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(54) **METHOD FOR ENHANCED OIL RECOVERY BY IN SITU CARBON DIOXIDE GENERATION**

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(57) **ABSTRACT**

The method for enhanced oil recovery by in situ carbon dioxide generation utilizes a chelating fluid injected into an oil reservoir through a fluid injection system. The chelating fluid is a low pH solution of a polyamino carboxylic acid chelating agent. The polyamino carboxylic acid chelating agent may have a concentration of about 5 wt %. The polyamino carboxylic acid chelating agent is preferably either an aqueous solution of H_2Na_2-ethylenediaminetetraacetic acid (pH 4.5), H_3-hydroxyethyl ethylenediamine triacetic acid (pH 2.5), or an aqueous solution of H_2NaHEDTA (pH 4). The injection of the chelating fluid may be preceded by flooding the core with seawater, and is followed by injection of either to seawater, a high pH chelating agent, or low salinity water to ensure maximal extraction of oil from the reservoir. The method is particularly for use in formations where the core of the reservoir has a carbonate rock matrix.

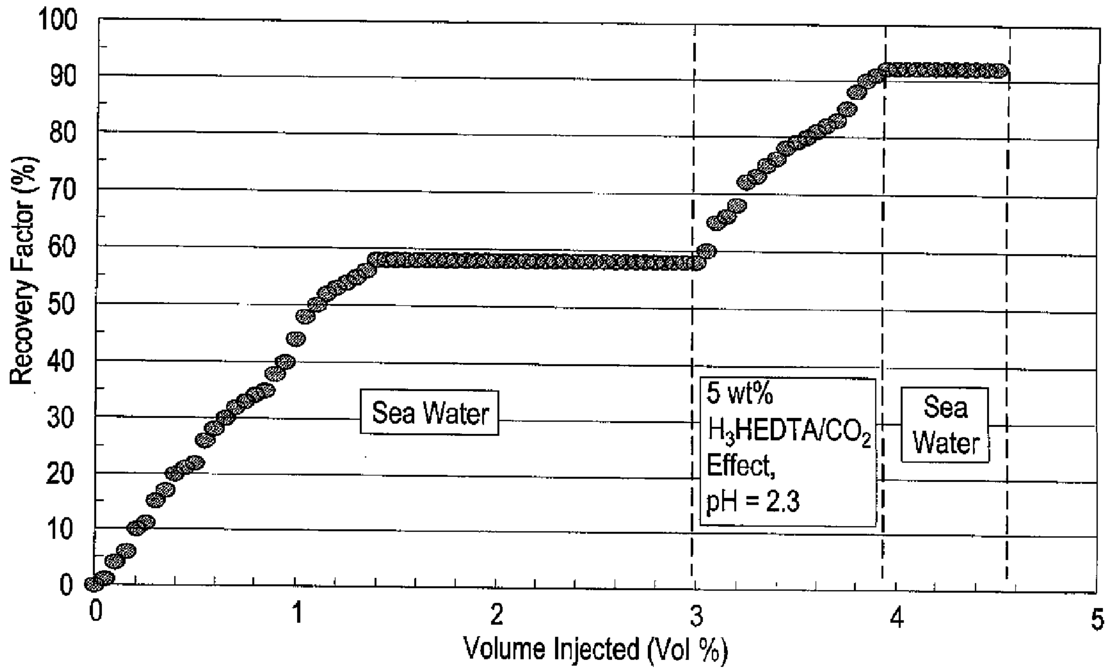
Recovery Factor (%)
Volume Injected (Vol %)
Sea Water
5 wt%
H_3HEDTA/CO_2
Effect,
pH = 2.3
Sea
Water

Fig. 1

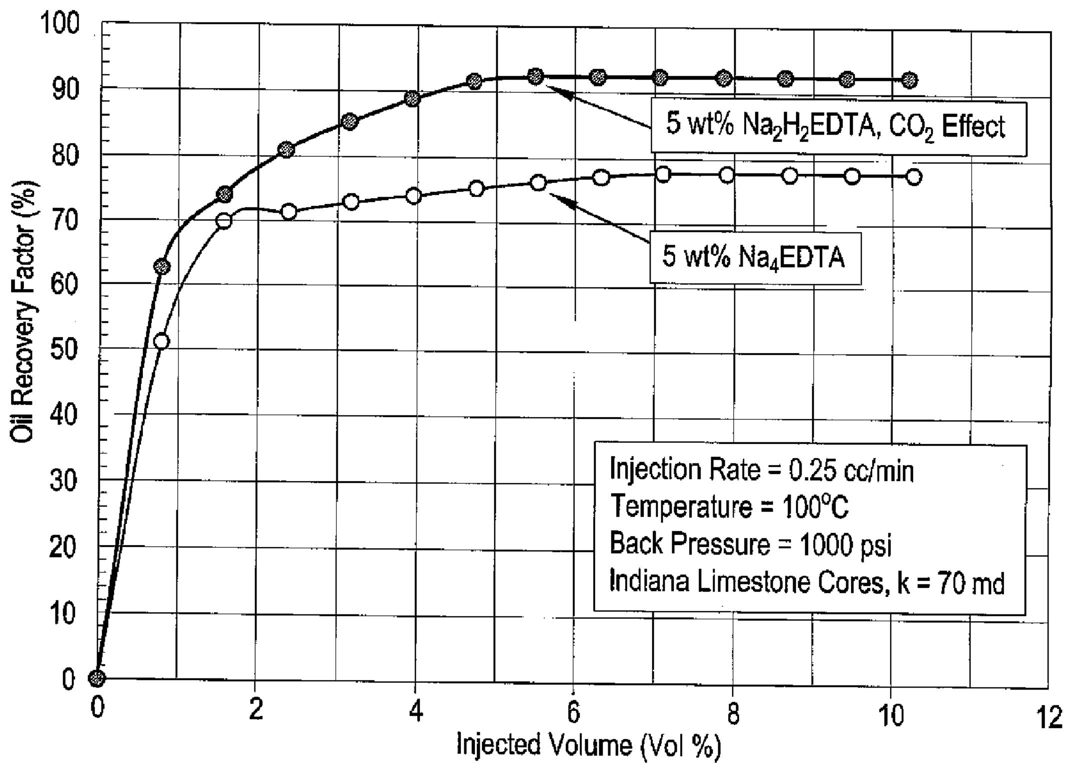
Oil Recovery Factor (%)
Injected Volume (Vol %)
5 wt% Na_2H_2EDTA, CO_2 Effect
5 wt% Na_4EDTA
Injection Rate = 0.25 cc/min
Temperature = 100°C
Back Pressure = 1000 psi
Indiana Limestone Cores, k = 70 md

Fig. 2

METHOD FOR ENHANCED OIL RECOVERY BY IN SITU CARBON DIOXIDE GENERATION

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to oil recovery operations, and particularly to a method for enhanced oil recovery by in situ carbon dioxide generation.

[0003] 2. Description of the Related Art

[0004] Enhanced oil recovery (EOR) is a technique for increasing the amount of crude oil that can be extracted from an oil field. Gas injection, or miscible flooding, is presently the most commonly used approach in enhanced oil recovery. Miscible flooding is a general term for injection processes that introduce miscible gases into the reservoir. A miscible displacement process maintains reservoir pressure and improves oil displacement because the interfacial tension between oil and water is reduced by removal of the interface between the two interacting fluids. This allows for total displacement efficiency. Gases used for miscible flooding include carbon dioxide, natural gas, and nitrogen.

[0005] The fluid most commonly used for miscible displacement is carbon dioxide because of its ability to reduce the oil viscosity, coupled with its relatively low cost, particularly when compared to the more costly liquefied petroleum gas. Oil displacement by carbon dioxide injection relies on the phase behavior of the mixtures of the gas and the crude, which is strongly dependent on reservoir temperature, pressure and crude oil composition. However, carbon dioxide flooding processes frequently experience viscous fingering and gravity override problems because of the very low density and viscosity of the carbon dioxide when compared to those of crude oil. As a result, sweep efficiency is decreased, compared with more dense and/or viscous fluids, and significant amounts of oil are left behind.

[0006] Enhanced oil recovery using carbon dioxide flooding typically requires the addition of mobility control agents to prevent the carbon dioxide from migrating to the upper part of the reservoir, particularly in thick reservoirs. This migration leaves the lower part of the reservoir unswept from oil. The need for mobility control during carbon dioxide flooding has motivated research into foam processes, which involve the injection of carbon dioxide together with an aqueous solution of a carbon dioxide-foaming agent.

[0007] Carbon dioxide has a very low viscosity compared with both oil and water. However, when carbon dioxide is in a dispersed phase, as in a foam, its apparent viscosity is greatly increased and its mobility is improved. In the past, it has been generally assumed that foam would preferentially impede flow in the higher permeability layers or fractures in the reservoir that had already been swept of their oil. In such a process, the unswept parts of the reservoir would remain at least as accessible and available to have their content displaced and forced into the production wells. The overall success of the foaming process depends on foam concentration, compatibility with the reservoir rock, stability in solution over long periods of time, and thermal stability. Surfactants have been used as foaming agents, but surfactants suffer from thermal stability problems, typically being unstable at temperatures exceeding 100° C.

[0008] Due to the problems involved in the injection of carbon dioxide into the reservoir, there has been significant interest in generating carbon dioxide in situ. One prior technique used ammonium carbamate to produce a significant amount of carbon dioxide when the temperature rose to 85° C. Using ammonium carbamate in a one-dimensional sand pack column resulted in the production of carbon dioxide in the column at temperatures between 80° C. and 90° C., along with decreases in oil viscosity. The additional injection of a 0.5 vol % of 3% ammonium carbamate solution with a polymer/surfactant chemical flood improved crude oil recovery by 9.7% original oil in place (OOIP), compared to a polymer/surfactant chemical flood without carbamate. However, there was negligible oil recovery in experiments without the presence of surfactants when using light oils, decane and Arrow crude oil. Overall, oil recovery by this process was very low, with only 43% residual oil recovery after surfactant/polymer injection.

[0009] Another method for generating carbon dioxide in situ involves the injection of sodium carbonate with hydrochloric acid (HCl) into the formation, followed by reaction over a 24 hour period. However, HCl is very corrosive. Thus, costly corrosion inhibitors need to be added. Further, the corrosion inhibitor may reverse the wettability of the formation, thus requiring water wetting agents to also be added. A further problem is that the HCl cannot be used in carbonate reservoirs due to the reaction between the HCl with the carbonate.

[0010] Thus, a method for enhanced oil recovery by in situ carbon dioxide generation solving the aforementioned problems is desired.

SUMMARY OF THE INVENTION

[0011] The method for enhanced oil recovery by in situ carbon dioxide generation utilizes a chelating fluid injected into an oil reservoir through a fluid injection system. The chelating fluid is a low pH solution of a polyamino carboxylic acid chelating agent. The polyamino carboxylic acid chelating agent may have a concentration of about 5 wt %. The polyamino carboxylic acid chelating agent is preferably either an aqueous solution of H_2Na_2-ethylenediaminetetraacetic acid (pH 4.5), H_3-hydroxyethyl ethylenediamine triacetic acid (pH 2.5), or an aqueous solution of $H_2NaHEDTA$ (pH 4). The chelating fluid may be injected at a rate of approximately 0.25 mL/min. The injection of the chelating fluid may be preceded by flooding the core with seawater, and is followed by injection of either seawater, a high pH chelating agent, or low salinity water to ensure maximal extraction of oil from the reservoir. The method is particularly for use in formations where the core of the reservoir has a carbonate rock matrix, since the carbon dioxide generation results from acidic liberation of carbon dioxide from the carbonate rock.

[0012] These and other features of the present invention will become readily apparent upon further review of the following specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a graph showing oil recovery using a low pH solution of H_3-hydroxyethyl ethylenediaminetriacetic acid for in situ carbon dioxide generation for enhanced oil recovery according to the present invention.

[0014] FIG. **2** is a graph showing oil recovery using a low pH solution of H_2Na_2-ethylenediaminetetraacetic acid for in situ carbon dioxide generation for enhanced oil recovery according to the present invention.

[0015] Similar reference characters denote corresponding features consistently throughout the attached drawings.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The method for enhanced oil recovery by in situ carbon dioxide generation utilizes a chelating fluid injected into an oil reservoir through a fluid injection system. The chelating fluid is a low pH solution of a polyamino carboxylic acid chelating agent. The polyamino carboxylic acid chelating agent may have a concentration of about 5 wt %. The polyamino carboxylic acid chelating agent is preferably either an aqueous solution of H_2Na_2-ethylenediaminetetraacetic acid (pH 4.5), H_3-hydroxyethyl ethylenediamine triacetic acid (pH 2.5), or an aqueous solution of $H_2NaHEDTA$ (pH 4). The chelating fluid may be injected at a rate of approximately 0.25 mL/min. The injection of the chelating fluid may be preceded by flooding the core with seawater, and is followed by injection of either seawater, a high pH chelating agent, or low salinity water to ensure maximal extraction of oil from the reservoir. The method is particularly for use in formations where the core of the reservoir has a carbonate rock (chalk and limestone) matrix (referred to as a carbonate reservoir), since the carbon dioxide generation results from acidic liberation of carbon dioxide from the carbonate rock.

[0017] First, the low pH chelating agent will react with the carbonate rock and produce CO_2 that will diffuse to the oil and increases oil mobility so that more oil will be produced. The acidic part of the chelating agent that includes the hydrogen ions will produce the carbon dioxide from the carbonate rock formations. Then, the high pH chelating agent, seawater, or low salinity water will displace the low pH chelating agent and the CO_2. The method does not require the use of surfactants or other additives, and eliminates the problem of gravity override. Only a small volume of the aqueous solution of the low pH chelating agent is needed to generate the carbon dioxide, and when the concentration is limited to about 5%, no additives are required to prevent corrosion.

[0018] In order to demonstrate the method, core flooding experiments were performed using Indiana limestone cores, each having a length of 5 inches, and a diameter of 1.5 inches. H_2Na_2-ethylenediaminetetraacetic acid (H_2Na_2-EDTA) with a pH of 4.5 and H_3-hydroxyethyl ethylenediaminetriacetic acid (H_3-HEDTA) with a pH of 2.5 were each tested as dual chelating agents and in situ carbon dioxide generating agents. Each agent was dissolved in water, and the solution was injected. The injection was followed by continuous injection of seawater or continuous injection of a high pH chelating agent.

[0019] FIG. **1** shows the effect of carbon dioxide generated from the use of the H_3-HEDTA chelating agent at 5 wt % concentration and a pH of 2.5. The experiment was performed at 100° C. and at an injection rate of 0.25 mL/min. The core was first flooded by seawater, which recovered 58% of the initial oil from the core (i.e., 42% of the oil remained inside the core). A single pore volume of 5 wt % H_3-HEDTA was injected into the core, and it recovered 34% oil from the oil in place or, in other words, 81% of the residual oil. One pore volume of 5 wt % H_3-HEDTA produced enough carbon dioxide to recover more than 80% of the residual oil.

[0020] FIG. **2** shows the results of a similar core flooding experiment with H_2Na_2-EDTA at a pH of 4.5. Continuous injection of this solution increased the oil recovery more than 90% from the initial oil in place. H_2Na_2-EDTA did not produce as much carbon dioxide as H_3-HEDTA, thus larger volumes of the H_2Na_2-EDTA solution were required to recover an equivalent amount of oil. Further, in FIG. **2**, H_2Na_2-EDTA was tested against a 5 wt % conventional chelating agent, Na_4-EDTA, with the H_2Na_2-EDTA solution clearly outperforming the conventional chelating solution of Na_4-EDTA.

[0021] 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.

We claim:

1. A method for enhanced oil recovery from a carbonate reservoir, comprising the steps of:

injecting an aqueous solution of a low pH polyamino carboxylic acid chelating agent into the core of the reservoir to generate the production of carbon dioxide in situ; and

subsequently injecting a fluid into the core to complete recovery of oil from the reservoir, the fluid being selected from the group consisting of seawater, a solution of a high pH chelating agent, and a low salinity fluid.

2. The method for enhanced oil recovery according to claim **1**, wherein the aqueous solution comprises an aqueous solution of H_2Na_2-ethylenediaminetetraacetic acid having a pH of about 4.5.

3. The method for enhanced oil recovery according to claim **1**, wherein the aqueous solution comprises an aqueous solution of H_3-hydroxyethyl ethylenediamine triacetic acid having a pH of about 2.5.

4. The method for enhanced oil recovery according to claim **1**, wherein the aqueous solution comprises an aqueous solution of $H_2NaHEDTA$ having a pH of about 4.

5. The method for enhanced oil recovery according to claim **1**, wherein the aqueous solution has a concentration of about 5 wt %.

6. The method for enhanced oil recovery according to claim **1**, wherein said step of injecting the aqueous solution further comprises injecting the aqueous solution of a low pH polyamino carboxylic acid chelating agent at a temperature of about 100° C. and at an injection rate of 0.25 mL/min.

7. The method for enhanced oil recovery according to claim **1**, further comprising the step of flooding the core of the carbonate reservoir with seawater prior to said step of injecting the aqueous solution of the low pH polyamino carboxylic acid chelating agent into the core.

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