formation. At the same time it may cover cleaning of the wellbore and descaling of the oil/gas production well and production equipment.

The present invention now provides fluids containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), a corrosion inhibitor, and a surfactant. The amount of GLDA and/or MGDA is preferably up to 30 wt%, based on the total weight of the fluid.

According to a first aspect of the present invention, there is provided a fluid suitable for treating carbonate formations containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), a corrosion inhibitor, and a surfactant, wherein the fluid is acidic.

According to a second aspect of the present invention, there is provided a kit of parts suitable for treating carbonate formations wherein one part contains an acidic fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), and a corrosion inhibitor, and the other part contains a fluid containing a surfactant, and, optionally, a mutual solvent.

According to a third aspect of the present invention, there is provided use of the fluid according to the first aspect above in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom, in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.

According to a fourth aspect of the present invention, there is provided use of the kit of parts according to the second aspect above in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom wherein the one part is introduced into the carbonate formation for the main treatment step and the other part for the preflush and/or postflush step, in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.

Moreover, the present invention relates to a kit of parts for a treatment process consisting of several stages, such as the pre-flush, main treatment and postflush stage, wherein one part of the kit of parts for one stage of the treatment process, contains a fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), and a corrosion inhibitor, and the other part of the kit of parts for the other stage of the treatment process, contains a surfactant, or wherein one part contains a fluid containing GLDA and/or MGDA and a corrosion inhibitor, and the other part contains a mutual solvent and a surfactant. A pre- or post-flush is a fluid stage pumped into the formation prior to or after the main treatment. The purposes of the pre- or post-flush include but are not limited to adjusting the wettability of the formation, displacing formation brines, adjusting the salinity of the formation, dissolving calcareous material and dissolving iron scales. Such a kit of parts can be conveniently used in the process of the invention, wherein the part containing a fluid containing a surfactant and, in one embodiment, a mutual solvent is used as a preflush and/or postflush fluid and the other part containing a fluid containing GLDA and a corrosion inhibitor is used as the main treatment fluid.

The invention in addition provides the use of the above fluids and kits of parts in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom and so

In the scheme of Table 2 the results of the corrosion study of 13Cr steel coupons (UNS S41000) are shown for the different solutions.

Table 2: Different chelate or acid solutions

Test no.	Chelate	pH	Temp. °C	Pressure (PSI)	Assay after corrosion test	6Hrs corrosion lbs/sq.ft
#01	GLDA	3.5	160	-	18.4 wt% as GLDA-NaH_3	0.0013
#02	GLDA	3.5	149	-	20.1 wt% as GLDA-NaH_3	0.0008
#03	HEDTA	3.7	149	-	24.4 wt% as HEDTA-NaH_2	0.3228
#04	GLDA	3.5	149	>1,000	20.1 wt% as GLDA-NaH_3	0.0009
#05	HEDTA	3.7	149	>1,000	16.0 wt% as HEDTA-NaH_2	0.5124
#06	MGDA	3.6	149	>1,000	22.7 wt% as MGDA-NaH_2	0.0878

The corrosion rates of HEDTA at 149°C and pressure 6.89 x 10^6Pa (1000 psi) are significantly higher than those of MGDA and much higher compared to GLDA. The corrosion rates of both HEDTA and MGDA at 149°C and pressure 6.89 x 10^6Pa (1000 psi) are higher than the generally accepted limit value in the oil and gas industry of 0.05 lbs/sq.ft (6-hour test period), which means that they will need a corrosion inhibitor for use in this industry. As MGDA is significantly better than HEDTA, it will require a much decreased amount of corrosion inhibitor for acceptable use in the above applications when used in line with the conditions of this Example. The 6-hour corrosion of GLDA for 13Cr steel (stainless steel S410, UNS 41000) at 149°C (300°F) is well below the generally accepted limit value in the oil and gas industry of 0.05 lbs/sq.ft. It can thus be concluded that it is possible to use GLDA in this field without the need to add a corrosion inhibitor.

Example 2

To study the effect of the combination of a corrosion inhibitor, cationic surfactant, and GLDA on the corrosion of Cr-13 steel (UNS S41000), a series of corrosion tests were performed using the method described in Example 1. The results expressed as the 6-hour metal loss at 163°C (325 °F) are shown in Figure 1. The cationic surfactant, Arquad C-35, consists of 35% cocotrimethyl ammonium chloride and water. Armohib 31 represents a group of widely used corrosion inhibitors for the oil and gas industry and consists of alkoxylated fatty amine salts, alkoxylated organic acid, and N, N'-dibutyl thiourea. The corrosion inhibitor and cationic surfactant are available from AkzoNobel Surface Chemistry.

The results show that the corrosion rate of GLDA is significantly less than for HEDTA under all studied conditions. In combination with 0.01 vol% of corrosion inhibitor and/or 6 vol% of cationic surfactant the corrosion rate of GLDA remains well below the acceptable limit of 0.05 lbs/sq.ft. Even in the absence of corrosion inhibitor acceptable results were obtained for this type of metallurgy, but for inferior quality metal types a minor amount of corrosion inhibitor is expected to be needed. For HEDTA 1.0 vol% corrosion inhibitor is not yet sufficient to reduce the corrosion rate below this limit. The results show that, in contrast to HEDTA, GLDA is surprisingly gentle to Cr-13 metal and that combining GLDA with corrosion inhibitor or cationic surfactant or not does not influence the corrosion rate.

Example 3

The corrosion experiment described in Example 2 was repeated with a different type of surfactant. Ethomeen C/22 is a cationic surfactant and consists of coco alkylamine ethoxylate with nearly 100% active ingredient and can be obtained from AkzoNobel Surface Chemistry. The results are shown in Figure 2 and show the same trend as in Figure 1. For HEDTA 1.0 vol% corrosion inhibitor is insufficient by far to reduce the corrosion rate below the generally accepted limit of 0.05 lbs/sq.ft.

In contrast to HEDTA, GLDA in combination with this cationic surfactant is surprisingly gentle to Cr-13 steel.

Example 4

General procedure coreflood tests

Figure 3 shows a schematic diagram for the core flooding apparatus. For each core flooding test a new piece of core with a diameter of 3.81 cm (1.5 inches) and a length of 15.24 or 50.8 cm (6 or 20 inches) was used. The cores were placed in the coreholder and shrinkable seals were used to prevent any leakage between the holder and the core.

An Enerpac hand hydraulic pump was used to pump the brine or test fluid through the core and to apply the required overburden pressure. The temperature of the preheated test fluids was controlled by a compact bench top CSC32 series, with a 0.1° resolution and an accuracy of ± 0.25% full scale ± 1°C. It uses a type K thermocouple and two Outputs (5 A 120 Vac SSR). A back pressure of 6.89×10^6 Pa (1,000 psi) was applied to keep CO_2 in solution.

The back pressure was controlled by a Mity-Mite back pressure regulator model S91-W and kept constant at $2.07 \times 10^6 - 2.76 \times 10^6$ Pa (300 - 400 psi) less than the overburden pressure. The pressure drop across the core was measured with a set of FOXBORO differential pressure transducers, models IDP10-A26E21F-M1, and monitored by lab view software. Two gauges were installed with ranges of 0-2.07×10^6 Pa (0-300 psi) and 0-1.03×10^7 Pa (0-1500 psi), respectively.

Before running a core flooding test, the core was first dried in an oven at 121°C (250°F) and weighted. Subsequently the core was saturated with water at a 1.03×10^7 Pa (1500 psi) overburden pressure and 3.45×10^6 Pa (500 psi) back pressure. The pore volume was calculated from the difference in weight of the dried and saturated core.

The core permeability before and after the treatment was calculated from the pressure drop using Darcy's equation for laminar, linear, and steady-state flow of Newtonian fluids in porous media:

cores that were treated with GLDA was 3.65 PV for the water-saturated core, and 3.10 PV for the oil-saturated core. The presence of oil in the core reduced the PV_{bt} for the cores treated with 0.6M GLDA at pH of 4, thus the GLDA performance was enhanced in the oil-saturated cores by creating a dominant wormhole. The enhancement in the performance can be attributed to the reduced contact area exposed to the reaction with GLDA. 2D CT scan images showed that the wormhole diameter was not affected by saturating the core with oil or water.

This Example again demonstrates that GLDA is similarly compatible with oil and with water.

Example 6

The procedure of Example 4 was used to compare the efficiency of 20 wt% GLDA at pH=4 with 15 wt% HCl in the stimulation of 50.8 cm (20-inch) Indiana limestone cores with an average initial permeability of 1 mD. As shown in Figure 4, at 121°C (250°F) the pore volume to breakthrough required for GLDA is significantly smaller in comparison with HCl, showing the advantage of this new stimulation fluid in terms of chemical need, chemical cost, and environmental impact. At 0.5 and 1 cm^3/min the HCl-treated core showed significant formation damage, as up to 5.08 cm (2 inches) of core were dissolved at the inlet side of the core.

Example 7

The core flooding procedure described in Example 4 was used to study the influence of the cationic surfactant and/or corrosion inhibitor on the performance of an acidizing treatment with 0.6M GLDA. Core flooding experiments with Indiana limestone with an initial permeability of 1 to 1.6 mD (milli Darcy) were carried out at 149°C (300°F) and an injection rate of 2 cm^3/min. The cationic surfactant that was used was Arquad C-35 ex Akzo Nobel Surface Chemistry, the corrosion inhibitor that was used was Armohib 31 ex Akzo Nobel Surface Chemistry. Based on the results of Example 2, the fluids containing GLDA were made with 0.1% of corrosion

Claims

1. Fluid suitable for treating carbonate formations containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), a corrosion inhibitor, and a surfactant.

2. Fluid of claim 1, wherein the amount of GLDA and/or MGDA is 5 to 30 wt% on the basis of the total weight of the fluid.

3. Fluid of claim 1 or 2, containing GLDA.

4. Fluid of any one of claims 1 to 3, wherein the corrosion inhibitor is present in an amount of 0.1-2 volume% on total fluid.

5. Fluid of any one of claims 1 to 4, wherein the corrosion inhibitor is selected from the group of amine compounds, quaternary ammonium compounds, and sulfur compounds.

6. Fluid of any one of claims 1 to 5, wherein the surfactant is present in an amount of 0.1-2 volume% on total fluid.

7. Fluid of any one of claims 1 to 6, wherein the surfactant is a nonionic or cationic surfactant.

8. Fluid of any one of claims 1 to 7, wherein the surfactant is selected from the group of quaternary ammonium compounds and derivatives thereof.

9. Fluid of any one of claims 1 to 8, containing water as a solvent for the other components.

10. Fluid of any one of claims 1 to 9, in addition containing a biocide and/or a bactericide.

11. Fluid of any one of claims 1 to 10, in addition containing a further additive from the group of mutual solvents, anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives, particulates, crosslinkers, salt substitutes, relative permeability modifiers, sulfide scavengers, fibres, and nanoparticles.

12. Fluid of any one of claims 1 to 11 having a pH of from 3.5 to 13.

13. Kit of parts suitable for treating carbonate formations wherein one part contains a fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), and a corrosion inhibitor, and the other part contains a fluid containing a surfactant, and, optionally, a mutual solvent.

14. Kit of parts of claim 13, wherein the amount of GLDA and/or MGDA is 5 to 30 wt% on the basis of the total weight of the fluid in the one part.

15. Kit of parts of claim 13 or 14, containing GLDA.

16. Kit of parts of any one of claims 13 to 15, wherein the corrosion inhibitor is present in an amount of 0.1-2 volume% on total fluid in the one part.

17. Kit of parts of any one of claims 13 to 16, wherein the corrosion inhibitor is selected from the group of amine compounds, quaternary ammonium compounds, and sulfur compounds.

18. Kit of parts of any one of claims 13 to 17, wherein the surfactant is present in an amount of 0.1-2 volume% on total fluid in the other part.

19. Kit of parts of any one of claims 13 to 18, wherein the surfactant is a nonionic or cationic surfactant.

20. Kit of parts of any one of claims 13 to 19, wherein the surfactant is selected from the group of quaternary ammonium compounds and derivatives thereof.

21. Kit of parts of any one of claims 13 to 20, containing water as a solvent for the other components.

22. Kit of parts of any one of claims 13 to 21, in addition containing a biocide and/or a bactericide.

23. Kit of parts of any one of claims 13 to 22, in addition containing a further additive from the group of mutual solvents, anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives, particulates, crosslinkers, salt substitutes, relative permeability modifiers, sulfide scavengers, fibres, and nanoparticles.

24. Kit of parts of any one of claims 13 to 23 wherein at least the fluid in the one part has a pH of from 3.5 to 13.

25. Use of the fluid of any one of claims 1 to 12 in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom.

26. Use of the fluid of any one of claims 1 to 12 in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.

27. Use of the kit of parts of any one of claims 13 to 24 in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom wherein the one part is introduced into the carbonate formation for the main treatment step and the other part for the preflush and/or postflush step.

28. Use of the kit of parts of any one claims 13 to 24 in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.

CLAIMS

1. A fluid suitable for treating carbonate formations containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), a corrosion inhibitor, and a surfactant, wherein the fluid is acidic.

2. The fluid of claim 1, wherein the amount of GLDA and/or MGDA is 5 to 30 wt% on the basis of the total weight of the fluid.

3. The fluid of claim 1 or claim 2, containing GLDA.

4. The fluid of any one of claims 1 to 3, wherein the corrosion inhibitor is present in an amount of 0.1-2 volume% on total fluid.

5. The fluid of any one of claims 1 to 4, wherein the corrosion inhibitor is selected from the group of amine compounds, quaternary ammonium compounds, and sulfur compounds.

6. The fluid of any one of claims 1 to 5, wherein the surfactant is present in an amount of 0.1-2 volume% on total fluid.

7. The fluid of any one of claims 1 to 6, wherein the surfactant is a nonionic or cationic surfactant.

8. The fluid of any one of claims 1 to 7, wherein the surfactant is selected from the group of quaternary ammonium compounds and derivatives thereof.

9. The fluid of any one of claims 1 to 8, in addition containing a biocide and/or a bactericide.

10. A kit of parts suitable for treating carbonate formations wherein one part contains an acidic fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA) and/or methylglycine N,N-diacetic acid or a salt thereof (MGDA), and a corrosion inhibitor, and the other part contains a fluid containing a surfactant, and, optionally, a mutual solvent.

11. The kit of parts of claim 10, wherein the amount of GLDA and/or MGDA is 5 to 30 wt% on the basis of the total weight of the fluid in the one part.

12. The kit of parts of claim 10 or claim 11, containing GLDA.

13. The kit of parts of any one of claims 10 to 12, wherein the corrosion inhibitor is present in an amount of 0.1-2 volume% on total fluid in the one part.

14. The kit of parts of any one of claims 10 to 13, wherein the corrosion inhibitor is selected from the group of amine compounds, quaternary ammonium compounds, and sulfur compounds.

15. The kit of parts of any one of claims 10 to 14, wherein the surfactant is present in an amount of 0.1-2 volume% on total fluid in the other part.

16. The kit of parts of any one of claims 10 to 15, wherein the surfactant is a nonionic or cationic surfactant.

17. The kit of parts of any one of claims 10 to 16, wherein the surfactant is selected from the group of quaternary ammonium compounds and derivatives thereof.

18. Use of the fluid of any one of claims 1 to 9 in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom, in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.

19. Use of the kit of parts of any one of claims 10 to 17 in treating a subterranean carbonate formation to increase the permeability thereof, remove small particles therefrom and/or remove inorganic scale therefrom wherein the one part is introduced into the carbonate formation for the main treatment step and the other part for the preflush and/or postflush step, in cleaning of the wellbore and/or descaling of the oil/gas production well and production equipment in the production of oil and/or gas from a subterranean carbonate formation.