ketone group (i.e., it is not an aldehyde functional group). Other functional groups may be present in the compound provided that they do not prevent deposition of carbonate material when this component is present in a treatment fluid.

-17-

The alpha ketocarboxylic acid may, for example, have the formula (X)



wherein R_1 and R_2 are independently selected from hydrogen, C_{1-6} alkyl, a hydrocarbyl
 5 ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10- membered heteroaryl
 ring and a 5- to 10- membered heterocyclyl ring, or wherein R_1 and R_2 , together with
 the carbon atom to which they are mutually attached, form a hydrocarbyl ring
 containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10- membered heteroaryl ring or
 a 5- to 10- membered heterocyclyl ring. Examples of particularly preferred alpha
 10 ketocarboxylic acids include pyruvic acid and 2-ketobutyric acid.

As used herein (for example in the formulae (X) and/or (Y) and/or with reference to the
 groups R_a and R_b), a hydrocarbyl ring containing 3 to 6 carbon atoms includes
 cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, with cyclopentyl and cyclohexyl
 15 being preferred and cyclohexyl being particularly preferred.

As used herein (for example in the formulae (X) and/or (Y) and/or with reference to the
 groups R_a and R_b), a C_{6-10} aryl ring is a monocyclic or polycyclic 6- to 10-membered
 aromatic hydrocarbon ring system having from 6 to 10 carbon atoms. Phenyl is
 20 preferred.

As used herein (for example in the formulae (X) and/or (Y) and/or with reference to the
 groups R_a and R_b), a 5- to 10- membered heteroaryl ring is a monocyclic or polycyclic
 5- to 10- membered aromatic ring system, such as a 5- or 6- membered ring, containing
 25 at least one heteroatom, for example 1, 2, 3 or 4 heteroatoms, selected from O, S and N.
 When the ring contains 4 heteroatoms these are preferably all nitrogen atoms.
 Examples of monocyclic heteroaryl groups include thienyl, furyl, pyrrolyl, imidazolyl,
 thiazolyl, isothiazolyl, pyrazolyl, oxazolyl, isoxazolyl, triazolyl, thiadiazolyl,

- oxadiazolyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl and tetrazolyl groups. Examples of polycyclic heteroaryl groups include benzothienyl, benzofuryl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzoxazolyl, benzisoxazolyl, benztriazolyl, indolyl, isoindolyl and indazolyl groups. Preferred polycyclic groups include indolyl, isoindolyl, benzimidazolyl, indazolyl, benzofuryl, benzothienyl, benzoxazolyl, benzisoxazolyl, benzothiazolyl and benzisothiazolyl groups, more preferably benzimidazolyl, benzoxazolyl and benzothiazolyl, most preferably benzothiazolyl. However, monocyclic heteroaryl groups are preferred.
- 10 Preferably the heteroaryl group is a 5- to 6- membered heteroaryl group. Particularly preferred heteroaryl groups are thienyl, pyrrolyl, imidazolyl, thiazolyl, isothiazolyl, pyrazolyl, oxazolyl, isoxazolyl, triazolyl, pyridinyl, pyridazinyl, pyrimidinyl and pyrazinyl groups. More preferred groups are thienyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, pyrrolyl and triazinyl, most preferably pyridinyl.
- 15 As used herein (for example in the formulae (X) and/or (Y) and/or with reference to the groups R_a and R_b), and a 5- to 10- membered heterocyclyl ring is a non-aromatic, saturated or unsaturated, monocyclic or polycyclic C₅₋₁₀ carbocyclic ring system in which one or more, for example 1, 2, 3 or 4, of the carbon atoms are replaced with a moiety selected from N, O, S, S(O) and S(O)₂. Preferably, the 5- to 10- membered heterocyclyl group is a 5- to 6- membered ring. Examples of heterocyclyl groups include azetidiny, oxetanyl, thietanyl, pyrrolidinyl, imidazolidinyl, oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolidinyl, tetrahydrofuranyl, tetrahydrothienyl, tetrahydropyranyl, tetrahydrothiopyranyl, dithiolanyl, dioxolanyl, pyrazolidinyl, piperidinyl, piperazinyl, hexahydropyrimidinyl, methylenedioxyphenyl, ethylenedioxyphenyl, thiomorpholinyl, S-oxo-thiomorpholinyl, S,S-dioxo-thiomorpholinyl, morpholinyl, 1,3-dioxolanyl, 1,4-dioxolanyl, trioxolanyl, trithianyl, imidazoliny, pyranyl, pyrazoliny, thioxolanyl, thioxothiazolidinyl, 1H-pyrazol-5-(4H)-onyl, 1,3,4-thiadiazol-2(3H)-thionyl, oxopyrrolidinyl, oxothiazolidinyl, oxopyrazolidinyl, succinimido and maleimido groups and moieties. Preferred heterocyclyl groups are pyrrolidinyl, imidazolidinyl, oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolidinyl, tetrahydrofuranyl, tetrahydrothienyl, tetrahydropyranyl,
- 20
- 25
- 30

tetrahydrothiopyranyl, dithiolanyl, dioxolanyl, pyrazolidinyl, piperidinyl, piperazinyl, hexahydropyrimidinyl, thiomorpholinyl and morpholinyl groups and moieties. More preferred heterocyclyl groups are tetrahydropyranyl, tetrahydrothiopyranyl, thiomorpholinyl, tetrahydrofuranyl, tetrahydrothienyl, piperidinyl, morpholinyl and pyrrolidinyl groups.

A beta oxocarboxylic acid ester or an alkylene carbonate can also be used without being combined with an amine in the system (III), i.e. as system (VI) or (VII), respectively. For processes based on (VI), preferred beta oxocarboxylic acid esters include those described elsewhere herein (for example, in the processes based on (III)); similarly, for processes based on (VII), preferred alkylene carbonates include those described elsewhere herein (for example, in the processes based on (III)).

In the case of processes based on (II) amino acids the further addition of (i) a hemiacetal or (ii) a hemiketal may be beneficial. The hemiacetal or hemiketal may be 1,3-dihydroxyacetone dimer or a reducing sugar comprising a monosaccharide, disaccharide, oligosaccharide or polysaccharide. 1,3-dihydroxyacetone dimer is a hemiacetal that reacts with sodium glycinate resulting in decarboxylation but is not a reducing sugar. The monosaccharide, disaccharide or oligosaccharide may be selected from glucose, fructose, galactose, xylose, ribose, arabinose, lyxose, allose, altrose, mannose, gulose, talose, lactulose, lactose, maltose, cellobiose or dextrin. Preferably the monosaccharide, disaccharide or oligosaccharide is glucose, fructose, dextrin or maltose. The reducing sugar can be produced *in situ* via the breakdown of a non-reducing di-, tri-, tetra-, oligo- or poly-saccharide using an enzyme or oxidising agent. The reducing sugars are assumed to exist primarily as rings in solution possessing either hemiketal and/or hemiacetal groups.

In the case of processes based on (II) amino acids or (IV) amino alkyl sulphonic acids, the further addition of a carbonyl compound is optional and may be beneficial. The optional carbonyl compound, if present, is typically also soluble in the treatment fluid.

-20-

Different carbonyl compounds may be effective with (II) amino acids or (IV) amino alkyl sulphonic acids.

In the case of processes based on (II) amino acids, the carbonyl compound may be selected from a $C_{i-2}O$ aldehyde, a $C_{i-2}O$ alpha carbonyl ketone, a $C_{i-2}O$ alpha hydroxy ketone, an alpha-oxocarboxylic acid, a beta-oxocarboxylic acid ester, an alkylene carbonate or a D-isoascorbate salt (the latter also commonly known as an erythorbate salt). Examples of such carbonyl compounds include carbonyl compounds selected from glyoxylic acid monohydrate, glyoxylic acid 50% wt. aqueous solution, pyruvic acid, 2-ketobutyric acid (these preceding four preferably being deprotonated, e.g. using sodium hydroxide), 4-hydroxybenzaldehyde, phthaldialdehyde, methyl cyclopentenolone, methyl acetoacetate, ethyl acetoacetate, ethylene carbonate, propylene carbonate, butylene carbonate, glycerine carbonate, sodium D-isoascorbate monohydrate, pyruvaldehyde, 2,2-dimethoxyacetaldehyde and hydroxyacetone.

15 An alpha hydroxyl ketone is also specifically known as an acyloin and generally as a ketol. The alpha carbonyl group of the alpha carbonyl ketone may be either an aldehyde (i.e. an alpha keto aldehyde) or a ketone (i.e. an alpha keto ketone also known as an alpha diketone.)

20 In the case of the amino alkyl sulphonic acids (IV), the carbonyl compound may be selected from an alpha-oxocarboxylic acid, a beta-oxocarboxylic acid ester or an alkylene carbonate. Preferably the carbonyl compound is glyoxylic acid monohydrate, glyoxylic acid 50% wt. aqueous solution, pyruvic acid, 2-ketobutyric acid, methyl acetoacetate, ethyl acetoacetate, ethylene carbonate, propylene carbonate, butylene carbonate or glycerine carbonate.

25

As with amino-acid based systems (II), it is also necessary for the carbonate deposition systems based on (III), (IV), (V), (VI) and (VII) to be run under alkaline conditions, where for example the alpha oxocarboxylic acid, alpha ketocarboxylic acid, amino alkyl sulphonic acid or amino acid will be in a deprotonated form. For example, in the process of the present invention at least one of the components (II), (III)(b)(i), (IV) and (V) may be present and be prepared by deprotonating the corresponding protonated

30

form of the component with at least a stoichiometric equivalent of base. The base may, for example, be sodium hydroxide or potassium hydroxide.

5 It is desirable that individual chemicals are selected such they are soluble to a sufficient extent in the treatment fluid to allow their entry into a permeable medium such as the rock matrix, to allow the treatment fluid to effectively deposit carbonate mineral within the permeable medium in order to achieve the desired effect such as consolidation, water or gas shut off etc. For example some potential candidate compounds such as dicarboxylates may form insoluble complexes with (I) cations of a metal having an
10 oxidation state of +2 or higher.

The currently most preferred treatment fluids comprise calcium ions as component (I) in combination with a component selected from lysine, glycine, sarcosine (i.e., amino acids belonging to the general group (II)) and taurine (i.e., an amino alkyl sulphonic
15 acid belonging to the general group (IV)). Preferably these treatment fluids further comprise a base, thus ensuring the required deprotonation of the carboxylic acid groups in the amino acids or the sulphonic acid group in the amino alkyl sulphonic acid, respectively.

20 The concentrations of the components (I) and (II), (III), (IV), (V), (VI) and (VII) in the treatment fluid will be selected to give the required rate of carbonate deposition and amount of carbonate deposition and extent of consolidation or permeability reduction of the formation within the duration of the treatment.

25 Before field use, the suitability of individual candidate systems under conditions relevant to the formation to be treated (particularly temperature) can routinely be determined in tests carried out by one skilled in the art.

In all cases, the consolidating mineral deposited is a carbonate or substantially a
30 carbonate. In some cases carbonate may be co-deposited with other poorly soluble materials produced during the carbonate deposition reactions. It will be understood that

-22-

as long as at least some carbonate is deposited, leading to consolidation or water or gas shut off etc. that the treatment fluids will fall within the scope of the present invention.

In certain embodiments, such as those discussed below, the treatment fluid may contain
5 components in addition to the components (I) and (II), (III), (IV), (V), (VI) or (VII). It
will of course be appreciated that any additional components present in the treatment
fluid must be compatible with the other components, in the sense that they must not
prevent the desired consolidation process from taking place. A skilled person would
generally be able easily to recognise whether particular additional components would be
10 compatible with the treatment fluid of the invention. However, if necessary this could
be routinely and easily confirmed by preparing a suitable test mixture containing the
additional components at issue and then checking whether deposition of carbonate
material still occurs in the required manner.

15 Following preparation of the treatment fluid and introduction of the treatment fluid into
the underground formation, the treatment fluid will normally undergo an increase in
temperature as it is heated by the formation. This will increase the rate of deposition of
the carbonate mineral as a solid consolidating material. The consolidating material is
preferably deposited on the internal surfaces of the formation, such as the surface of
20 individual sand particles, and results in an increase in the strength of the formation.
Similarly, deposition of the consolidating material may be used to strengthen proppant
packs in propped fractures or gravel in gravel packs. All substances present in the
treatment fluid will preferably be soluble in the treatment fluid to at least a
concentration that will be useful in the process of the present invention (that is, a
25 concentration that will result in a degree of deposition of consolidating material
effective for consolidation).

In order to facilitate ready penetration into the formation to be consolidated, the
treatment fluid will normally be particulate-free and have low viscosity. There may
30 however be some cases where use of a particulate-containing treatment fluid or a higher
viscosity treatment fluid might be beneficial to produce a desired consolidating material
(for example, for seeding or nucleation purposes or where the process of the present

invention is combined with the use of other consolidation processes requiring the use of particulates e.g. nanoparticle based consolidation processes). The use of particulate containing fluids, including in some embodiments the use of particulates large enough to block pore throats, is therefore not excluded from the scope of the present invention.

5

The treatment may be carried out at any suitable stage during completion or production or injection of the well. The treatment may be carried out on new wells or those that have been already been produced or injected.

- 10 The treatment fluid is normally prepared at the surface by mixing the components (I) and (II), (III), (IV), (V), (VI) or (VII) and any other optional components into a solvent such as water or brine by any method such as will be known to those skilled in the art. Water is usually used as the solvent, but the solvent could also be a water-miscible solvent or a mixture of water with one or more water-miscible solvents. In some cases
- 15 the treatment fluid may be an emulsion or microemulsion including non-polar solvents or hydrocarbons and suitable emulsifying agents or surfactants.

- Following preparation of the treatment fluid, it is placed in the formation using a suitable method such as will be known to those skilled in the art, for example pumping
- 20 via a drillstring, by bullheading, or by coiled tubing. The well penetrating the formation may be cased and perforated or openhole. In the case of treating formations adjacent to an openhole well, including formations adjacent to a horizontal well, it may be necessary to remove any filter cake present at the formation face (particularly in the case of a newly drilled well) by any suitable method, such as will be known to those
- 25 skilled in the art, before introducing the treatment fluid, so that the treatment fluid can enter the formation. In the case of treating formations adjacent to a cased and perforated wellbore it may be necessary to remove any damage in the vicinity of the perforations and adjacent formation by any suitable method such as will be known to those skilled in the art, before introducing the treatment fluid, so that the treatment fluid can enter the
- 30 formation.

The fluid is placed sufficiently far into the formation to be treated to give an adequate degree of sand control. The degree of consolidation (formation strengthening) required and the depth to which consolidation is required will be readily determinable by one skilled in the art of designing such treatments.

5

Generally, the degree of strengthening obtained with the treatment fluid formulation to be used on the formation will be determined in a laboratory evaluation ahead of the treatment to assist in design of the treatment. The extent of consolidation may conveniently be investigated by measuring the unconfined compressive strength of the formation with and without treatment, for example using cores cut from the formation.

10

The effectiveness of the process may also be assessed or estimated using model systems such as the consolidation of loose sand or glass beads or through core tests run on cores cut from poorly consolidated outcrop sandstones.

15

After placement of the treatment fluid in the formation, the fluid is left for a sufficient period of time for the deposition of consolidating material to occur. This will normally take a period of a day to a few weeks (for example from 1 to 28 days and preferably from 2 to 14 days), but may take place over a shorter or longer period of time depending on the specific formulation and temperature. In the case of those treatment fluids capable of depositing carbonate mineral at the fastest rates, deposition may be essentially complete within less than a day or even within a period of minutes or hours.

20

25

The temperature at which the treatment is carried out is generally an important determinant of the rate of the deposition reactions. Normally, consolidation will proceed at the prevailing temperature of the formation. The treatment fluid as introduced will normally (although not in all cases) be at a lower temperature than the formation and will increase in temperature with time. It is well known that the rate of chemical reactions generally increases at higher temperatures. The process of the present invention may however be used in low temperature formations without additional heating if sufficient time is allowed for the carbonate deposition to occur.

30

Deposition can proceed at temperatures as low as room temperature (about 20 °C) or even lower.

In some situations where the process of the present invention is operated, it may be advantageous to increase the rate at which the process proceeds and deposits a mineral as a consolidant by increasing the temperature of the treatment fluid in the formation adjacent to a wellbore. This may be achieved by supplying heat via the wellbore. Methods of supplying heat include, but are not limited to, injection or circulation of hot water, steam or hydrocarbons through the wellbore, or carrying out exothermic chemical reactions in or adjacent to the wellbore. Suitable methods of providing heat to the wellbore and adjacent formation will be well known to those skilled in the art.

10

The aim of the process of the present invention is to consolidate the formation to a sufficient extent to provide sand control and minimise or remove the need for mechanical sand control. The process will increase the unconfined compressive strength of the formation. As a consequence of the deposition of consolidating material, the permeability of the formation may be reduced to at least some extent. The process is normally applied to formations from which it is intended to produce hydrocarbons or water, or to inject hydrocarbons or water, and therefore it is desirable that the formation retains at least sufficient permeability for production or injection to take place. It will be understood by those skilled in the art that deposition of sufficient consolidant in the formation to reduce the permeability to the point at which production or injection could be sealed off could also have oilfield, water well or other applications for treating underground formations. These may include, but not be limited to, water or gas shut off or the grouting of tunnels. Accordingly, another embodiment of the present invention is to seal off the formation to prevent production or injection. It will be understood that more than one treatment may need to be applied to the formation in order to achieve this or it may be necessary to continuously inject treatment fluid over a prolonged period of time.

25

To assist the deposition of carbonate onto formation rock, gravel, proppant or other surfaces, a water wetting agent may be introduced into the underground formation prior to or at the same time as introducing the treatment fluid into the underground formation.

30

-26-

As normally applied, a relatively slow rate of deposition of consolidating material is generally to be preferred as this will facilitate placement of the treatment fluid deep into the formation before any consolidating material is deposited. Deposition is also more likely to deposit carbonate mineral on internal surfaces rather than result in the precipitation of discrete particles into the bulk fluid. The former will strengthen the formation, whereas the latter will generally result in permeability reduction due to mechanisms such as the blocking of pore throats. Thus, in consolidation embodiments carbonate mineral is typically allowed to be deposited from the fluid over a period of from 1 to 28 days, or from 4 to 28 days, such as from 2 to 14 days. In shut-off applications, carbonate mineral may typically be deposited over a period of minutes to several days, such as from 1 hour to 4 days. Deposition time will obviously be a function of the specific system, temperature, concentration etc.

Using an adequately mixed treatment fluid, deposition of the consolidating material will take place homogeneously throughout the treatment fluid and therefore throughout the region of the formation into which the treatment fluid has been placed. This should result in uniform consolidation of the formation.

The consolidation treatment may be applied to any poorly consolidated formation with which an individual treatment fluid is compatible. In addition to poorly consolidated sands or sandstones, it will be apparent to those skilled in the art that the process may also be applied to other poorly consolidated zones or formations such as unconsolidated clays, shale or the like. Wells drilled into the consolidated formation may be used for the production or injection of hydrocarbons or water.

In some embodiments, the process of the present invention may be used to consolidate the formation behind induced or natural fracture faces or proppant within propped fractures.

The process may also be used to deposit material on surfaces other than sand, sandstone, clays, shale etc. present in the formation. In particular, it may also be used to deposit carbonate mineral in frac packs, gravel packs, propped fractures, or the like for

-27-

the purposes of consolidation of the gravel, proppant or the like. The process may be used for remedial treatments of resin coated gravel or proppant in gravel packs or propped fractures etc where the resin coatings have failed or been removed by other chemical treatments.

5

The deposition of consolidating material in the formation increases the amount of cementation or adhesion between the sand grains within the sandstone. Deposition is favoured at surfaces and at the contact points between sand grains due to surface energy considerations. Deposition of consolidant on the existing cementation on sand grains that are already cemented together will lead to strengthening of the formation.

10

Optionally, the treatment fluid may further comprise one or more other components if this assists in the deposition of the consolidating carbonate.

15

The presence of suitable nucleating materials may also assist in ensuring deposition takes place on the existing cementation. Such materials may be incorporated into the treatment fluid or introduced into the formation ahead of the treatment fluid.

20

Suitable nucleating materials will be any material that preferentially binds or associates to the particles or cementation already present in the formation, and which acts as a nucleating material for consolidants of the present invention. Suitable nucleating materials include, but are not limited to, polymers such as polysaccharides and proteins and micro- particles (micro-crystals) of the consolidant being deposited. Suitable effective materials will be known to those skilled in the art. The effectiveness of different materials will be readily determinable by suitable tests. Organic-inorganic (carbonate) composites may be stronger than just carbonate alone (Rodriguez-Navarro, C. Et al. (2003). Conservation of Ornamental Stone by *Myxococcus xanthus* - Induced Carbonate Biomineralization. Applied and Environmental Microbiology, Vol. 69 No 4 pp 2182-2193).

25

30

-28-

The use of polymers in or with the treatment fluid of the present invention may therefore be advantageous as it may result in the deposition of a consolidant stronger than the carbonate mineral in isolation.

5 Where the consolidant that is deposited is essentially the same mineral as the existing cementation or nucleating material, deposition onto the existing cementation will be particularly favoured. For example, where calcium carbonate is deposited as a consolidant, the presence of existing calcium carbonate in the cementation is expected to provide an excellent surface for nucleation and deposition of the new calcium
10 carbonate.

In some situations, it may be useful to incorporate materials that have the opposite effect to nucleating agents, i.e. act as delaying agents which inhibit, modify or regulate the deposition of the consolidating material to at least some extent. These may be any
15 materials that prevent, slow, modify or inhibit deposition of the consolidating mineral at the concentration at which they are used.

Particularly useful will be scale inhibitors, such as will be known to those skilled in the art and which are generally used to prevent deposition of oilfield scales. Oil field scale
20 inhibitors include phosphate esters, phosphonates, sulfonates, and polyacrylates. Other scale inhibitors include copolymers and terpolymers of acrylates, sulfonates and phosphonates, phosphinico polycarboxylic acids (PPCA) and mixtures thereof. Particularly useful scale inhibitors include 2-hydroxyethyl imino bis methylene phosphonic acid, fatty amine phosphonates, triethanolamine phosphate ester, DETA
25 phosphonate (pentaphosphonates) and TETA phosphonate (hexaphosphonates). Other examples of suitable scale inhibitors include diethylenetriamine penta(methylene) phosphonic acid, DETPMP, polyphosphino-carboxylic acids (PPCAs) and polymers such as polyacrylate (PAA) and poly vinyl sulphonate (PVS), sulphonated polyacrylates (VS-Co), phosphonomethylated polyamines (PMPA) and combinations thereof.

30

Many known scale inhibitors are proprietary chemicals are generally composed of materials which fall into one of three chemical classes: (1) low molecular weight

polycarboxylates, including polyacrylates and polymaleates; (2) inorganic polyphosphates and phosphate esters; and (3) phosphonates. Each class has properties which make certain materials desirable depending on the specific conditions.

5 Introduction of such materials into the formation ahead of, or contained in the treatment fluid, may retard deposition of consolidant and allow consolidation deeper into the formation. In the case of scale inhibitors, dilution of the scale inhibitor to below the minimum inhibitory concentration (MIC) will generally be needed in order for mineral deposition to occur.

10

It will be understood by those skilled in the art that the morphology of any carbonate crystals deposited can be influenced by the type of surface on which they grow and also by the type and concentration of the chemicals present in the treatment fluid. The morphology of the carbonate crystals deposited may not be important, as long as
15 consolidation proceeds to the desired extent. Methods of adjusting the morphology of carbonate crystals by addition of chemicals is well established and therefore a skilled person could, if desired, routinely seek to obtain carbonate crystals in a particular morphology by judicious choice of additional chemicals in the treatment fluid.

20 In general, use of treatment formulations that deposit consolidant at a relatively slow rate is preferred as this is more likely to result in effective consolidation. Effective consolidation may reduce the permeability of the formation to some extent but this is an acceptable trade-off if the treatment results in strengthening of the formation. It is noteworthy in the process of the present invention that deposition is very slow. Despite
25 rather low yields of consolidant compared to other systems, good consolidation is obtained.

Deposition of consolidant from the treatment fluid at too rapid a rate may result in the deposition of discrete carbonate particles in the treatment fluid, which could potentially
30 block pore throats and substantially reduce the permeability of the formation but without giving the same degree of strengthening obtained from a slower deposition at surfaces. It will be understood by those skilled in the art that the deposition of material

for blocking of pore throats or sealing off of the formation is potentially useful and capable of industrial application. Operation of the process in such a manner may therefore result in blocking of pore throats leading to sealing off of the formation to production or injection.

5

The deposition of mineral onto the sand grains or other internal surfaces of the underground formation increases the amount of cementing materials and will generally increase the unconfined compressive strength of the formation. Following consolidation of the formation, wells penetrating the formation may if desired be put on production or injection.

10

The deposited carbonate will normally have a low solubility in water so that during production or injection the consolidant is not dissolved by water leading to a reduction in the amount of consolidant and a reduction in the strength of the formation with time.

15

If dissolution of the consolidant occurs at a higher than desirable rate, as determined by laboratory or field determinations, re-consolidation of the formation using more treatment fluid may be required.

Normally, all substances used in the process of the present invention will be technical or agricultural feed grade to reduce the cost of the process.

20

Suitable concentrations of substances used in the process of the present invention will depend on the required amount of consolidant to be deposited in the formation. This will depend on the particular combination of substances chosen. Typical concentrations of component (I) include from 1 to 25% w/v measured in terms of the weight of a salt comprising the cations and in which form the cations have been supplied to the treatment fluid). Suitable such concentrations of component (I) include from 1 to 20% w/v and from 3 to 15% w/v, such as about 5% w/v or about 10% w/v. Typical concentrations of component (II) include from 1 to 25% w/v. Suitable such concentrations of component (II) include from 1 to 20% w/v and from 3 to 15% w/v, such as about 2% w/v or about 10% w/v. Typical concentrations of components (III)(a), (III)(b), (IV), (V), (VI) and (VII) range from about 0.2% w/v to 10% w/v.

25

30

The concentrations used will also depend on the solubility of the components in the treatment fluid. Consolidant yield will typically be of the order of 0.2 to 100 grams per litre of treatment fluid (preferably 1 to 50 grams per litre) although higher or lower concentrations may be appropriate in some situations.

Any nucleating materials or scaling modifiers regulators or inhibitors will be used at a suitable concentration to give the desired effect and suitable concentrations will be understood by those skilled in the art or may be readily determined by suitable laboratory evaluations.

Some mixing of reservoir fluids and treatment fluid will occur in the formation. Possible dilution of the concentration of the chemical species in the treatment is therefore expected to occur and the initial concentration of these chemical species may be increased to compensate for the expected dilution. However, in many cases the formation water or formation rock will contain appreciable concentrations of a chemical species that may be useful in the process of the present invention and this will also be taken into account by persons designing the treatments and skilled in the art. For example, there is frequently a high concentration of soluble calcium in many formation waters.

More than one type of (I) cations of a metal having an oxidation state of +2, and more than one source of (II) amino acid having at least one deprotonated carboxylic acid group (or substance capable of generating an amino acid having at least one deprotonated carboxylic acid group *in situ*), may be used in the treatment fluid, which may lead to the deposition of more than one type of carbonate mineral in the formation.

Similarly, more than one type of (I) cations of a metal having an oxidation state of +2, and more than one source of: (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; (V)

-32-

an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$; (VI) a beta oxocarboxylic acid ester; and (VII) an alkylene carbonate; may be used in the treatment fluid, which may lead to the deposition of more than one type of carbonate mineral in the formation.

5

The process of the present invention may be applied to any well drilled into an underground formation but is particularly intended for use in poorly consolidated formations. Types of well may include vertical, deviated, inclined or horizontal wells. The wells may be cased and perforated, openhole, or completed using any other type of completion.

10

The process of the present invention may, if desired, be used in conjunction with mechanical and/or other chemical methods of sand control such as will be known to those skilled in the art. The process may be used before, after or at the same time as the other methods of sand control as is appropriate for the particular case.

15

Where a formation is sensitive to, and may be damaged by introduced fluids this will generally be taken into account in formulating treatment fluids of the present invention. For example, where clay swelling is a problem, suitable inhibitors may be incorporated in the fluid to inhibit the swelling. These may include chelating agents or other chemicals such as $CaCl_2$ and $AlCl_3$. Such inhibitors may be incorporated into the treatment formulation, if compatible with the other components in the treatment formulation and still allowing consolidation to occur.

20

The process as generally operated involves the deposition of consolidant from an aqueous solution onto a water-wet surface. It may therefore be beneficial to treat the formation ahead of a treatment with any agents that are commonly used to remove hydrocarbons from the formation surfaces in the zone of the formation to be consolidated, leaving a water-wet surface. Agents that can achieve this include, but are not limited to, solvents, mutual solvents and surfactants including hydrocarbon micro emulsifying surfactants. Suitable agents may also be incorporated into the treatment fluid if compatible, for example where an emulsion or microemulsion

30

treatment fluid is used. The use of microemulsions may be particularly beneficial in cleaning and water wetting surfaces. Other additives that may be useful in the process of the present invention include viscosity modifying agents and fines suspenders but any other additives that are recognised as providing a benefit to the treatment by those skilled in the art may also be used. Such additives or chemicals may be introduced ahead of the treatment fluid, incorporated into the treatment fluid, or used after the treatment fluid as long as they are compatible with the consolidation process.

In a preferred aspect of the present invention, the treatment fluid further comprises one or more additional components, such as a water-wetting agent, a clay swelling inhibitor, a nucleating material or a delaying agent.

Consolidants that are particularly usefully deposited using the process of the present invention include carbonates of the type that are typically already present as cementing material in sandstone formations (for example calcium carbonate or calcium magnesium carbonate). Such minerals are low solubility and will dissolve from the formation at a negligible or acceptably low rate during injection or production operations.

In another embodiment of the present invention, an enzyme or any other catalyst capable of accelerating the deposition of the carbonate from the treatment fluid is also included in the treatment fluid. An advantage of incorporating an enzyme or other catalyst into the treatment fluid in this manner is that the process of the invention can be carried out without the need for an increase in temperature in the treatment fluid once it is in the underground formation. This embodiment of the invention is therefore particularly useful in applications where the underground formation is not at a significantly higher temperature than the ambient temperature outside the wellbore, and/or where it is inconvenient or otherwise undesirable to heat up the treatment fluid when it has been introduced into the formation. One specific application in which this embodiment of the invention may be useful is in grouting applications in tunnels conducted at ambient temperature.

In one preferred aspect of the present invention, the catalyst is a copper salt, for example a copper (II) salt, e.g. copper chloride dihydrate. In another preferred aspect of the present invention, the catalyst is an enzyme.

5 In a further embodiment, treatment fluids of the present invention may optionally contain an oxidising agent if its presence will increase the rate of deposition of carbonate. Suitable oxidizing agents may include but not be limited to, hydrogen peroxide, urea hydrogen peroxide, sodium perborate, sodium hypochlorite, sodium bromate, ozone or an organic peroxide such as tert-butyl hydroperoxide.

10

For example an alpha-oxocarboxylic acid can be produced *in situ* via the oxidation of an alpha-hydroxy carboxylic acid i.e. oxidation of glycolic acid to glyoxylic acid and oxidation of lactic acid to pyruvic acid. Oxidation can be achieved either with a suitable oxidising agent or an oxidase enzyme.

15

In a further aspect of the invention as described above, the treatment fluid may optionally be used as a drilling fluid (or drilling mud or drill-in fluid) that can achieve consolidation during or following drilling. In such an embodiment it is necessary that the treatment fluid will also fulfil the requirements of a drilling fluid.

20

Required functions of a drilling fluid include: control of formation pressure; lubrication of the drill string; cooling of the drill bit; suspension of solids under static and dynamic conditions and the removal of drilled cuttings from the hole. The term drilling should be taken to include under-reaming and similar operations.

25

In this further embodiment of the present invention components (i) and (ii) of the treatment fluid will enter the formation during drilling as part of the fluid spurt loss that occurs as a filter cake is deposited on the inside of the wellbore. A drilling fluid is normally formulated to minimise the loss of fluid to the formation, by incorporating
30 particulate materials into the fluid which, in combination with fines generated during the drilling process and viscosifying polymers (if present) contribute to the build up of a

filter cake. Fluid spurt loss is the loss of fluid to the formation that takes place as the filter cake builds up.

5 However, in the case of the present invention it is generally advantageous to formulate the treatment fluid used as a drilling fluid to give a larger spurt loss than is normally obtained and therefore to obtain consolidation around the wellbore to a greater depth than would otherwise be the case. Accordingly, it will generally be desirable not to incorporate particulate materials into treatment fluids used as drilling fluids in the present invention, or alternatively to use only low concentrations of particulate
10 materials or particles of such a size that a larger spurt loss occurs than is generally the case for standard drilling fluids.

High loadings of particulate materials are intended to reduce the spurt loss and low or zero loadings will increase the spurt loss. Filtrate is estimated to penetrate into the
15 formation to depths of 30 to 60 cm even in the case of normally formulated drilling muds, although the penetration of particulates is generally much less than this. With drilling fluids formulated to give high spurt losses deeper penetration will generally occur. After deposition of the filter cake, some further fluid loss to the formation may occur, but this is likely to be limited.

20 The treatment fluid used as a drilling fluid will be prepared at the surface, generally in the mud pits, by any method which would be known to those skilled in the art. If the rate of carbonate deposition is slow enough components (I) and (II), (III), (IV), (V), (VI) or (VII) may be incorporated directly into the treatment fluid used as a drilling
25 fluid. Alternatively if the rate of deposition of carbonate mineral is fast enough to result in unacceptable levels of the consolidating material being deposited in the bulk drilling fluid, one or more of these substances may be introduced and mixed into the drilling fluid lower down the drilling assembly, so that more of the consolidating material is produced in the formation after spurt loss has taken place. Introduction and mixing into
30 the drilling fluid lower down the drilling assembly may be achieved by any method that is known to those skilled in the art. It may also be preferable in this embodiment to make use of a component that is generated *in-situ* in the treatment fluid from another

substance (e.g., use as component (II) of a substance capable of generating an amino acid having at least one deprotonated carboxylic acid group *in situ*) and/or a treatment fluid which only becomes alkaline *in situ*, since these will also generally delay the onset of consolidation.

5

During drilling, using treatment fluids formulated as drilling fluids according to the process of the present invention, it will generally be desirable to monitor the composition of the treatment fluid to measure the concentrations of the chemical substance(s) (I)-(VII) (e.g., (I) and (II)) and any nucleation material(s) or delaying substances incorporated into the treatment fluid. After formulating a treatment fluid as a drilling fluid and during drilling, some consolidant may be deposited within the drilling fluid. Any solid materials produced within the bulk treatment fluid during drilling will remain as part of the drilling fluid or be deposited as part of the filter cake. Deposition of consolidant in the treatment fluid will reduce the concentration of those consolidant forming chemicals within the bulk treatment fluid and therefore their concentration in the fluid spurt loss. The monitoring of individual chemicals in the bulk treatment fluid will indicate what chemicals might need to have their concentration increased (or where the pH is important in achieving consolidation what pH adjustment may be needed) in order to maintain the effectiveness of the treatment fluid that will deposit the required amount of consolidant in the formation. Methods of monitoring and replacement of chemicals consumed in the reaction will be such methods as are generally well known to those skilled in the art.

For the avoidance of doubt, it is emphasised that the treatment fluid of the present invention is as defined in relation to the process of the present invention. Therefore preferred features of the treatment fluids as referred to in relation to the process of the present invention (e.g., in relation to the identity of components (I)-(VII), the alkaline characteristics of the fluid, the solvent(s) and also optional components of the fluid) apply equally to the treatment fluids of the present invention. Furthermore, typically in the use of the present invention, the treatment fluid is as described in respect of the process of the present invention. Therefore preferred features of the treatment fluid as

30

-37-

referred to in relation to the process of the present invention apply equally to the treatment fluid in the use of the present invention.

The skilled person would appreciate that the process for consolidating an underground
5 formation of the present invention can also be applied in other applications where
deposition of carbonate material from a fluid may be desirable. For example, coating or
impregnating objects such as building stonework and statues with carbonate material
may sometimes be desirable for preservation and/or strengthening purposes. The
present invention therefore extends to a process for depositing carbonate material from
10 a fluid. Typically the deposition occurs onto a surface that is in contact with the
treatment fluid. For example, an object having the surface to be modified may be
submerged in the treatment fluid. The treatment fluid itself is as defined in the context
of the process for consolidating an underground formation. The deposition process also
proceeds in a directly analogous manner to that in the process for consolidating an
15 underground formation.

The present invention has the numerous advantages. It provides novel processes based
on generally cheap, readily available components that are easy to store, transport and
mix and are generally low hazard, low toxicity and environmentally acceptable. The
20 processes are easy to apply and may be applied to new wells or to wells that have
already been produced in order to strengthen the formation or frac packs, gravel packs,
propped fractures or the like and reduce or prevent sand or fines production.

The processes may also be used for remedial treatments of previously consolidated
25 gravel or proppant packs where consolidation was incomplete or has failed. In some
embodiments the process can be used to strengthen the formation during or following
drilling, through use of the treatment fluid as a drilling fluid. The process may be
readily applied to long formation intervals. The processes may be used in cased and
perforated or openhole wells. The process can achieve effective consolidation while
30 retaining useful levels of permeability.

In other embodiments the invention may be used to substantially reduce the permeability, even to the point of shutting off production or injection. The process may also be used for other underground applications such as grouting of tunnels. Other applications that will be apparent to those skilled in the art include; ground

5 consolidation in areas of poor soil consolidation; strengthening of embankments, dykes, dams or artificial islands; consolidating shore lines or cliff faces for combatting coastal erosion; strengthening of, and/or filling cracks in, brickwork, plaster, building foundations, concrete or road surfaces; setting of foundry moulds; sealing fractures in pipelines; restoring and/or conserving stone monuments, art, statuary or objects;

10 increasing the speed at which concrete, grout and/or plaster sets; or incorporating carbonate mineral into composite materials. Other potential applications include depositing a protective layer of CaCO_3 on to clay or shale surfaces to act as a clay or shale swelling inhibitors or the deposition of protective surfaces on internal pipe work.

15 Another advantage of the present invention is that the carbonate consolidants may be readily removed by simple acidizing if required (either partly or wholly) if for example permeability reduction is more than considered desirable. This is in marked contrast to the situation where resins have been used for consolidation as they are generally very difficult to remove.

20

The invention is further illustrated in the following examples. Examples 1 to 12 relate to processes based on (I) and (II). Tables 1 and 2 relates to processes based on (I) and (II), (III), (IV), (V), (VI) or (VII).

25 **Example 1. Deposition of calcium carbonate.**

A treatment fluid comprising deionised water containing 10% w/v sodium glycinate (glycine sodium salt hydrate) and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. The initial pH, measured at room temperature was 10.54. On heating to 60 °C, a white precipitate was slowly deposited

30 on the internal surface of the glass tube (that part of the tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid

to the white precipitate resulted in evolution of gas. The same treatment fluid maintained at ambient temperature (approximately 20 °C) also deposited calcium carbonate but at a much slower rate (at least 10 days).

5 **Example 2. Deposition of calcium carbonate.**

A treatment fluid comprising deionised water containing 10% w/v L-histidine with a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 60 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the
10 tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

Example 3. Deposition of calcium carbonate.

15 A treatment fluid comprising deionised water containing 10% w/v β-alanine with a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 60 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the
20 tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

Example 4. Deposition of calcium carbonate.

25 A treatment fluid comprising deionised water containing 10% w/v L-alanine with a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 60 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the
tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition
30 of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

Example 5. Deposition of calcium carbonate.

A treatment fluid comprising deionised water containing 10% w/v DL-serine with a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 60 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

10

Example 6. Deposition of calcium carbonate.

A treatment fluid comprising deionised water containing 10% w/v L-glutamic acid with a stoichiometric amount of sodium hydroxide (2 equivalents) and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 60 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the tube in contact with the treatment fluid) over a period of 3 days. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

20

Example 7. Deposition of calcium carbonate.

A treatment fluid comprising deionised water containing 10% w/v L-aspartic acid with a stoichiometric amount of sodium hydroxide (2 equivalents) and 10% w/v calcium chloride dihydrate was prepared and placed in stoppered pyrex boiling tubes. On heating to 80 °C, a white precipitate was slowly deposited on the internal surface of the glass tube (that part of the tube in contact with the treatment fluid) over a period of 100 hours. The precipitate was collected, washed and identified as calcium carbonate using FT-IR analysis. Addition of 4M hydrochloric acid to the white precipitate resulted in evolution of gas.

30

Example 8. Consolidation of glass beads

An uncoloured, clear and transparent treatment fluid comprising deionised water containing 10% w/v sodium glycinate (glycine sodium salt hydrate) and 10% w/v calcium chloride dihydrate was prepared and introduced into an Ofite double ended HPHT cell assembly (Cat No. 170-46) containing a ceramic disc (2.5 x 0.25", 10 micron, 2 Darcy permeability) and 60 ml bed volume of glass beads of diameter 200 to 300 micron so that the beads were submerged in approximately 90 ml of the treatment fluid. The initial pH, measured at room temperature was 10.54. The beads and treatment fluid were stirred to remove any air bubbles. Before adding the beads and treatment fluid the inside of an Ofite HPHT cell was lined with a thin coating of silicon grease, then a thin sheet of PTFE, to prevent the glass beads sticking to the stainless steel internal surface of the cell and allow recovery of any consolidated material. The top was placed on the HPHT cell. The bottom valve, initially closed, was opened to allow 20 ml of treatment fluid to pass through the bottom valve dropwise. The top and bottom valves were both closed and the HPHT cell heated to 60 °C. After 11 days, both valves on the HPHT cell were opened and clear, spent treatment fluid freely drained from the cell, indicating that permeability was retained within both the beads and the ceramic disc. Both ends were removed. The ceramic disc was also removed. The bed of glass beads was found to have been effectively consolidated. The consolidated beads were removed from the HPHT cell as a single large cylindrical block using a plunger comprised of a steel tube and a plastic disc. Addition of 4M hydrochloric acid to the consolidated beads resulted in evolution of gas and the beads fell apart.

Example 9. Consolidation of glass beads

An uncoloured, clear and transparent treatment fluid comprising deionised water containing 10% w/v glycine plus a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and introduced into an Ofite double ended HPHT cell assembly (Cat No. 170-46) containing a ceramic disc (2.5 x 0.25", 10 micron, 2 Darcy permeability) and 60 ml bed volume of glass beads of diameter 200 to 300 micron so that the beads were submerged in approximately 90 ml of the treatment fluid. The beads and treatment fluid were stirred to remove any air bubbles. Before adding the beads and treatment fluid the inside of an Ofite HPHT cell was lined with a

-42-

thin coating of silicon grease, then a thin sheet of PTFE, to prevent the glass beads sticking to the stainless steel internal surface of the cell and allow recovery of any consolidated material. The top was placed on the HPHT cell. The bottom valve, initially closed, was opened to allow 20 ml of treatment fluid to pass through the bottom valve. The top and bottom valves were both closed and the HPHT cell heated to 60 °C. After 14 days, both valves on the HPHT cell were opened and clear, spent treatment fluid freely drained from the cell, indicating that permeability was retained within both the beads and the ceramic disc. Both ends were removed. The ceramic disc was also removed. The bed of glass beads was found to have been effectively consolidated. The consolidated beads were removed from the HPHT cell as a single large cylindrical block using a plunger comprised of a steel tube and a plastic disc. Addition of 4M hydrochloric acid to the consolidated beads resulted in evolution of gas and the beads fell apart.

15 **Example 10. Consolidation of glass beads**

An uncoloured, clear and transparent treatment fluid comprising deionised water containing 5% w/v glycine plus a stoichiometric amount of sodium hydroxide and 10% w/v calcium chloride dihydrate was prepared and introduced into an Ofite double ended HPHT cell assembly (Cat No. 170-46) containing a ceramic disc (2.5 x 0.25", 10 micron, 2 Darcy permeability) and 60 ml bed volume of glass beads of diameter 200 to 300 micron so that the beads were submerged in approximately 90 ml of the treatment fluid. The initial pH, measured at room temperature was 10.54. The beads and treatment fluid were stirred to remove any air bubbles. Before adding the beads and treatment fluid the inside of an Ofite HPHT cell was lined with a thin coating of silicon grease, then a thin sheet of PTFE, to prevent the glass beads sticking to the stainless steel internal surface of the cell and allow recovery of any consolidated material. The top was placed on the HPHT cell. The bottom valve, initially closed, was opened to allow 20 ml of treatment fluid to pass through the bottom valve. The top and bottom valves were both closed and the HPHT cell heated to 60 °C. After 14 days, both valves on the HPHT cell were opened and clear, spent treatment fluid freely drained from the cell, indicating that permeability was retained within both the beads and the ceramic disc. Both ends were removed. The ceramic disc was also removed. The bed of glass

beads was found to have been effectively consolidated. The consolidated beads were removed from the HPHT cell as a single large cylindrical block using a plunger comprised of a steel tube and a plastic disc. Addition of 4M hydrochloric acid to the consolidated beads resulted in evolution of gas and the beads fell apart.

5

Example 11 . Yield of consolidant

The dry weight yield of consolidant was estimated using large stoppered pyrex boiling tubes containing reaction mixtures incubated at either 60° C or 80° C for up to 528 hours (22 days). The yield at 528 hours was as follows.

10

Formulation	Temp ° C	Yield g/l at 528 hours
5% w/v CaCl ₂ .2H ₂ O + 5% w/v Glycine sodium salt hydrate	60	1.75
5% w/v CaCl ₂ .2H ₂ O + 5% w/v Glycine sodium salt hydrate	80	3.65
5% w/v CaCl ₂ .2H ₂ O + 10% w/v Glycine sodium salt hydrate	60	2.6
5% w/v CaCl ₂ .2H ₂ O + 10% w/v Glycine sodium salt hydrate	80	4.5

It should be noted that at the point the experiment was terminated (528 hours), increases in yield were still being observed i.e. the reaction had not gone to completion.

15 **Example 12.** Effect of copper chloride on yield of consolidant

The effect of including copper (II)chloride (CuCl₂) at 51.5 mM in a 5% w/v CaCl₂.2H₂O + 10% w/v Glycine sodium salt hydrate formulation was investigated. The yield after 66 hours at 60° C was 4.10 g against 1.55 g in a control without copper.

20 The above examples are for illustration only and are not for the purpose of limiting the scope of the present invention. It will be understood by those skilled in the art that other salts, other concentrations, other shut-in periods and other temperatures may also result in useful levels of consolidation.

Table 1. Summary of reagent combinations observed to result in calcium carbonate deposition.

Reagent 1	Reagent 2
3-Aminobutyric acid	N/A
2-Amino-2-(hydroxymethyl)-1,3-propanediol	GLYX, EAA, MAA
2-Oxobutyric acid	N/A
Acetone oxime	GLYX
Ammonia	GLYX
Beta alanine	N/A, GLYX, EAA, MAA
Bis(2-hydroxypropyl)amine	GLYX, EAA
Creatine monohydrate	EAA
Diethanolamine	GLYX
Diethylenetriamine	GLYX, EAA
Diglycine	N/A
DL-Methionine	N/A
DL-Serine	N/A, EAA, MCPTL
DL-Valine	N/A, EAA, MCPTL
Ethanolamine	N/A, GLYX, EAA*, MAA*, PC*
Formamidine acetate	GLYX, EAA
Gamma aminobutyric acid	N/A
Glycine	N/A, PYRV, GLYX, 4-HBA, PDA, MAA*, EAA*, SDIA, GL, FR, RB, ML, DX, MCPTL, HA, 1,3-DHAD, PC*, EC*, BC*, GC*, HP, UHP, PYRVLD, IVALD
Glycine anhydride	N/A
Guanidine hydrochloride	GLYX
Iminodiacetic acid	N/A, GLYX, SDIA, PC, EAA
L-Alanine	N/A, EAA, GLYX
L-Arginine	N/A, GLYX, EAA, MCPTL

L-Aspartic acid	N/A
L-Glutamic acid	N/A, GLYX, EAA
L-Histidine	N/A
L-Lysine	N/A, GLYX, MCPTL, EAA
L-Threonine	N/A, GLYX
N-methyl ethano lamine	EAA, MAA, GL, FR
Polyethyleneimine	GC, GLYX, MCPTL, GL, SDIA, EAA, MAA
Polyethyleneimine acetic acid sodium salt	GLYX
Potassium formate	EAA, MAA
Pyruvic acid	N/A
Sarcosine	N/A, GLYX, PC, EAA, MAA, MCPTL, SDIA
Sodium acetate	GC, PC, EAA, MAA
Taurine	N/A, GLYOX, EAA
Triglycine	N/A
Urea	GLYX, GC, EAA, MAA, N/A

The above table shows reagent combinations observed to result in calcium carbonate deposition. All reactions were performed in the presence of enough NaOH to fully deprotonate the reagents. All mixtures contained 5% w/v $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and were heated at 60°C in closed vessels. Observations were made over periods of up to 14 days. The concentrations of Reagent 1 and Reagent 2 used in the experiments reported in Table 1 were in the range of 0.2% w/v to 10% w/v. When any of the chemicals listed under reagent 2 are marked with an asterisk * it means that the reaction was also observed to precipitate CaCO_3 at room temperature.

10

Whenever N/A is listed under reagent 2, it means that using reagent 1 without a second reagent was observed to result in the deposition of calcium carbonate.

List of reagent 2 abbreviations for Table 1:

Abbreviation	Chemical name
1,3-DHAD	1,3-Dihydroxyacetone dimer
4-HBA	4-Hydroxybenzaldehyde
BC	Butylene carbonate
DX	Dextrin
EAA	Ethylacetoacetate
EC	Ethylene carbonate
FR	D-(-)-Fructose
GC	Glycerine carbonate
GL	D-(+)-Glucose
GLYX	Glyoxylic acid
HA	Hydroxyacetone
HP	Hydrogen peroxide
IVALD	Isovaleraldehyde
MAA	Methylacetoacetate
MCPTL	Methyl cyclopentenolone
ML	D-(+)-Maltose
PC	Propylene carbonate
PDA	Phthaldialdehyde
PYRV	Pyruvic acid
PYRVLD	Pyruvaldehyde
RB	D-(-)-Ribose
SDIA	Sodium D-Isoascorbate
UHP	Urea hydrogen peroxide

Table 2 below provides a summary of selected reactions shown to deposit calcium carbonate. The table in particular provides a qualitative assessment of rate and extent of carbonate deposition and scaling and the ability of the scale to consolidate glass beads and sand. All reactions in Table 2 were performed in the presence of 5g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

-47-

and made up to a total of 100ml in deionised water. All reactions were subsequently heated in closed vessels at 60°C for up to 14 days.

Table 2

No	Generic reaction type	Specific example	Formulation used	A	B	C	D	E
1	Amino acid	Glycine	10g Glycine + 71.6ml 2M NaOH sol.	1	1	2	4-5	3-4
2	Amino acid	Lysine	10g L-Lysine monohydrochloride + 57.49ml 2M NaOH sol.	1	1	2	5	4
3	Amino acid	Glutamic acid	10g L-Glutamic acid + 71.37ml 2M NaOH sol.	1	1	2	4-5	3-4
4	N-Alkylamino acid	Sarcosine	10g Sarcosine + 60.33ml 2M NaOH sol.	1	1	2	4-5	3-4
5	Aminoalkyl sulphonic acid	Taurine	10g Taurine + 42.95ml 2M NaOH sol.	1	1	2	4-5	n/a
6	Amino acid + Copper salt	Glycine + Copper chloride dihydrate	10g Glycine + 71.6ml 2M NaOH sol. + 0.17g CuCl ₂ .2H ₂ O	2	2	2	n/a	n/a
7	Secondary alkyl amine + alpha oxocarboxylic acid	Diethanolamine + Glyoxylic acid	6g Diethanolamine hydrochloride + 4.48ml Glyoxylic acid 50% wt. sol. + 41.44ml 2M NaOH sol.	2	3	4	n/a	2
8	Amino acid + alpha diketone	Glycine + Methyl cyclopentenolone	2g Glycine + 14.32ml 2M NaOH sol. + 2g Methyl cyclopentenolone	2	3	3	1	n/a
9	Ammonia precursor + alpha oxocarboxylic acid	Urea + Glyoxylic acid	2g Urea + 2.99ml Glyoxylic acid 50% wt. sol. + 13.51ml 2M NaOH sol.	2	3	3	1	n/a
10	Primary alkyl amine + alpha oxocarboxylic acid	Monoethanolamine + Glyoxylic acid	6g Monoethanolamine hydrochloride + 4.48ml Glyoxylic acid 50% wt. sol. + 51.01ml 2M NaOH sol.	2-3	3	4	2	2-3
11	N-Alkyl amino acid + alpha oxocarboxylic acid	Sarcosine + Glyoxylic acid	4g Sarcosine + 2.99ml Glyoxylic acid 50% wt. sol. + 37.64ml 2M NaOH sol.	2-3	3	4	3-4	2
12	Beta amino acid + alpha oxocarboxylic acid	Beta-alanine + Glyoxylic acid	2g Beta-alanine + 2.99ml Glyoxylic acid 50% wt. sol. + 24.73ml 2M NaOH sol.	2-3	3	4	2	n/a

13	Amino acid + Beta oxocarboxylic acid ester	Glycine + Ethylacetoacetate	2g Glycine + 14.32ml 2M NaOH sol. + 1.94ml Ethyl acetoacetate	2-3	3	5	2	n/a
14	Alpha ketocarboxylic acid	Pyruvic acid	7.89ml Pyruvic acid + 56.78ml 2M NaOH sol.	2-3	5	3	n/a	n/a
15	Aminoacid + Hemiacetal	Glycine + Glucose	2g Glycine + 14.32ml 2M NaOH sol. + 2g D-(+)-Glucose	2-3	3	3	2	n/a
16	Amino acid + aldehyde	Glycine + 4-Hydroxybenzaldehyde	2g Glycine + 14.32ml 2M NaOH sol. + 2g 4-Hydroxybenzaldehyde	2-3	3	3	n/a	n/a
17	Amino acid + Isoascorbate	Glycine + Sodium D-isoascorbate	2g Glycine + 14.32ml 2M NaOH sol. + 2g Sodium D-isoascorbate	3	3	3	2	n/a
18	Primary alkyl amine + Beta oxocarboxylic acid ester	Ethanolamine + Ethylacetoacetate	2g Monoethanolamine hydrochloride + 10.25ml 2M NaOH sol. + 1.94ml Ethylacetoacetate	3-4	3	1	n/a	n/a
19	Aminoacid + alpha oxocarboxylic acid	Glycine + Glyoxylic acid	2g Glycine + 2.99ml Glyoxylic acid 50% wt. sol. + 27.82ml 2M NaOH sol.	3-4	4	3	2	n/a
20	Amino acid + Oxidising agent	Glycine + Hydrogen peroxide	2g Glycine + 14.32ml 2M NaOH sol. + 1.77ml H ₂ O ₂ 35% wt. sol.	3-4	5	1	1	n/a
21	N-Alkyl amino acid + Alkylene carbonate	Sarcosine + Propylene carbonate	4g Sarcosine + 14.32ml 2M NaOH sol. + 1.6ml Propylene carbonate	3-4	4	2	n/a	2
22	Primary alkyl amine + Alkylene carbonate	Ethanolamine + Propylene carbonate	2g Monoethanolamine hydrochloride + 10.25ml 2M NaOH sol. + 1.6ml Propylene carbonate	4	4	1	n/a	n/a
23	Amino acid + Alkylene carbonate	Glycine + Propylene carbonate	2g Glycine + 14.32ml 2M NaOH sol. + 1.6ml Propylene carbonate	5	5	1	n/a	n/a

Key to Table 2:

n/a = Observation has not been made

	Criterion scored	Range of score lowest to highest	
Column A	Relative rate of CaCO ₃ precipitation	1 = Slowest relative rate of CaCO ₃ precipitation	5 = Fastest relative rate of CaCO ₃ precipitation
Column B	Relative yield of CaCO ₃ precipitate	1 = Lowest relative yield of CaCO ₃	5 = Highest relative yield of CaCO ₃
Column C	Relative ability to create a layer of CaCO ₃ scale on various surfaces including glass and plastic (based on the consistency and thickness of the scale.)	1 = Worst relative scaling ability	5 = Best relative scaling ability
Column D	Relative ability to consolidate 200-300µm diameter spherical glass beads (based on the relative unconfined compressive strength of the resultant consolidated mass.)	1 = Worst relative degree of consolidation	5 = Best relative degree of consolidation
Column E	Relative ability to consolidate various types of natural and artificial sand (based on the relative unconfined compressive strength of the resultant consolidated mass.)	1 = Worst relative degree of consolidation	5 = Best relative degree of consolidation

5

It will be understood by those skilled in the art that the examples given in Table 1 and Table 2 do not limit the scope of the present invention. There are many other potential combinations of chemicals as defined by the claims. While all of the examples are

known to be able to deposit a carbonate mineral (in these examples, calcium carbonate) as shown in Table 2 there is generally an inverse relationship between the rate of deposition and the quality of the consolidation obtained i.e. the best consolidation may be achieved by systems that scale relatively slowly and deposit relatively low quantities
5 of carbonate mineral.

In Table 2 examples 1-5 gave good consolidation over a 2 week period at 60°C whereas example 23 deposited significant amounts of carbonate within a 10 minute period at room temperature (22°C). At 60°C examples 1-5 are suited to consolidation. Examples
10 18-23 may be more suitable for shut-off applications.

It will be understood by those skilled in the art that these examples indicate the situation prevailing at the test temperature of 60°C. The results obtained at other temperatures or (for example) using different concentrations of reagents may differ. Factors that
15 influence the rate of deposition of carbonate, quantity of carbonate deposited, quality of scaling of surfaces and extent of consolidation of glass beads and sand may include the concentration of individual reagents, the ratio between the reagents, the type of base used to deprotonate the acidic reagents, the type of metal (e.g. calcium) salt, temperature, treatment period, type of substrate being treated and the presence of any
20 additional components such as surfactants, solvents, mutual solvents etc.

It will also be understood by those skilled in the art that the amount of each reagent used and the ratio between reagents in each of the reactions mentioned in the above table do not necessarily represent the optimum formulation to achieve the best possible degree of
25 consolidation or scaling, the highest rate of precipitation or the greatest yield of precipitate. The examples are indicative of preferred reagent combinations which have been observed to precipitate CaCO_3 at a range of different rates. Other criteria for selecting preferred reagents include price, availability, stability, toxicity and storage, transport and handling requirements. Most of the relatively slow carbonate depositing
30 systems exhibit a delay before deposition begins, which is advantageous when placing the treatment fluids of the present invention into an underground formation.

CLAIMS

1. A process for consolidating an underground formation, which process comprises:
 - 5 (a) introducing a treatment fluid into an underground formation, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid:
 - (II) an amino acid having at least one deprotonated carboxylic acid group;
 - 10 (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{O}^-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester;
 - (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group;
 - 15 (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{O}^-$;
 - (VI) a beta oxocarboxylic acid ester; and
 - (VII) an alkylene carbonate;
 - 20 (b) allowing carbonate mineral to be deposited from the fluid, thereby consolidating the underground formation.
2. A process according to Claim 1 wherein at least one of the components (II),
25 (III)(a), (III)(b)(i), (IV) or (V) is present and is generated *in-situ* in the treatment fluid from another substance.
3. A process according to claim 1 or 2, wherein said cations of a metal having an oxidation state of +2 or higher are group II metal or transition metal cations.
- 30 4. A process according to claim 1 or 2, wherein said cations of a metal having an oxidation state of +2 or higher are selected from magnesium, calcium, strontium,

-52-

barium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminium, silver and zirconium cations.

5. A process according to any of the preceding claims, wherein said cations of a metal are provided in the form of a chloride, bromide, nitrate, propionate, lactate, acetate or formate salt.
6. A process according to any of the preceding claims, wherein at least one of the components (II), (III)(b)(i), (IV) or (V) is present and is prepared by deprotonating the corresponding protonated form of the component with at least a stoichiometric equivalent of base.
7. A process according to claim 6, wherein said base is sodium or potassium hydroxide.
8. A process according to any one of the preceding claims, wherein in (II) said amino acid having at least one deprotonated carboxylic acid group does not contain a terminal amide group.
9. A process according to any one of the preceding claims, wherein in (II) said amino acid having at least one deprotonated carboxylic acid group is a deprotonated form of glycine, histidine, B-alanine, alanine, serine, glutamic acid, aspartic acid, threonine, sarcosine, lysine, methionine, arginine, valine, iminodiacetic acid, 3-aminobutanoic acid or gamma aminobutyric acid, and preferably is a deprotonated form of glycine, glutamic acid, sarcosine or lysine.
10. A process according to claim 1, wherein said treatment fluid comprises (I) calcium chloride and (II) glycine, glutamic acid, sarcosine or lysine.
11. A process according to any one of the preceding claims, wherein the component (II) is generated *in-situ* in the treatment fluid from another substance selected from di-, tri-, tetra-, oligo- or poly-peptides, including diglycine, triglycine,

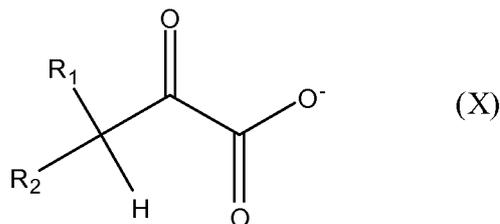
tetraglycine and polyglycine, polyaspartic acid, cyclic dipeptides, cyclic oligo peptides, esters of amino acids, amides of amino acids and proteins.

12. A process according to any of the preceding claims wherein said treatment fluid
5 comprises at least the components (I) and (II) and additionally comprises a carbonyl compound that is soluble in the treatment fluid.
13. A process according to claim 12, wherein said carbonyl compound is selected
10 from a $C_{i-2}O$ aldehyde, a $C_{i-2}O$ alpha carbonyl ketone, a $C_{i-2}O$ alpha hydroxy ketone, an alpha oxocarboxylic acid, a beta oxocarboxylic acid ester, an alkylene carbonate and a D-isoascorbate salt.
14. A process according to claim 12, wherein said carbonyl compound is selected
15 from glyoxylic acid monohydrate, glyoxylic acid 50% wt. aqueous solution, pyruvic acid, 2-ketobutyric acid, 4-hydroxybenzaldehyde, phthaldialdehyde, methyl cyclopentenolone, methyl acetoacetate, ethyl acetoacetate, ethylene carbonate, propylene carbonate, butylene carbonate, glycerine carbonate, sodium D-isoascorbate monohydrate, pyruvaldehyde, 2,2-dimethoxyacetaldehyde and hydroxyacetone.
20
15. A process according to any of the preceding claims wherein said treatment fluid
comprises at least the components (I) and (II) and additionally comprises at least one of (i) a hemiacetal or (ii) a hemiketal.
- 25 16. A process according to claim 15, wherein the hemiacetal or hemiketal is 1,3-dihydroxyacetone dimer or a reducing sugar comprising a monosaccharide, disaccharide, oligosaccharide or polysaccharide.
17. A process according to claim 16, wherein the monosaccharide, disaccharide or
30 oligosaccharide is selected from glucose, fructose, galactose, xylose, ribose, arabinose, lyxose, allose, altrose, mannose, gulose, talose, lactulose, lactose, maltose, cellobiose or dextrin, and preferably wherein the

monosaccharide, disaccharide or oligosaccharide is glucose, fructose, dextrin or maltose.

18. A process according to any one of the preceding claims, wherein in (III) the
5 amine is a primary or secondary amine that does not contain any terminal amide functional groups.
19. A process according to claim 18, wherein the primary or secondary amine is selected from monoethanolamine (MEA), diethanolamine (DEA)
10 diethylenetriamine (DETA), triethylenetetramine (TETA), N-methylethanolamine, 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris), bis(2-hydroxypropyl)amine, 2-amino-2-methyl-1,3-propanediol and polyethyleneimine (PEI).
- 15 20. A process according to any one of the preceding claims, wherein in (III) the amine is provided in the form of a salt, which salt releases the amine under alkaline conditions.
21. A process according to claim 20, wherein said salt is ethanolamine
20 hydrochloride, Tris-hydrochloride or diethanolamine hydrochloride.
22. A process according to any one of the preceding claims, wherein in (IV) said amino alkyl sulphonic acid having at least one deprotonated sulphonic acid
25 group is a deprotonated form of 2-amino ethane sulphonic acid.
23. A process according to any one of the preceding claims, wherein said treatment fluid comprises at least the components (I) and (IV) and additionally comprises a carbonyl compound that is soluble in the treatment fluid.
- 30 24. A process according to claim 23, wherein said carbonyl compound is selected from an alpha oxocarboxylic acid, a beta oxocarboxylic acid ester or an alkylene carbonate.

25. A process according to claim 23 wherein said carbonyl compound is selected from glyoxylic acid monohydrate, glyoxylic acid 50% wt. aqueous solution, pyruvic acid, 2-ketobutyric acid, methyl acetoacetate, ethyl acetoacetate, ethylene carbonate, propylene carbonate, butylene carbonate and glycerine carbonate.
- 5
26. A process according to any one of the preceding claims, wherein the, or each, alpha oxocarboxylic acid present in the treatment fluid is selected from glyoxylic acid, pyruvic acid and 2-ketobutyric acid.
- 10
27. A process according to any one of the preceding claims wherein in (V) the alpha ketocarboxylic acid has the formula (X)



- 15 wherein R_1 and R_2 are independently selected from hydrogen, C_{1-6} alkyl, a hydrocarbyl ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10-membered heteroaryl ring and a 5- to 10-membered heterocyclyl ring, or wherein R_1 and R_2 , together with the carbon atom to which they are mutually attached, form a hydrocarbyl ring containing 3 to 6 carbon atoms, a C_{6-10} aryl ring, a 5- to 10-membered heteroaryl ring or a 5- to 10-membered heterocyclyl ring.
- 20
28. A process according to claim 27, wherein the alpha ketocarboxylic acid is selected from pyruvic acid and 2-ketobutyric acid.
- 25
29. A process according to any of the preceding claims, wherein (i) consolidation proceeds at the prevailing temperature of the underground formation or (ii) the

process comprises supplying heat to the underground formation, thereby accelerating the rate of deposition of carbonate material.

- 5 30. A process according to any of one the preceding claims, which comprises introducing a water wetting agent into the underground formation prior to or at the same time as introducing the treatment fluid into the underground formation, and wherein said water wetting agent is preferably a surfactant such as a microemulsifying surfactant, a solvent or a mutual solvent.
- 10 31. A process according to any of the preceding claims, wherein: the strength of the formation is increased by the deposition of said carbonate material; and/or the permeability of the underground formation is reduced by the deposition of said carbonate material, and/or rock particles, sand, gravel or proppant are consolidated by the deposition of said carbonate material.
- 15 32. A process according to any of the preceding claims, which comprises substantially sealing off the underground formation to production or injection.
- 20 33. A process according to any of the preceding claims, which comprises a remedial treatment of resin-coated gravel or resin-coated proppant.
- 25 34. A process according to any of the preceding claims, wherein the treatment is carried out on (a) a new well or (b) a well that has already been produced or injected.
- 30 35. A process according to any of the preceding claims, which comprises the grouting of tunnels.
36. A process according to any of the preceding claims, wherein the treatment fluid further comprises a catalyst for increasing the rate of deposition of the carbonate mineral.

37. A process according to claim 36, wherein the catalyst is a copper salt or an enzyme.
38. A process according to any of the preceding claims, wherein the treatment fluid
5 further comprises an oxidising agent for increasing the rate of deposition of the carbonate mineral.
39. A process according to claim 1, which process is for consolidating an
10 underground formation during or following drilling and which process comprises:
- drilling a well with the treatment fluid after said step of introducing the treatment fluid into the underground formation, and such that at least a portion of the treatment fluid enters the formation; and
 - allowing carbonate mineral to be deposited, thereby consolidating the
15 underground formation, during or following said drilling.
40. A process according to any of the preceding claims, wherein a viscosity modifier, a fines suspender, a clay swelling inhibitor or a nucleating material is introduced into the formation ahead of or in conjunction *with* the treatment fluid.
20
41. A process according to any of the preceding claims, wherein a delaying agent is introduced into the formation ahead of or in conjunction with the treatment fluid, and wherein the delaying agent is preferably a scale inhibitor.
- 25 42. Use of a treatment fluid for consolidating an underground formation with a consolidating material, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid:
- (II) an amino acid having at least one deprotonated carboxylic acid group;
 - 30 (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula

-58-

-C(=O)-C(=O)-O⁻, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester;

(IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group;

5 (V) an alpha ketocarboxylic acid that contains a functional group of the formula -C(=O)-C(=O)-O⁻;

(VI) a beta oxocarboxylic acid ester; and

(VII) an alkylene carbonate;

and which treatment fluid is alkaline or is capable of becoming alkaline *in situ*.

10

43. A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid:

(II) an amino acid having at least one deprotonated carboxylic acid group;

15 (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula -C(=O)-C(=O)-O⁻, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester;

(IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group;

20

(V) an alpha ketocarboxylic acid that contains a functional group of the formula -C(=O)-C(=O)-O⁻;

(VI) a beta oxocarboxylic acid ester; and

(VII) an alkylene carbonate;

25

and which treatment fluid is alkaline or is capable of becoming alkaline *in situ* in an underground formation.

44. A treatment fluid according to claim 43, which treatment fluid further comprises one or more of a water-wetting agent, a surfactant, a microemulsifying
30 surfactant, a solvent, a mutual solvent, a viscosity modifier, a fines suspender, a clay swelling inhibitor and a nucleating material.

45. A process for depositing carbonate material from a fluid, which process comprises:
- (a) providing a fluid comprising (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid:
- 5 (II) an amino acid having at least one deprotonated carboxylic acid group;
- (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$, (ii) an alkylene carbonate and (iii) a beta
- 10 oxocarboxylic acid ester;
- (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group;
- (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O^-$;
- 15 (VI) a beta oxocarboxylic acid ester; and
- (VII) an alkylene carbonate;
- and which treatment fluid is alkaline or is capable of becoming alkaline; and
- (b) allowing carbonate mineral to be deposited from said fluid, if necessary after said fluid has become alkaline.
- 20
46. A process according to claim 45, which is a process for substantially sealing off an underground formation to production or injection and which comprises:
- (a2) introducing the fluid provided in (a) into an underground formation; and
- (b) allowing carbonate mineral to be deposited from the fluid, thereby substantially
- 25 sealing off the underground formation to production or injection.
47. A process according to claim 45, which is a process for:
- ground consolidation in areas of poor soil consolidation;
 - strengthening of embankments, dykes, dams or artificial islands;
 - 30 - consolidating shore lines or cliff faces for combatting coastal erosion;
 - strengthening of, and/or filling cracks in, brickwork, plaster, building foundations, concrete or road surfaces;

-60-

- setting of foundry moulds;
 - sealing fractures in pipelines;
 - restoring and/or conserving stone monuments, art, statuary or objects;
 - increasing the speed at which concrete, grout and/or plaster sets; or
- 5 - incorporating carbonate mineral into composite materials.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/052712

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/56
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C09K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STEFAN FOX ET AL: "Coordinated of Biologically Important [alpha]-Amino Acids to Calcium(II) at High pH: Insights from Crystal Structures of Calcium [alpha]-Aminocarboxylates", INORGANIC CHEMISTRY, vol. 46, no. 3, 1 February 2007 (2007-02-01), pages 818-824, XP55050850, ISSN: 0020-1669, DOI: 10.1021/ic061838b	43,44
A	experimental part; figures 1-4 the whole document	1-42, 45-47
X	US 1 994 050 A (TEIKICHI SATO, TOKYO, JAPAN) 12 March 1935 (1935-03-12)	43,44
A	page 1, left-hand column, lines 36-39 the whole document	1-42, 45-47

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

10 April 2013

Date of mailing of the international search report

18/04/2013

Name and mailing address of the ISA/

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

Authorized officer

Straub, Thomas

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/052712

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	F. MANOLIA, J. KANAKISA, P. MALKAJB, E. DALASA: "The effect of amino acids on the crystal growth of calcium carbonate" , JOURNAL OF CRYSTAL GROWTH, vol . 236, 14 November 2001 (2001-11-14) , pages 363-370, XP002690862 ,	43,44
A	page 364, left-hand column abstract the whole document	1-42 , 45-47
Y	wo 99/05394 AI (CLEANSORB LTD [GB] ; HARRIS RALPH EDMUND [GB] ; MCKAY IAN DONALD [GB]) 4 February 1999 (1999-02-04)	1,42 ,45
A	examples 1,2 the whole document	2-41 ,43 , 44,46,47
Y	RODRIGUEZ-NAVARRO CARLOS ET AL: "Conservation of ornamental stone by Myxococcus xanthus-induced carbonate biomineralization" , APPLIED AND ENVIRONMENTAL MICROBIOLOGY, AMERICAN SOCIETY FOR MICROBIOLOGY, US, vol . 69, no. 4, 1 April 2003 (2003-04-01) , pages 2182-2193 , XP002448928, ISSN: 0099-2240, DOI : 10.1128/AEM.69.4.2182-2193.2003	1,42 ,45
A	cited in the application page 2189 , last line - page 2190, line 3 the whole document	2-41 ,43 , 44,46,47
A	wo 2005/124097 AI (STATOIL ASA [NO] ; CHAMPION TECHNOLOGY INC [US] ; KOTLAR HANS KRISTIAN []) 29 December 2005 (2005-12-29) claims 1, 10, 11, 15 the whole document	1-47
A	EP 0 644 257 A2 (ROHM & HAAS [US]) 22 March 1995 (1995-03-22) page 16 - page 18 the whole document	1-47
X	US 2008/176770 AI (SANDERS MICHAEL W [US] ET AL) 24 July 2008 (2008-07-24)	43,44
A	paragraphs [0054] - [0055] , [0061] , [0062] the whole document	1-42 , 45-47
X	US 4 976 315 A (PRUKOP GABRIEL [US] ET AL) 11 December 1990 (1990-12-11)	43,44
A	column 3, line 60 - column 4, line 20 the whole document	1-42 , 45-47
	-/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/052712

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 717 875 A (WEISS WALTER J)	43,44
A	13 September 1955 (1955-09-13) claims 1,4,6	1-42, 45-47

X	US 4 439 328 A (MOITY RANDOLPH M [US])	43,44
A	27 March 1984 (1984-03-27) example 4	1-42, 45-47

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/GB2012/052712
--

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 1994050	A	12-03-1935	NONE

Wo 9905394	AI	04-02 -1999	AU 8351698 A 16-02-1999
			CA 2296357 AI 04-02-1999
			GB 2345077 A 28-06-2000
			US 6401819 BI 11-06-2002
			wo 9905394 AI 04-02-1999

Wo 2005124097	AI	29-12 -2005	AU 2005254779 AI 29-12-2005
			CA 2569810 AI 29-12-2005
			GB 2430002 A 14-03-2007
			US 2009014178 AI 15-01-2009
			wo 2005124097 AI 29-12-2005

EP 0644257	A2	22-03-1995	AT 180012 T 15-05- 1999
			BR 9403790 A 02-05- 1995
			CA 2132112 AI 22-03- 1995
			CN 1108266 A 13-09- 1995
			DE 69418403 DI 17-06- 1999
			DE 69418403 T2 30-12- 1999
			EP 0644257 A2 22-03- 1995
			JP 3481697 B2 22-12- 2003
			JP H07216084 A 15-08- 1995
			TR 28856 A 23-09- 1997
			US 5552514 A 03-09- 1996
			US 5554721 A 10-09- 1996
			US 5556938 A 17-09- 1996

US 2008176770	AI	24-07 -2008	US 2008176770 AI 24-07 -2008
			US 2011152133 AI 23-06 -2011

US 4976315	A	11-12 -1990	NONE

US 2717875	A	13-09 -1955	NONE

US 4439328	A	27-03 -1984	NONE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB20 12/0527 12

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (II) an amino acid having at least one deprotonated carboxylic acid group; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.
Plus method claims 1 and 45 as well as use claim 42.

2. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (III) (a) ammonia or an amine; and (b) at least one of (i) an alpha oxocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O-$, (ii) an alkylene carbonate and (iii) a beta oxocarboxylic acid ester; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.
Plus method claims 1 and 45 as well as use claim 42.

3. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (IV) an amino alkyl sulphonic acid having at least one deprotonated sulphonic acid group; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.
Plus method claims 1 and 45 as well as use claim 42.

4. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (V) an alpha ketocarboxylic acid that contains a functional group of the formula $-C(=O)-C(=O)-O-$; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.
Plus method claims 1 and 45 as well as use claim 42.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

5. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (VI) a beta oxocarboxylic acid ester; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.

Plus method claims 1 and 45 as well as use claim 42.

6. claims: 1-47 (partially)

A treatment fluid, which treatment fluid comprises (I) cations of a metal having an oxidation state of +2 or higher and at least one of the following (II) to (VII) which is soluble in the treatment fluid: (VII) an alkylene carbonate; and which treatment fluid is alkaline or is capable of becoming alkaline in situ in an underground formation.

Plus method claims 1 and 45 as well as use claim 42.
