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Laboratory Investigation of Indepth Gel Placement for Carbon Dioxide Flooding in Carbonate Porous Media

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Proposal

This paper presents the results of an investigation on the application of gel placement in an attempt to reduce the permeability of a carbonate porous medium to water and supercritical carbon dioxide, as encountered in the CO₂ flooding of carbonate reservoirs. The high and low molecular weight polyacrylamide polymers with chromium (III), as crosslinker, were used for this study. Since sodium lactate is commonly used for increasing gelation time at elevated temperatures, additional experiments were conducted by adding sodium lactate to the gel solution with a ratio of polymer to sodium lactate equal to one.

Experiments were conducted at 1200 psi and 40 °C, with and without the presence of residual oil in order to investigate any role the residual oil might play in the performance of gel. Performance and stability of above gel systems for reducing the permeability of the carbonate medium to the injected water and carbon dioxide was tested in a series of flow experiments by alternatively injecting several pore volumes of water and carbon dioxide into the porous media in several cycles.

The porous medium used was crushed carbonate with initial permeability of over 10 Darcies. For all experiments the presence of Sor led to lower residual resistance factors (RRF). Nevertheless, RRFs were between 100 and few thousands for all experiments conducted. The results obtained are clear indication of the effectiveness of these gel systems for conformance control purposes during carbon dioxide flooding projects in carbonate reservoirs.

Introduction

Application of gel treatment is an attempt to reduce or block channeling through the fractures or high permeability layers of oil reservoirs. This technique can divert fluid flow to lower permeability zones and improve the oil recovery. This method

has been applied over last few decades as one of the most effective tools for controlling water and gas production. The polymer-gel technology has been applied successfully in many reservoirs, resulting in fracture sealing, water and gas shut-off, and permeability modification.⁷ The objective of gel placement and similar blocking-agent treatments are to reduce channeling through fractures or high-permeability zones of oil reservoirs without significantly damaging hydrocarbon productivity and improve the overall oil recovery from the flooding process. The goal of gel treatments is to maximize gel penetration and permeability reduction in high permeable zones while minimizing gel penetration and permeability reduction in less permeable zones or hydrocarbon producing zones.¹ Although no treatment has been found that reduces water permeability without effecting on oil permeability,² gel treatments are one of the most aggressive types of conformance control or profile modification techniques. The main advantages of using gels over the other methods such as cements or mechanical plugs, is their flexibility for pumping without a work-over rig, high control of setting time, a deeper penetration into the formation, ease of cleaning, lack of milling time, and an easy removal from the well-bore by water recirculation.³ Gels can be applied to both injection and production wells.⁴ Injection well treatments are often larger than producing well treatments, then the goal is to fill as large a portion of the conductive channels from injector to producers as possible.⁵ In order to ensure an effective blocking of high permeable regions, gel systems have to be placed deep enough into the target zones.⁶

Polyacrylamide polymers cross-linked with chromium (III) have been used primarily to treat fracture systems, casing leaks, near well-bore regions, water shut-off and permeability reduction in reservoirs. Hence, experiments were designed to investigate the stability and performance of several polyacrylamide based gel systems by alternatively injecting water and carbon dioxide through the gelled porous media. The residual resistance factor, RRF (the ratio of the permeability before gelation to the permeability after gelation), was measured for each gel system against the flow of water and carbon dioxide. Gel systems made of high-molecular weight polyacrylamide (Alcoflood 935)-chromium (III) and low-molecular weight polyacrylamide (Alcoflood 254S)-chromium (III) were tested during this research. The goal of this research was to study the stability and resistance of each of the above gel systems for reducing the permeability of a carbonate medium to water and carbon dioxide.

Sodium lactate is used for increasing the gelation time for the polyacrylamide-chromium (III) gel systems at elevated reservoir temperatures. Hence, a series of experiments were conducted to investigate the effect of the presence of sodium lactate on the performance of the gel systems studied. The optimum amount of sodium lactate for our experiments was determined through conducting a set of gelation time measurement experiments at various sodium lactate concentrations.

Also, the potential role of residual oil saturation on the blocking ability of gels against injected water and carbon dioxide was investigated and some of the results are presented in this paper.

The findings of this study will be used to improve our understanding of the behavior and application of gel systems for improving the conformance of water and carbon dioxide in oil reservoirs, especially for heterogeneous and fractured carbonate reservoirs that are considered for CO₂-EOR projects.

Gel Systems and Gelation Time

The time it takes for sufficient reaction between the polymer and crosslinker species to occur, resulting in a substantial rise in viscosity of the gelant solution and formation of the semi-solid gel material, is called gelation time. Gelation time is of a great practical significance, since it determines the amount of time available for injecting gelling solution into reservoir and cleaning the injection lines after mixing the polymer and crosslinker at the surface.

The gelation time for various gel systems is determined through measuring the viscosities of gelling solutions with time. The time it takes for the viscosity of the gelling solution to go beyond the range of the instrument used for measuring viscosity is reported as gelation time. Since gelation time is affected by both temperature and composition of the gel systems, the gelation time measurement experiments were performed at various temperatures and concentrations.

The compositions of the gel systems investigated in this study are as follows:

1. Gel System One: A mixture of 7500 ppm high-molecular weight polyacrylamide (Alcoflood 935), 300 ppm chromium(III) and 1% sodium chloride concentrations.
2. Gel System Two: A mixture of 7500 ppm high-molecular weight polyacrylamide (Alcoflood 935), 300 ppm chromium(III), various concentrations of sodium lactate and 1% sodium chloride concentrations.
3. Gel System Three: Mixtures of 4 wt% and 5 wt% of low molecular weight polyacrylamide (Alcoflood 254S) and chromium(III) with a ratio of 1:12 crosslinker to polymer.

The high-molecular weight polyacrylamide with a molecular mass of approximately 7 million Daltons and degree of hydrolysis of 30% and the low-molecular weight polyacrylamide (Alcoflood 254S) with molecular mass of approximately 500 thousand Daltons were provided by Ciba and were used as received. Chromium(III) from an 11.5 % active chromium acetate solution was used as crosslinker, and Fisher Scientific provided sodium chloride.

Figure 1 presents the results of gelation time measurements for Gel System Three at two different concentrations and two temperatures. The results demonstrate gelation time decrease significantly by increasing the temperature or polymer concentration. However, the presence of sodium lactate increases the gelation time (Figure 2). Figure 3 shows the results of gelation time for Gel System One and Gel System Two, respectively. The results illustrated in Figure 4 indicates that gelation time for Alcoflood-935-Cr (III) gel system increases by increasing the concentration of sodium lactate.

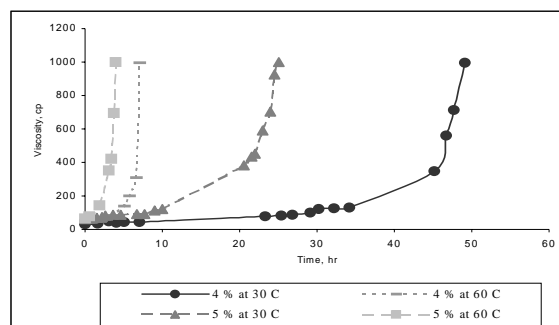


Figure 1: Gelation time of AF-254S at different conditions

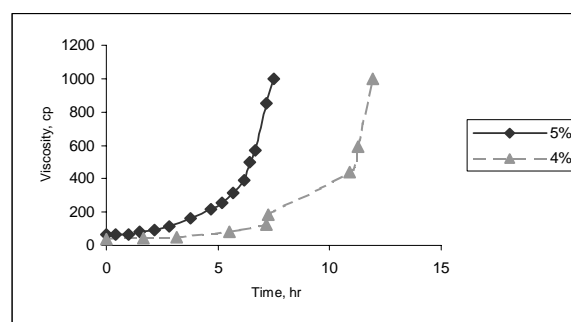


Figure 2: Gelation time of AF-254S + sodium lactate at 60 °C

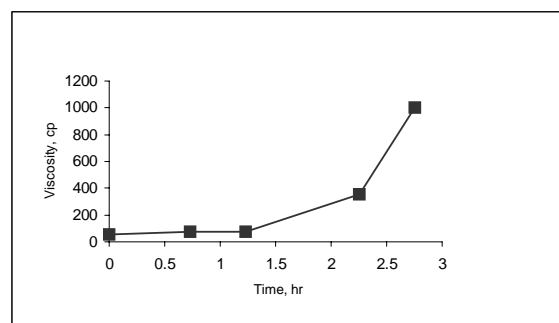


Figure 3: Gelation time of AF-935 without the presence of sodium lactate at 60 °C

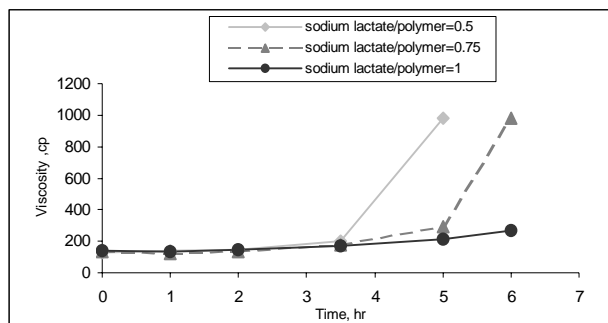


Figure 4: Gelation time of AF-935 at the presence of sodium lactate at 60 °C

Experimental Set Up

Figure 5 presents the schematic diagram for the experimental set up. An ISCO – 500 D-syringe pump was used to inject both brine and carbon dioxide into the porous media. In order to inject oil or gelant, two transfer cylinders and necessary valves were used. A TEMCO high-pressure core holder, Hessler Type, was used for this series of experiments. The crushed carbonate-pack, as the carbonate medium, was enclosed inside a rubber sleeve that was five centimeter in diameter. The ends of the rubber sleeve (crushed carbonate-pack) were sealed with specially designed and manufactured caps and were confined by clamps. Two 1/8" stainless steel tubes were connected to each end in order to wash the inlet and outlet lines after gel injection. A stainless steel transfer cylinder was used for applying the overburden pressure. The transfer cylinder was composed of two compartments separated by a floating piston. The side that was connected to the core holder was filled with fresh water and the other side was connected to a high-pressure nitrogen cylinder. At each step of the experiments, the overburden pressure was adjusted about 300 psi above the injection pressure and was monitored via a pressure gauge.

Validyne pressure transducers were used to measure and monitor the pressure drop across the crushed carbonate-pack, and the measured data was collected via a Validyne data collecting board that was installed in a desktop computer.

All experiments were performed in an air-bath at constant temperature of 40 °C and pressure of 1200 psi. In order to maintain a constant temperature throughout the experiments, an electric heater was connected to a temperature controller and two small fans were placed inside the air bath for circulation purposes. A backpressure regulator was used to maintain a pressure of 1200-1250 psi inside the crushed carbonate-pack. The backpressure was connected to a high-pressure nitrogen cylinder (dome gas).

The pressure readings were recorded across the sand-pack at various brine injection rates. Post-gelation carbon dioxide injection was conducted at constant rate of 2 mL/min in all experiments. The effective permeability and residual resistance factor for post-gelation brine and carbon dioxide injection were calculated and performance of the gel systems used was investigated.

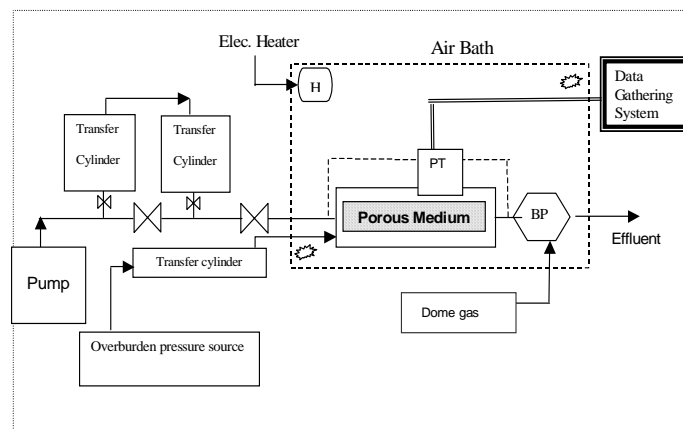


Figure 5. The schematic representation of the experimental set up

Experimental Procedure

The objective of this study is to investigate the stability and performance of the gel systems by alternatively injecting water and carbon dioxide through the gelled carbonate media. The general procedure used for the flow experiment is presented as follows:

1. Determine the initial permeability of the medium to brine.
2. Prepare the gelling solution and inject several pore volumes of gelant into the porous medium.
3. Wash the inlet and outlet tubing and shut-in the porous medium for sufficient time to allow gel to set.
4. Determine the brine permeability and the residual resistance factor for brine at atmospheric pressure.
5. Increase the backpressure to about 1200 psi.
6. Inject brine into the gelled carbonate-pack (step #1 of each cycle).
7. Determine the brine permeability and the residual resistance factor for brine.
8. Inject carbon dioxide at 2 mL/min and determine carbon dioxide permeability and the residual resistance factor for carbon dioxide (step # 2 of each cycle).
9. Repeat steps 8 to 11.

Results and Discussion

The stability and performance of gel systems with various compositions were studied by injecting carbon dioxide and water through the gelled porous media alternately, simulating the water-alternating-gas (WAG) process. The following gel systems were tested in this study: 1) Alcoflood 935-Cr (III) without the presence of residual oil, 2) Alcoflood 935-Cr (III) with presence of residual oil, 3) Alcoflood 935-Cr (III) with presence of sodium lactate, and 4) Alcoflood 254S-Cr (III) with presence of residual oil.

Alcoflood 935-Cr(III) Gel System. A crushed carbonate medium, 21 cm long and 5 cm in diameter, was used for this set of experiments performed at a constant temperature of 40 °C. The post gelation permeability measurements for injected water were compared to the initial permeability to brine, which was 14.74 Darcy. However, the initial permeability to

carbon dioxide at the residual water saturation was 2.8 Darcy. This value was used to compare the post-gelation permeability measurements to carbon dioxide to and calculate the residual resistance factor (RRF) in the subsequent cycles.

The gel used in this study contained 7500 ppm Alcoflood 935 HPAM, 300 ppm Cr (III), and 1% NaCl. Approximately three pore volumes of the gelling solution was injected into the porous medium at 4 mL/min. In order to monitor the gelation inside the pore space, effluent sample was collected and kept in the air bath to be used as an indicator for gelation inside the carbonate medium. The inlet and outlet tubes were washed with brine and the system was shut-in for sufficient time to allow the gel to set at 40 °C. The solution was defined as a gel when significant elastic behavior was observed in the effluent samples.

Post gelation brine injection was initiated by injecting brine into the gelled medium at various flow rates to determine the stability and resistance of the gel to brine injection, at atmospheric pressure. The permeabilities and residual resistance factors (ratio of the permeability to brine before gel placement to the permeability to brine after gel placement, RRF) were calculated and are presented in Table 1. The elastic behavior of the flow through the gelled porous medium is presented in Figure 6 where a linear relationship between injection rates versus effective permeability is demonstrated.

Table 1: Permeability and residual resistance factors to brine, for AF-935-Cr(III) gel system at 40 °C and atmospheric pressure

Initial permeability to brine = 14.74 Darcy

$Q, \text{ mL/min}$	$K, \text{ md}$	RRF
0.1	2	76000
0.2	4	41770
0.3	4	33068
0.4	6	25381
0.5	6	23206
0.5	8	193377
0.4	7	19725
0.3	7	20692
0.2	5	21755
0.1	5	27847

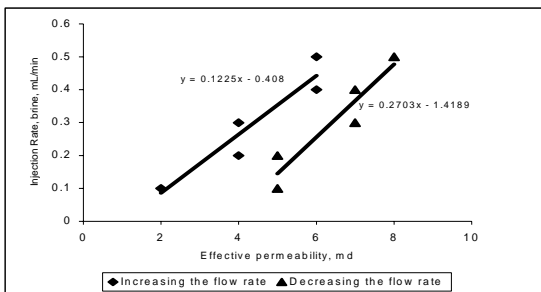


Figure 6: Injection rate vs. effective permeability to brine

Next, the system was pressurized to 1200 psi by connecting the backpressure and continuous injection of brine at a rate of 0.3 mL/min. Then, brine and carbon dioxide were injected into the gelled medium through four cycles. In the first step of each cycle (i.e. post gelation brine injection at high-pressure) brine was injected at a series of increasing flow rates followed by decreasing rates and the permeability to brine was measured for each injection flow rate. In the second step of each cycle carbon dioxide was injected at a rate of 2 mL/min into the gelled medium and the post gelation permeability to CO₂ was measured. Samples of pressure data obtained for a typical cycle of experiment is presented in Figures 7 and 8.

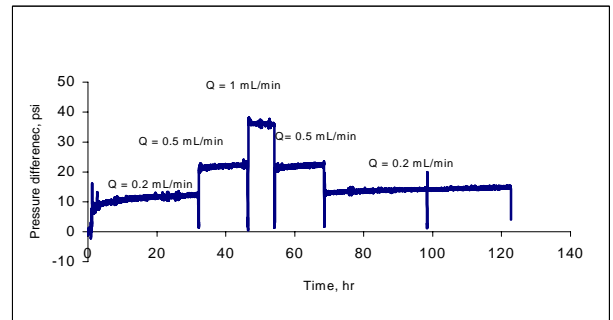


Figure 7: Sample results for pressure difference during the post gelation brine injection of each cycle at 1200 psi and 40 °C

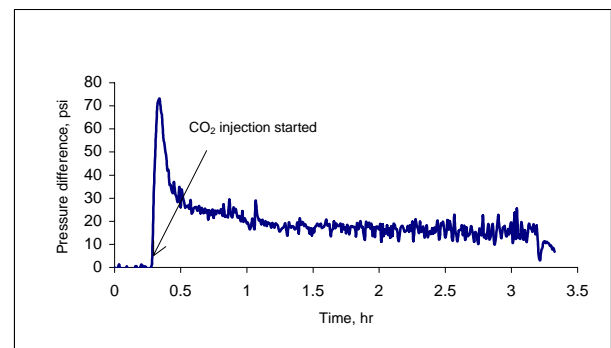


Figure 8: Sample results for pressure difference during the post gelation carbon dioxide injection of each cycle at 1200 psi and 40 °C

A summary of the results for the four cycles of this set of experiments is presented in Table 2. Although permeabilities were increased during the alternate injection of brine and carbon dioxide, the permeability to flow of both brine and carbon dioxide were reduced greatly after gel treatments. Overall, this gel system demonstrated a very high stability against injection of brine and carbon dioxide in the carbonate medium.

Table 2: Permeabilities and residual resistance factors to brine and CO₂ for AF-935-Cr(III) gel system at 40 °C and 1200 psi

Initial permeability to brine = 14.74 Darcy

Initial permeability to CO₂=2.8 Darcy

	Brine injection at 0.5 mL/min		CO ₂ injection at 2 mL/min	
	K, md	RRF	K, md	RRF
Post gelation brine injection	0.64	23206	-----	-----
Cycle 1	-----	-----	0.82	3415
Cycle 2	3.5	4258	0.73	3835
Cycle 3	5.6	2599	0.94	2979
Cycle 4	8.4	1740	1	2800

Alcoflood 935-Cr (III) at the Presence of Residual Oil. In order to investigate any role the residual oil saturation might play in the performance of the gel placement, a carbonate medium was saturated with crude oil at the irreducible water saturation. The permeability to brine at residual oil saturation was measured as 2.43 Darcy. This value was used as the base value to compare the post-gelation values of permeabilities against the flow of both brine and carbon dioxide. A gelling solution of 7500 ppm polymer, 300 ppm Cr(III) and 1 wt% brine was prepared and about 4 pore volumes of this solution was injected into the sand-pack. Effluent samples were collected and kept in the air bath as indicators for gelation inside the porous medium. Complete gelation in the sand-pack was determined when the gel in the effluent samples showed significant elastic behavior. After the gelation was complete, brine was injected into the gelled medium and the stability of the gel in presence of brine injection was studied.

After pressurizing the core holder to 1200 psi, four cycles of brine and carbon dioxide were injected into the gelled medium, as explained previously. Table 3 presents the summary of results for the four cycles of this experiment. As the results illustrate, the effective permeability increased and residual resistance factors decreased for both brine and carbon dioxide for cycles one through four. However, the gel system tested was able to reduce the permeability to both carbon dioxide and brine very effectively, with RRF values in the range of few hundreds for brine and few thousands for the injected carbon dioxide.

Table 3: Permeabilities and residual resistance factors to brine and CO₂ for AF-935-Cr(III) gel system with the presence of S_{or}, at 40 °C and 1200 psi

Base permeability at S_{or} = 2.43 Darcy

	Brine injection at 0.5 mL/min		CO ₂ injection at 2 mL/min	
	K, md	RRF	K, md	RRF
Post gelation brine injection	5.5	445	-----	-----
Cycle 1	10.9	224	0.6	3877
Cycle 2	14.9	163	1.5	1572
Cycle 3	20	122	1.9	1258
Cycle 4	21.9	111	2.4	1027

Alcoflood 935-Cr(III)-Sodium Lactate Gel System. Sodium lactate is commonly used for increasing gelation time at elevated temperatures. The stability and performance of the polyacrylamide (Alcoflood-935)-chromium (III) gel system in the presence of sodium lactate was investigated by adding sodium lactate to the gelling solution.

The initial permeability to brine and carbon dioxide were determined as 13.66 and 2.6 Darcy, respectively. These values were used as the basis to compare the values of post-gelation permeabilities and calculating RRFs to brine and carbon dioxide. A hydrogel made of 7500 ppm polymer (Alcoflood 935), 300 ppm Cr(III) and sodium lactate with a ratio of polymer to sodium lactate equal to one in 1 wt% brine solution was prepared. Approximately 3 pore volume of this solution was injected into the porous medium.

Visual observations on the gel formed from the effluent samples collected indicated that not only this gel system had longer gelation time, but also it was more fluid and weaker than other gel systems when no sodium lactate was present.

The performance and stability of this gel system for reducing the permeability of the carbonate medium to the injected brine and carbon dioxide was tested again by injecting four cycles of brine followed by carbon dioxide.

Figure 9 shows the pressure gradient during post gelation brine injection at atmospheric pressure. The long tail and fluctuations of pressure readings is indicative of the weak and fluid characteristics of this gel system. It was also observed that some gel was washed out of the system. These observations indicated that this gel system was unstable, and the gel might be moving inside the porous media during the brine injection.

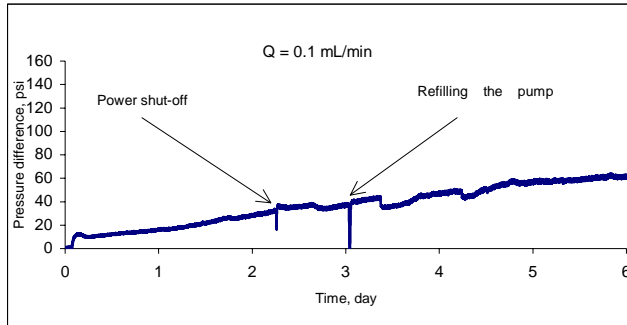


Figure 9: Post gelation brine injection at different flow rates for AF-935-Cr (III) + sodium lactate gel system at atmospheric pressure

After the system pressure was increased to 1200 psi, brine and carbon dioxide were injected into the gelled medium in four cycles. Table 4 shows the summary of results for the four cycles performed on this gel system. The results show that the trend in change in permeabilities and RRFs are different from previous gel systems. This behavior can be attributed to the physical properties of this gel system which is different from the other gels studied. Nevertheless, the results obtained indicated a good stability in the performance of this gel system.

Table 4: Permeabilities and residual resistance factors for AF-935-Cr (III) + sodium lactate gel system at 40 °C and 1200 psi

Initial Permeability to brine = 13.66 Darcy

Initial Permeability to CO₂ = 2.6 Darcy

	Brine injection at 0.5 mL/min		CO ₂ injection at 2 mL/min	
	K, md	RRF	K, md	RRF
Post gelation brine injection	0.53	25807	----	----
Cycle 1	0.85	16129	2.4	1083
Cycle 2	2.7	4973	2.3	1130
Cycle 3	1.84	7393	1.83	1420
Cycle 4	1.63	8373	1.73	1503

Alcoflood 254S-Cr (III) with the Presence of Residual Oil.

The next gel system tested, at the presence of residual oil saturation, was made of a low molecular weight polyacrylamide polymer (Alcoflood 254S) and Cr(III) as the crosslinker. The absolute permeability of the porous medium was determined as 13.23 Darcy. The effective permeabilities to brine, in the presence of residual oil saturation, and carbon dioxide were determined as 2.49 and 1.95 Darcy, respectively. The effective permeability to brine and CO₂ before gel placement was used as the basis of comparison for the post-gelation permeabilities.

The gel solution was prepared (5 wt% polymer, and a ratio of 1:12 chromium to polymer) and approximately 3 pore volume of the solution was injected into the porous medium.

The visual observations of the gel formed from the samples collected from the effluent indicated that this gel system is very rigid and could be characterized as a ringing-gel.

Then, brine and carbon dioxide were injected into the gelled medium through four cycles (post gelation injection), and performance of the gel was examined. As the results in Table 5 illustrate, the values of effective permeability after gel placement through cycles two to four are virtually the same. In other words, the gel structure inside the gelled medium did not change significantly as a result of repeating the cycles. The results indicate a very good performance for this gel system against the flow of carbon dioxide and moderate blocking effect against the flow of brine.

Table 5: Permeabilities and residual resistance factors to flow of brine and carbon dioxide for AF-254S-Cr (III) gel system with presence of S_{or} at 40 °C and 1200 psi

Effective permeability to brine at S_{or} = 2.49 Darcy

Effective Permeability to CO₂ = 1.95 Darcy

	Brine injection at 0.5 mL/min		CO ₂ injection at 2 mL/min	
	K, md	RRF	K, md	RRF
Post gelation brine injection	7.1	353	----	----
Cycle 1	14.9	1679	0.38	5131
Cycle 2	20.5	122	0.5	3900
Cycle 3	21.2	118	0.53	3679
Cycle 4	21.5	116	0.54	3611

Discussion. For the gel systems presented in this paper, the presence of residual oil saturation increases the permeability of the gelled medium to flow of fluids, especially to the flow of brine. It is believed that at the presence of residual oil saturation, the injected gelling solution cannot access small pores, which are filled with residual oil. Therefore, some pathways remain open for fluid to flow through during the post gelation experiments. As a result, permeability reduction was less when residual oil saturation was present.

The addition of sodium lactate to the gel system increases the gelation time and leads to a more fluid gel. However, in both cases (with and without addition of sodium lactate) a good stability in the performance of the gel systems as a means of blocking the high permeability zones against the flow of both brine and carbon dioxide was observed.

Conclusions

Based on the experiments conducted and the observations made during this study the following conclusions were made:

1. AlcoFlood 935-Cr(III) gel system, with and without the presence of residual oil saturation reduces the effective permeability to both brine and carbon dioxide in carbonate porous media effectively. The residual

resistance factors of few hundred to few thousands were observed.

2. RRF values of approximately 3000 were measured for the flow of CO₂ in a porous medium gelled with AlcoFlood 935-Cr(III) gel system without the presence of residual oil saturation.
3. AlcoFlood 935-Cr (III) gel system in the presence of residual oil saturation reduces the effective permeability to brine from an initial permeability of 2.43 Darcy (permeability to brine at residual oil saturation) to 21.9 md after several cycles of alternatively injecting water and CO₂ (in a carbonate medium).
4. AlcoFlood 935-Cr (III) gel system, at the presence of residual oil saturation, reduces the effective permeability to carbon dioxide to 2.4 md after several cycles of injecting water and CO₂, alternatively (in a carbonate medium).
5. The presence of sodium lactate leads to a more fluid gel. However, this gel system can effectively block the flow of brine and carbon dioxide in the carbonate media.
6. AlcoFlood 254S-Cr(III) gel system at the presence of residual oil saturation reduces the effective permeability to brine from 2.49 Darcy to 21.5 md after several cycles of injecting water and CO₂ in a carbonate medium.
7. AF-935-Cr (III) gel system at the presence of residual oil saturation reduces the effective permeability to carbon dioxide to 0.54 md after several cycles of injecting water and CO₂, alternatively in a carbonate medium.
8. The results of the Alcoflood 935-chromium (III) gel system with sodium lactate showed that the gel structure was fluid and weak and moved in the porous media.
9. The results reveal that the gel systems tested in this paper can significantly reduce the permeability to flow of both brine and carbon dioxide in the carbonate porous media.

Acknowledgments

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Nomenclature

ppm = parts per million

RRF = residual resistance factor

Q = injection rate, mL/min

K = permeability, Darcy

S_{or} = residual oil saturation

PV = pore volume

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