Further Insights into the Performance of Silylated Polyacrylamide-Based Relative Permeability Modifiers in Carbonate Reservoirs and Influencing Factors

Liming Qin, Matthew B. Myers, Claus Otto, Michael Verrall, Zhiqi Zhong, Eghan Arjomand, Ali Saeedi,* and Colin D. Wood*

Cite This: ACS Omega 2021, 6, 13671−13683

Metrics & More | Article Recommendations

ABSTRACT: We have previously used surface chemistry analysis techniques to optimize the functionalization of carbonate rocks with a silylated polyacrylamide-based relative permeability modifier (RPM). The RPM is expected to selectively reduce the permeability to water in a hydrocarbon reservoir setting, resulting in a reduction in the amount of produced water while maintaining the production of oil/gas. This study will focus on using core flooding techniques with brine/crude oil under reservoir conditions (i.e., 1500 psi pore pressure and 60 °C temperature) to understand the impact of a silylated polyacrylamide-based RPM on the fluid transport properties in carbonate rocks. The effects of RPM concentration, brine salinity, rock permeability, and pore structure on permeability characteristics were studied. Scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDX) provided visual images of the polymer adsorbed onto the rock surfaces and confirmed the attachment of the polymer on the surface of the rock pore space after treatment. The relative percentage of Si increased from 1.65 to 13.55%, and the relative percentage of N increased to 4.54%. Core flooding showed that increasing the PAM-co-AA (poly acrylamide-co-acrylic acid partial sodium salt) concentration resulted in residual resistance factors for oil (RRF_{oil}) and brine (RRF_{brine}) that were greater than 1. However, there was a modest decrease in the disproportionate permeability reduction (DRP) ratio (RRF_{brine}/RRF_{oil}) from 1.75 to 1.60 when the polymer concentration was increased from 0.05 to 0.1 wt %. Furthermore, the RRF_{brine} values decreased slightly from 120 to 62 with increasing salinity (i.e., 1−10% NaCl) because of electrostatic shielding caused by charged ions in brine and the RPM. The cross-over points of relative permeability in these four samples shifted to the right because of the larger decrease in relative water permeability compared with relative oil permeability. End-point relative permeability to water in sample C-5 decreased by 80%, showing a reduction greater than that in the sample C-2 (i.e., 74%). Kr curves indicated a stronger formation damage in sample C-1, C-2, and C-4 than in sample C-5. Rock samples with a higher initial permeability exhibited a higher RRF_{brine} to RRF_{oil} ratio (i.e., 3.05) under similar test conditions. This can be attributed to a larger pore radius, which was verified by nuclear magnetic resonance (NMR) measurements. Furthermore, a detailed mechanism has been proposed to understand the effects of the RPM on fluid transport in porous carbonate cores. In this study, SEM−EDX and NMR measurements combined with core flooding tests provide insights into the performance of silylated polyacrylamide-based RPMs and benefit its future implementation in carbonate reservoirs.

1. INTRODUCTION

Relative permeability modifiers (RPMs) are commonly composed of polymers or gels that act to reduce the production of unwanted water when they are applied in an oil/gas reservoir.\textsuperscript{1−6} Many RPM strategies use an uncross-linked...
copolymers containing partially hydrolyzed polyacrylamide (resulting in a combination of acrylate and acrylamide in the polymer backbone), which contains both positive and negative charges. These uncross-linked polymers with their long chains and charged ions can adsorb onto a rock surface. When a cross-linking agent is added to the polyacrylamide (called a gelant), the RPM forms a gel in situ that can be used to diminish water permeability substantially. For sandstone reservoirs, there are reports of several successful RPM formulations reported in the literature.7−9

However, the precise mechanism enabling the disproportionate reduction in oil and water permeability (i.e., the proportional decrease in permeability to water is greater than the proportional decrease in permeability to oil) with RPM formulations still remains mostly unresolved.10−12 Many researchers have conducted flooding tests using either sandstones or sand packs with different types of gels.7−22 Based on these experiments, there are several dominant mechanisms that are common among the different studies. Early in the development of RPM formulations, some investigators observed significant retention of polymers and proposed an adsorption–entanglement mechanism during polymer flooding.23 Under this mechanism, with continuous fluid flow, the polymer would adsorb onto pore surfaces initially and subsequently become entangled until the polymer solution in the cores achieves a hydrodynamic equilibrium. Simultaneously, another phenomenon termed bridge adsorption can occur in smaller pore throats during polymer flooding.7,26 In this case, macromolecules extend across pore throats via elongational forces, resulting in attachment to pore wall surfaces.26 These may lead to a decrease in pore size, resulting in permeability reduction.26 A shrinking–swelling or dehydration mechanism can provide another possible mechanism for polymer-induced permeability reduction during two-phase (crude oil and water) flow.12,26,29 With this mechanism, consecutive crude oil flooding would result in decreased water saturation causing polymer shrinking (or dehydrating), leading to an increase in oil permeability.15

Recently, many researchers have focused on exploring the mechanisms of disproportionate permeability reduction (DPR) using a gel to reduce water permeability substantially in sandstone reservoirs.10−12 They have identified several probable mechanisms (i.e., oil and water aggregated pathways, wall effect, oil droplet model, gel hydration, and dehydration10−12). For cross-linked gels, the gel hydration/dehydration mechanism is based on the swelling (or hydration) of the gel in the presence of water (which impedes water flow) and the deswelling (or dehydration) of the polymers in the presence of crude oil (which promotes the flow of oil).10−12 The other mechanisms are based on wettability and other phenomena. This viewpoint has been solely supported by microscopic observations,10,11,14 which may have little relevance in practical applications in the field. In addition, the performance of RPMs would be influenced by many factors (i.e., brine salinity, mineral compositions, pore sizes and structure,26 oil and water permeability,30 and wettability30).

Regardless of the precise mechanism, to date, very little research has been done utilizing RPM formulations in carbonate rocks.31,32 This can be attributed to the significant differences (i.e., mineral compositions, pore structure, and permeability characteristics) between carbonate rocks and sandstones. Aiming at making a new RPM applied in carbonate rocks, based on our previous studies,31,33 we have shown that we can efficiently functionalize/immobilize polyacrylamides onto the pore surface of carbonate rocks.31,33,34 In our previous study, sodium silicate was used to functionalize the carbonate surface with silicate groups, and then, 2-aminopropyltriethoxysilane (APTES) reacted with the Si−O bonds to functionalize the surface with amine groups.31,33,34 An organic linker such as formaldehyde can then be used to attach the polyacrylamide to the surface (i.e., the amides within the polyacrylamide would attach via the organic linker to the amines on the rock surface). The aim of this study was to further investigate the performance of this silylated polyacrylamide-based RPM formulation using flooding experiments on the carbonate core samples at reservoir-like conditions (i.e., 1500 psi, 60 °C). The end-point relative permeability to oil and brine as well as residual resistant factors have been calculated using recorded data from these core flooding experiments. Furthermore, some key factors influencing the performance of RPM including PAM-co-AA (i.e., poly (acrylamide-co-acrylic acid) partial sodium salt) concentration, brine salinity, rock permeability, and pore structure have been evaluated using scanning electron microscopy (SEM) and T2 nuclear magnetic resonance (NMR) relaxometry. These data presented will aid in developing a better understanding of the mechanisms that allow the RPM to perform as intended.

2. RESULTS AND DISCUSSION

2.1. SEM—Energy Dispersive Spectroscopy Analysis Post RPM Flooding. SEM—energy dispersive spectroscopy (EDX) measurements can be utilized for observing the morphological characteristics of polymer and quantitatively determining the elemental compositions in mineral surfaces after the treatment.35,36 Figure 1 shows the SEM images of sample A-7 flooded by deionized water and the RPM3 mixture (made from deionized water). These images confirm the existence of the RPM in the gray dark areas and spots associated with amine-functionalized carbonate rocks.
with intergranular pores compared to the relatively bright calcite crystals and matrixes. As indicated in Figure 1a, the polymer even exists in the smaller pores (i.e., less than 20 μm).

Figure 1b, c shows the dark gray areas filled with the polymer in the larger pores (i.e., more than 50 μm). Hence, the SEM images demonstrate that the RPM strongly adheres onto the carbonate rock surfaces after water flooding. After the RPM treatment and the brine flooding of samples A-2 and A-3, the SEM images were captured (see Figure 2). Figure 2a shows that the polymer was present in the intergranular pores and throats along with calcite grain edges as well in sample A-3. Figure 2b indicates a mixture of polymer and precipitated salt adhered onto the calcite crystal in sample A-2. Figure 2c of sample A-3 clearly depicts the morphology characteristics of polymer in the pores at a high resolution (40 μm × 40 μm field of view).

To further verify the existing polymer in the pores, three spectra of picked sites using EDX analysis were collected to analyze the element compositions including C, N, O, Na, Si, Cl, and Ca. As indicated in Figure 3, the distribution of spectrum 1 at the picked site (i.e., 1 μm × 1 μm) on the surface of the calcite crystal shows a larger peak for Ca, O, Na, and Cl relative to other elements. By contrast, spectrum 2 of another site (see Figure 3) shows that the peak height of Si and N exhibited a significant increase after the RPM treatment as these two elements originate from the RPM formulation. This was observed in sample A-3, as shown in Figure 4 as well, implying the immobilized polymer on the rock surfaces. In addition, the relative percentage of each element was quantified through spectrum analysis, as depicted in Table 1. It was also clearly shown that after the RPM treatment, the relative percentage of Si increased from 1.65 to 13.55%, and the relative percentage of N increased to 4.54%. Hence, the EDX analysis further illustrates the existence of RPMs in these pores after exposure to reservoir conditions.

2.2. Permeability, RRFbrine and RRFoil Calculation. Brine/RPM core flooding (type A and B) and brine/crude oil/RPM (type C) core flooding tests have been deployed under reservoir conditions (1500 psi, 60 °C). For brine/RPM core flooding tests, the brine permeability before and after the RPM treatment was calculated by Darcy’s law. For the two-phase (crude oil and brine) flow of imbibition and drainage, the end-point effective permeability to oil and brine before and after the RPM treatment was calculated using Darcy’s law as well (see Eq. 1).

\[
K_{oil,brine} = \frac{Q \times \mu \times L}{A \times \Delta P}
\]

(1)

where \(K_{oil,brine}\) (Darcy) is the end-point effective permeability (for either oil or brine); \(Q\) (cm³/s) is the flow rate; \(\mu\) (cp) is the fluid viscosity; \(L\) (cm) is the length; \(A\) (cm²) is the cross-section area; and \(\Delta P\) (atm) is the differential pressure.

The residual resistance factor (RRF) to crude oil (RRFoil) and brine (RRFbrine) is commonly used for evaluating permeability reduction after the RPM treatment. At the same injection rate, the RRFoil and RRFbrine were expressed as the following eqs 2 and 3. These two indicators (RRFbrine and RRFoil) can reveal the changes of the end-point relative permeability before and after the RPM treatment. The end-point relative permeability was acquired by the ratio between oil/brine effective permeability and absolute brine permeability.
The polymer can lead to undesirably large reductions in the Δ crude oil or brine after RPM injection; di can be seen in Table 5. All the processed results are shown in Tables 2 and 3. When the polymer concentration will likely need to be less. The RPM formulation we used in a previous study had a higher concentration of a polymer of 0.6 wt % (and correspondingly higher amounts of formaldehyde, sodium silicate, and APTES) and a higher viscosity; however, there was a concern that 0.6 wt % might cause a blockage of high-permeability channels in the carbonate core sample when PAM-co-AA is immobilized onto the pore walls after the RPM flooding. As a result, for all the RPM formulations used in this study, a polymer concentration less than 0.3 wt % was used. The brine permeability before and after RPM treatments is given in Table 2 and Figure 5. With the increasing concentration of RPM, the RRF value increased notably with the polymer concentration after RPM flooding for both 1 and 5% salinity brine (with the exception of A-6). A-6 has a significantly lower initial absolute brine permeability compared to A-5, and this may be associated with this anomalous result. Sample A-7 (where only deionized water was used) treated with RPM3 (i.e., 0.15 wt % PAM-co-AA) presented the highest RRF value of 29.44, suggesting that brine initially in the rock may impact the surface functionalization and thus the achieved RRF differences before and after the RPM treatment; this is discussed later in the manuscript. In addition, the adsorption thickness of the RPM onto rock surfaces was quantitatively calculated using Eqs. 4 and 5. The results indicate that the increasing concentration of RPM can yield higher thickness, as can be seen in Figure 6. Sample A-3 has the highest adsorption thickness (i.e., 25 μm) compared with sample A-1 and A-2 after the RPM treatment.

Table 1. Element Compositions of Spectra at Picked Sites on the Surfaces

| spectrum label | C (%) | N (%) | O (%) | Na (%) | Si (%) | Cl (%) | Ca (%) | others (%) |
|----------------|-------|-------|-------|--------|--------|--------|--------|------------|
| spectrum 1     | 12.68 |       | 32.71 | 9.22   | 1.65   | 4.29   | 39.15  | 0.30       |
| spectrum 2     | 25.58 | 2.50  | 29.4  | 9.28   | 15.35  | 3.43   | 0.91   |            |
| spectrum 3     | 26.13 | 4.54  | 25.36 | 8.12   | 12.44  | 12.49  | 10.91  | 0.01       |

“Note: three spectrums were acquired by EDX analysis, and the spot size with each spectrum was 1 μm. Compared with spectrum 1, the relative percentage of C, N, Cl, and Si increased, and the relative percentage of Ca and O decreased.

Table 2. Results of Brine or DI Water /RPM Core Flooding at 1 mL/min

| sample ID   | RPM | salinity (NaCl wt %) | K before, oil (mD) | K after, oil (mD) | RRF |
|-------------|-----|----------------------|--------------------|-------------------|-----|
| A-1 RPM1    | 1   | 57.98                | 26.92              | 2.15              |     |
| A-2 RPM1    | 1   | 118.7                | 45.1               | 2.63              |     |
| A-3 RPM3    | 1   | 121.79               | 23.49              | 5.18              |     |
| A-4 RPM1    | 5   | 155.33               | 88.98              | 1.79              |     |
| A-5 RPM2    | 5   | 223.8                | 36.52              | 6.13              |     |
| A-6 RPM5    | 5   | 105.85               | 25.67              | 4.12              |     |
| A-7 RPM3    |     | 91.27                | 3.1                | 29.44             |     |
| B-1 RPM3    |     | 278.6                | 2.88               | 96.7              |     |

“Note: K before, brine or DI permeability before the RPM treatment; K after, brine or DI permeability after the RPM treatment. Rock details can be seen in Table 5.

Table 3. Results of End-Point Relative Permeability to Oil and Brine

| sample ID | Ko (mD) | RPM | salinity (NaCl wt %) | K before, oil | K after, oil | RRF oil | RRF brine | DPR ratio |
|-----------|---------|-----|----------------------|---------------|--------------|---------|----------|-----------|
| C-1       | 101.95  | RPM2 | 2                     | 0.215         | 0.078        | 0.071   | 0.016    | 2.75      | 4.40      | 1.60      |
| C-2       | 55.37   | RPM1 | 2                     | 0.244         | 0.118        | 0.078   | 0.022    | 2.07      | 3.62      | 1.75      |
| C-3       | 125.28  | RPM1 | 6                     | 0.125         | 0.056        | 0.028   | 0.006    | 2.22      | 4.39      | 1.98      |
| C-4       | 152.4   | RPM2 | 2                     | 0.069         | 0.021        | 0.023   | 0.003    | 3.23      | 7.89      | 2.44      |
| C-5       | 121.65  | RPM1 | 2                     | 0.080         | 0.049        | 0.036   | 0.007    | 1.64      | 4.99      | 3.05      |

“Note: Ko, absolute brine permeability; K before, end-point relative permeability to oil before RPM treatment; K after, end-point relative permeability to oil after RPM treatment; ΔP before, end-point relative permeability to brine before RPM treatment; ΔP after, end-point relative permeability to brine after RPM treatment. Rock details can be seen in Table 5.
where, $r_{ave}$ ($\mu m$) is the pore radius, $K_{brine}$ (md) is the brine permeability, $RRF_{brine}$ is the residual assistant factor to brine, $e$ ($\mu m$) is the adsorption thickness.

2.3.2. Brine/Oil Flooding (Sample C-1 to C-2, C4 to C5). The concentration of the RPM has a similar impact on two-phase flow (i.e., crude oil/brine) compared to brine/RPM flooding. On comparing two lower-permeability samples (C-1 with RPM2 and C-2 with RPM1), sample C-1 with a higher concentration of polymer exhibits higher $RRF_{oil}$ and $RRF_{brine}$ values. However, there was a modest decrease in the DPR ratio from 1.75 to 1.60 when the polymer concentration was increased. A very similar behavior was observed when the results for C-4 and C-5 are compared. $RRF_{oil}$ and $RRF_{brine}$ increased significantly with a higher concentration of PAM-co-AA at 2 wt % salinity brine. Despite having higher RRF values with a higher concentration of PAM-co-AA, the DPR value decreased modestly, suggesting that a lower concentration of PAM-co-AA (i.e., RPM1) may exhibit better performance overall. This is possibly because increasing the concentration of the polymer has a strong resistance for water, whereas it would impact the oil permeability as well.

2.4. Effect of Brine Salinity. 2.4.1. Brine or Deionized Water Flooding (Sample A-1 to A-7, B-1). Brine salinity is a crucial factor influencing the behavior of polymers after RPM flooding because of the effect of ionic strength on the polymer in the RPM.\(^{39}\) Particularly, it is noted that brine salinity would inevitably impact the adsorption of chemical reagents (i.e., PAM-co-AA) while RPM mixes with brine. RPM and brine flooding tests using three salinity levels (1, 5, and 10 wt % NaCl) have been deployed. With respect to deionized water displacement, the use of deionized water flooding is a benchmark experiment to understand the influential difference between brine and deionized water. Comparing A-1 to A-3 (i.e., RPM1 at 1 and 5 wt % brine, respectively) and comparing A-3 to A-6 (i.e., RPM3 at 1 and 5 wt %, respectively), a decrease in the RRF value is observed, as shown in Table 2. This suggests that brine concentration might be impacting the surface functionalization with the polymer. It is also possible that the change in brine composition affects the swelling of the RPM and hence the observed RRF value. For this reason, we have conducted a series of experiments (namely, on core sample B-1) where the brine salinity is varied from 0 to 10 wt % on the same core sample. However, comparing A-2 to A-5 (i.e., RPM2 at 1 and 5 wt %, respectively), an increase in the RRF value was observed. This could be attributed to the higher permeability sample (namely, sample A-5) which possibly has better pore connectivity and porosity, allowing for improved polymer functionalization.

As illustrated in Table 2, the comparison of brine and deionized water flooding results clearly demonstrates that the brine has a slightly negative effect on RPM surface functionalization. The RRF value of sample A-7 flooded by deionized water increased to over 25 after the RPM displacement, but this sample which was never exposed to brine has a considerably larger RRF value compared to any of the other samples (A-1 to A-6), once again suggesting that brine negatively impacts polymer functionalization. By contrast, $RRF_{brine}$ of samples flooded by different salinity of brine was in the range from 1 to 7 (see Table 2).

However, for samples A-1 to A-7, the brine salinity already present in the sample can cause both the surface functionalization and the RPM behavior in multiphase flow to change. This makes it difficult to differentiate between the two effects. To further elucidate the effect of brine on the RPM without considering rock characteristics alone, we used one sample saturated with deionized water and then treated it with RPM3; after surface functionalization, the sample was flooded with deionized water and the increasing level of brine (1, 2, 5, 6, and 10%). The results of these experiments with sample B-1 at
different flow rates of 1, 2, and 3 mL/min are given in Figure 7. Generally, higher salinity values and higher flow rates resulted in a decrease in the RRF value. The decrease caused by the flow rate was possibly due to the further loss of the adsorbed RPM or elasticity and the deformability of polymer layers. The effect of brine concentration on the RRF value is explained by the mechanism of polymer mixing with brine, as shown in Figure 8. In brief, the polymer chains stretch in deionized water because of the induced charge repulsion of carboxylate ions along the polymer backbone, thus causing permeability reduction. After the polymer is exposed to brine, some of the monovalent ions (i.e., Na⁺, K⁺) present in the brine weaken the electrostatic repulsion between the carboxylate because of the presence of electrostatic shielding. In this way, the carboxylate chains collapse, causing the permeability to increase (thus reducing the RRF). Increasing brine salinity makes this effect more significant. In field applications, it may be useful to undertake measures to reduce the brine concentrations in the RPM-treated zones of the formation to achieve better surface functionalization.

2.4.2. Brine/Oil Flooding (Sample C-3 to C-4). To determine the impact of different brine salinity on the behavior of RPM, 2 and 6 wt % salinity brine have been used for core flooding tests, as shown in Table 3. The results indicate that when the samples are treated using the same RPM (i.e., RPM2), the sample flooded with 6 wt % brine has relatively lower values of both RRF_{brine} and RRF_{oil} than those samples flooded by 2 wt % brine after the RPM treatment. Therefore, during brine/oil/RPM flooding, brine would simultaneously cause a reduction of RRF_{brine} and RRF_{oil} showing the similar effect on the RPM, as observed in brine/RPM flooding.

2.5. Effect of Permeability/Pore Structure. Because of the inherent heterogeneities of carbonate rocks, it is challenging to accurately find consistent cores, so it can be observed that the performance of the RPM varied with rock properties while using the same concentration of polymers under the same experimental conditions (i.e., temperature, pressure, and salinity).

2.5.1. Brine or Deionized Water Flooding (Sample A-7 and B-1; A2, A5, and A6). Upon comparing samples A-7 and B-1, A-7 has a lower initial absolute brine permeability (i.e., 223.8 to 378.4 mD); A-7 has a significantly lower RRF value compared to B-1 for distilled water. A similar trend was also observed comparing samples A-2 and A-5 both treated with RPM2. Despite sample A-5 being flooded by higher-salinity (i.e., 5 wt % NaCl) brine, which on its own would cause a decrease in RRF, the RRF value actually increases for sample A-5 compared to A-2, and this can be attributed to the difference in permeability as well. Furthermore, sample A-5 yields a higher RRF than sample A-6, which was treated by a higher concentration of the RPM (i.e., RPM3); on its own, a higher concentration of RPM is expected to yield a higher RRF value because of the increased polymer functionalization. The higher permeability of A-5 compared to both A-2 and A-6 is the likely explanation for this anomalous behavior. This is possibly because a relatively higher fraction of larger pores would contribute greatly to the brine absolute permeability compared to smaller pores. In addition, low-field NMR measurements were performed to understand the distribution of pore sizes because of the correlation between the transverse relaxation time (T₂) and pore size. The carbonate rock pores can be categorized as micropores (T₂ < 100 ms), mesopores, and macropores (T₂ > 100 ms). In this study, four sections (<10 ms, 10−100 ms, 100–1000 ms, and >1000 ms) of the T₂ spectrum were divided in order to compare these samples in detail, as indicated in Table 4. Sample A-5 has the relatively higher increment porosity at T₂ > 1000 ms.
Performing the history matching in the Sendra software package. The results indicated that after the RPM treatment, the cross-over points of relative permeability in these four samples shifted to the right side because of the larger decrease in water relative permeability compared with oil relative permeability, as indicated in Figure 10. In addition, irreducible water saturation increased slightly because of the adsorption of the RPM after the RPM treatment. A minor increase in residual oil saturation (Sor) as well was possibly caused by the hysteresis effect. End-point relative permeability to water in sample C-5 decreased by 80%, as indicated in Table 3, showing reduction higher than that in sample C-2 (i.e., 74%). This result is favorably correspondent with the variations of the RRF values. However, Kr curves also indicated stronger formation damage in samples C-1, C-2, and C-4 than in sample C-5. This was possibly caused by the stronger polymer adsorption (i.e., RPM2), precipitation, hysteresis, or compaction. However, the effect of RPM is the main role based on experimental observations and related literature.\textsuperscript{17,21,27} Additionally, based on the recent literature in sandstone rocks,\textsuperscript{9,47,48} DPR ratios varied from 2 to 4 and RRF\textsubscript{oil} ranged from 1.2 to 4 while using polymers as RPM materials. Therefore, the newly developed RPM in carbonate rocks is comparable to these RPMs used in sandstone rocks.

**3. CONCLUSIONS**

In this study, a series of core floods have been designed and performed in order to verify the effectiveness of a novel RPM under reservoir conditions (1500 psi, 60 °C) and explore the key influencing factors including the concentration of PAM-co-AA, brine salinity, rock permeability, and pore structure. Some conclusions are described as follows:

1. It has been observed that the polymer exists clearly in larger pores and smaller pores from the SEM images after RPM treatments. The increase in the relative proportion

| Table 4. Porosity Distribution at Different Ranges of T\textsubscript{2} in the Samples\textsuperscript{a} |
|---------------------------------|-------|-------|-------|
| T\textsubscript{2} (ms) | A-2   | A-5   | A-6   |
| <10               | 2.34  | 0.58  | 2.46  |
| 10–100           | 0.455 | 0.41  | 0.45  |
| 100–1000         | 8.34  | 7.59  | 8.45  |
| >10000          | 0.41  | 2.64  | 0.59  |

Note: Porosity distribution was determined in four ranges of T\textsubscript{2} relaxation time. T\textsubscript{2} relaxation time increased by the pore radius. Larger porosity in the higher T\textsubscript{2} range indicates more pores with a higher pore radius.

and fall in the range of 2–5%, whereas these samples have a lower increment porosity at T\textsubscript{2} < 100 ms in comparison with sample A-2 and A-6, as can be seen in Figure 9. This indicates that sample A-6 has a higher average pore radius associated with mesopores or macropores, leading to a higher permeability. Furthermore, a larger number of pores with higher surface areas can benefit RPM adsorption, which can cause a higher permeability reduction.

2.5.2. Brine/Oil Flooding (Sample C1 to C4, C2 to C5). The increase in rock permeability would individually promote permeability reduction without considering other conditions (i.e., polymer concentration and salinity), resulting in an increase in RRF\textsubscript{oil} and RRF\textsubscript{brine}.\textsuperscript{7} Comparing the results from sample C-1 and C-4 where the same salinity and RPM formulation are used (i.e., RPM2), an increase in the absolute brine permeability (i.e., comparing C-4 with C-1) causes a marked increase in both RRF\textsubscript{oil} (from 2.75 to 3.23) and RRF\textsubscript{brine} (from 4.40 to 7.89). This is consistent with the literature results, and interestingly, an increase in the rock permeability caused an increase in the DPR ratio as well. This trend was also observed when samples C-5 and C-2 were flooded at similar experimental conditions (2% salinity and RPM1 with 0.05 wt % polymer), as can be seen in Table 3, whereas sample C-5 exhibits a higher RRF\textsubscript{brine} (from 3.62 to 4.99) and lower RRF\textsubscript{oil} (from 2.07 to 1.64). The disproportionate ratio of sample C-5 is approximately 3.05, indicating a higher water permeability reduction in high permeable samples with less impact on crude oil permeability. The variations of the disproportionate ratio in these samples show that initial permeability plays an essential role in the performance of the RPM. Hence, it seems that relatively higher permeable samples have a higher DPR ratio. Relative permeability correlated with water saturation was calculated using the Sigmund and McCaffery\textsuperscript{16} model after

![Figure 9. T\textsubscript{2} relaxation time of carbonate rock samples. Sample A-6 has the higher T\textsubscript{2} spectrum peak compared with samples A-2 and A-5, indicating a larger pore radius.](https://doi.org/10.1021/acsomega.1c00820)
of elements (N wt %, Si wt %, and C wt %) of rock surfaces provided evidence that the RPM exhibits good adsorption onto carbonate rocks.

(2) Increasing the concentration of PAM-co-AA in RPM can result in higher values of RRFoil and RRFbrine because of the strong chemical adsorption of RPM. RPM1 with a concentration of 0.5% wt polymer has less impact on oil permeability because of RRFoil less than 2, indicating lower oil permeability reduction while significantly reducing the water permeability.

(3) RRFbrine decreased by increasing brine salinity after the RPM treatment. Increasing the salinity of brine can mitigate electrostatic repulsion because of electrostatic shielding at a high brine salinity. However, RRFbrine can reach up to 50 and 45 at the flow rate of 2 and 3 cc/min while using 10% salinity brine, showing good performance at a higher salinity as well.

(4) After the RPM treatment, the cross-over points of relative permeability in these four samples shifted to the right because of larger decrease in relative water permeability compared with relative oil permeability. Brine/ RPM flooding showed that higher permeable samples have higher RRFbrine. NMR measurements provided evidence that the sample with a higher permeability has a larger pore radius which can probably benefit the adsorption of RPM. Two-phase flooding also showed that high permeable samples have higher disproportionate ratios (RRFbrine/RRFoil), indicating reducing water permeability more than oil permeability.

(5) The main mechanism causing a disproportionate ratio is due to polymer hydration and swelling caused by RPM adsorption. Moreover, some water in smaller pores was possibly shut off by bridge adsorption after RPM flooding.

4. EXPERIMENTS AND METHODS

4.1. Core Samples and Materials. Thirteen Indiana carbonate cores (Kocurek Industries, USA) were used for core flooding tests. These cores are composed approximately of calcite (98.16 wt % on average). Prior to use, all the samples were cleaned using methanol and toluene to remove the contaminants (i.e., salt and organic matter) via the Dean–Stark extraction method for 24 h. After drying in an oven for another 24 h at 60 °C, the petrophysical parameters were measured using an automated gas pore-perm apparatus, as shown in Table 5.

4.2. RPM Preparation. All chemicals purchased for RPM formulation are of reagent grade, which were purchased from Sigma-Aldrich (Australia) and were used as received without further purification. The chemicals include formaldehyde (36 wt %), PAM-co-AA (poly (acrylamide-co-acrylic acid) partial...
sodium salt, $M_w$ 520,000, $M_n$ 150,000 (typical), 80 wt % sodium silicate (determined by gravity analysis, 12−13 wt % silicon, 10 wt % of NaOH) and APTES (99 wt %). RPM formulations (based on our previous work)\textsuperscript{34} with three different concentrations of PAM-co-AA were used, and the exact compositions of these (i.e., RPM1, RPM2, and RPM3) are shown in Table 6 and Figure 12. As an example, the method for using RPM1 formulation is as follows. As described in our previous study,\textsuperscript{34} this silylated polyacrylamide-based RPM consists of two main chemical parts containing the adsorption component (sodium silicate and APTES) and the polymer component. First, 0.1252 g of PAM-co-AA was added to 3.13 g of deionized water to give a 4 wt % solution. After subsequent stirring using a magnetic stirrer in a small glass vial at room temperature for 30 min, 0.05 g of 36 wt % formaldehyde was added to the PAM-co-PAA solution and kept for another 30 min. Next, in a separate beaker, 1.19 g of 80 wt % sodium silicate solution was mixed with 50 g of deionized water. Then, 0.81 g of APTES was added to this diluted sodium silicate solution and mixed thoroughly. Water (194.83 g) was then added to the sodium silicate/APTES mixture in a glass jar. Finally, the previously prepared polymer/formaldehyde solution was added into this mixture which was thoroughly mixed.

![Figure 11](https://doi.org/10.1021/acsomega.1c00820)

**Figure 11.** Schematic of RPM flowing through porous carbonate cores: (a) oil and water were injected, and irreducible water existed in smaller and dead pores, (b) RPM transported in larger pores, and bridge adsorption occurred, (c) water permeability decreased because of the hydration of polymer, (d) RPM dehydrated because of oil displacement.

### Table 5. Petrophysical Properties of the Samples

| Sample ID | Pore Volume (cm$^3$) | Porosity (%) | $K_{gs}$ (md) |
|-----------|---------------------|--------------|---------------|
| A-1       | 16.48               | 19.04        | 160.1         |
| A-2       | 15.78               | 18.07        | 316.4         |
| A-3       | 13.76               | 16.14        | 246.58        |
| A-4       | 12.95               | 15.12        | 369.53        |
| A-5       | 13.5                | 15.68        | 381.96        |
| A-6       | 15.55               | 17.7         | 272.11        |
| A-7       | 17.2                | 19.54        | 223.77        |
| B-1       | 12.84               | 15.01        | 378.43        |
| C-1       | 15.84               | 18.07        | 131.6         |
| C-2       | 16.03               | 18.22        | 118.78        |
| C-3       | 15.12               | 17.37        | 228.53        |
| C-4       | 13.12               | 15.31        | 265.08        |
| C-5       | 13.56               | 15.85        | 251.91        |

### Table 6. Amount of Each Chemical Formulating RPM\textsuperscript{a}

| RPM  | Total Weight (g) | Sodium Silicate Solution (g) | APTES (g) | PAM-co-AA Solution (4 wt %) (g) | Formaldehyde Solution (36 wt %) (g) | Deionized Water (g) | Concentration of PAM-co-AA (wt %) |
|------|------------------|-------------------------------|-----------|----------------------------------|-------------------------------------|---------------------|----------------------------------|
| RPM1 | 250              | 1.19                          | 0.81      | 3.13                             | 0.05                                | 244.82              | 0.05                             |
| RPM2 | 200              | 1.76                          | 1.19      | 5.00                             | 0.07                                | 191.98              | 0.10                             |
| RPM3 | 200              | 2.66                          | 1.91      | 7.50                             | 0.10                                | 187.83              | 0.15                             |

\textsuperscript{a}Note: RPMs (RPM1, RPM2, and RPM3) present three concentrations of PAM-co-AA. The amount of each chemical increased by the same ratio.
The whole RPM1 solution was kept for 30 min before being injected into the core samples.

4.3. SEM–EDX Measurements. SEM coupled with an Oxford EDX detector analysis has been carried out to perform the microscopic observations of the treated carbonate cores by the RPM. After the three core samples (A-7, A-3, and A-2) were flooded and treated with RPMs and then flooded with brine (or distilled water in the case of A-7), they were then dried in an oven for 24 h at 60 °C prior to the SEM analysis. Next, the prepared samples were measured by SEM–EDX, and some microm-scale images were captured. EDX spectra were obtained at three representative sites and were used to quantitatively calculate the weight percentage of each element.

4.4. NMR Measurements. A low-field NMR (2 MHz) instrument was used to measure the transverse relaxation time (T2) for water within the pore space to understand the porosity distribution and quantitative pore size distribution. The echo numbers and scanning times for all the samples are 50,000 and 64, respectively. The waiting time (T1w) and echo time (T2) were set at 500 and 0.1 ms, respectively. The NMR instrument was calibrated using brine standard prior to the analysis of rock samples. To prepare the samples for NMR analysis, the rock sample was vacuumed using a pump for 24 h. To ensure that full brine saturation was achieved.

4.5. Core Flooding Tests. 4.5.1. Crude Oil and Brine. Texas light oil was used for the core flooding test during the drainage process. The viscosity at 60 °C is approximately 10.5 cp, and the compositions of this oil include 31.7 wt % asphaltenes, 26.3 wt % naphthenes, 2.8 wt % wax, and 3.9 wt % sulfur. Five brine salinity levels (1, 2, 5, 6, and 10 wt % NaCl) were used during brine flooding. The brine viscosity under core flooding conditions (i.e., 1500 psi at 60 °C) is shown in Table 7.

4.5.2. Core Flooding Procedures. Figure 13 depicts the schematic of the core flooding apparatus, and Table 2 describes the experimental conditions of core flooding tests. According to the recent literature referring to the RPM flooding tests, the procedures for brine saturating the samples and the core flooding tests are summarized as follows:

1. The core plug inside a Viton sleeve was placed into the core holder and then transferred into an oven set to 60 °C.
2. The confining pressure was set at 2500 psi using a syringe pump. After this, the pore pressure line (including the rock sample) was vacuumsed using a pump for 24 h.
3. The prepared brine (concentrations given in Tables 4 and 5) was injected using a syringe pump until the injection pressure increased to 1500 psi, which is close to the outlet back pressure (1500 psi) controlled using a back pressure regulator. Afterward, the sample was aged for 24 h to ensure that full brine saturation was achieved.
4. Brine was injected at the rate of 1 cc/min, and the permeability was determined from the stabilized inlet and outlet pressure values and reported as the absolute brine permeability.

This is followed by three different types of flooding experiments which were conducted on the brine saturated samples which look at concentration and salinity effects (details provided below) before and after the RPM treatment and then oil-displacing brine end-point permeability before and after the treatment (details provided below).

4.5.3. Experiments with the Concentration Effect (Samples A-1 to A-7). Two PVs (pore volumes) of the RPM (made from deionized water) were initially injected at 0.5 cc/min to displace brine saturated in the sample. After the whole equipment was aged for 14 h, the brine was injected at 1 cc/min to displace the RPM and ceased once the differential pressure remained steady. The brine permeability at 1 cc/min before and after the RPM treatment can be calculated via Darcy’s law. After the core flooding tests, the three samples (A-7, A-3, and A-2) were analyzed by SEM–EDX.

4.5.4. Experiments to Study the Salinity Effect (Sample B-1). Two PVs (pore volumes) of RPM3 (made from di-ionized water) were injected at 0.5 cc/min to displace deionized water saturated in the sample. After the sample was aged for 24 h, deionized water was injected at 2 cc/min to displace the RPM and ceased once the differential pressure remained steady. Then, different salinity levels of brine (1, 2, 5, 6, and 10%) in a sequence were injected at 1, 2, and 3 cc/min. Each salinity brine was aged for 24 h and then flooded again.

4.5.5. Experiments with Two-Phase Flow (Samples C-1 to C-5). Crude oil was injected at 1 cc/min to displace the brine (concentrations given in Table 5) until the pressure remained steady at residual water saturation (S_w). Brine was then reinjected at 1 cc/min again to displace oil and ceased when the differential pressure remained the same at the residual oil saturation (S_o). To decrease the hysteresis effect, the oil and brine were injected separately at 1 cc/min for many cycles and...
ceased until the differential pressure at the \( S_w \) and \( S_o \) end points remained relatively unchanged. Next, two PVs of the RPM was injected at 0.5 cc/min and subsequently aged for 24 h. Then, 4 to 5 PVs of brine were injected to displace the RPM until brine flowed from the cores. Afterward, crude oil was injected again at 1 cc/min to displace the brine, and the inlet with outlet pressure points were recorded. Finally, the oil and brine permeability (\( K_w \) and \( K_b \)) at \( S_o \) and \( S_w \) before and after the RPM treatment was derived.

■ AUTHOR INFORMATION

Corresponding Authors

Ali Saeedi — Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia; orcid.org/0000-0002-9499-8769; Phone: 61-8-9266 4988; Email: Ali.Saeedi@Curtin.edu.au

Colin D. Wood — Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia; CSIRO Australian Resources Research Centre, Kensington, Western Australia 6151, Australia; orcid.org/0000-0001-6160-0112; Phone: 61-8-6436 8701; Email: Colin.Wood@csiro.au

Authors

Liming Qin — Department of Petroleum Engineering, Curtin University, Perth, Western Australia 6102, Australia; Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia; CSIRO Australian Resources Research Centre, Kensington, Western Australia 6151, Australia; orcid.org/0000-0003-0855-801X

Matthew B. Myers — CSIRO Australian Resources Research Centre, Kensington, Western Australia 6151, Australia; orcid.org/0000-0002-5889-4196

Claus Otto — Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia

Michael Verrall — CSIRO Australian Resources Research Centre, Kensington, Western Australia 6151, Australia

Zhiqi Zhong — Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia

Eghan Arjomand — Curtin University Oil and Gas Innovation Centre (CUOGIC), Curtin University, Perth, Western Australia 6102, Australia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00820

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully thank Curtin University Oil and Gas Innovation Centre (CUOGIC) for providing funding for this research. The authors also would like to acknowledge the help from Prores AS for granting us access to their core-flood interpretation software package, Sendra.

■ REFERENCES

(1) Grattoni, C. A.; Luckham, P. F.; Jing, X. D.; Norman, L.; Zimmerman, R. W. Polymers as relative permeability modifiers: adsorption and the dynamic formation of thick polyacrylamide layers. J. Petrol. Sci. Eng. 2004, 45, 233–245.

(2) Alfarge, D. K.; Wei, M. Z.; Bai, B. J. Numerical simulation study of factors affecting relative permeability modification for water-shutoff treatments. Fuel 2017, 207, 226–239.

(3) Al-Hulail, I.; Shakeel, M.; Bingham, A.; Zeghouani, M.; Rahal, R.; Al-Taq, A.; Al-Rustum, A., Water Control in High-Water-Cut Oil Wells using Relative Permeability Modifiers: A Saudi Lab Study. In SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Society of Petroleum Engineers: Dammam, Saudi Arabia, 2017; 8.

(4) Nelson, S. G.; Kafayan, L. J.; Rittenberry, W. M., The Application of a New and Unique Relative Permeability Modifier in Selectively Reducing Water Production. In SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers: Denver, CO, 2003; p 7.

Figure 13. Schematic diagram of the core flooding apparatus. Two syringe pumps were used for controlling the injection pressure and confining pressure. The effluent was collected using a fluid collector. The fluids (oil and brine) were maintained in the oven, and the RPM was kept outside the oven. A laptop recorded the pressure drop.
(5) Cornwall, C. K.; Boughey, A., Relative Permeability Modifier (RPM): Suitability Screening With Reservoir Core Under Reservoir Conditions. SPE International Symposium and Exhibition on Formation Damage Control, Society of Petroleum Engineers: Lafayette, LA, 2008; 9.

(6) Vasquez, J.; Eoff, L., A Relative Permeability Modifier for Water Control: Candidate Selection, Case Histories, and Lessons Learned after more than 3,000 Well Interventions. In SPE European Formation Damage Conference & Exhibition, Society of Petroleum Engineers: Noordwijk, The Netherlands, 2013; 13.

(7) Liang, J.; Seright, R. S. Wall-effect/gel-droplet model of disproportionate permeability reduction. SPE J. 2001, 6, 268−272.

(8) Song, Z. J.; Hou, J. R.; Zhang, L. Y.; Chen, Z. Y.; Li, M. Experimental study on disproportionate permeability reduction caused by non-recovered fracturing fluids in tight oil reservoirs. Fuel 2018, 226, 627−634.

(9) Seright, R. S. Disproportionate Permeability Reduction With Pore-Filling Gels. SPE J. 2009, 14, 5−13.

(10) Liang, J.-T.; Sun, H.; Seright, R. S. Why Do Gels Reduce Water Permeability More Than Oil Permeability? SPE Reserv. Eng. 1995, 10, 252−286.

(11) Liang, J.-T.; Seright, R. S. Further Investigations of Why Gels Reduce Water Permeability More Than Oil Permeability. SPE-37249-PA 1997, 12, 225−230.

(12) Willhite, G. P.; Zhu, H.; Natarajan, D.; McCool, C. S.; Green, D. W. Mechanisms causing disproportionate permeability reduction in porous media treated with chromium acetate/HPAM gels. SPE J. 2002, 7, 100−108.

(13) Salehi, M. B.; Soleimanian, M.; Moghadam, A. M. Examination of disproportionate permeability reduction mechanism on rupture of hydrogels performance. Colloid Surf. A 2019, 560, 1−8.

(14) Seright, R. S.; Liang, J.; Lindquist, W. B.; Dunsuir, J. H. Characterizing disproportionate permeability reduction using synchrotron X-ray computed microtomography. SPE Reserv. Eval. Eng. 2002, 5, 355−364.

(15) Stavland, A.; Ekran, S.; Hettetriver, K. O.; Jakobsen, S. R.; Schmidt, T.; Schilling, B. Disproportionate permeability reduction is not a panacea. SPE Reserv. Eval. Eng. 1998, 1, 359−366.

(16) Askarinezhad, R.; Hatzignatiou, D. G.; Stavland, A. Disproportionate Permeability Reduction of Water-Soluble Silicate Gels: Importance of Formation Wettability. SPE Prod. Oper. 2017, 32, 362−373.

(17) Song, Z. J.; Liu, L. B.; Wei, M. Z.; Bai, B. J.; Hou, J. R.; Li, Z. P.; Hu, Y. P. Effect of polymer on disproportionate permeability reduction to gas and water for fractured shales. Fuel 2015, 143, 28−37.

(18) Nguyen, T. Q.; Green, D. W.; Willhite, G. P.; McCool, C. S. Effects of gelant composition and pressure gradients of water and oil on disproportionate permeability reduction of sandpacks treated with polyacrylamide-chromium acetate gels. SPE J. 2006, 11, 145−157.

(19) Governing mechanism of disproportionate permeability reduction. J. Petrol. Technol. 2001, 53 (1), 39−39, DOI: 10.2118/120118−MS-JPT.

(20) Ye, Z. B.; He, E. Q.; Xie, S. Y.; Han, L. J.; Chen, H.; Luo, P. Y.; Shu, Z.; Shi, L. T.; Lai, N. J. The mechanism study of disproportionate permeability reduction by hydrophobically associating water-soluble polymer gel. J. Petrol. Sci. Eng. 2010, 72, 64−66.

(21) Liang, B.; Jiang, H. Q.; Li, J. J.; Chen, F. Z.; Miao, W. P.; Yang, H. X.; Qiao, Y.; Chen, W. B. Mechanism Study of Disproportionate Permeability Reduction Using Nuclear Magnetic Resonance T2. Energy Fuels 2018, 32, 4959−4968.

(22) Bekbauov, B. E.; Kaltryav, A.; Wojtanowicza, A. K.; Panfilov, M. Numerical Modeling of the Effects of Disproportionate Permeability Reduction Water-Shutoff Treatments on Water Coning. J. Energy Resour.-ASME 2013, 135, No. 011101.

(23) Seright, R. S.; Prodanovic, M.; Lindquist, W. B. X-ray computed microtomography studies of fluid partitioning in drainage and imbibition before and after gel placement: Disproportionate permeability reduction. SPE J. 2006, 11, 159−170.

(24) Al-Sharji, H. H.; Grattoni, C. A.; Dawe, R. A.; Zimmerman, R. W. Disproportionate Permeability Reduction Due to Polymer Adsorption Entanglement. In SPE European Formation Damage Conference, Society of Petroleum Engineers: The Hague, The Netherlands, 2001; 11.

(25) Cohen, Y.; Metzner, A. B. Adsorption effects in the flow of polymer solutions through capillaries. Macromolecules 1982, 15, 1425−1429.

(26) Zaitoun, A.; Chauveau, G., Effect of Pore Structure and Residual Oil on Polymer Bridging Adsorption. In SPE/DOE Improved Oil Recovery Symposium, Society of Petroleum Engineers: Tulsa, OK, 1998; 15.

(27) Zaitoun, A.; Kohler, N., Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. In SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers: Houston, TX, 1988; p 14.

(28) Mennella, A.; Chiappa, L.; Bryant, S. L.; Burrufato, G., Pore-scale Mechanism for Selective Permeability Reduction by Polymer Injection. In SPE/DOE Improved Oil Recovery Symposium, Society of Petroleum Engineers: Tulsa, OK, 1998; 12.

(29) Nguyen, T. Q.; Green, D. W.; Willhite, G. P.; McCool, C. S., Effect of Composition of a Polyacrylamide-Chromium(III) Acetate Gel on the Magnitude of Gel Dehydration and Disproportionate Permeability Reduction. In SPE/DOE Symposium on Improved Oil Recovery, Society of Petroleum Engineers: Tulsa, OK, 2004; 17.

(30) Chiappa, L.; Mennella, A.; Lockhart, T. P.; Burrufato, G., Polymer adsorption at the brine/rock interface: the role of electrostatic interactions and wettability. J. Petrol. Sci. Eng. 1999, 24, 113−122.

(31) Wood, C.; K.; Karen; Pham, Khoa; Al-muntasheeri, G. A. Method for chemically adsorbing to carbonate surfaces; 2012.

(32) Seright, R. S.; Martin, F. D. Impact of GELation Ph, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel. SPE Reserv. Eval. Eng. 1993, 8, 43−50.

(33) Ayman, R.; Al-Nakkhi, M.B., Ayman, Almohsin, Hamed, Al-Badiary, A. Breakthrough Water Shutoff System for Super-K Zones in Carbonate Ghawar Field: Adsorption and Polymer System. In Abu Dhabi International Petroleum Exhibition & Conference, Society of Petroleum Engineers: Abu Dhabi, UAE, 2016.

(34) Qin, L.; Arjomand, E.; Myers, M. B.; Otto, C.; Pejicic, B.; Heath, C.; Saeedi, A.; Wood, C. Mechanistic Aspects of Polymeric Relative Permeability Modifier Adsorption onto Carbonate Rocks. Energy Fuels 2020, 12065.

(35) Afolabi, R. O.; Oluyemi, G. F.; Officer, St.; Ugwu, J. O. Hydrophobically associating polymers for enhanced oil recovery : Part A: A review on the effects of some key reservoir conditions. J. Petrol. Sci. Eng. 2019, 180, 681−698.

(36) Jain, R.; Mahto, V.; Sharma, V. P. Evaluation of polyacrylamide-grafted-polyethylene glycol/silica nanocomposite as potential additive in water based drilling mud for reactive shale formation. J. Nat. Gas Sci. Eng. 2015, 26, 526−537.

(37) Seright, R. S. How Much Polymer Should Be Injected During a Polymer Flood? Review of Previous and Current Practices. SPE J. 2017, 22, 1−18.

(38) Kerrans, C.; Tinker, S. W.; SEPM, Sequence stratigraphy and characterization of carbonate reservoirs. SEPM: Tulsa, OK, 1997.

(39) Yao, C. J.; Wang, D.; Wang, J.; Hou, J.; Lei, G. L.; Steenhuis, T. S. Effect of Ionic Strength on the Transport and Retention of Polyacrylamide Microspheres in Reservoir Water Shutoff Treatment. Ind. Eng. Chem. Res. 2017, 56, 8158−8168.

(40) Al-Shajalee, F.; Arif, M.; Sari, A.; Wood, C.; Al-Bayati, D.; Xie, Q.; Saeedi, A. Low-Salinity-Assisted Cationic Polyacrylamide Water Shutoff in Low-Permeability Sandstone Gas Reservoirs. Energy Fuels 2020, 34, 5524−5536.

(41) Mao, J. C.; Tan, H. Z.; Yang, B.; Zhang, W. L.; Yang, X. J.; Zhang, Y.; Zhang, H. Novel Hydrophobic Associating Polymer with Good Salt Tolerance. Polymers 2018, 10 (2).

(42) Regnet, J. B.; David, C.; Robion, P.; Menendez, B. Microstructures and physical properties in carbonate rocks: A comprehensive review. Mar. Petrol. Geol. 2019, 103, 366−376.
Wei, D.; Gao, Z. Q.; Fan, T. L.; Meng, M. M.; Chen, Y.; Li, Y. B.; Zhang, C. J. New Insight into the Characteristics of Tight Carbonate based on Nuclear Magnetic Resonance. *Energy Fuels* 2018, 32, 2962–2972.

Wei, D.; Gao, Z. Q.; Zhang, C.; Fan, T. L.; Karubandika, G. M.; Meng, M. M. Pore characteristics of the carbonate shoal from fractal perspective. *J. Petrol. Sci. Eng.* 2019, 174, 1249–1260.

Vincent, B.; Fleury, M.; Santerre, Y.; Brigaud, B. NMR relaxation of neritic carbonates: An integrated petrophysical and petrographical approach. *J. Appl. Geophys.* 2011, 74, 38–58.

Sigmund, P. M.; McCaffery, F. G. An Improved Unsteady-State Procedure for Determining the Relative-Permeability Characteristics of Heterogeneous Porous Media (includes associated papers 8028 and 8777). *SPE-5556-PA* 1979, 19, 15–28.

Maffra, D. A.; Freitas, T. C.; da Cruz, G. F.; de Siqueira, F. D.; do Rosario, F. F. Evaluation of Barium Sulfate Scale Inhibition Using Relative Permeability Modifier Polymers as Adsorption Enhancer for Mature Offshore Well Treatments in Campos Basin, Brazil. *Ind. Eng. Chem. Res.* 2018, 57, 11493–11504.

Abbas, A.; Saaid, I. M.; Shafian, S. R. M. Novel Relative Permeability Modifier using Polymer Grafted Nanoclay. *Energy Fuels* 2020, 34, 2703–2709.

Freire-Gormaly, M.; Ellis, J. S.; MacLean, H. L.; Bazylik, A. Pore Structure Characterization of Indiana Limestone and Pink Dolomite from Pore Network Reconstructions. *Oil Gas Sci. Technol.* 2016, 71, 53.

Kestin, J.; Khalifa, H. E.; Correia, R. J. Tables of the Dynamic and Kinematic Viscosity of Aqueous NaCl Solutions in the Temperature-Range 20–150 °C and the Pressure Range 0.1–35 Mpa. *J. Phys. Chem. Ref. Data* 1981, 10, 71–88.