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In-situ Generation of CO_2 to Eliminate the Problem of Gravity Override in EOR of Carbonate Reservoirs

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Abstract

Carbon dioxide (CO_2) injection into hydrocarbon reservoir is reported by many researchers to be one of the best enhanced oil recovery techniques. CO_2 for enhanced oil recovery has favorable characteristics such as miscibility between CO_2 and oil under most reservoir conditions, intermediate component extraction and heavy oil viscosity reduction which is named CO_2 flooding process. As a result of viscous fingering and gravity override, sweep efficiency decreases and significant amounts of oil are left behind during CO_2 flooding. Foaming was used to increase the injected CO_2 viscosity but a lot of problems were encountered with the foaming agents such as stability and thermal stability, etc.

In this paper we will introduce a new method of generating CO_2 *in-situ* in carbonate reservoirs during enhanced oil recovery processes. The generation process includes the injection of low pH HEDTA or EDTA chelating agents followed by sea water, high pH chelating agents, or low salinity water. First the low pH chelating agent will react with the carbonate rock and produce CO_2 that will diffuse to the oil and increases the oil mobility and in turn more oil will be produced. The chelating agents used are H_2Na_2EDTA (pH = 4.5), H_3HEDTA (pH = 2.5), and $H_2NaHEDTA$ (pH = 4). The acid part which contains the hydrogen ions will attack the carbonate rock and produce CO_2 that will increase the oil recovery, and then the high pH chelating agent or even sea water can be used to displace the low pH chelating agent and CO_2.

The experimental results showed that about 90% of the oil in place was recovered from the carbonate cores without using of surfactants or any other additives. The new method will eliminate the problem of gravity override which is the main problem of CO_2 EOR. The chelating agent can be placed in the whole reservoir by introducing a low reactive form of these chemicals or by encapsulating these chemicals to start reacting with the reservoir after the placement is complete. The reaction of the encapsulated chemicals can be triggered by temperature or any other triggering mechanism.

Keywords: Gravity; Chelating agents; CO_2 injection

Introduction

Enhanced oil recovery using CO_2 flooding required a mobility control agent otherwise CO_2 will migrate to the upper part of the reservoir especially for thick reservoirs and the lower part of the reservoir will remain unswept from oil. CO_2 injection into hydrocarbon reservoir is reported by many researchers to be one of the best enhanced oil recoveries [31-3].

CO_2 for enhanced oil recovery has favorable characteristics such as miscibility between CO_2 and oil under most reservoir conditions, intermediate component extraction and heavy oil viscosity reduction. However, CO_2 flooding processes frequently experience viscous fingering and gravity override problems because of the very low CO_2 density and viscosity when compared to the crude oil [4]. As a result, sweep efficiency decreases and significant amounts of oil are left behind [5-7].

The need for mobility control during CO_2 flooding motivated a lot of investigators to look for foam processes, which involves the injection of CO_2 together with an aqueous solution of a CO_2 -foaming agent [5]. CO_2 has a very low viscosity in comparison to oil and water. However, when CO_2 is a dispersed phase, as in foam, its apparent viscosity is greatly increased and its mobility will be improved [8]. From the time when the use of foam in reservoirs was first proposed in a patent by Bond and Holbrook which is reported by [10], it was usually implicitly assumed without specific mention, that foam would preferentially impede flow in the higher permeability layers or fractures in the reservoir that had already been swept of their oil [11]. Also it was assumed without evidence that 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 foaming process success depends on foam concentration, compatibility with the reservoir rock, stability in solution for long time, and thermal stability. Surfactants have been used as foaming agents but the main problem with surfactants is the thermal stability, they cannot stand for temperatures more than 100°C.

Gravity Override during CO_2 Injection

Gravity override is a phenomenon of multiphase flow in petroleum reservoirs [12]. Less dense fluid flows on the top of the reservoir part and moredenser fluid flows at the bottom. For example, in a steam flood, steam flows on the top and condensed liquid flows at the bottom of the zone. Gravity override ends up with sweep inhomogeneities.

During any CO_2 injection process usually the recovery can be increased by an earlier development of miscibility with the reservoir fluid and alleviation of CO_2 override. Gravity override phenomena will accelerate the breakthrough of the injected gas and resulted in bypassing the trapped oil in the reservoir and poor sweep efficiency. In relatively homogeneous formations gravity override become more severe. Many techniques are being used in the industry to enhance the displacement of gas injection projects instead of continuous gas injection (CGI). The first practice to enhance the sweep efficiency and enhance a gravity stable gas injection was water alternative gas injection (WAG) [12]. In WAG application water and gas are injected sequentially through the same well. The problem of WAG process is the segregation of water and gas after being injected into the reservoir. In order to increase the injectivity and distance before complete segregation, methods were introduced such as Surfactant-Alternating-Gas (SAG) Foam, and Foam assisted WAG.

Other techniques in the last 5 years tried to working in harmony with nature by utilizing the natural buoyancy tendency of injected gas to displace oil downwards which resulted in an excellent gravity stable gas injection [14]. Figure 1 shows one of these practices which take advantage of the density difference between injected gas and reservoir oil by utilizing the horizontal well technology. The density difference can be effectively used as an advantage in dipping reservoirs [15].

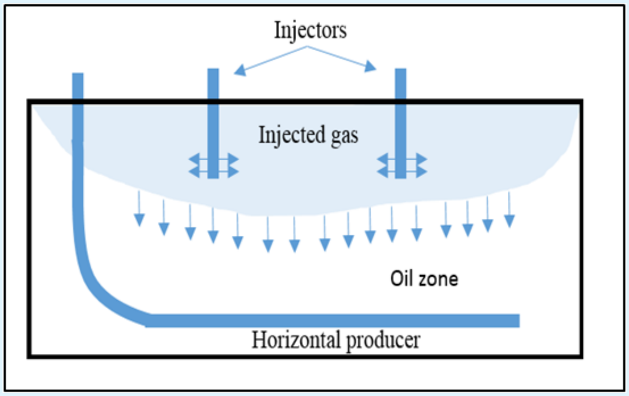

Figure 1: Schematic of the gas assisted gravity drainage (GAGD) process.

Previous Methods to Generate CO_2 *In-situ*

Shiau et al. developed a method to generate CO_2 *in-situ* [15]. The purpose of their study is to investigate compounds that can generate carbon dioxide *in-situ*. They used ammonium carbamate to produce a significant amount of carbon dioxide when the temperature is elevated to 85°C. In contrast, negligible CO_2 is detected while heating up the methyl carbamate to a similar temperature range. Ammonium carbamate results in the production of CO_2 in column studies at 80°C and 90°C and also results in a decrease in oil viscosity. The additional injection of a 0.5 PV of 3% ammonium carbamate solution with a polymer /surfactant chemical flood improved crude oil recovery by 9.7% OOIP compared to a polymer/surfactant chemical flood without carbamate. However, there is negligible oil recovery without the presence of surfactant for studies using light oils, decane and Arrow crude oil. They used this method in sand pack column but they did not try it with actual cores. The recovery from this method was very low compared to the recovery of the new method that we are introducing. The maximum recovery they got in their experiment was 43% from the residual oil recovery after surfactant/polymer injection; in our method we recovered more than 80% from the residual oil after sea water injection. Our method is very simple and there is no need for complex additives.

Gumersky introduced a new method to generate CO_2 *in-situ*, this method includes the injection of sodium carbonate with hydrochloric acid (HCl) into the formation and wait for 24 hours for the reaction to occur then the CO_2 will be generated [17]. The problem with this method is that HCl is very corrosive; therefore, corrosion inhibitors should be added (high cost). The corrosion inhibitor may reverse the wettability of the formation and make it oil wet, in turn water wetting agents should be added. A lot of additives should be used in this method, also it cannot be used in carbonate reservoirs because HCl will react with carbonate immediately when injected and the sodium carbonate will remain in the reservoir without reaction and it will cause damage. In addition, this method is very expensive and uncontrollable.

Chelating Agents

Chelating agents contain different functional groups (carboxyl, hydroxyl, ether, primary amine, tertiary amine, thiol, nitro, nitroso, and sulphine etc.) which have the ability of grabbing the metal ion and form a stable complex. Dissociated carboxyl group turns out to be the best sequestering group. Tertiary amine is the most promising group among the neutral groups [18]. The distribution of ionic species depends on the equilibrium constants for each of the dissociation reactions and on the solution pH. The basic idea behind these chelating agents is the sequestration of metal ions and preventing any metal precipitation in carbonate formations. The conjugate bases of the chelating agents have the ability to chelate different ions such as iron and calcite which present in reaction solutions. The stability of the calcium chelate influences the ability of the chelating agent to dissolve calcite [19-20]. Structure of chelating agents used in petroleum industry is shown in Figure 2.

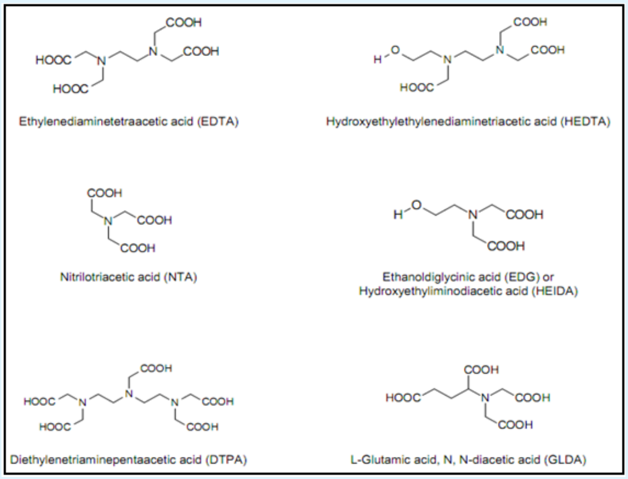

Figure 2: Structure of chelating agents used in petroleum industry.

The distribution of ionic species for EDTA at room temperature is shown in Figure 3. At a pH of approximately 4.5, EDTA is in the form of H_2Y^{2-}. At higher pH values of about 8.5 and 13 EDTA successively deprotonates to the HY^{-3} and Y^{-4} species respectively [19].

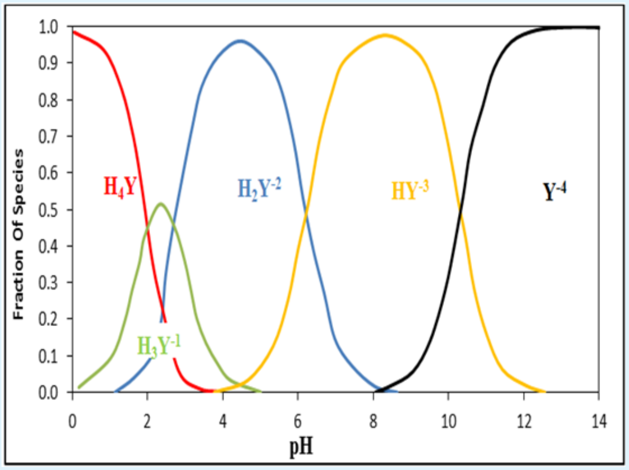

Figure 3: Distribution of ionic species of EDTA at room temperature.

New Method of Generating *In-situ* CO_2

Usually weak acids are used to stimulate production and injection wells drilled in high temperature reservoirs.

This time we tried to use few of these acids at low concentrations for another objective. From simple chemistry it is well known that one of the products of acid reaction with carbonate is CO_2. If we force the reaction between the injected acid and the reservoir rock to occur deeper in the reservoir we will end up with an *in-situ* generated CO_2. The generated gas now has the best opportunity to swell the nearby residual oil and release it from the rock surface.

The objective of this work is to generate CO_2 *in-situ* by injecting low pH HEDTA or EDTA chelating agents followed by sea water, high pH chelating agents, or low salinity water. First the low pH chelating agent will react with the carbonate rock and produce CO_2 that will diffuse to the oil and increases the oil mobility in turn more oil will be produced. The chelating agents used in the current invention are H_2Na_2EDTA (pH = 4.5), H_3HEDTA (pH = 2.5), and $H_2NaHEDTA$ (pH = 4). The acid part which contains the hydrogen ions will attack the carbonate rock and produce CO_2 that will increase the oil recovery, and then the high pH chelating agent or even sea water can be used to displace the low pH chelating agent and CO_2. The flooding work showed that about 90% of the oil in place can be recovered from the carbonate cores without using of surfactants or any other additives. The new method will eliminate the problem of gravity override which is the main problem of CO_2 EOR.

Experimental Work

The coreflooding experiments were performed using Indiana limestone cores 6 in length and 1.5 in diameter.

Core #	L (cm)	D (cm)	Dry Wt. (gm)	Bulk Vol. (cc)	Saturated Wt. (gm)	Porosity (%)	Perm (mD)	Pore Vol (cc)
EOR-1	15.000	3.720	347.53	163.03	383.45	19.38	70	31.59
EOR-2	15.000	3.720	347.42	163.03	383.58	19.51	70	31.80
EOR-3	15.000	3.720	347.53	163.03	383.45	19.38	185	31.59

Table 1: Properties of the core samples used for the *in-situ* CO_2 flooding tests.

Table 1 shows the properties of the Indiana limestone samples used in the flooding tests. A dead crude oil (API=30) for this study from one of the Saudi Arabia fields; the oil composition is shown in Table 2, more properties of the crude oil are shown in Figure 4. H_2Na_2EDTA (pH = 4.5), H_3HEDTA (pH=2.5) were used to generate CO_2 *in-situ* when reacting with the carbonate matrix while a high pH chelating agent Na_4EDTA (pH = 12) was used to show the effect of generated CO_2.

Component	Moles	Mole%
C5	0.00216	1.23
C6	0.007434	4.23
C7	0.018767	10.67
C8	0.027806	15.81
C9	0.025519	14.51
C10	0.025371	14.43
C11	0.019607	11.15
C12+	0.049211	27.98

Table 2- Fluid composition for UTMN crude oil.

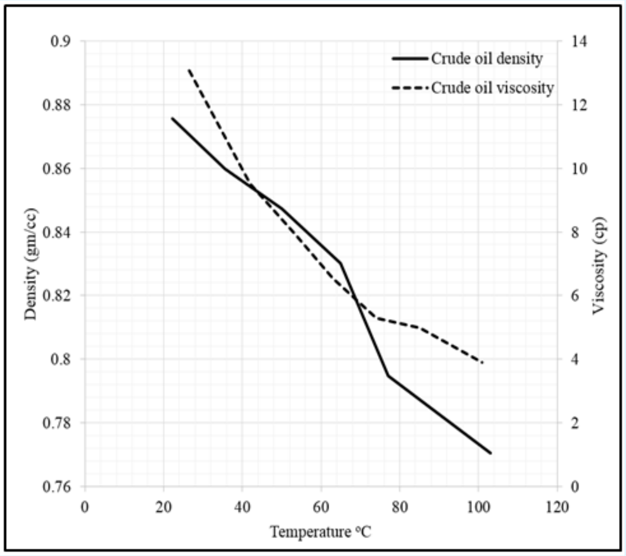

Figure 4: Density and viscosity of the crude oil as a function of temperature.

Na_4EDTA was diluted using sea water (53670 ppm TDS) while the other chelating agents were diluted using distilled water. The *in-situ* generated CO_2 can be followed by seawater or continuous injection of high pH chelating agent to get more oil recovery. The concentration of the chelating agents used was 5 wt% therefore, no other additives are required to protect against corrosion. The experiments were performed at 100°C, 0.25 cc/min injection rate, 1000 psi back pressure and net overburden pressure of 500 psi using the core flooding setup Figure 5.

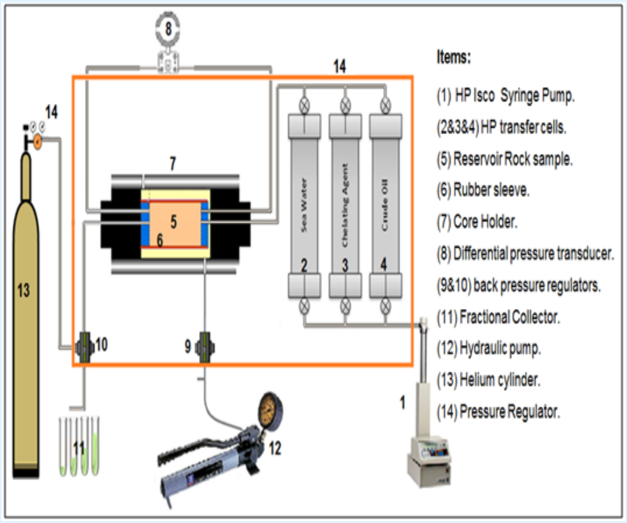

Figure 5: Flooding Setup used for the study.

Two senarios where applied, the Chelating agetnt system as injected from the beginning of the core flooding the in the forst scenario while it was preceded by seawater in the second scenario and the recovery difference is reported. I addition the effect of injecting a high pH chelating agent after 1PV low pH chelating agent is reported. Table 3 shows the EOR system used for each core sample.

Core Sample	Experiment	*In-situ* CO_2	pH
EOR-1	Flooded with 5wt% Na_4EDTA till no more recovery	No	12
EOR-2	Flooded with 5wt% H_2Na_2EDTA	yes	4.5
EOR-3	Flooded with sea water followed by 1 PV of 5wt% H_3HEDTA then sea water	yes	2.5

Table 3- EOR system for each core sample.

Results and Discussion

The injection of one pore volume of 5wt% H_3HEDTA (pH=2.5) was able to recover 34% additional oil from the original oil in place or 81% from the residual oil Figure 6 in the EOR-11 Indiana limestone sample.

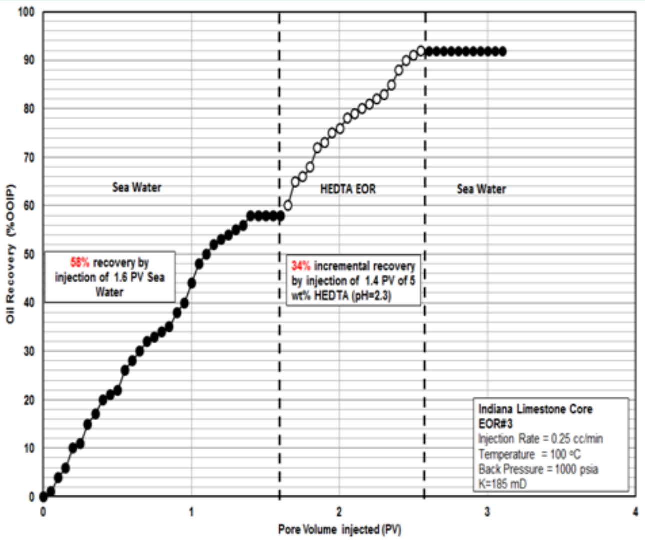

Figure 6: Oil recovery by the *in-situ* generation of CO_2 using H_3HEDTA (pH=2.5) from core#3.

The injected pore volume of 5 wt% H_3HEDTA was able to produce enough amount of CO_2 to recover more than 80% of the residual oil. For H_2Na_2EDTA (pH 4.5) continuous injection, the oil recovery increased up to 90% from the initial oil in place Figure 7.

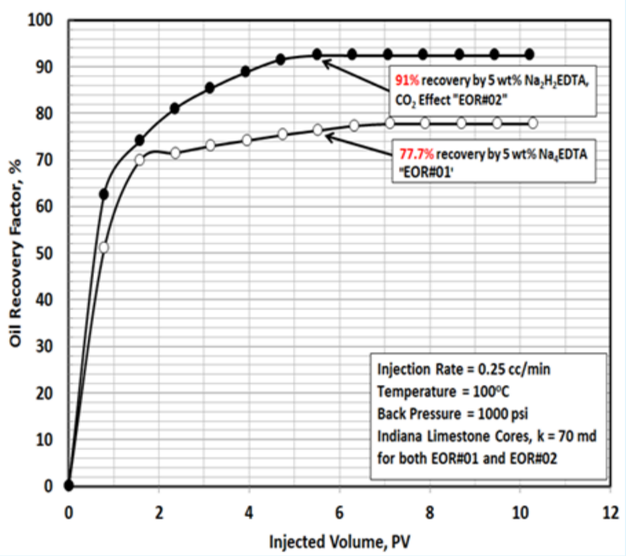

Figure 7: Oil recovery by the *in-situ* generation of CO_2 using H_2Na_2EDTA (pH=4.5; EOR#02) vs. Oil recovery using Na_4EDTA (pH=12; EOR#01).

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H_2Na_2EDTA was not powerful as H_3HEDTA in producing CO_2; therefore, more volumes of H_2Na_2EDTA were injected to recover additional oil equal to that recovered with H_3HEDTA. This process can be controlled by proper design of the concentration, pH, and chelating agent type to maximize the oil recovery as much as possible. The effect of generated CO_2 on recovery can be highlighted by comparing the recovery from EOR-2 to the recovery from the sister core EOR-1in which a higher pH fluid is used (Na_4EDTA). The CT scan for the EOR-2 core sample after flooding Figure 8 shows a dominating wormhole generated in the core due to the interaction between the low pH EDTA solution and the calcite matrix while no such effect occurred in the high pH solution flooded sample Figure 9.

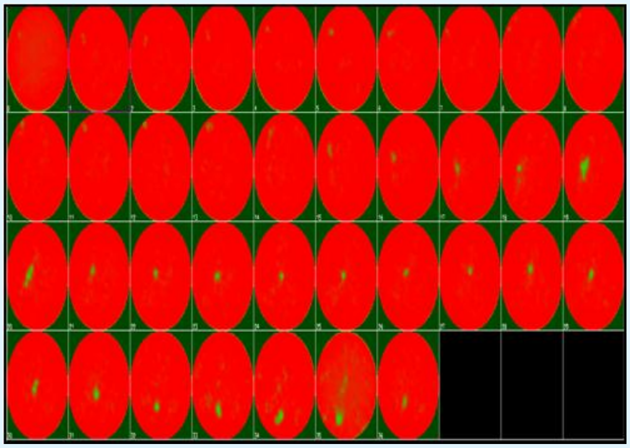

Figure 8: CT scans of core # EOR#02 after low pH Na_2H_2EDTA solution injection.

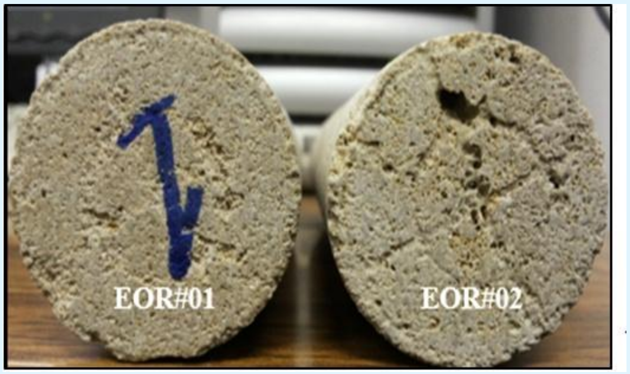

Figure 9: Wormholes created in the Low pH EDTA flooded Core (pH = 4.5; right core) compared to the High pH EDTA flooded one (pH = 12; left core).

The increased recovery observed from the flooding experiments can be attributed torock dissolution, interfacial tension reduction, oil swelling and wettability alteration. Rock dissolution due to the injection of low pH solution enhanced the productions by leaching the crude oil which is adsorbed in the rock surface. Even the injection of high pH solution (chelating agent diluted in sea water) was observed to cause rock surface dissolution based on the effluent analysis [22,23]. Comparing the recovery usinghigh pH and low pH solutions, the increasing contribution of rock dissolution by the low pH solution increased the recovery from EOR-2 core sample simultaneously with the slow released CO_2 due to the reaction between low pH solution and carbonate rock. The generated CO_2 can enhance viscosity reduction as a result of dissolution of the CO_2 in crude oil. Swelling effect of CO_2 increases the oil volume and reduces the interfacial tension which enhanced the production of the oil. The most important aspect when upscaling this approach to field application is the need to prevent the injected chemicals to react directly at the sand face. Encapsulation of the injected chemicals can be studied with the aim that we can force the generation if CO_2 to be deeper in the reservoir where most of the residual oil is trapped.

Conclusions

Based on the performed core flooding experiments:

- *In-situ* generated carbon dioxide technique can be used to avoid gravity override during gas injection EOR.
- *In-situ* generated CO_2 using acidic chelating agents diluted in deionized water was able to increase the recovery by 30% of the OOIP.
- The effect of CO_2 on swelling the oil in addition to more dissolution is the difference in the performance of High pH and low pH chelating agent.
- Unlike the High pH chelating agents, the sea water cannot be used to dilute the low pH chelating agents due to stability issues [24].

This work represents the first step towards a new application in field scale. More work has to be done considering different types of chelating agents and testing it compatibility and stability under reservoir conditions. During EOR the injected fluids will remain in contact with the formation for years after reaction. Sea water can be tested to be used as a diluting bulk solution for these chemicals so that another step can be taken towards the application of a cost effective *in-situ* generated CO_2 for EOR purposes. Reservoir simulation can be carried out to evaluate the reservoir performance under such practice.

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