US 20150000916A1

(19) **United States**

(12) **Patent Application Publication**

**Mahmoud et al.**

(10) **Pub. No.: US 2015/0000916 A1**

(43) **Pub. Date: Jan. 1, 2015**

(54) **ENHANCED OIL RECOVERY USING SEAWATER AND EDTA**

(71) Applicant: **KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS**, Dhahran (SA)

(72) Inventors: **Mohamed Ahmed Nasr El-Din Mahmoud**, Dhahran (SA); **HASAN SALMAN AL-HASHIM**, DHAHRAN (SA); **ABDULLAH SAAD SULTAN**, DHAHRAN (SA); **MOHAMMED ATTIA GADALLAH**, DHAHRAN (SA)

(21) Appl. No.: **13/932,986**

(22) Filed: **Jul. 1, 2013**

**Publication Classification**

(51) **Int. Cl.**
*E21B 43/20* (2006.01)

(52) **U.S. Cl.**
CPC ..... ***E21B 43/20*** (2013.01)
USPC ..... **166/305.1**

(57) **ABSTRACT**

The enhanced oil recovery using seawater and EDTA (ethylenediaminetetraacetic acid) is a method that uses injection of EDTA in seawater to enhance the recovery of oil from sandstone reservoirs. The EDTA may be introduced into seawater during the initial extraction of oil from the reservoir by seawater injection, or a solution of EDTA in seawater may be used to flush residual oil from the reservoir after the initial extraction by seawater injection. In either case, the EDTA is present in about 1.0 wt % to about 5.0 wt % of the seawater solution, and the solution has a pH of between 10.5 and 11.0.

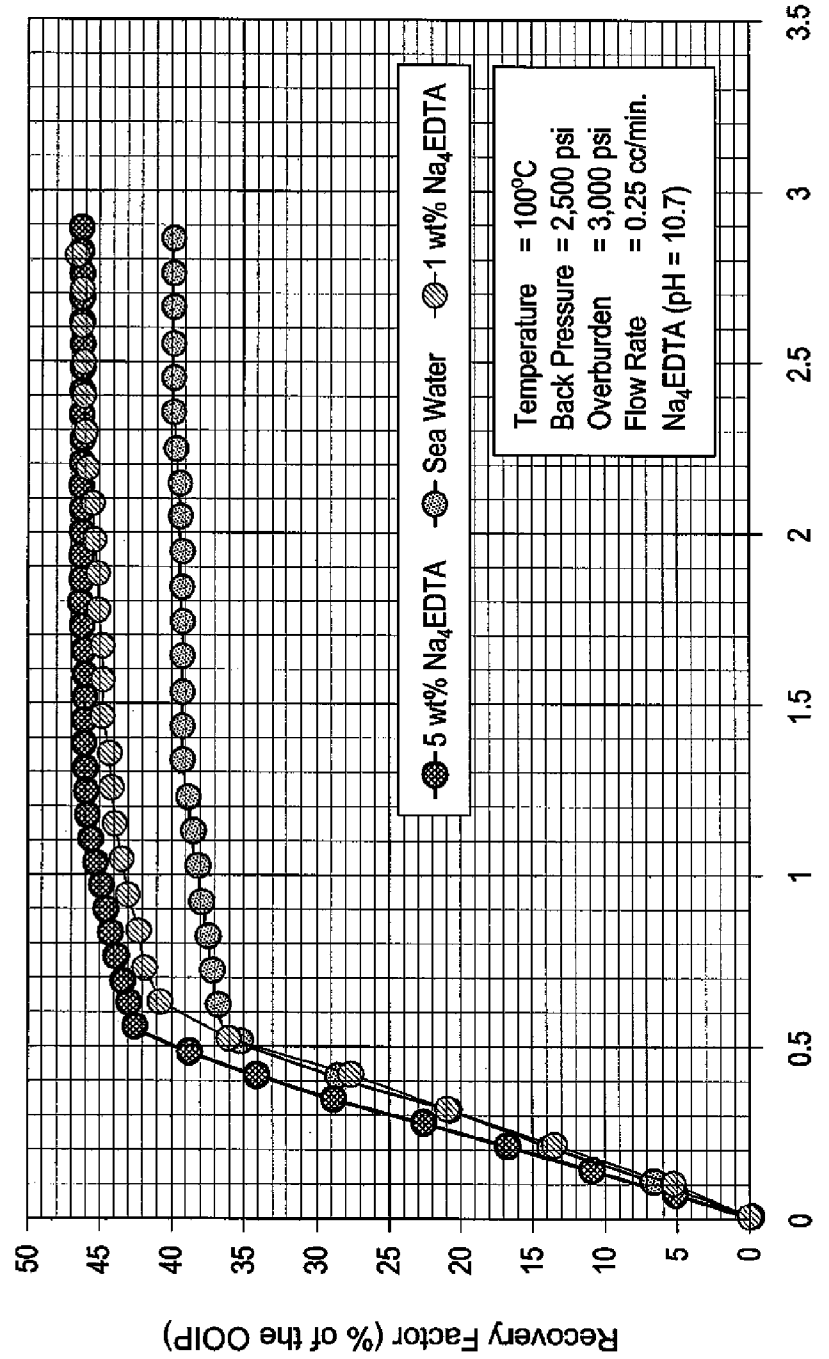
Recovery Factor (% of the OOIP)
0
5
10
15
20
25
30
35
40
45
50
0
0.5
1
1.5
2
2.5
3
3.5
PV Injected
5 wt% Na4EDTA
Sea Water
1 wt% Na4EDTA
Temperature = 100°C
Back Pressure = 2,500 psi
Overburden = 3,000 psi
Flow Rate = 0.25 cc/min.
Na4EDTA (pH = 10.7)

*Fig. 1*

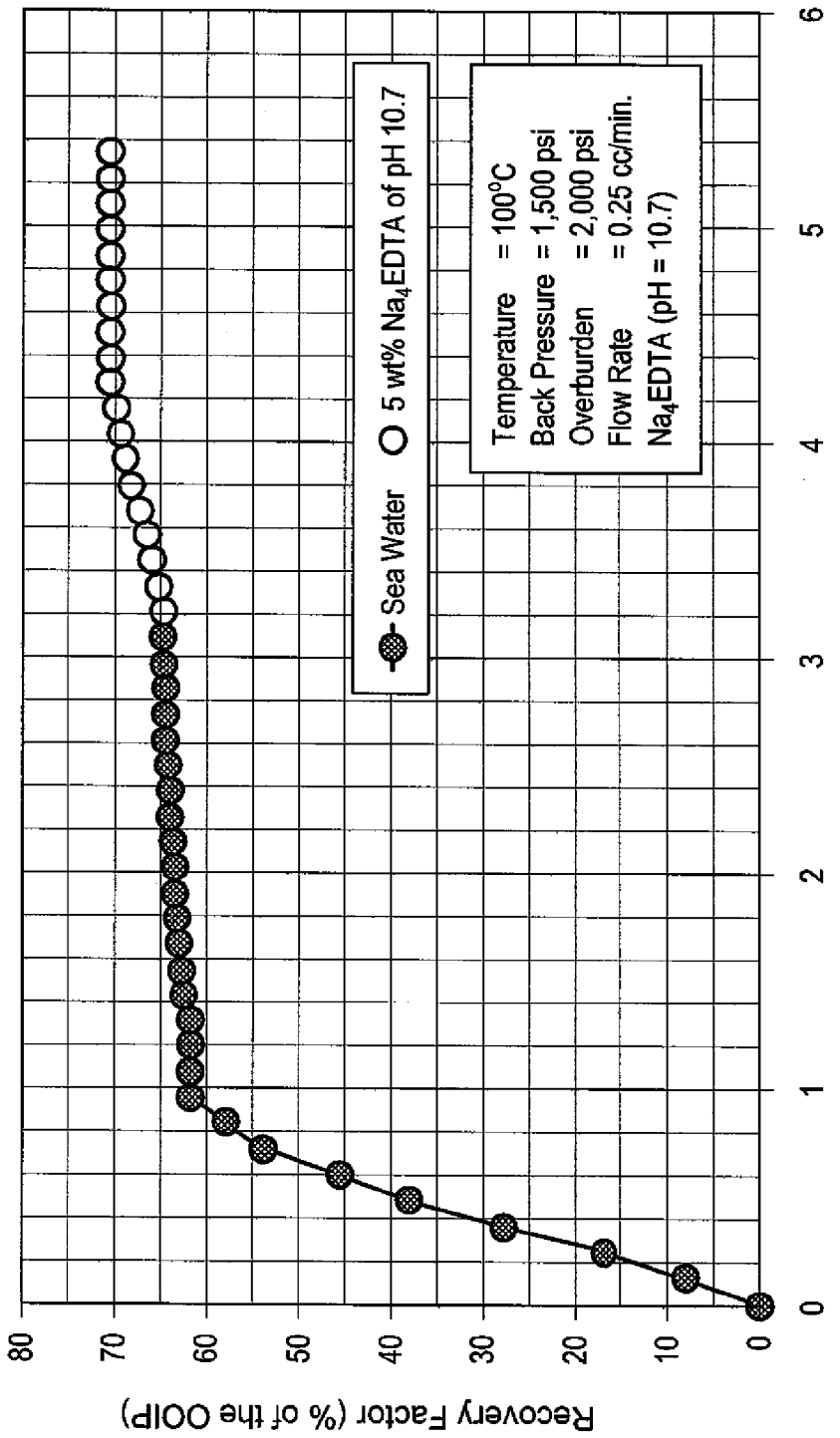
Recovery Factor (% of the OOIP)
0
10
20
30
40
50
60
70
80
PV Injected
0
1
2
3
4
5
6
Sea Water
5 wt% Na4EDTA of pH 10.7
Temperature = 100°C
Back Pressure = 1,500 psi
Overburden = 2,000 psi
Flow Rate = 0.25 cc/min.
Na4EDTA (pH = 10.7)

*Fig. 2*

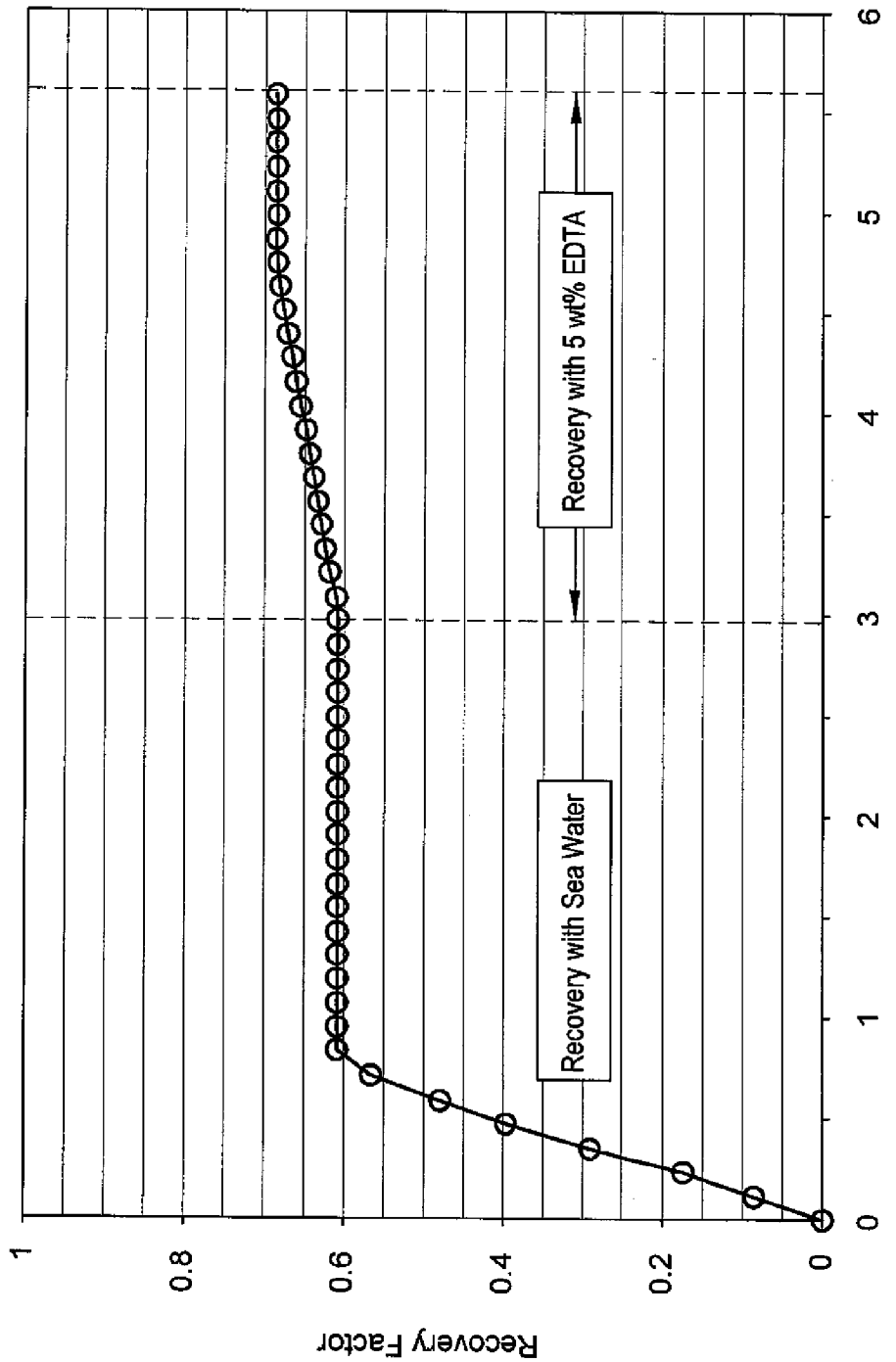
Recovery Factor
0
0.2
0.4
0.6
0.8
1
Injected Volume (PV)
0
1
2
3
4
5
6
Recovery with Sea Water
Recovery with 5 wt% EDTA

*Fig. 3*

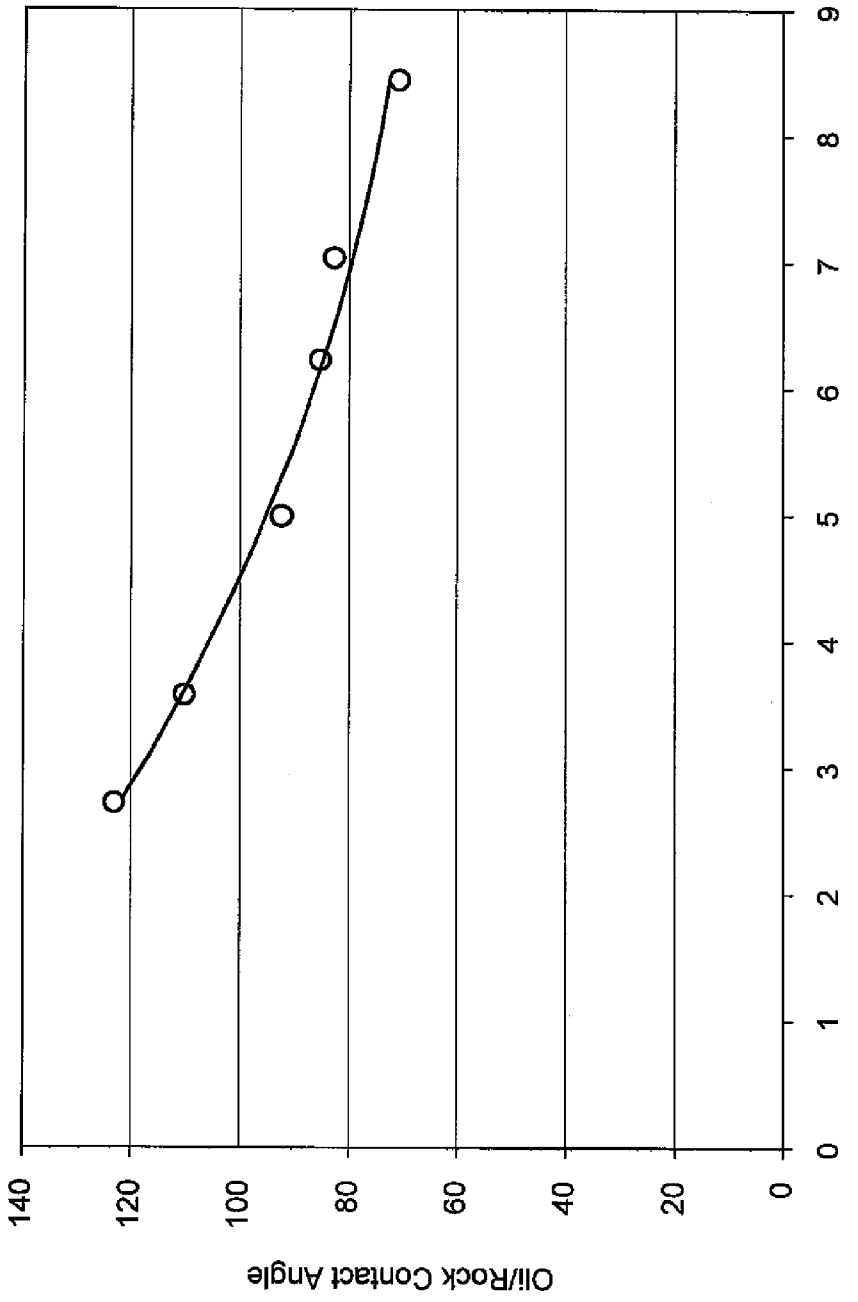
Oil/Rock Contact Angle
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
pH of the Solution

*Fig. 4*

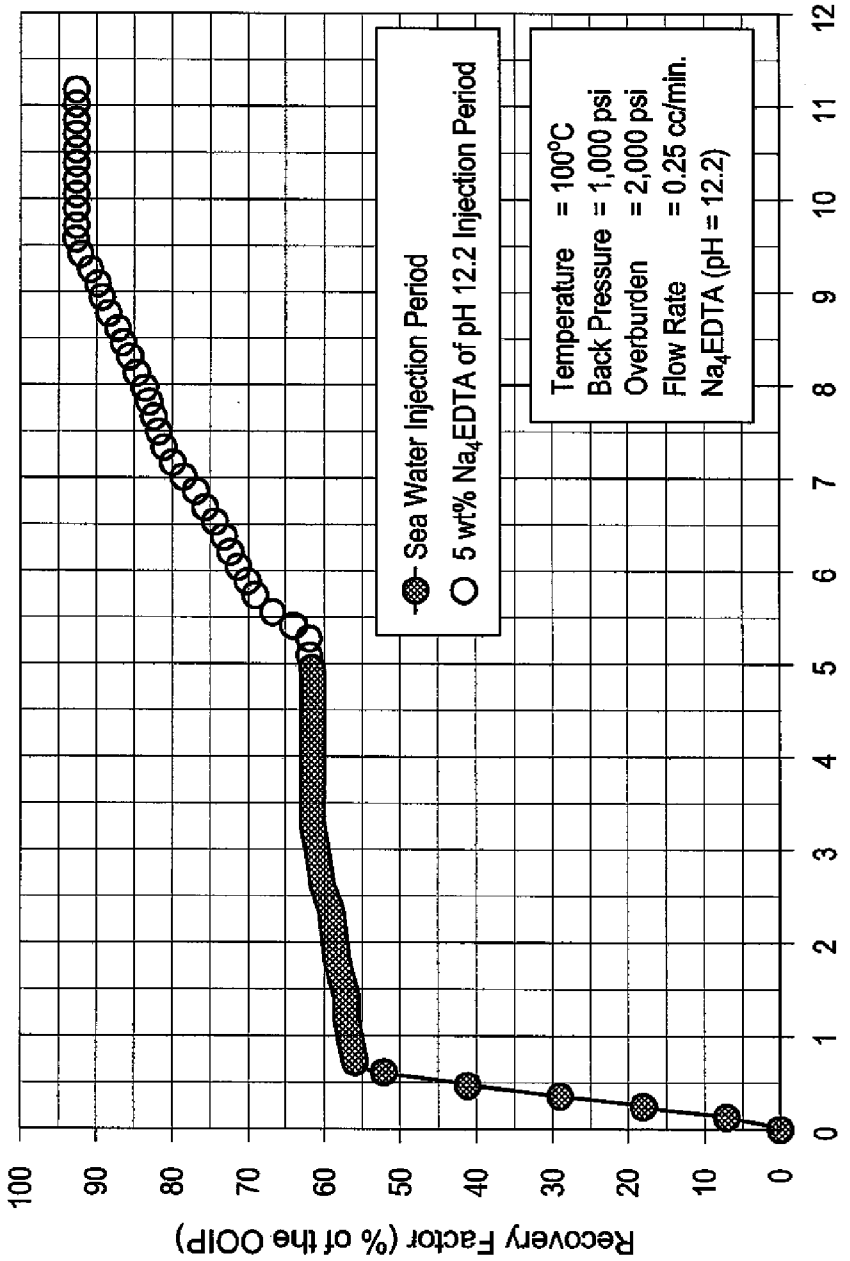
Recovery Factor (% of the OOIP)
PV Injected
Sea Water Injection Period
5 wt% $Na_4EDTA$ of pH 12.2 Injection Period
Temperature = 100°C
Back Pressure = 1,000 psi
Overburden = 2,000 psi
Flow Rate = 0.25 cc/min.
$Na_4EDTA$ (pH = 12.2)

*Fig. 5*

# ENHANCED OIL RECOVERY USING SEAWATER AND EDTA

## BACKGROUND OF THE INVENTION

**[0001]** 1. Field of the Invention

**[0002]** The present invention relates to the enhancement of oil recovery in oil reservoirs, and particularly to enhanced oil recovery using seawater and EDTA (ethylenediaminetetraacetic acid) that enhances oil recovery in seawater injection systems by adding EDTA to the seawater.

**[0003]** 2. Description of the Related Art

**[0004]** One method of enhancing oil recovery from oil reservoirs involves injecting water into the reservoir. In many areas, seawater provides the most economical and abundant source of water. However, seawater contains sulfates, which can precipitate calcium sulfate and other insoluble or slightly soluble sulfates from minerals in the formation brine of sandstone reservoirs. These sulfates develop into formations of scale, which constrict the injection and pumping equipment, reducing the recovery of oil and requiring shutdown to clean or replace machinery. Various attempts are being used to improve oil recovery in reservoirs that use seawater injection, e.g., by diluting the seawater with fresh water to form "smart water" or low salinity water. Nevertheless, there is still a need for cost effective methods of enhancing oil recovery from oil reservoirs using seawater injection systems, particularly in regions where fresh water is a scarce and valuable commodity.

**[0005]** Thus, enhanced oil recovery using seawater and EDTA solving the aforementioned problems is desired.

## SUMMARY OF THE INVENTION

**[0006]** The enhanced oil recovery using seawater and EDTA (ethylenediaminetetraacetic acid) is a method that uses injection of EDTA in seawater to enhance the recovery of oil from sandstone reservoirs. The EDTA may be introduced into seawater during the initial extraction of oil from the reservoir by seawater injection, or a solution of EDTA in seawater may be used to flush residual oil from the reservoir after the initial extraction by seawater injection. In either case, the EDTA is present in about 1.0 wt % to about 5.0 wt % of the seawater solution, and the solution has a pH of between 10.5 and 11.0.

**[0007]** These and other features of the present invention will become readily apparent upon further review of the following specification.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0008]** FIG. **1** is a graph showing a comparison of the oil recovery factor for core flooding experiments performed at a temperature of 100° C. at a rate of 0.25 mL/min in Berea sandstone cores between a control seawater sample, a solution of seawater with 1.0 wt % ethylenediaminetetraacetic acid (EDTA), and a solution of seawater with 5.0 wt % EDTA, each of the examples showing initial extraction of oil from the sandstone cores.

**[0009]** FIG. **2** is a graph showing the oil recovery factor for core flooding experiments performed at a temperature of 100° C. at a rate of 0.25 mL/min in 3-inch Berea sandstone cores by a solution of seawater with 5.0 wt % EDTA, showing the recovery of residual oil after initial seawater flooding.

**[0010]** FIG. **3** is a graph showing the oil recovery factor for core flooding experiments performed at a temperature of 100° C. at a rate of 0.25 mL/min in 5-inch Berea sandstone cores by a solution of seawater with 5.0 wt % EDTA, showing the recovery of residual oil after initial seawater flooding.

**[0011]** FIG. **4** is a graph showing the oil/rock contact angle as a function of pH of a core flooding solution.

**[0012]** FIG. **5** is a graph showing the oil recovery factor for core flooding experiments performed at a temperature of 100° C. at a rate of 0.25 mL/min in Berea sandstone cores by a solution of seawater with 5.0 wt % EDTA and with a pH of 12.2, showing the recovery of residual oil after initial seawater flooding.

**[0013]** Similar reference characters denote corresponding features consistently throughout the attached drawings.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0014]** The enhanced oil recovery using seawater and EDTA (ethylenediaminetetraacetic acid) is a method that uses injection of EDTA in seawater to enhance the recovery of oil from sandstone reservoirs. The EDTA may be introduced into seawater during the initial extraction of oil from the reservoir by seawater injection, or a solution of EDTA in seawater may be used to flush residual oil from the reservoir after the initial extraction by seawater injection. In either case, the EDTA is present in about 1.0 wt % to about 5.0 wt % of the seawater solution, and the solution has a pH of between 10.5 and 11.0. The method is demonstrated by the following experiments.

**[0015]** As a control, untreated seawater with a high sulfate content was injected into a Berea sandstone core, which was initially saturated with a composition that simulates a typical formation brine. The contents of the seawater and the connate water (water that is trapped in the pores of sedimentary rocks, i.e., formation brine) are shown below in Table 1. Calcium sulfate in mineral form was found to have precipitated in the sandstone core, as expected.

TABLE 1

Composition of Seawater and Formation Brine (Connate Water)

| Ions | Connate Water (ppm) | Seawater (ppm) |
|---|---|---|
| Sodium | 59,491 | 18,300 |
| Calcium | 19,040 | 650 |
| Magnesium | 2,439 | 2,110 |
| Sulfate | 350 | 4,290 |
| Chloride | 132,060 | 32,200 |
| Bicarbonate | 354 | 120 |
| TDS | 213,734 | 57,670 |

**[0016]** Core flooding experiments were performed using Berea sandstone cores, each core having a diameter of 1.5 inches and a length of either 3 or 6 inches. The permeability of the cores was each approximately 100 mD, and porosity was approximately 18%. All the experiments were performed at 100° C. Formation brine (i.e., connate water) having the properties shown above in Table 1 was injected through the cores, and then oil was injected to stabilize the initial water saturation $S_{wi}$ under a back pressure of 2,000 psi. The difference between the overburden pressure and the injection pressure (i.e., the effective stress) was kept constant at 500 psi. The flow rate was 0.25 mL/min through the different flooding stages. Seawater was injected to recover the oil from the three and six inches core samples.

**[0017]** Core flooding experiments were then performed with a chelating fluid formed from a solution of seawater

having the composition shown in Table 1 and 1.0 wt % ethylenediaminetetraacetic acid (EDTA, in the form of the sodium salt, $Na_4EDTA$) added to the seawater, and then a solution of 5 wt % EDTA in seawater to test the effect of the concentration of EDTA. The EDTA was used both to recover residual oil after seawater flooding, and to enhance the recovery of oil during the initial seawater flooding. The pH values of the different flooding fluids are shown in Table 2.

TABLE 2

pH Values of Different Flooding Solutions

| Solution | pH |
|---|---|
| Seawater | 7.50 |
| 1.0 wt % EDTA + Seawater | 10.5 |
| 5.0 wt % EDTA + Seawater | 11 |

**[0018]** FIG. **1** shows the recovery of oil from the core flooding experiments using three different fluids at 100° C. and 0.25 mL/min for the recovery of oil during the initial flooding of the cores. The recovery factor from the control seawater was 40%, and the recovery factor from the 1.0 wt % EDTA solution was 46%. The increase in the recovery from 40 to 46% that was achieved by the addition of EDTA was due to the cation exchange between the rock surface and the solution, and also the pH increase by 2.35 units, from the seawater value of 7.5 to 9.85 (for the EDTA solution). Increasing the pH reduces the interfacial tension (IFT) of the solution. Adding EDTA at a concentration of 5.0 wt % gave a 47% recovery. This 1% increase in recovery over the 1.0 wt % solution is due to the increase in chelation, which increased the viscosity of the solution. This effect is detailed below in Table 3. Increasing the solution viscosity will control the mobility of the injected fluid, and this mobility control increased the recovery by 1%.

TABLE 3

Viscosity and Density of 5.0 wt % EDTA Solution Prepared in De-ionized Water at 70° F.

| Calcium Concentration (ppm) | Viscosity (cP) | Density (g/mL) |
|---|---|---|
| 0 | 1.45 | 1.101 |
| 5000 | 1.64 | 1.115 |
| 10000 | 1.98 | 1.134 |
| 20000 | 2.14 | 1.187 |
| 30000 | 2.67 | 1.221 |

**[0019]** FIG. **2** shows the recovery of oil from the core flooding experiments using first, initial recovery of oil by seawater flooding, followed by second, recovery of residual oil from the core by the 5.0 wt % EDTA solution in seawater at 100° C. and 0.25 mL/min in the three-inch long cores. Seawater alone was able to recover 54% of the initial oil, and the EDTA solution recovered an additional 7% of the residual oil. The same experiment was repeated using the six-inch long cores, and the recovery increased almost by the same percentage, as shown in FIG. **3**.

**[0020]** Table 4 below shows the interfacial tension (IFT) of Arabian light oil measured as a function of pH. Increasing the solution pH decreases the IFT between oil and rock. In the present method, the pH of the solution is 11. By utilizing a high pH solution, oil recovery is enhanced by a decrease in the IFT. Additionally, it was found that the contact angle was greatly affected by the pH of the flooding fluid, as illustrated in FIG. **4**. Increasing the pH of the solution to 11 can decrease the contact angle to 70°, which, in terms of wettability, is a water-wet state. The high pH (of about 11) of the present EDTA solutions aids in changing the wettability to more water-wet and reduces the IFT, thus allowing for greater oil recovery.

TABLE 4

IFT of Arabian Light Oil at Varying pH Values

| pH | IFT (N/m) |
|---|---|
| 2 | 15.8 |
| 3 | 17 |
| 4 | 20.2 |
| 4.5 | 17.8 |
| 5.1 | 20 |
| 7 | 13.9 |
| 9.21 | 5.4 |
| 10 | 5.2 |
| 13 | 0.1 |

**[0021]** It is thought that the addition of EDTA acted in a manner similar to low salinity water flooding, forcing the rock to release cations to replace the cation shortage in the flooding solution, thus changing the wettability to a greater water-wet state. Further, the EDTA acted as a surfactant, since it contains four carboxylic groups, thus reducing the interfacial tension of the seawater. Additionally, the viscosity of the EDTA rises when it chelates cations from the solution, and this increases the viscosity of seawater and aids in controlling the mobility of injected water. Importantly, the EDTA leaches all calcium in the solution, thus eliminating the possibility of calcium sulfate precipitation and maintaining the injectivity in the reservoir at a constant level.

**[0022]** FIG. **5** shows the oil recovery factor for core flooding experiments performed at a temperature of 100° C. at a rate of 0.25 mL/min in Berea sandstone cores by a solution of seawater with 5.0 wt % EDTA and with an increased pH of 12.2, showing the recovery of residual oil after initial seawater flooding. Recovery of 29% of the original oil in place and almost 75% of the residual oil after sea water flooding was attained by injecting 5 PV of EDTA (pH 12.2). The increase in oil recovery compared to the previous cases can be attributed to the high pH value of the EDTA in this case.

**[0023]** It is to be understood that the present invention is not limited to the embodiments described above, but encompasses any and all embodiments within the scope of the following claims.

**1**. A method for enhanced oil recovery from a sandstone oil reservoir, comprising the step of injecting a solution consisting of an effective amount of ethylenediaminetetraacetic acid (EDTA) in seawater into the reservoir for chelating cations in the formation brine to prevent scaling caused by mixing the seawater with the formation brine.

**2**. The method for enhanced oil recovery according to claim **1**, wherein the effective amount of EDTA comprises about 1 wt % EDTA.

**3**. The method for enhanced oil recovery according to claim **1**, wherein the effective amount of EDTA comprises about 5 wt % EDTA.

**4**. The method for enhanced oil recovery according to claim **1**, wherein the solution has a pH of about 11.

**5**. The method for enhanced oil recovery according to claim **1**, wherein the step of injecting the solution comprises injecting the solution for the initial recovery of oil from the reservoir.

**6**. The method for enhanced oil recovery according to claim **1**, wherein the step of injecting the solution comprises injecting the solution containing the EDTA after the initial recovery of oil from the reservoir by seawater flooding in order to recover residual oil from the reservoir.

**7**. A method for enhanced oil recovery from a sandstone oil reservoir, comprising the step of injecting a solution consisting of between 1 wt % and 5 wt % ethylenediaminetetraacetic acid (EDTA) in seawater into the reservoir, the solution having a pH of about 11.

**8**. The method for enhanced oil recovery according to claim **7**, wherein the solution comprises 1 wt % EDTA.

**9**. The method for enhanced oil recovery according to claim **7**, wherein the solution comprises 5 wt % EDTA.

**10**. The method for enhanced oil recovery according to claim **7**, wherein the step of injecting the solution comprises injecting the solution for the initial recovery of oil from the reservoir.

**11**. The method for enhanced oil recovery according to claim **7**, wherein the step of injecting the solution comprises injecting the solution containing the EDTA after the initial recovery of oil from the reservoir by seawater flooding in order to recover residual oil from the reservoir.

* * * * *