



(86) **Date de dépôt PCT/PCT Filing Date:** 2015/01/12  
(87) **Date publication PCT/PCT Publication Date:** 2015/07/23  
(85) **Entrée phase nationale/National Entry:** 2016/07/12  
(86) **N° demande PCT/PCT Application No.:** GB 2015/050047  
(87) **N° publication PCT/PCT Publication No.:** 2015/107328  
(30) **Priorité/Priority:** 2014/01/17 (GB1400802.3)

(51) **Cl.Int./Int.Cl. C09K 8/52** (2006.01),  
**C09K 8/72** (2006.01)  
(71) **Demandeur/Applicant:**  
CLEANSORB LIMITED, GB  
(72) **Inventeurs/Inventors:**  
HARRIS, RALPH EDMUND, GB;  
HOLDSWORTH, DUNCAN, GB  
(74) **Agent:** NORTON ROSE FULBRIGHT CANADA  
LLP/S.E.N.C.R.L., S.R.L.

(54) **Titre : PROCEDE D'ACIDIFICATION**  
(54) **Title: PROCESS FOR ACIDIZING**

(57) **Abrégé/Abstract:**

The invention relates to in-situ acidizing processes that involve the dissolution of an acid-soluble material. Treatment fluids have been identified that can effectively dissolve acid-soluble materials at low temperatures, such as temperatures of 30 °C or lower. In some embodiments, the processes may also be usefully employed at higher temperatures. The processes and treatment fluids of the invention can advantageously be used to dissolve acid-soluble materials, including filter cakes, in underground formations.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau(43) International Publication Date  
23 July 2015 (23.07.2015)(10) International Publication Number  
**WO 2015/107328 A1**

- (51) **International Patent Classification:**  
C09K 8/52 (2006.01) C09K 8/72 (2006.01)
- (21) **International Application Number:**  
PCT/GB2015/050047
- (22) **International Filing Date:**  
12 January 2015 (12.01.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
1400802.3 17 January 2014 (17.01.2014) GB
- (71) **Applicant:** CLEANSORB LIMITED [GB/GB]; 1J Merrow Business Centre, Merrow Lane, Guildford, Surrey GU4 7WA (GB).
- (72) **Inventors:** HARRIS, Ralph Edmund; c/o Cleansorb Limited, 1J Merrow Business Centre, Merrow Lane, Guildford, Surrey GU4 7WA (GB). HOLDSWORTH, Duncan; c/o Cleansorb Limited, 1J Merrow Business Centre, Merrow Lane, Guildford, Surrey GU4 7WA (GB).
- (74) **Agent:** KEEN, Celia Mary; 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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report (Art. 21(3))

(54) **Title:** PROCESS FOR ACIDIZING

(57) **Abstract:** The invention relates to in-situ acidizing processes that involve the dissolution of an acid-soluble material. Treatment fluids have been identified that can effectively dissolve acid-soluble materials at low temperatures, such as temperatures of 30 °C or lower. In some embodiments, the processes may also be usefully employed at higher temperatures. The processes and treatment fluids of the invention can advantageously be used to dissolve acid-soluble materials, including filter cakes, in underground formations.



WO 2015/107328 A1

## Process for acidizing

### Background to the invention

5 The use of acidizing systems based on acid precursors has become widespread in oilfield chemical treatments over the last decade or so. Producing organic acid in-situ from acid precursors, rather than using an organic or mineral acid directly, can deliver excellent zonal coverage. In addition the use of acid precursors offers considerable health, safety and environmental advantages.

10

Treatment formulations based on acid precursors are generally designed to deliver a certain amount of acid from the treatment fluid within a desired timescale at the prevailing temperature. The acid produced from the acid precursor is available to solubilise at least a portion of the targeted acid-soluble materials, for example carbonate rock, carbonate scale  
15 or carbonate components of drill-in fluid filter cakes, so that they can be removed from the treated zone in the form of dissolved salts.

The most commonly used acid precursors are carboxylic acid esters, particularly esters of formic, acetic and lactic acid. These are suited to use in different temperature ranges.

20

They have a relatively high yield of acid, with the acid precursors and the products of acidizing all being soluble.

If using these acid precursors in the absence of an enzyme or other catalyst, the typical temperature range in which acetic and lactic acid precursors are used is from about 85 °C  
25 and preferably from about 100 °C up to about 160 °C. Precursors of formic acid hydrolyse more readily than precursors of acetic or lactic acid, so can generate acid in-situ at lower temperatures. The typical temperature range in which precursors of formic acid are used is from about 30 °C to about 120 °C.

30

The rate of acid generation from precursors of formic, acetic or lactic acid may, if desired, be increased using a suitable enzyme catalyst such as a lipase, esterase or protease enzyme (US 5,678,632). Treatment formulations are designed to give acceptable rates of acid generation and therefore acceptable treatment (shut-in) times under the conditions of use.

Unfortunately, at temperatures lower than about 30 °C acidizing based on the most commonly used acid precursors can proceed more slowly than is generally acceptable to operators.

5

For example, at 27 °C it typically takes about 6 days to convert a formic acid precursor, used at 10% w/v in a treatment fluid, to formic acid. This can be reduced to about 2 days by incorporating enough of a suitable enzyme into the treatment formulation. However, this increases the cost.

10

There are a number of low temperature underground formations found worldwide at temperatures below about 30 °C. For example some formations in Canada and Russia are at temperatures as low as 7 °C. At such low temperatures, acidizing treatments based on formic acid precursors, even those containing ester-hydrolysing enzymes, would require long shut-in periods likely to be unacceptable to operators.

15

Another problem associated with the use of formic acid precursors in dense formate brines is the potential for precipitation of calcium salts. In such treatments, the solubility of calcium formate may be exceeded, resulting in the precipitation of calcium formate as a solid in the treatment fluid. US 2013/0213659 teaches that by including a suitable chelant or an alkyl glucoside surfactant in the treatment fluid, precipitation of calcium formate when acidizing with a formic acid precursor in dense formate brines may be avoided.

20

There is a continuing need for acidizing processes that are low hazard and that are based on environmentally acceptable components.

25

There is a specific need for in-situ acidizing processes that are effective within acceptable treatment timescales at low temperatures, particularly at temperatures in the range from about 5 °C to about 30 °C, for oilfield and other applications. Furthermore, it is necessary to avoid the precipitation of solid by-products, such as acid salts, as the acidizing process takes place.

30

### **Summary of the invention**

It is an object of the present invention to provide a simple and effective acidizing method for dissolving acid-soluble material within an underground formation or dissolving acid soluble material in tubulars, tanks, pipelines, reverse osmosis units and the like.

- 5 It is a particular object of the present invention to provide simple and effective methods for the effective treatment of filter cakes, including their treatment over long horizontal intervals.

10 It is a further object of the present invention to provide methods that are environmentally acceptable by utilising components that are of low environmental impact.

It is a still further object of the present invention to provide methods that are effective at low temperatures, for example temperatures of 30 °C or lower.

- 15 Further still, it is an object of the present invention to provide methods that do not suffer from precipitation of acid salts when the acidizing process is underway.

The inventors have now found that these objects can be achieved by using glucono delta lactone, as an acid precursor, in combination with a salt effective for preventing the precipitation of, and/or dissolving, alkaline earth metal salts of gluconic acid. In particular, the inventors have found that glucono delta lactone is an acid precursor that generates gluconic acid at rates that are useable for acidizing at temperatures below about 30° C. Although such acidizing has the potential to produce alkaline earth salts of gluconic acid, which have low solubility and are therefore liable to precipitate, the addition of the salt component is effective for preventing the precipitation of, and/or redissolving, alkaline earth metal salts of gluconic acid. Consequently, sufficiently high concentrations of glucono delta lactone can be incorporated into a treatment fluid to enable production of sufficient gluconic acid to achieve effective acidizing (without precipitation of gluconic acid salts).

30

Specifically, the present invention provides an acidizing process which comprises:

- (a) providing a treatment fluid that comprises dissolved glucono delta lactone;
- (b) contacting the treatment fluid with an acid-soluble material; and

(c) allowing the glucono delta lactone to hydrolyse to produce gluconic acid and the gluconic acid to dissolve at least a portion of the acid-soluble material; wherein during or following the step (c) the treatment fluid comprises a dissolved salt effective for preventing precipitation of alkaline earth metal salts of gluconic acid and/or  
5 dissolving precipitated alkaline earth metal salts of gluconic acid.

The present invention also provides a treatment fluid effective for dissolving acid-soluble material, which treatment fluid comprises: (i) glucono delta lactone; and (ii) at least one of sodium lactate, sodium acetate, potassium lactate, potassium acetate, ammonium lactate  
10 and ammonium acetate.

The present invention thus provides an in-situ acidizing process that is effective at low temperature. It provides an in-situ acidizing process that proceeds at faster rates than processes based on esters of formic acid. It also provides a process where glucono delta  
15 lactone may be used for acidizing at concentrations higher than a few percent by weight, without encountering the problem of precipitation of poorly soluble gluconate salts. It may be used for the acid treatment of underground formations, including water- or hydrocarbon-bearing formations, particularly those at temperatures lower than 30° C.

## 20 **Description of the Figures**

Figure 1 shows the evolution of carbon dioxide gas (ml) from calcium carbonate as a function of time (hours) when using a treatment fluid of the invention, as described in more detail in Example 3.

25

## **Detailed description of the invention**

The process of the present invention may be used to dissolve carbonate rocks, fluid loss additives, drill-in fluid components or scales, including, but not being limited to, calcium  
30 carbonate, magnesium carbonate, calcium magnesium carbonate, chalk, limestone, marble or dolomite. The acid-soluble material normally contains at least one alkaline earth metal, such as at least one of calcium and magnesium. The acid-soluble material thus normally releases alkaline earth metal ions, for example at least one of calcium or magnesium ions,

when it is dissolved by an acid (e.g., the gluconic acid or an acid generated from another acid precursor).

5 The process may be applied to hydrocarbon reservoirs, such as oil or gas reservoirs, or to water reservoirs in underground formations, where specific acidizing applications include deep matrix acidizing, acidizing of natural fracture networks, or filter cake treatment, including the treatment of filter cakes produced from drilling with water-based or oil-based drill-in fluids.

10 The process may also be used for the acid treatment of acid-soluble materials such as scales in tubulars, tanks, pipelines, reverse osmosis units and the like, particularly at low ambient temperatures.

15 The glucono delta lactone used in the present invention is an acid precursor that generates gluconic acid by hydrolysis in a treatment fluid at temperatures below 30° C (although it can of course also generate gluconic acid at higher temperatures and typically does so rapidly). Gluconic acid is capable of dissolving the acid-soluble materials described herein.

20 Two potential barriers to the use of glucono delta lactone as an acid precursor for use in dissolving acid-soluble materials have been overcome in order to arrive at the present invention. A first barrier is that glucono delta lactone suffers from a comparatively poor acid yield on a weight basis and therefore has limited dissolving capacity. In particular, only one gluconic acid molecule is produced per molecule of delta glucono lactone, compared to two formic acid molecules per molecule of a typical formic acid precursor. In addition gluconic acid is a larger molecule than formic acid. This means that the dissolving power of glucono delta lactone on a weight basis is only about half that of typical formic acid precursors. It therefore must typically be included in larger amounts by weight than would a typical formic acid precursor.

30

This first barrier can be overcome by ensuring that a sufficient amount by weight of glucono delta lactone is incorporated into the treatment fluid. The second barrier is the low solubility of alkaline earth salts of gluconic acid. Such salts can be formed when alkaline earth metal ions are released from an acid-soluble material containing alkaline

earth metal, as it is dissolved by an acid (e.g. by the gluconic acid). For example, the solubility of calcium gluconate is only about 3.5% by weight. This means that acidizing a calcium carbonate material with more than a few percent glucono delta lactone would, if no further steps were taken, result in the precipitation of calcium gluconate within the treatment fluid as acidizing proceeded, which is highly undesirable.

The present invention solves this problem by including a salt that is effective for preventing precipitation of alkaline earth metal salts of gluconic acid and/or dissolving precipitated alkaline earth metal salts of gluconic acid. This means that it becomes possible to incorporate a sufficiently large amount of glucono delta lactone to achieve effective acidizing, while still avoiding subsequent long-term precipitation of alkaline earth metal salts of gluconic acid when the acidizing is underway.

Sufficient glucono delta lactone is incorporated into the treatment fluid to deliver the required amount of gluconic acid when fully hydrolysed. Typically this will be a minimum of 2 to 3% w/v glucono delta lactone (for example at least 2% w/v) and preferably 5 to 20% w/v, although higher or lower amounts may be used if desired.

The salt effective for preventing the precipitation of, or dissolving precipitates of, alkaline earth metal salts of gluconic acid in the treatment fluid must be present (dissolved) in the treatment fluid during or following the step (c), i.e. after the treatment fluid has been contacted with the acid-soluble material in the step (b). This ensures that it can act to at least reduce and preferably prevent precipitation of gluconic acid salts as the acidizing proceeds, and/or can redissolve any gluconic acid salts that may already have precipitated. Typically the salt is present in the treatment fluid during or following the step (c) in an amount sufficient to prevent the precipitation of alkaline earth metal salts of gluconic acid and to redissolve any alkaline earth metal salts of gluconic acid that have precipitated.

In a first embodiment, the treatment fluid provided in the step (a) already comprises the salt. In this first embodiment, a salt effective for preventing the precipitation of alkaline earth metal salts of gluconic acid in the treatment fluid at the target temperature is selected and is incorporated into the treatment fluid at the desired concentration. The treatment fluid provided in the step (a) thus comprises both the glucono delta lactone and the salt. Preferably the weight ratio of the glucono delta lactone and the salt in the treatment fluid is

from 10:1 to 1:5, although other weight ratios are possible. For example, the weight ratio of the glucono delta lactone and the salt in the treatment fluid may be from 3:1 to 1:3, e.g. from 2:1 to 1:2. This weight ratio typically refers to the treatment fluid that is provided in the step (a), i.e. prior to it being contacted with the acid-soluble material. Typically in this  
5 embodiment the presence of the salt throughout the process means that precipitates of gluconic acid salts do not form, i.e. the salt is effective for preventing precipitation of the gluconic acid salts.

Salts effective for preventing the precipitation of alkaline earth metal salts of gluconic acid  
10 that may be added directly to the treatment fluid may be readily identified by carrying out suitable laboratory tests (to confirm the absence of insoluble gluconate salts following acidizing). Preferred salts are lactate or acetate salts including sodium lactate, sodium acetate, potassium lactate, potassium acetate, ammonium lactate, ammonium acetate, calcium acetate or magnesium acetate. Most preferred are sodium acetate and sodium  
15 lactate. If a lactate salt is used, the lactate may be D-lactate, L-lactate or DL-lactate. For example, if sodium lactate is used then it may be sodium D-lactate, sodium L-lactate or sodium DL-lactate.

In a second embodiment, the required salt is instead formed in-situ during or following the  
20 step (c). In particular, the salt may be generated within the treatment fluid when it comes into contact with acid soluble material in the zone to be treated. For example, a suitable salt may be generated in-situ by providing a treatment fluid in the step (a) that contains a suitable acid precursor in addition to the glucono delta lactone. This acid precursor is typically an organic acid precursor (e.g. an ester, orthoester, polyester or polyorthoester)  
25 that may hydrolyse to form an organic acid. In the presence of suitable acid-soluble materials (for example, calcium carbonate or magnesium carbonate) the organic acid generated may react to form the required salt.

In particular, the salt may be generated in-situ in the treatment fluid during or following  
30 the step (c) by a reaction between a portion of the acid-soluble material and an acid generated from an acid precursor (other than glucono delta lactone) that is comprised in the treatment fluid in the step (a).

Organic acid precursors suitable for generating suitable salts may be readily identified by carrying out suitable laboratory tests (to confirm the absence of insoluble gluconate salts following acidizing). Preferred organic acid precursors are esters of lactic or acetic acid and polyesters which hydrolyse to generate lactic acid. Most preferred are acetate esters of  
5 glycerol, ethylene glycol or diethylene glycol, lactate esters of C1-C4 alcohols and polylactic acid. The resulting salt generated in-situ in the treatment fluid during or following the step (c) is thus preferably selected from lactate or acetate salts including calcium lactate, magnesium lactate, calcium acetate or magnesium acetate. Most preferred are calcium acetate and calcium lactate. If the resulting salt generated in-situ in the  
10 treatment fluid is a lactate salt then the lactate may be D-lactate, L-lactate or DL-lactate.

Preferably the acid precursor in the treatment fluid provided in the step (a) is present in an amount sufficient to generate salt such that the weight ratio of the glucono delta lactone and the salt is from 10:1 to 1:5, although other weight ratios are possible. For example, the  
15 weight ratio of the glucono delta lactone and the salt may be from 3:1 to 1:3, e.g. from 2:1 to 1:2.

It will be appreciated that depending on the relative rate at which the acid precursor and the glucono delta lactone hydrolyse, it is possible that sufficient glucono delta lactone may  
20 have reacted with acid-soluble material to initiate precipitation of some alkaline earth metal salt of gluconic acid before sufficient hydrolysis of acid precursor has occurred to yields salts that prevent such precipitation. In this case, some precipitation of gluconic acid salt may initially occur, with the precipitate then redissolving as more of the organic acid precursor hydrolyses. Thus, the dissolved salt present in the treatment fluid  
25 during/following step (c) may either be one that is effective simply for preventing precipitation (including initially) of the alkaline earth metal salts of gluconic acid. Alternatively, it may be effective both for: (i) dissolving precipitated alkaline earth metal salts of gluconic acid; and (ii) for preventing precipitation of (further) alkaline earth metal salts of gluconic acid. For the avoidance of doubt, it is emphasised that the process of the  
30 present invention provides for both possibilities.

Normally, all components of the treatment fluid will be soluble in the treatment fluid at their concentration of use, i.e. they will be dissolved in the treatment fluid. They may, if not soluble, be dispersed in the treatment fluid.

The treatment fluid may be prepared by any method known to one skilled in the art. Generally the components may be mixed in any order. It will be understood by those skilled in the art that treatment fluids used to treat underground formations typically need  
5 to be made up at a certain density.

The treatment fluid is normally prepared by dissolving the components in suitable water. Examples include city (drinking) water, produced water, sea water or oilfield brines, such as will be well known to those skilled in the art. The treatment fluid is therefore normally  
10 an aqueous treatment fluid, i.e. a treatment fluid that comprises water (e.g. at least 50 wt% water). References herein to solubility also refer to solubility in water, unless otherwise specified.

If using an organic acid precursor such as an ester above the concentration at which it is  
15 fully soluble, it is not outside of the scope of the present invention that an emulsion of the organic acid precursor may be present.

After preparing the treatment fluid, it is introduced into the target zone by any method known to those skilled in the art. This may include introduction into an underground  
20 formation, for example via the drill string, coiled tubing, work string or by bullheading. It may also include introduction into tubulars, tanks, pipelines, reverse osmosis units and the like.

The process may be used when acidizing with glucono delta lactone. Acidizing  
25 applications may include, but not be limited to, acidizing of underground formations, including treatment of filter cakes in openhole wellbores, particularly those with sand control completions, treatment of formation damage such as scales containing acid-soluble components, treatments directed at increasing the permeability or porosity of the underground formation, for example by dissolving carbonate rock in the rock matrix or  
30 natural or induced fractures, including acid fracturing treatments, or treatments to dissolve acid-soluble material in pipelines, tubulars or tanks.

The volume of treatment fluid to be used will be appropriate to the type of treatment and will be known to those skilled in art.

The treatment fluid is then left for a period long enough for the desired amount of gluconic acid to be produced from the delta glucono lactone and (optionally) for organic acid to be produced from any precursor of another organic acid included as a component of a system used for generating salts effective for preventing the precipitation of alkaline earth metal salts of gluconic acid. When generating gluconic acid at temperatures in the range of between about 5 °C and about 30 °C a shut in period of between 6 hours and 7 days will normally be sufficient, depending on the specific temperature at which the treatment is conducted. The temperature in the step (c) of the process of the invention may, for example, be 30 °C or lower, for example from 5 to 30 °C, from 5 to 25 °C or even from 5 to 20 °C.

While the process of the present invention is particularly suited to acidizing at low temperatures, particularly those below about 30°C, it may also be operated at higher temperatures. In particular, in acid fracturing treatments there is a need for a rapid reaction rate so that the acid may etch fracture faces. Use of treatment fluids of the present invention at a sufficiently high temperature may permit sufficiently high rates of generation of gluconic acid to etch fracture faces in acid fracturing, while avoiding the deposition of alkaline earth metal salts of gluconic acid. One familiar with the art of acid fracturing would be able to design acid fracturing treatments based on the treatment fluids of the present invention. In a preferred embodiment, suitable forms (for example prills or fibres) of polyesters may be incorporated into treatment fluids of the present invention used for acid fracturing. These hydrolyse to generate lactic acid, leading to the formation of salts effective for preventing the precipitation of alkaline earth metal salts of gluconic acid but may also assist with acidizing.

It will be understood by one skilled in the art that, at the end of treatments according to the present invention, there will be no precipitated alkaline earth metal salt of gluconate present in the spent treatment fluid. It is not outside the scope of the present invention that a precipitate may form and then subsequently dissolve (for example as hydrolysis of an acetate or lactate ester and subsequent reaction of the acid with calcium carbonate results in formation of calcium acetate or calcium lactate). One skilled in the art will understand that in some treatment situations, for example filter cake cleanup or acid fracturing, there

may be benefits in forming a temporary precipitate as this may prevent premature leak-off of the well treatment fluid.

5 Normally, the rate of gluconic acid generation from hydrolysis of the glucono delta lactone does not require any acceleration. Optionally, a suitable enzyme may be incorporated to increase the rate of hydrolysis as taught by US 5,678,632.

All chemicals used in the process of the present invention will normally be technical grade to reduce the cost of the process.

10

The treatment fluid may contain further chemical additives such as are commonly used in acidizing applications, including but not being limited to surfactants, foaming and chelating agents if their inclusion is deemed to be beneficial and if they are compatible with the other components of the treatment fluid. Other chemical additives considered  
15 useful in the treatment fluids of the present invention are biostatic agents and biocidal agents.

The present invention has the following particular advantages over the prior art:

20 The method provides a simple, effective and convenient way of acidizing, particularly at low temperatures.

In some embodiments of the invention, all of the components of the treatment fluids are generally environmentally acceptable and of low environmental impact. This potentially  
25 makes the system much more suitable for use in sensitive environments, for example arctic environments than conventional acidising systems.

Glucono delta lactone is Generally Recognised as Safe (GRAS) in the US. The preferred salts that are effective for preventing the precipitation of alkaline earth metal salts of  
30 gluconic acid, sodium acetate and sodium lactate, are also both GRAS.

In Europe, sodium acetate is on the OSPAR List of Substances Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment (PLONOR).

Preferred organic acid precursors suitable for generating salts effective for preventing the precipitation of alkaline earth metal salts of gluconic acid are acetate and lactate esters and polyesters which hydrolyse to generate lactic acid. These esters and polyesters are generally low hazard. In particular, acetate esters such as glycerol diacetate and glycerol triacetate are low toxicity with high flash point.

Another advantage of the system is that gluconate, a product of the system, is effective as an iron control agent, corrosion inhibitor, scale inhibitor or nucleation / crystal growth inhibitor.

10

The following examples illustrate the invention.

### Examples

15 **Example 1** - Comparison of solubility of calcium gluconate and calcium formate.

The dissolving capacities of delta glucono lactone and Acidgen<sup>TM</sup> FG (a formic acid precursor commercially available from Cleansorb Limited of Guildford, UK) and their capacity for precipitation of calcium salts is shown in Table 1.

20

Table 1

Acid precursor	Percent at which used (w/v)	Acid produced	Calculated dissolving capacity for calcium carbonate (g/l) at 100% conversion of acid precursor to organic acid	Calcium salt precipitated following acidising of calcium carbonate in fresh water
Glucono delta lactone	1	Gluconic	2.8	No
Glucono delta lactone	2	Gluconic	5.6	No

Glucono delta lactone	3	Gluconic	8.4	Yes
Glucono delta lactone	5	Gluconic	14.0	Yes
Glucono delta lactone	10	Gluconic	28.0	Yes
Acidgen FG*	5	Formic	30.8	No
Acidgen FG	10	Formic	61.7	No
Acidgen FG	15	Formic	92.5	No

\* Acidgen<sup>TM</sup> FG is a proprietary formic acid precursor available from Cleansorb Limited.

**Example 2** - Effect of incorporating sodium acetate or sodium lactate on precipitate formation

5

100ml solutions were prepared in deionised water in 100ml Duran bottles: 2.7g of laboratory grade CaCO<sub>3</sub> was added to each solution. Acidizing was allowed to proceed at room temperature (approximately 25 °C) for 65 hours. To simulate the effect of low temperature spent acidizing solutions were placed in a refrigerator at 5 °C and observed at 20 hours for the presence of any precipitate.

10

These results indicated that in the absence of sodium acetate or sodium lactate, calcium gluconate was precipitated from the spent acidizing solution at 5 °C, but the inclusion of either sodium acetate or sodium lactate in the acidizing formulation prevented the deposition of a precipitate.

15

Table 2

Acidizing solution based on	Percent at which used (w/v)	Additional component	Percent at which used (w/v)	Calcium salt precipitated at 5 °C following acidising
Glucono delta lactone	10	None	Not applicable	Yes

Glucono delta lactone	10	Sodium acetate	5	No
Glucono delta lactone	10	Sodium lactate 60% solution	10.8	No
Glucono delta lactone	22	None	Not applicable	Yes
Glucono delta lactone	22	Sodium acetate	5	No
Glucono delta lactone	22	Sodium lactate 60% solution	10.8	No

**Example 3** - Carbon dioxide release from calcium carbonate acidized with a solution of glucono delta lactone and sodium acetate

- 5 A 250ml graduated glass measuring cylinder was filled with tap water, inverted with the top covered and then sat in a tub of water. The end of some plastic tubing was positioned under the inverted cylinder. The other end of the tubing was attached to a large bore needle which was inserted in to a sealed Wheaton bottle holding 0.983g CaCO<sub>3</sub>, 100ml of deionised water containing 3.6g D-(+)-Gluconic acid  $\delta$ -lactone + 1.8g sodium acetate and
- 10 a magnetic stirring bar. The experiment was conducted at room temperature 26 °C $\pm$ 1 °C.

The Wheaton bottle was placed on a magnetic stirring platform and stirred whilst observing the volume of evolved CO<sub>2</sub> collected in the inverted cylinder. After 8 hours and 45 minutes all of the CaCO<sub>3</sub> had been dissolved.

15

The results (Figure 1) show that acidizing with glucono delta lactone proceeded over several hours, indicating that this lactone gives useful rates of in-situ acid generation at room temperature.

## Claims

1. An acidizing process which comprises:
  - (a) providing a treatment fluid that comprises dissolved glucono delta lactone;
  - 5 (b) contacting the treatment fluid with an acid-soluble material; and
  - (c) allowing the glucono delta lactone to hydrolyse to produce gluconic acid and the gluconic acid to dissolve at least a portion of the acid-soluble material;wherein during or following the step (c) the treatment fluid comprises a dissolved salt effective for preventing precipitation of alkaline earth metal salts of gluconic acid and/or  
10 dissolving precipitated alkaline earth metal salts of gluconic acid.
2. A process according to claim 1 wherein the salt is a lactate or acetate salt.
3. A process according to claim 1 or 2 wherein the treatment fluid already comprises the  
15 salt in the step (a).
4. A process according to claim 3, wherein the salt is at least one of sodium lactate, sodium acetate, potassium lactate, potassium acetate, ammonium lactate, ammonium acetate, calcium acetate and magnesium acetate.  
20
5. A process according to claim 1 or 2 wherein the salt is generated in-situ in the treatment fluid during or following the step (c) by a reaction between a portion of the acid-soluble material and an acid generated from an acid precursor that is comprised in the treatment fluid in the step (a).  
25
6. A process according to claim 5 wherein the acid precursor is an ester of acetic or lactic acid or a polyester which hydrolyses to generate lactic acid.
7. A process according to claim 5 or 6 wherein the salt is at least one of calcium lactate,  
30 magnesium lactate, calcium acetate and magnesium acetate.
8. A process according to any of the preceding claims wherein the acid-soluble material comprises at least one of calcium carbonate, magnesium carbonate, calcium magnesium carbonate, chalk, limestone, marble and dolomite.

9. A process according to any of the preceding claims wherein the concentration of glucono delta lactone in the treatment fluid in the step (a) is at least 2% w/v.
- 5 10. A process according to any of the preceding claims wherein the salt is present in the treatment fluid during or following the step (c) in an amount sufficient to prevent the precipitation of alkaline earth metal salts of gluconic acid and to dissolve any precipitated alkaline earth metal salts of gluconic acid.
- 10 11. A process according to any of the preceding claims wherein the weight ratio of the glucono delta lactone and the salt in the treatment fluid is from 10:1 to 1:5.
12. A process according to claim 11 wherein the weight ratio of the glucono delta lactone and the salt in the treatment fluid is from 3:1 to 1:3.
- 15 13. A process according to any one of the preceding claims wherein the temperature in the step (c) is 30 °C or less.
14. A process according to claim 13 wherein the temperature is from 5 to 30 °C.
- 20 15. A process according to any one of the preceding claims wherein the acid-soluble material is in an underground formation and the step (b) comprises introducing the treatment fluid into the underground formation in order to contact the treatment fluid with the acid-soluble material.
- 25 16. A process according to claim 15, wherein the acid-soluble material comprises a filter cake in an openhole wellbore.
17. A process according to claim 15 or 16, which comprises increasing the permeability and/or porosity of the underground formation.
- 30 18. A process according to claim 15, which is an acid fracturing process.

19. A process according to any one of claims 1 to 14 wherein the acid-soluble material is in a pipeline, tubular or tank and the step (b) comprises introducing the treatment fluid into the pipeline, tubular or tank in order to contact the treatment fluid with the acid-soluble material

5

20. A treatment fluid effective for dissolving acid-soluble material, which treatment fluid comprises: (i) glucono delta lactone; and (ii) at least one of sodium lactate, sodium acetate, potassium lactate, potassium acetate, ammonium lactate, ammonium acetate, calcium acetate and magnesium acetate.

10

21. A treatment fluid according to claim 20, which further comprises at least one chemical additive selected from surfactants, foaming agents, chelating agents, biostatic agents and biocidal agents.

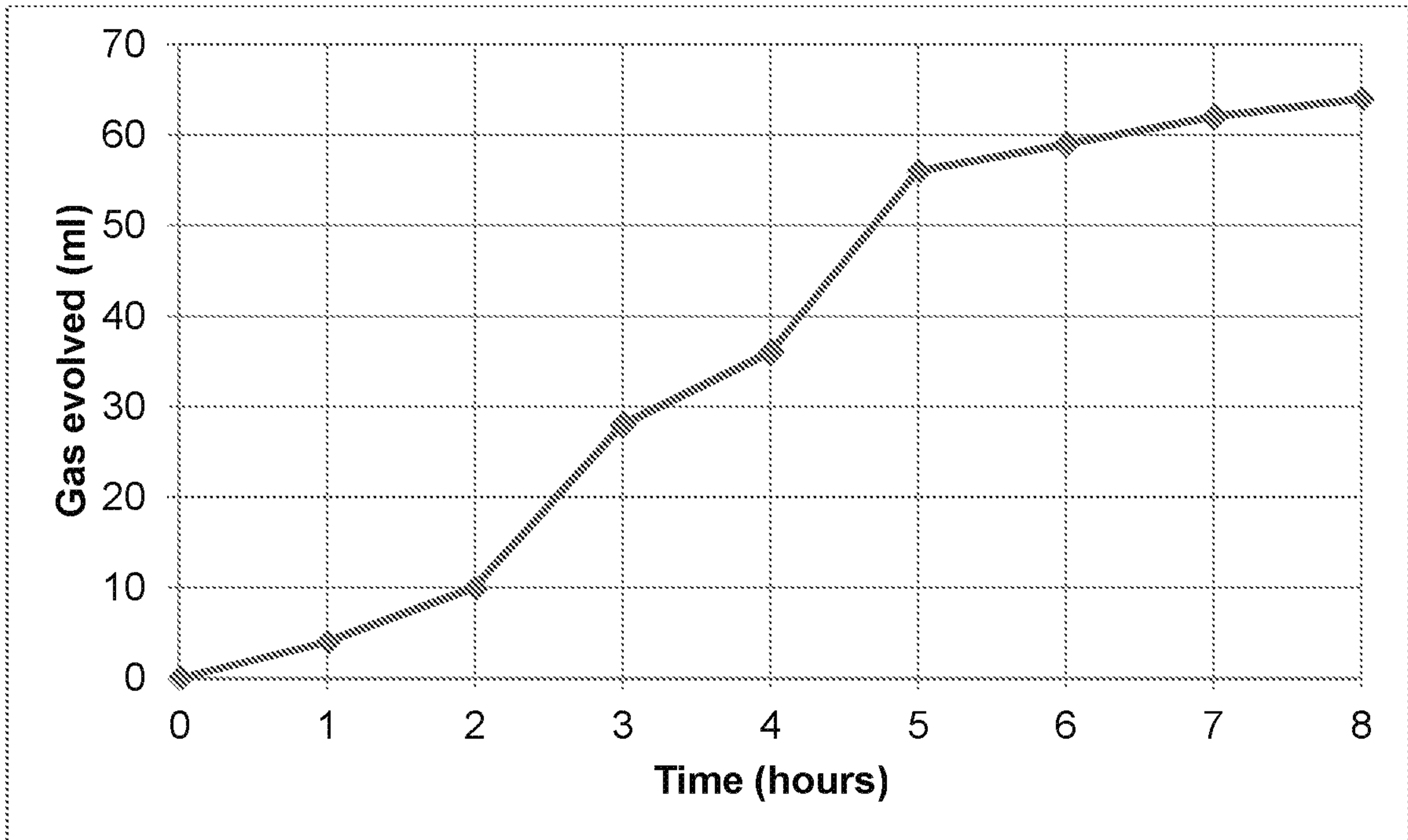


Figure 1