Comprehensive Investigation of Dynamic Characteristics of Amphoteric Surfactant–Sulfonated Polymer Solution on Carbonate Rocks in Reservoir Conditions

Xianmin Zhou, Muhammad Shahzad Kamal, and Alhasan B. Fuseni

ABSTRACT: To recover the remaining oil after water flooding, amphoteric surfactant–sulfonated polymer (S-P) flooding has attracted attention as a tertiary oil recovery technique. Oil recovery by S-P flooding not only is influenced by reservoir heterogeneity but also depends on chemical adsorption and interactions of S-P solution with the surface of rocks. This paper presents comprehensive laboratory results related to the dynamic adsorption, resistance factor (RF), residual resistance factor (RRF), and adsorbed layer thickness of S-P solution on the surface of carbonate rocks. Three core flooding experiments were conducted. The S-P solution was composed of an amphoteric surfactant (0.2 wt %) and sulfonated polymer solution (0.2 wt %) in seawater. The S-P solution was injected until the effluent concentration reached the inlet concentration. Seawater was injected after S-P injection to displace S-P solution until the effluent concentration reduced to a minimum value or constant value for desorption study. Total organic carbon (TOC) and Hyamine methods were used to determine the adsorption of the polymer and surfactant, respectively. The individual amount of dynamic adsorption and the total amount of adsorption of S-P solution onto carbonate rock were determined and compared with the results of single adsorption of a surfactant solution published previously. The residual resistance factor, resistance factor, and adsorbed layer thickness of the S-P solution on carbonate rocks were calculated based on the differential pressure before and after injecting the S-P solution. We found that the dynamic adsorption, RF, RRF, and adsorbed layer thickness of the S-P solution strongly depends on pore geometry or reservoir properties. Some of the relationships are proposed for the first time. The loss of injectivity and liquid permeability during S-P solution injection are evaluated in detail in this paper. This paper presents insights into the dynamic adsorption, residual resistance factor, resistance factor, adsorbed layer thickness, and injectivity of S-P solution on carbonate rocks with reservoir parameters, which could help in designing the chemical enhanced oil recovery process in carbonate reservoirs.

1. INTRODUCTION

Surfactant–polymer (S-P) flooding is a major enhanced oil recovery (EOR) technique for improving volumetric sweep efficiency and reducing residual oil saturation (ROS) after water flooding.1–5 The S-P slug could change wetting behavior by the interaction of rock/oil/surfactant and also provide improved mobility control.6–10 One of the major problems of S-P floods is the loss of chemicals in the formation due to retention/adsorption. This loss of surfactant has a direct influence on the oil recovery and economics of the EOR process. Many researchers have investigated and measured quantitatively the adsorption of the surfactant and polymer solution onto the surface of sandstone cores and the factors...
affecting the adsorption. However, only a few studies were conducted for carbonate cores.

1.1. Dynamic Adsorption and Permeability Reduction of Polymer Solution. Adsorption and permeability reduction of polymer solution plays an important role in the design of formulation for field application of surfactant—polymer flooding. The adsorption process is complex and depends strongly on the chemical solution concentration, salt concentration, pH, reservoir temperature, injection rate, pore structure, and wettability of the rocks. Brosota et al.11 addressed the effect of core wettability and residual oil saturations on polymer retention. Two types of polymers (polyacrylamides and polysaccharides) were used for their study. It was found that the effect of nonionic polyacrylamide and polysaccharide was stronger than that of anionic polyacrylamide. In oil-wet cores, adsorption decreased considerably in the presence of oil, while it increased slightly in water-wet cores.

Zheng et al.6 examined the effect of polymer adsorption on recovery in Berea sandstone and reservoir sandstone cores using steady-state and unsteady-state core flooding experiments. The measurements of polymer adsorption and relative permeability were performed. The results showed that the relative permeability reduction to the water phase in the presence of residual oil is higher than at water saturation of 100%, and polymer adsorption and relative permeability reduction increase with an increase in the polymer concentration. Relative permeability reduction is a function of polymer adsorption. The relative permeability curve exhibits an "s-type curve".

Experimental investigation of the influence of an adsorption-polymer layer on two-phase flow behavior through porous media based on the relative permeability at endpoints and capillary pressure has been reported by Barreau et al.12 and Zaitoun and Kohler.13 Barreau et al.12 experimentally determined relative permeability and capillary pressure after injection of water-soluble polymer solutions by an unsteady-state flow test for water-wet and oil-wet sandstone cores in ambient conditions. Synthetic brine, mineral oil, and high-molecular-weight nonionic polyacrylamide (HPAM) were used for core flooding tests. The conclusions related to polymer adsorption from the investigation are as follows: due to polymer adsorption, the relative permeability to water was reduced much more than the relative permeability to oil, and the effect of polymer adsorption on the relative permeability was the same for both water-wet and oil-wet cores.

Zaitoun and Kohler13 investigated the effect of an adsorbed polymer layer on a two-phase flow through sandstone cores. Two different polymers, PAM and polysaccharide G, were used in their study. Core flooding tests were conducted at a temperature of 36 and 60 °C. The main conclusions have shown that the quantity of adsorption of polymers on wet-sand and sandstone was almost the same as at full water saturation. However, the permeability reduction was enhanced due to trapped oil droplets and the relative permeability to oil is little affected by the presence of the adsorbed polymer in the core.

Al-Sharji et al.14 and Ogunberu et al.15 reported the effect of polymer adsorption on permeability reduction in the glass micromodels. Al-Sharji et al.14 described the mechanisms of polymer adsorption and lubrication in both water-wet and oil-wet glass models. Synthetic seawater as a water phase, commercial kerosene as an oil phase, and a cationic polyacrylamide polymer (CPAM) were used for flooding tests at a temperature of 70 °C. Ogunberu et al.15 presented the results of improvement of the adsorbed polymer layer in increasing the shear rate as "flow-induced adsorption". The critical shear rate for the polymer used was approximately 300 s⁻¹ in the absence of mechanical degradation.

Amro et al.16 investigated the effect of polymer adsorption using two types of polymers (polyacrylamide and xanthan gum) on sandstone cores in ambient conditions. The resistance factor (RF) and residual resistance factor (RRF) with different polymer concentrations were measured in the range of a frontal velocity of 2.5 to 8 ft./day. The results showed that the RF decreased with an increase in frontal velocity. The retention of the polymer on sandstone cores strongly depends on the frontal velocity of the polymer solution. Han et al.17 reported the injectivity of polymer solutions into carbonate rocks under reservoir conditions. The results showed that the RF was enhanced by increasing the flow rate, while the RRF was reduced slightly with the flow rate. The adsorbed polymer layer thickness was reduced with the frontal velocity at a concentration of 0.2 wt % but found to be constant for a polymer concentration of 0.1 wt % and a decrease in polymer concentrations.

Zhang et al.18 reported the effect of the polymer concentration on the dynamic retention of the HPAM polymer. The results showed that the dynamic retention of such polymers on sandstone rock is instantaneous and irreversible, and they analyzed the concentration-related retention mechanism in the three regions (dilute, semi-dilute, and fully concentrated regions).

Wever et al.19 studied the polymer dynamic retention on the actual sandstone reservoir rocks with and without a residual oil phase using HPAM. Five core flooding experiments were conducted at different temperatures. They found that higher polymer retention occurred in the rock without residual oil, and then the rock with residual oil resulted lower polymer retention, which was approximately 10 times lower for medium to low permeable rocks. The existence of residual oil in the rock strongly affects the dynamic adsorption of the polymer.

Ferreira et al.20 investigated the dynamic adsorption and readsoption of polymers on outcrop sandstone cores in a concentration range of 100 to 2000 ppm. The virgin and polymer flooded cores were used to measure the dynamic adsorption and readsoption of the polymer solution, respectively, and the effect of the permeability of rock on adsorption in reservoir conditions. The behavior of polymer adsorption in virgin cores can be characterized by type IV isotherm. A type I isotherm described polymer readsoption characteristics on the surface of the polymer flooded rock. The permeability reduction in the virgin core was higher than that in the polymer-flooded core during the process of adsorption and readsoption tests.21

1.2. Dynamic Adsorption of Surfactant Solution. The loss of surfactant in the form of adsorption and trapping during surfactant flooding as a tertiary oil recovery process for the reservoirs is the most critical issue that influences its success or failure.22,23 The surfactant retention in both sandstone and carbonate reservoirs depends on many factors that can be divided into two categories. One is determined by the properties of the chemicals themselves such as the type of surfactant, surfactant equivalent weight, ionic strength, PH, etc.24–27 The other is related to test conditions such as the type of rock, type of clay and clay content, surfactant
concentration, salinity of brine, injection rate, test temperature, etc.\textsuperscript{22,26,28–33} Kamal et al.\textsuperscript{27} and Belhaj et al.\textsuperscript{34} reviewed static adsorption of different surfactants and described adsorption and retention mechanisms of adsorbing surfactants onto the surface of minerals and how to apply them to the tertiary oil recovery as a displacing agent. For the dynamic adsorption of surfactants, very little work has appeared in the literature.\textsuperscript{22,33} Kulkarni et al.\textsuperscript{32} studied the effect of temperature and ionic strength on the adsorption of surfactants and reported that adsorption increased with an increase in temperature at low ionic strength. Zhou et al.\textsuperscript{22} investigated the dynamic adsorption of amphoteric surfactants on carbonate rocks. Core flooding experiments were conducted at reservoir conditions. The concentrations of surfactant solutions were 0.1, 0.2, 0.3, and 0.5 wt % in seawater. It was also found that the adsorption is a function of the surfactant initial concentration.

Solairaj et al.\textsuperscript{33} reported a comprehensive study of dynamic adsorption and retention for a variety of new-generation surfactants using three types of rocks from different outcrops, Berea and Bentheimer sandstone for sandstone formation, Silurian dolomite and Estillades limestone for carbonate formation, and one sand pack. Fifty-four core flooding experiments were carried out to measure and analyze the adsorption and retention of surfactants with different concentrations. They systematically analyzed the effect of various factors on dynamic adsorption and retention such as the acid number, pH, mobility ratio, co-solvent concentration, temperature, salinity, and surfactant molecular weight using a regression study. The results show that the retention of anionic surfactants was similar on both sandstone and carbonate rocks and decreased with an increase in pH or oil reactivity.

Ngo et al.\textsuperscript{35} measured the dynamic adsorption and desorption of surfactant sodium dodecyl benzene sulfonate in Berea sandstone to discuss the effect of the degree of the reversibility of surfactants by use of a reservoir simulator. Their results showed that the dynamic adsorption and desorption of surfactants increased with an increase in the concentration of surfactants and the effect of the reversibility of surfactant adsorption on oil production was different due to reservoir types.

1.3. Dynamic Adsorption of Surfactant–Polymer Solution. Austad et al.\textsuperscript{36} studied the effect of a polymer (xanthan and An125) on the adsorption of a surfactant (alkylpropoxylxythoxyl sulfate) onto sandstone cores using dynamic laboratory experiments using injection of water with and without a polymer. The long-term circulation and short-term experiments were carried out at 50 °C and 1 atm. Dynamic adsorption regimes in the long-term circulation experiments were affected by the presence of xanthan, which caused a 20% reduction in the adsorption. However, this reduction depends on the surfactant concentration.

Osterloh et al.\textsuperscript{37} reported experimental results of an anionic surfactant and polyethylene glycol (PEG) on Berea sandstone. Static and dynamic adsorption experiments were performed.

The results of the dynamic adsorption showed that adsorption of a 1.5 wt % surfactant in the absence and presence of 0.5 wt % PEG was 0.92 and 0.24 mg/g, respectively.

Wang et al.\textsuperscript{38} investigated the dynamic adsorption of surfactants in the presence of a polymer in carbonate rocks. Three kinds of dynamic adsorption of surfactants were studied such as in injecting surfactant solution only into the carbonate rocks, in use of a polymer slug followed by surfactant solution injection, and in co-injection of a surfactant and polymer. The results showed that the dynamic adsorption of the surfactant is the highest in the case of surfactant injection. In the other two cases, the adsorption density was similar to each other. Compared to the dynamic adsorption of the three cases, the injection of the surfactant solution only yields the maximum adsorption value and then polymer slug and co-injection strategies can reduce the dynamic adsorption by approximately 50%.

In this study, we focus on testing these dynamic characteristic parameters of the amphoteric surfactant–sulfonated polymer solution and evaluate their relationship to the pore geometry parameter or reservoir quality index (RQI) for carbonate rocks under particular conditions. These dynamic characteristic parameters include the individual amounts of dynamic adsorption and the total amount of adsorption of such a solution and adsorbed layer thickness onto the carbonate rock, and we compare the results with those of single adsorption of surfactant solution published previously. The resistance factor, RRF, and adsorbed layer thickness of S-P solution on carbonate rocks were calculated based on the differential pressure before and after injecting the S-P solution. The loss of injectivity and liquid permeability during S-P solution injection are evaluated in detail in this paper.

This paper presents insights into the dynamic characteristics of S-P solution on carbonate rocks with reservoir parameters, which could benefit application design for chemical EOR processes in the carbonate reservoirs.

2. RESULTS AND DISCUSSION

2.1. Dynamic Adsorption of a Surfactant with and without a Polymer. The amount of adsorption of the surfactant solution without a polymer onto carbonate rocks was reported in the previous study.\textsuperscript{22} The combined concentration of the S-P solution used in this study was a 0.4 wt % (0.2% surfactant and 0.2% polymer). Core flooding experiments were conducted at reservoir conditions at a temperature of 100 °C, a pore pressure of 3100 psi, and a flow rate of 0.5 cc/min, which respond to the frontal velocities in the range from 7 to 15 ft./day as listed in Table 1.

Figure 1 shows the concentration profile of S-P and the polymer versus the pore volume injected. The blue diamond symbol shows the total dynamic adsorption and desorption on the rock versus the pore volume injected during S-P solution and post seawater injections, while the cross symbol represents the polymer. The amount of total dynamic adsorption of S-P
and dynamic adsorption of the polymer onto rocks was calculated using the method reported earlier.\textsuperscript{22}

Table 1 shows the total adsorption density ($\Gamma_{ta}$), surfactant adsorption density ($\Gamma_{sa}$), and polymer adsorption density ($\Gamma_{pa}$) on the surface of carbonate rock. The amount of adsorption of the polymer is slightly less than that of the surfactant in S-P flooding. In this study, the ratio of the amount of polymer adsorption, $\Gamma_{pa}$, and surfactant adsorption, $\Gamma_{sa}$, to the total amount of S-P adsorption is defined as the relative adsorption. The values of relative adsorption of the surfactant ($\Gamma_{rsa}$) and polymer ($\Gamma_{rpa}$) are listed in Table 1. The surfactant adsorption is 9\% higher than polymer adsorption for core plugs O and P and 1.7\% for low permeability core plug Q.

Figure 2 shows the dynamic adsorption onto carbonate rocks for the S-P solution with different pore geometry parameters. Figure 3 shows the effect of pore geometry $\sqrt{K/\Phi}$ on adsorption of the S-P solution and surfactant desorption onto carbonate rocks. Both the total S-P adsorption and adsorption of the surfactant from a previous study\textsuperscript{22} are functions of pore geometry. Both values of dynamic adsorption versus pore geometry are mixed, which can be expressed by the same functional expression as shown in Figure 3. However, when the adsorption of the surfactant in S-P solution is considered, the difference between the adsorption of the surfactant in S-P and surfactant solutions is observed. Comparison of the dynamic adsorption of surfactant with and without a polymer is presented in Figure 4, which has shown that the effect of the polymer on adsorption of surfactants onto carbonate rocks is a function of the pore geometry $\sqrt{K/\Phi}$. The account of adsorption of the surfactant in the S-P solution is much lower than that of the surfactant solution alone because the dynamic adsorption of surfactant in the S-P solution was affected by the presence of the polymer. It is well known that the interaction between the polymer and carbonate rock occurs during the S-P flooding process. The large surface area of carbonate rock presents a positive charge, which provides the place to adsorb the adsorbents of the polymer in the S-P solution by electrostatic attraction and entrapment. Therefore, the surfactant dynamic adsorption is reduced by approximately 50\% in the equilibrium adsorption of the surfactant. Referring to Figure 4, we found that the degree of influence of the polymer on dynamic adsorption of surfactants in the S-P solution depends on the pore geometry. When the value of pore geometry is small, the presence of the polymer has a great influence on the dynamic adsorption of surfactants. With increasing pore geometry, such an influence becomes a small value as shown in Figure 4.

The effect of the reservoir quality index (RQI) on adsorption is shown in Figure 5. The trends of adsorption such as the total dynamic adsorption, surfactant dynamic adsorption, and polymer dynamic adsorption of S-P solution...
versus the RQI are similar to those of the dynamic adsorption of a single-surfactant solution, which indicates that dynamic adsorptions decreased with the increase in the reservoir quality index. The difference of the S-P solution and surfactant solution for dynamic adsorption behavior may be that the adsorption of a single-surfactant solution is linear with the reservoir quality index, while the dynamic adsorption of S-P solution is nonlinear. This may be related to the interactions of the S-P solution and the surface of carbonate rock. All core flooding tests were conducted at 0.5 cc/min in reservoir conditions. The values of frontal velocity, RQI, $\Gamma_{ta}$, $\Gamma_{pa}$, $\Gamma_{sa}$, $\Gamma_{rpa}$, and $\Gamma_{rsa}$ are listed in Table 1. $\Gamma_{ta}$, $\Gamma_{pa}$, and $\Gamma_{sa}$ are the total dynamic adsorption, polymer dynamic adsorption, and surfactant dynamic adsorption, respectively. $\Gamma_{rpa}$ and $\Gamma_{rsa}$ are relative dynamic adsorption based on the total dynamic adsorption of the S-P solution.

2.2. Resistance Factor and Residual Resistance Factor. In this study, the RF and RRF of the S-P solutions are determined experimentally using different stages of the core flooding process (before and after S-P solution injection). The equations described by Zhou et al. (2019) for a polymer solution in the previous study are used to calculate the dynamic parameters of S-P solution. Adsorbed layer thickness ($\varepsilon_h$) of the S-P solution on the surface of carbonate rocks are calculated through the RRF and rock data such as permeability and porosity.

The resistance factor, RRF, and adsorbed layer thickness ($\varepsilon_h$) of the S-P solution on carbonate rocks with a mixture solution of 0.2 wt % surfactant and 0.2 wt % polymer are listed in Table 2. Differential pressures ($\Delta P_{sw}$, $\Delta P_{sp}$, and $\Delta P_{psw}$) are recorded by pressure transducers during the process of seawater, S-P solution, and post seawater flooding and listed in Table 2 as well. Figure 6 shows an example of the profile of differential pressures versus the pore volume injected during S-P solution and post seawater flooding processes for core plug Q. The injection history of core plug Q is as follows: seawater injection, S-P solution injection, and post seawater injection. At each step of the injection process, a stable differential pressure has been obtained, that is, 2.15 psi for seawater flooding, 120.62 psi for S-P solution injection, and 15.2 psi for post seawater injection. Comparing the differential pressure in the case of seawater injection with that of post seawater injection, we found that the differential pressure of the post seawater injection was 7 times that of initial seawater flooding, which indicates that co-retention of S-P solution occurred and the adsorption film formed during the S-P injection. The values of the RF and RRF are calculated by the use of the stabilized differential pressures for S-P and post seawater injection based on the differential pressure across the core plug in initial seawater flooding. The RF is equal to 55.74, and the value of RRF is 7.02.

The effect of the RQI on the RRF of the S-P solution on carbonate rocks is shown in Figure 7. Two groups of experimental values are compared in Figure 8. One indicated with the black triangle shows the RRF of the polymer solution of 0.2 wt % in seawater on carbonate rocks from the literature. The same polymer was used in our study. The red circles indicate the results of the current study for S-P solution flooding. The results obtained in this study have great agreement with our previous results for single-polymer

Table 2. Dynamic Characteristics of S-P Solution onto Carbonate Rocks

| core plugs | frontal velocity (R/D) | RQI (µm) | $\Delta P_{sw}$ (psi) | $\Delta P_{sp}$ (psi) | $\Delta P_{psw}$ (psi) | RF | RRF | $\varepsilon_h$ (µm) |
|------------|------------------------|----------|----------------------|----------------------|----------------------|----|-----|------------------|
| O          | 8.5                    | 1.1      | 0.178                | 4.92                 | 0.441                | 27.64 | 2.48 | 0.444            |
| P          | 7.6                    | 2        | 0.036                | 0.46                 | 0.065                | 127.2 | 1.81 | 0.7              |
| Q          | 13.86                  | 0.5      | 2.154                | 120.62               | 15.2                 | 55.74 | 7.02 | 0.333            |

Figure 5. Effect of reservoir quality on adsorption.

Figure 6. Differential pressure profile vs pore volume injected of S-P solution and post seawater.

Figure 7. RRF of the S-P solution vs RQI.
injection. It was shown that the RRF is strongly dependent on the pore geometry parameter and decreases with an increase in the pore geometry parameter.

The relationship between dynamic adsorption and the RRF of the S-P solution on carbonate rocks is reported for the first time as shown in Figure 9. During the process of the S-P or polymer solution injection, the total dynamic adsorption of the S-P solution onto the surface of rocks is usually accompanied by phenomena of viscoelasticity and entrapment, which result in the increases of the RF, and the sweep efficiency can be improved. Therefore, the S-P adsorption from its solution plays an important role in mobility control. As a result, the S-P dynamic adsorption increases with an increase in the residual resistant factor for the S-P solution in carbonate rock. Figure 10 shows the RRF as a function of frontal velocity. Both the relationships, dynamic adsorption of S-P solution versus the RRF and RRF versus frontal velocity, can fit a quadratic polynomial.

The adsorbed layer thickness of the S-P solution was calculated using the RRF as a function of differential pressure across the core plug during primary seawater, S-P, and post seawater injection. The S-P adsorbed layer thickness, $\varepsilon_h$, is deduced from the measurement of the RRF, assuming that the effective or hydrodynamic pore radius, $\sqrt{8k/\Phi}$, is reduced by an impenetrable S-P layer with thickness, $\varepsilon_h$ ($\mu m$), defined as:

$$\varepsilon_h = (8K_b/\Phi)^{0.5}(1 - (RRF)^{-0.25})$$

$$= (8K_b/\Phi)^{0.5}(1 - (\Delta P_{psw}/\Delta P_{sw})^{-0.25})$$

(1)

where $K_b$ is the initial permeability to seawater ($\mu m^2$), $\Phi$ is the porosity of core plug (fraction), $\Delta P_{psw}$ is the differential pressure across the core plug during seawater injection (psi), and $\Delta P_{sw}$ is the differential pressure across the core plug during post seawater injection (psi).

Plotting the S-P adsorbed layer thickness as a function of geometry $\sqrt{8k/\Phi}$, a power-law correlation is found. For a specific concentration of solution and carbonate rock system in this study, the power-law expression is as follows:

$$\varepsilon_h/1 - (RRF)^{-0.25} = a[(K/\Phi)^{0.5}]$$

(2)

Figure 12 shows the effect of pore geometry on S-P adsorbed layer thickness for the S-P solution of 0.4 wt % by use of 0.2 wt % amphoteric surfactant and 0.2 wt % sulfonated polymer in a seawater/carbonate rock system. The parameters
The injectivity index, which is the ratio of the frontal velocity to the injection pressure gradient, is presented in the literature in detail. These values are listed in Table 3. The injectivity loss can be calculated by the equation below

\[ I_{\text{loss}} = (1 - \frac{I_{sp}}{I_{sw}}) \times 100 \]  

where \( I_{\text{loss}} \) is the injectivity loss during S-P solution injection, \( I_{sp} \) is the injectivity of S-P solution, and \( I_{sw} \) is seawater injectivity. The injectivity loss is listed in Table 3 as well. Figure 14 shows the comparison of the injectivities of S-P solution and post seawater injection with those of seawater injection, which is a function of the RQI for carbonate rock. The relationship between the seawater, S-P solution, and post seawater injectivities and the reservoir quality index is a quadratic function. The injection capacities increase with the increase in the reservoir quality index for three kinds of injection processes as shown in Figure 14. According to the results in Table 3, we found that the injectivity loss of S-P solution injection is 96.4% for core plug O, 92.2% for core plug P, and 98.2% for core plug Q. The relationship between the injectivity loss of S-P solution and the reservoir quality index is shown in Figure 15. These results show that the reservoir properties strongly affect S-P injectivity. In the post seawater injection, the loss of injectivity may be caused by the retention of S-P solution, which results in the increase of differential pressure across the core plug compared with that of the initial seawater. The injectivity loss of the S-P solution is shown in Figure 15.

The liquid permeability loss can be presented as

\[ K_{\text{loss}} = \left(1 - \frac{k_{sp}}{k_{sw}}\right) \times 100 \]  

where \( K_{\text{loss}} \) is the S-P solution permeability loss (%) and \( k_{sw} \) and \( k_{sp} \) are the primary seawater permeability and S-P solution permeability of the core plug (mD), respectively. The S-P solution permeability is calculated using a steady differential pressure across the core plug when the injected S-P concentration of S-P is equal to the concentration in the effluence. The values of permeability loss are listed in Table 3. The relationship between permeability loss of S-P solution in the core plug and the reservoir quality index is shown in Figure 15. The results reveal that permeability loss decreases with the increase in the reservoir quality index.

The parameters obtained in this work such as dynamic characteristics, adsorption, retention, RF, RRF, injectivity, and permeability reduction of S-P solution can be applied directly.
results of adsorption of surfactant solution and decreases with an increase in the pore geometry parameter or reservoir quality index.
3. The amount of adsorption of surfactants in surfactant–polymer solution onto carbonate rock is much less than that of surfactants in a single-surfactant solution at a lower value of pore geometry. With the increasing pore geometry parameter, the effect of the polymer on adsorption of the surfactant becomes significantly small.
4. The relationships between dynamic adsorptions and adsorbed layer thickness of S-P solution on the carbonate rock and the reservoir quality index were obtained experimentally for the first time. With an increase in the reservoir index, both the dynamic adsorptions, surfactant adsorption and polymer adsorption, and adsorbed layer thickness decreased. Both correlations can be expressed by the power-law equation.
5. Both the resistance factor and residual resistance factor were decreased with the increase in the reservoir quality index for carbonate rocks.
6. The relationship between surfactant–polymer adsorption and the residual resistance factor shows that surfactant–polymer adsorption increases with increasing the residual resistance factor.

### 3. CONCLUSIONS

Core flooding tests with a solution of an amphoteric surfactant and a sulfonated polyacrylamide in seawater were conducted in carbonate rocks with different permeabilities ranging from 30 to 1200 mD in reservoir conditions. Based on these core flooding results and the concentration analysis of surfactant–polymer effluents, the following conclusions can be drawn:

1. The total amount of surfactant–polymer adsorption was in the range of 0.258 to 0.645 mg/g-rock for carbonate rocks with a pore geometry parameter from 64 to 15 μm or a reservoir quality index from 0.5 to 2 μm. The relative adsorption to the surfactant in the S-P solution is higher than that of the polymer.
2. The total adsorption of the surfactant–polymer solution onto carbonate rock is in good agreement with previous

### 4. EXPERIMENTAL WORK

#### 4.1. Fluids.

Two types of brines were used in this study. One was the formation water, and the other was seawater. The components for both brines are listed in Table 4. The total dissolved solids (TDS) of formation water and seawater are 213,734 and 57,670 ppm, respectively. These waters were synthesized using laboratory-grade salts. The viscosities of brines at ambient and reservoir temperatures are listed in Table 5.

The surfactant used for this study is a betaine-based amphoteric surfactant with a molecular weight of 430 g/mol. The surfactant was compatible with the formation water and

| core plugs | core length (cm) | flow rate (R/D) | RQI (μm) | ΔPsw (psi) | ΔPsp (psi) | ΔPpsw (psi) | Isw ((R/D)/(psi/ft)) | Isw (ft/D)/(psi/ft) | Πsw (psi) | Πsp (psi) | Ksw (psi) |
|-----------|----------------|----------------|----------|------------|------------|------------|--------------------|---------------------|-----------|-----------|-----------|
| O         | 5.88           | 8.5            | 1.1      | 0.178      | 4.92       | 0.441      | 9.22               | 0.333               | 3.72      | 96.38     | 70.10     |
| P         | 5.78           | 7.6            | 2        | 0.036      | 0.46       | 0.065      | 40.11              | 3.139               | 22.22     | 92.17     | 48.44     |
| Q         | 7.02           | 13.86          | 0.5      | 2.154      | 120.62     | 15.2       | 1.48               | 0.026               | 0.21      | 98.21     | 84.76     |

Figure 14. Comparison of injectivities of seawater, S-P solution, and post seawater injection.

Figure 15. Injectivity and liquid permeability loss as a function of the reservoir quality index for S-P solution injection.
seawater. The concentration of the surfactant used was 0.2 wt % in seawater. The polymer selected for the tests was sulfonated polyacrylamide. It is a copolymer of acrylamide and acrylamido tert-butyl sulfonate. The molecular weight was approximately 12 million g/mol. The polymer was dissolved in seawater at concentrations of 0.2 wt % for the tests. The ratio of the surfactant solution to the polymer solution is 1:1. The viscosities of the surfactant and polymer are listed in Table 5.

4.2. Core Flooding. All core flooding experiments were conducted using carbonate core plugs from a carbonate reservoir. The saturation of the core plug was conducted with formation brine using a standard saturation procedure. The core plugs were placed in brine to achieve the ionic equilibrium. The physical data of the core plugs are listed in Table 6. The term \((K/\Phi)^0.5\) in Table 6 presents the pore geometry parameter of core plugs used in this study.

The core flooding tests for dynamic adsorption were performed at a constant concentration of the solution (0.4 wt %). The concentration of both the surfactant and polymer was 0.2 wt %. For brine permeability, \(K_{db}\) the confining and back pressures were 1300 and 300 psi, respectively. Three different flow rates (0.5, 1.0, and 2.0 cc/min) were used for permeability measurements. After the permeability measurement, the temperature was increased to 100 °C. The pore pressure and confining pressure were maintained at 3100 and 4400 psi, respectively. In primary seawater flooding, 10 pore volumes (PVs) of seawater were injected. The differential pressure \(\Delta P_{sw}\) was recorded using different transducers. In the next stage, 5–10 PVs of the S-P solution was injected. Approximately 6 PVs of seawater were flooded in the post seawater flooding stage. The flow rate for both S-P solution and post seawater flooding was 0.5 cc/min. The effluents were collected after every 4 min using a dedicated fraction collector. The effluent in the odd tube was used for concentration analysis of the total adsorbed S-P, and the effluent in the even tube was for concentration analysis of the adsorbed polymer.

4.3. Effluent Analysis. 4.3.1. Concentration of S-P Effluents. A total organic carbon analyzer, TOC-VCPH, made by Shimadzu was used to determine the concentration of the surfactant and polymer solution. The instrument measures the concentration of both the total carbon (TC) and the inorganic carbon (IC), which includes dissolved carbon dioxide and carbonic salts in brine. The total organic carbon (TOC) is obtained by subtracting IC from the TC. This method has been widely used to determine polymer concentrations or the concentrations of mixed polymer/surfactant solutions in the literature.40,41 We used this method to determine the concentrations of polymer/surfactant solutions. In this method, a calibration curve was first created using the known concentration of surfactants by measuring the TOC. This calibration curve was used to measure the unknown effluent concentration.

4.3.2. Concentration of the Polymer in Effluents. The Hyamine method, also widely used, is a less hazardous procedure and gives reliable results if the appropriate dilution is used.42,43 This method is turbidometric and relies on the reaction of the amide group in the polymer with the cationic surfactant. The reaction produces a precipitate of the hydrolyzed polyacrylamide, which can then be measured by the absorbance of light at a particular wavelength. The relative ease of implementing this method and the fact that it does not involve any hazardous chemicals make it an attractive choice in polymer analysis. In this study, the Hyamine method was chosen to analyze the concentration of the sulfonated polymer mixed with the amphoteric surfactant. Figure 16 shows a linear relationship between the polymer concentration and absorbance, which is the calibration curve. The amount of absorbance of the polymer in the effluent was calculated using an equation shown in Figure 16 when the value of the absorbance of the polymer in the effluent is determined by the Hyamine method.

| Table 4. Recipes of Formation Water and Seawater |
|-----------------------------------------------|
| component | formation water (g/L) | seawater (g/L) |
| NaCl       | 150.446                | 41.041         |
| CaCl₂·2H₂O | 69.841                 | 2.384          |
| MgCl₂·6H₂O | 20.396                 | 17.645         |
| Na₂SO₄     | 0.518                  | 6.343          |
| NaHCO₃     | 0.487                  | 0.165          |
| total dissolved solids | 213,734 | 57,670 |

| Table 5. Viscosities of Formation Water, Seawater, and S-P Solution |
|---------------------------------------------------------------|
| temperature (°C) | formation water | seawater | S-P solution, 0.4 wt % |
|------------------|-----------------|----------|-----------------------|
| 25               | 1.45            | 1.038    | 11.34                 |
| 102              | 0.476           | 0.299    | 3.39                  |

| Table 6. Properties of Carbonate Core Plugs |
|---------------------------------------------|
| core | L (cm) | D (cm) | PV (cc) | Φ (fra.) | \(K_{db}\) (mD) | \(K_b\) (mD) | \((K/\Phi)^0.5\) |
|------|--------|--------|---------|---------|---------------|--------------|-----------------|
| O    | 5.88   | 3.8    | 16.336  | 0.245   | 285.53        | 146.35       | 34.14           |
| P    | 5.78   | 3.8    | 17.95   | 0.274   | 1120          | 892.36       | 63.93           |
| Q    | 7.02   | 3.8    | 11.57   | 0.15    | 32.4          | 13.98        | 14.69           |

Figure 16. Calibration curve for polymer concentration analysis.
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