Mechanistic Study on the Decrease in Injectivity during Salt-Resistant Polymer Flooding

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ABSTRACT: According to numerous laboratory experiments and field applications, polymer flooding can effectively modify the liquid absorption profile and increase the sweep efficiency, thereby enhancing the oil recovery. However, long-term injection of polymers decreases the effective permeability of the reservoir and plugs the formation pores, resulting in irreversible reservoir damage. In the development process, polymer types and concentrations must be selected according to the reservoir to avoid problems such as plugging of the formation pores. This study was aimed at clarifying the degree of plugging and the injection limit of the reservoir when a salt-resistant polymer (SRP) is used in production processes of the Daqing Oilfield. To this end, oil displacement experiments, dynamic and static adsorption experiments, and SEM observations were performed using representative reservoir fluid and core samples. The static adsorption of "medium-molecular" SRP reached equilibrium after 36 h, and the saturated adsorption capacity was 3.56 mg/g, which was approximately 2–5 times the dynamic adsorption capacity. For medium-molecular SRP, with a molecular mass of 7 million, the lower limit of the core permeability was 20–40 mD. When the permeability was less than 100 mD, the SRP concentration injected into the core could not exceed 900 mg/L. The oil displacement capacity of SRP decreased owing to the macromolecular hydration radius and the strong aggregation effect of SRP. Polymer adsorption and the retention of sand-carrying critically decreased water permeability. This study provides insights into SRP flooding under different geological conditions in the Daqing Oilfield and can help clarify the molecular mass and concentration of polymers with changes in the reservoir conditions.

INTRODUCTION

The development of oil resources is influenced by a variety of elements, such as the oil and gas reserves, types of oil and gas, geological conditions, and development stage.1 Water can be injected into the formation as an inexpensive and simple flooding agent to replenish the formation energy and push crude oil through piston action. However, reservoirs are heterogenous, and high-permeability reservoirs exhibit low seepage resistance. The high-permeability layer absorbs more liquid than the medium and low permeability layers under the same injection pressure. This phenomenon gradually intensifies with the injection time until the injection of water in the high-permeability layer is inefficient or even ineffective.2 The recovery of water flooding depends on the swept volume and oil displacement efficiency. The oil recovery and oil displacement efficiency can be increased at a certain swept volume. Consequently, most oil fields introduce chemical reagents to lower the permeability of the high-permeability layer and enhance the oil displacement efficiency to increase the oil recovery.3 Polymer flooding, as a representative EOR technique, is extensively employed in many oilfields, owing to its wide range of material sources, easy synthetic methods, high oil displacement efficiency, and low cost.4,5 Following injection, the polymer can selectively seal the high-permeability zone and lower its permeability. At a constant injection rate, the injection pressure increases throughout the well, increasing the adsorption differential pressure and liquid absorption volume in the medium- and low-permeability zones. This framework is typically appropriate for reservoirs with high oil saturation and medium heterogeneity. China conducted field testing of polymer flooding in the oilfields of Daqing, Dagang,6 Liaohe,7 and Shengli8 and obtained exceptional stimulation results. However, after the polymer enters the low- and medium-permeability layers, it remains in those layers, thereby increasing the permeability resistance.9 The increase in permeability resistance is substantially greater than that of the high-
permeability layer for the same injection volume. The injection pressure increases with the amount of adsorbed polymer in the reservoir.\textsuperscript{10–12} To prevent polymer loss owing to reservoir fractures, the injection pressure must be lower than the fracturing pressure. Consequently, in the case of continuous polymer injection, once the injection pressure exceeds the top limit, the adsorption pressure difference in each layer at the injection end progressively decreases, and the injectivity of the polymer injection well gradually diminishes and even approaches zero. For example, in the case of the Daqing Oilfield, the reservoir permeability is usually less than 200 mD. The injection rate of most polymer injection wells was lower than the injection allocation rate for several years and decreased significantly after production (Figure 1), increasing the cost of polymer flooding and decreasing the economic effect of polymer flooding to enhance oil recovery. Although nanoparticles can be mixed with polymers to alleviate this problem, large-scale rollout remains a distant possibility.\textsuperscript{15,14}

The decrease in the polymer injectivity can be primarily attributed to polymer obstruction in pipelines and formation during polymer flooding.\textsuperscript{15–17} The location and mechanism of plugging in the polymer flooding process have been examined to increase the polymer flooding efficiency and design a polymer flooding reservoir plugging system. Clogging may occur in the polymer flooding process owing to several reasons. “Fisheye” scaling may occur near the well area of the polymer injection well because of the low solubility of the dry polymer powder or deviation in the construction means.\textsuperscript{18–20} Adsorption and trapping of injected polymers in the reservoir, particularly at tiny pore openings, can limit the reservoir permeability.\textsuperscript{21–24} The water used to manufacture the polymer may be incompatible with formation water, resulting in inorganic scaling. Moreover, the polymer may be stranded in the oil layer winding, generating large obstruction and limiting the progress of polymer flooding. SRB bacteria in water can proliferate using polymers as an energy source, resulting in bacterial obstruction and inorganic scale blockage if the injected water quality is not adequately high.\textsuperscript{25–27} The existing studies mainly focused on theoretically analyzing the mechanism of plugging formation. However, the compatibility of polymer and reservoir conditions is a key factor influencing the occurrence of plugging in the polymer flooding process in oil fields.\textsuperscript{28–30} Consequently, it is crucial to investigate the injectivity of the polymer utilized in each oil field under the appropriate reservoir geological circumstances and polymer compatibility with the formation conditions and degree of plugging.\textsuperscript{31}

This study was aimed at clarifying the degree of reservoir plugging and the injection limit for the case in which a salt-resistant polymer (SRP) is used in the Daqing Oilfield. To this end, the injection ability of SRPs with different molecular weights and concentrations for different types of cores and permeability conditions was simulated by displacement experiments. The main factors influencing the adsorption capacity of the SRP were determined by measuring the adsorption retention of polymers in porous media in dynamic and static conditions. The mechanism of the decrease in the polymer injection ability was analyzed from the aspects of the polymer molecular size, aggregation state, and adsorption. This research can provide a basis for the optimal molecular weight and concentration of polymers for the SRP flooding of reservoirs in the Daqing Oilfield and theoretical guidance for the study of plugging systems.

### EXPERIMENTAL MATERIALS AND METHODS

**Materials.** The polymer solution used in this study was a “medium-molecular” SRP with a molecular mass of $700 \times 10^4$. The polymer structure is shown in Figure 2. The polymer is a product provided by the Daqing Oilfield and has a commercial application value. Moreover, the high-molecular partially hydrolyzed polyacrylamide (PHPAM) with a molecular mass of $14 \times 10^6$ and ultrahigh-molecular PHPAM with a molecular mass of $25 \times 10^6$ were used. The sand sample was a natural core sand sample from the Gaotaizi Reservoir (more than 40 mesh). Crude oil with a viscosity of 6.0 mPa·s was derived from the

![Figure 1. Decrease in the injectivity of polymer injection wells in the Daqing Oilfield.](image-url)
Daqing Gaotaizi oilfield. The water samples included samples of clean injection water and deeply treated sewage from the Daqing Oilfield. Tables 1, 2 summarize the water quality analysis results. The sizes of the artificial and natural cores are 25 × 100 mm and 25 × 100 mm (70–100 mm), respectively. The reservoir temperature in the Daqing Oilfield is approximately 45 °C; therefore, the experimental temperature was set as 45 °C.

**Methods. Preparation of Polymer Solution.** The medium-molecular SRP solution was sheared with clear water to prepare a 5000 mg/L polymer mother solution, and the shear duration was measured at a viscosity retention rate of 60%. The other two polymer solutions were sheared at the same rate and the same duration. Subsequently, a 75-mesh filter was used to filter the polymer solution. Finally, the oilfield effluent was used to dilute the polymer mother solution to the target concentration of 900 mg/L.

**Polymer Flooding Experiment.** The changes in the pressure of artificial cores with different permeability levels during water flooding, polymer flooding, and subsequent water flooding were measured through an indoor core simulation experiment at a polymer solution concentration of 900 mg/L, and the resistance coefficient and residual resistance coefficient were calculated. The following steps were adopted:

1) Device connection: using the appropriate method, connect the flooding device, pressure detection device, and generated-liquid collection device; check for air and liquid leakage at each point; and verify that no leaking point exists.

2) Core vacuuming: after drying, weigh the core and attach it to the vacuuming apparatus. Initiate the timer when the vacuum gauge on the vacuum pump decreases to less than 0.098 MPa, and vacuum the core constantly. For an artificial homogenous long core and a natural core, the vacuuming time must be 8 h and at least 5 h, respectively.

3) Water saturation: seal the outlet end of the valve, connect the inlet end of the valve to the acid burette, slowly inject saturated water into the core, gradually open the outlet end of the valve, and swiftly close the valve when water flows out. Track the amount of injected water.

4) Water permeability measurement: vary the flooding rates, inject the simulated formation water into the core at a consistent rate, record the stable pressure difference, and use Darcy’s law to compute the effective core permeability.

5) Crude oil saturation: replace the core with simulated oil until the water yield is zero and record the amount of saturated oil at this point.

6) Water injection: inject water at a steady rate, shift the core to the desired water production rate, and record the injection pressure, oil production rate, and liquid production rate.

7) Polymer injection: perform a constant speed injection of 6.0 PV polymer solution. Monitor the injection pressure, oil production rate, and liquid production rate, and obtain samples of the generated fluid at regular intervals to determine the polymer content.

8) Subsequent water flooding: continue to infuse 6.0 PV water at a steady pace and record the injection pressure, oil production rate, and liquid production rate.

The resistance coefficient and residual resistance coefficient are technical indicators that specify the quantity of polymer retained in a porous medium. These parameters can be mathematically represented as follows:

\[ F_R = \frac{\Delta P_1}{\Delta P} \]  \hspace{1cm} (1)

\[ F_{RR} = \frac{\Delta P_2}{\Delta P_3} \]  \hspace{1cm} (2)

where \( F_R \) is the resistance coefficient; \( F_{RR} \) is the residual resistance coefficient; \( \Delta P_1 \) is the difference in the water drive pressure; \( \Delta P_2 \) is the difference in the polymer flooding pressure; and \( \Delta P_3 \) is the differential pressure in the subsequent water flooding.

The \( F_R \) and \( F_{RR} \) test flow and experimental equipment are illustrated in Figure 3. The experimental equipment included advection pumps, pressure sensors, core grippers, hand pumps, and intermediate vessels. Parts other than the advection pump and the hand pump were maintained at a temperature at 45 °C in a constant temperature box. The system error of the experiment included the instrument error of the injection pump, intermediate vessel, and pressure gauge, and the same set of experimental equipment was used in the experimental process to minimize the influence of the system error on the experimental results. The characteristics of artificial cores used in various core permeability studies are listed in Table 3.

The system errors of this experiment included instrument errors such as those of the injection pumps, intermediate containers, and pressure gauges. The same set of experimental equipment was used in the experiment to minimize the influence of system errors on the experimental results.

**Polymer Adsorption Experiment.** The physicochemical interaction between the polymer and formation rock and fluid is critical in the effective implementation of polymer flooding and chemical flooding with the polymer as the principal agent. Static and dynamic adsorption tests were performed based on the polymer adsorption theory. The adsorption behavior of the SRP solution on the natural core and dynamic retention characteristics in porous media were investigated, and the adsorption process and variables influencing the polymer solution were examined.

**Static Adsorption. Experimental Procedure.**

Table 1. Water Quality Analysis of Clean Water

| ions       | Ca^{2+} | Mg^{2+} | Cl⁻   | HCO₃⁻ | CO₃²⁻ | SO₄²⁻ | K⁺ + Na⁺ | total |
|------------|---------|---------|-------|-------|-------|-------|---------|-------|
| concentration (mg/L) | 45.69   | 29.18   | 124.11| 512.5 | 0     | 5.76  | 168.82  | 886.06|
1) Certain amounts of core sand and the polymer solution were added to a tapered bottle with a plug, and the overall weight of the conical bottle was recorded.

2) For a certain period, the conical bottle was placed in an incubator at 45 °C. The conical flask was oscillated at regular intervals to ensure that the adsorbent was completely immersed in the solution.

3) The solution was shaken in the conical container and poured into the centrifugal tube. The samples were centrifuged for 30 min at 3000−4000 rpm. Subsequently, using the absorbance method, the polymer concentration in the clear liquid was measured three times, and the results were averaged.

**Variation in the Adsorption Capacity of the Polymer Solution with Time.** The reservoir temperature (45 °C) in the Gaotaizi polymer flooding test region was simulated, and the adsorption capacity at various adsorption durations was determined using a natural core under a constant liquid−solid ratio. The durations of the trial were 12, 24, 36, and 48 h.

**Static Adsorption of Polymer Solutions at Different Liquid−Solid Ratios.** The reservoir temperature (45 °C) was simulated in the Daqing polymer flooding test area, natural cores were used to assess the static adsorption capacity at various liquid−solid ratios, and the corresponding liquid−solid ratio was determined at a steady adsorption capacity. The liquid to solid ratios were 3, 5, 10, 15, and 20 mg/L, with a standing time of 36 h.

**Static Adsorption of Polymer Solutions with Different Concentrations.** The static adsorption capacity of three polymer solutions with concentrations of 300, 600, 900, 1200, and 1500 mg/L was measured using natural cores at a temperature of 45 °C.

**Dynamic Adsorption. Experimental Method.** The sand-filled tube core with a diameter of 2.5 cm and length of 10 cm...
was dried and weighed to saturate the formation water, and the permeability of the formation water was measured. The polymer solution was injected at a flow rate of 1 mL/min, and the produced polymer concentration was measured until it was equal to that of the injected polymer. The formation water was injected at a constant rate, and samples were collected from the core outlet until no polymer was detected in the core-produced fluid.

Using the material balance approach, the quantity of the polymer retained in the formation was estimated using eq 3.

$$Q = \left( \rho_0 V_0 - \sum_{i=1}^{n} \rho_i V_i \right) / W$$

where $Q$ is the polymer retained in the core, $\mu g/g$; $\rho_0$ is the injected polymer solution concentration, $mg/L$; $V_0$ is the cumulative volume of the injected polymer solution, $mL$; $\rho_i$ is the polymer concentration of the $i$th outflow sample at the core outlet, $mg/L$; $V_i$ is the volume of the $i$th outflow sample, $mL$; $n$ is the number of outflow samples collected at the core outlet; and $W$ is the core dry mass, g. The error in the polymer dynamic and static adsorption experiment was mainly the mass measurement error. The electronic balance used in the experiment was accurate to $10^{-4}$ mg, which satisfied the experimental requirements.

The error in the polymer dynamic and static adsorption experiment was mainly the mass measurement error. The electronic balance used in the experiment was accurate to $10^{-4}$ mg, which satisfied the experimental requirements.

**Experimental Design.** The reservoir temperature (45 °C) in the Gaotaizi polymer flooding test region was simulated. Natural cores with permeabilities of 100, 300, and 500 mD were used to perform flooding tests with the medium-molecular SRP with a polymer solution concentration of 900 mg/L. The dynamic adsorption capacity was investigated at various adsorption periods.

![Injection pressure curves of different polymers in cores with different permeabilities.](image-url)

![Table 4. $F_R$ and $F_{RR}$ after Polymer Solution Flooding ($C_p = 900$ mg/L)](table-url)

| polymer              | viscosity (mPa s, 10 s$^{-1}$) | permeability ($\times 10^{-3}$) | resistance coefficient ($F_R$) | residual resistance coefficient ($F_{RR}$) | decrease in the permeability (%) |
|----------------------|--------------------------------|---------------------------------|-------------------------------|--------------------------------------------|---------------------------------|
| medium-molecular SRP | 52.6                           | 22.5                            | blocking                      | blocking                                   | 100                             |
|                      | 40.9                            | 50.1                            | 12.4                          | 92.0                                       |
|                      | 62.7                            | 38.3                            | 11.2                          | 91.4                                       |
|                      | 110.6                           | 24.6                            | 9.8                           | 89.7                                       |
|                      | 310.5                           | 20.5                            | 8.2                           | 87.8                                       |
| high-molecular PHPAM | 24.7                           | 19.5                            | blocking                      | blocking                                   | 100                             |
|                      | 42.4                            | 40.1                            | 7.2                           | 86.2                                       |
|                      | 69.2                            | 35.6                            | 5.7                           | 83.2                                       |
|                      | 103.8                           | 22.4                            | 4.9                           | 80.6                                       |
| ultrahigh-molecular PHPAM | 36.2                     | 24.8                            | blocking                      | blocking                                   | 100                             |
|                      | 45.7                            | 22.4                            | blocking                      | blocking                                   | 100                             |
|                      | 65.9                            | 50.3                            | 10.0                          | 90.1                                       |
|                      | 114.2                           | 33.0                            | 7.6                           | 86.7                                       |
occupies all the pores. After subsequent water flooding, the injection end gradually increases until the polymer solution continuously enters the low-permeability pores, the pressure at the permeability pores in the core. As the polymer solution flows, the resistance when it flowed in the pores. When the polymer solution first appeared from the outlet end, it occupied the high-permeability pores in the core. As the polymer solution continuously enters the low-permeability pores, the pressure at the injection end gradually increases until the polymer solution occupies all the pores. After subsequent water flooding was initiated, the pressure at the injection end rapidly decreased. After 1 PV of water was injected, the pressure at the injection end gradually decreased and stabilized. However, the polymer molecules were adsorbed on the surface of the sand particles, resulting in a higher pressure at the injection end after subsequent water flooding than that during the previous water flooding.

The calculated resistance coefficient (FR), residual resistance coefficient (FRR), and decrease in the core permeability for each group of experiments are presented in Table 4. The FR of the medium-molecular SRP is larger than that of the high-molecular PHPAM but smaller than that of the ultrahigh-molecular PHPAM. Under the same permeability conditions, the resistance coefficient was not proportional to the molecular weight of the polymer but proportional to the apparent viscosity in the porous medium. This phenomenon occurred because during the flow of the polymer, the stretching effect was dominant, resulting in an increased apparent viscosity and FR. Table 4 indicates that the FRR of the SRP ranged between 8 and 12, whereas that of the PHPAM was less than 10. Under the same permeability conditions, the FRR of the medium-molecular SRP was higher than that of the high-molecular PHPAM and ultrahigh-molecular PHPAM. In other words, the retention capacity of the SRP was higher than that of the PHPAM. Experiments demonstrated that polymer adsorption and retention in the core was irreversible, thereby decreasing the core permeability. The core permeability decreased by 92.0% when the 40.9 mD core was displaced by the medium-molecular SRP solution, and the displacement of the 22.5 mD core led to core plugging. Therefore, the lower limit of the permeability of the medium-molecular SRP solution-flooded core was 20–40 mD. In general, when choosing the SRP, the formation permeability must be determined in accordance with the polymer solution; otherwise, the formation may be irreversibly damaged.

**Natural Core.** High-permeability and medium—low permeability channels coexist in natural cores, and the degree of mineral cementation is not uniform, which renders the pore structure complex. Therefore, core flooding experiments must be performed using natural cores with different permeability levels. Subsequent water flooding was performed to sample the core, and the resistance coefficient was calculated based on the pressure change at the injection end. After these experiments were conducted using different permeability cores, the results are shown in Table 5. The FR of the Long Core Displaced by the Medium-Molecular SRP was calculated based on the pressure change at the injection end. The calculated FR is higher than that of the Natural Core. The FR of the Natural Core is 9.25, whereas that of the Long Core is 4.30.

**Table 5. F_R and F_RR of the Natural Core Displaced by Medium-Molecular SRP (Cp = 0.9 g/L)**

| polymer       | viscosity (mPa·s, 10 s⁻¹) | permeability (×10⁻³ μm²) | resistance coefficient (F_R) | residual resistance coefficient (F_RR) | decrease in the permeability (%) |
|---------------|--------------------------|--------------------------|-----------------------------|----------------------------------------|---------------------------------|
| medium-molecular SRP | 52.6                     | 108.3                    | 66.8                        | 33.8                                   | 97.0                            |
|               |                          | 315.2                    | 44.7                        | 22.6                                   | 95.5                            |
|               |                          | 489.6                    | 26.8                        | 13.2                                   | 92.5                            |

**Table 6. F_R and F_RR of the Long Core Displaced by the Medium-Molecular SRP**

| permeability level (mD) | polymer concentration (mg/L) | permeability (×10⁻³ μm²) | EOR (%) | resistance coefficient (F_R) | residual resistance coefficient (F_RR) | decrease in the permeability (%) |
|-------------------------|------------------------------|--------------------------|---------|-----------------------------|----------------------------------------|---------------------------------|
| 300                     | 600                          | 296                      | 8.80    | 9.36                        | 4.1                                    | 75.60                           |
|                         | 900                          | 310.5                    | 14.60   | 20.5                        | 8.2                                    | 87.80                           |
|                         | 1200                         | 284                      | 19.20   | 31.7                        | 11.6                                   | 91.38                           |
| 100                     | 600                          | 94                       | 6.50    | 20.8                        | 9.0                                    | 88.90                           |
|                         | 900                          | 110.6                    | 8.80    | 24.6                        | 9.8                                    | 89.70                           |
|                         | 1200                         | 85.2                     | 10.30   | 33.1                        | 13.1                                   | 92.40                           |
| 50                      | 600                          | 45                       | 4.30    | 38.2                        | 12.0                                   | 91.69                           |
|                         | 900                          | 40.9                     | 5.90    | 50.1                        | 12.4                                   | 92.00                           |
|                         | 1200                         | 43.5                     | 7.50    | 55.8                        | 15.2                                   | 93.42                           |

**RESULTS AND DISCUSSION**

**Polymer Flooding Experiment. Formation Permeability. Artificial Core.** Flooding experiments were conducted using artificial cores with different permeabilities, and the polymer concentration was 900 mg/L. Figure 4 shows the change in the pressure at the injection end recorded during the experiment. Since the polymer injection, the pressure at the injection end rapidly increased, and after the injection of approximately 2 PV of polymer, the pressure increase rate at the injection end decreased and stabilized. This phenomenon occurred owing to the high viscosity of the polymer solution, which generated high resistance when it flowed in the pores. When the polymer solution first appeared from the outlet end, it occupied the high-permeability pores in the core. As the polymer solution continuously enters the low-permeability pores, the pressure at the injection end gradually increases until the polymer solution occupies all the pores. After subsequent water flooding was initiated, the pressure at the injection end rapidly decreased. After 1 PV of water was injected, the pressure at the injection end gradually decreased and stabilized. However, the polymer molecules were adsorbed on the surface of the sand particles, resulting in a higher pressure at the injection end after subsequent water flooding than that during the previous water flooding.

![Medium-Molecular SRP Flooding](https://doi.org/10.1021/acsomega.2c00296)

**Figure 5. Medium-molecular SRP flooding with different permeability natural core injection pressures.**

**Table 5. F_R and F_RR of the Natural Core Displaced by Medium-Molecular SRP (Cp = 0.9 g/L)**
The intermolecular entanglement intensifies and decreases in the permeability are presented in Table 5. No permeability, respectively. This slightly decreased. In addition to the in low-permeability formations, although the polymer viscosity did not considerably decrease the injection pressure of polymers high-permeability cores. Decreasing the polymer concentration were considerably greater than those of the 100 and 300 mD permeability for core adsorption but did not lead to obstruction. The injection pressure increased during the concentration increased, and the network topology became more compact. The injection pressure increased during the flooding process, and a larger amount of polymer remained in the rock. Increasing the polymer intermolecular force increased the adsorption but did not lead to obstruction.

The $F_R$ and $F_{RR}$ values of the 300 and 100 mD cores were only slightly different, but those of the 50 mD low-permeability cores were considerably greater than those of the 100 and 300 mD high-permeability cores. Decreasing the polymer concentration did not considerably decrease the injection pressure of polymers in low-permeability formations, although the polymer viscosity decreased. In addition to the influencing factors, specifically, the polymer adsorption and high viscosity, the consistency between the polymer molecular size and the rock pore size (particularly, the pore throat) considerably influenced polymer molecular retention.

In general, decreasing the polymer solution concentration can decrease the injection pressure of polymer flooding, which influences the microscopic oil displacement efficiency of polymer flooding. Consequently, to achieve the highest oil flooding efficiency, a suitable polymer concentration must be used. The suitable polymer concentration of cores with varying permeability can be preliminarily calculated using Figure 6. When the permeability is less than 100 mD, the SRP concentration injected into the core must not be greater than 900 mg/L; otherwise, the injectivity would considerably decrease.

### Polymer Adsorption Experiment

Polymer Concentration. The polymer concentration considerably influences the perceived viscosity of the polymer. SRP flooding simulation studies with various quantities of medium-molecular SRP were performed. The $F_R$, $F_{RR}$, and decrease in the permeability for core flooding with different polymer concentrations and permeabilities are shown in Table 6 and Figure 6. The intermolecular entanglement intensified as the polymer concentration increased, and the network topology became more compact. The injection pressure increased during the flooding process, and a larger amount of polymer remained in the rock. Increasing the polymer intermolecular force increased the adsorption but did not lead to obstruction.

Table 7. Polymer Solution Standing for Different Time Adsorption Capacities

| polymer                  | time (h) | absorbance | concentration loss (mg/L) | adsorption quality (mg) | sand quality (g) | adsorption capacity (mg/g) |
|--------------------------|----------|------------|---------------------------|-------------------------|-----------------|----------------------------|
| medium-molecular SRP     | 12.00    | 0.37       | 151.00                    | 6.04                    | 4.00            | 1.51                       |
|                          | 24.00    | 0.35       | 225.00                    | 9.00                    | 4.00            | 2.25                       |
|                          | 36.00    | 0.35       | 328.13                    | 13.13                   | 4.00            | 3.28                       |
|                          | 48.00    | 0.34       | 356.25                    | 14.25                   | 4.00            | 3.56                       |
| high-molecular PHPAM     | 12.00    | 0.48       | 71.05                     | 2.84                    | 4.00            | 0.71                       |
|                          | 24.00    | 0.45       | 153.00                    | 6.12                    | 4.00            | 1.53                       |
|                          | 36.00    | 0.40       | 260.53                    | 10.42                   | 4.00            | 2.61                       |
|                          | 48.00    | 0.39       | 276.32                    | 11.05                   | 4.00            | 2.76                       |
| ultrahigh-molecular PHPAM| 12.00    | 0.44       | 48.57                     | 1.94                    | 4.00            | 0.49                       |
|                          | 24.00    | 0.39       | 172.00                    | 6.88                    | 4.00            | 1.72                       |
|                          | 36.00    | 0.35       | 267.14                    | 10.69                   | 4.00            | 2.67                       |
|                          | 48.00    | 0.33       | 288.00                    | 11.52                   | 4.00            | 2.88                       |

Figure 6. $F_R$ and $F_{RR}$ of polymer flooding of cores with different permeabilities.

Figure 8 presents the static adsorption values of polymer solutions at various liquid—solid ratios. In the static adsorption experiment, the polymer adsorption capacity increased with the liquid—solid ratio. The adsorption capacity of polymers with a low and high liquid—solid ratios significantly decreased. As the liquid—solid ratio increased, the static
adsorption capacity progressively increased and stabilized. When a suitable polymer solution was used, the static adsorption capacity of the sand particles was limited by their surface area.

**Static Adsorption of Polymer Solutions with Different Concentrations.** Table 8 presents the statistical experimental data of polymer solutions with different concentrations after standing for 36 h, and Figure 9 shows the isothermal static adsorption curve of polymer solutions with different concentrations. When the polymer concentration increased from 300 to 900 mg/L, the static adsorption capacity of the polymer increased. When the polymer concentration exceeded 900 mg/L, because of the limitation of the solid–liquid ratio, the static adsorption amount saturated and did not increase with the polymer concentration. At different concentrations, the adsorption capacity of the medium-molecular ASPAM was greater than that of high-molecular and ultrahigh-molecular PHPAM. This phenomenon occurred because the molecular chain of medium-molecular ASPAM was shorter than those of the other two polymers and could thus enter the finer pore roars and be adsorbed in the pores. The adsorption loss of the polymer could be decreased by decreasing the polymer solution concentration, and the injection pressure of the polymer solution could be decreased. However, the effect of decreasing the concentration on the viscosity of the polymer entering the reservoir must be considered.

**Dynamic Adsorption.** The dynamic adsorption capacity test results of the polymer solution are shown in Table 9. Table 9 shows that the static adsorption capacity of the medium-molecular SRP is approximately 2–5 times that of the dynamic adsorption capacity. This phenomenon could be attributed to the fluid shearing effect in the dynamic adsorption. The chains are shorter, and the intertwining phenomenon weakens. Consequently, the adsorption capacity is less than that in the static adsorption. Sameer Al-Hajri highlighted the large difference in the static and dynamic adsorption amounts of various polymers in the core. For a given type and concentration of the polymer solution, lower core permeability corresponds to a smaller pore size and larger dynamic adsorption capacity. Because the molecular structure of the polymer does not change, the polymer adsorption capacity on the surface of the medium does not change, although the spatial structure formed by its entanglement increases the adsorption layer thickness. The external force balance is the main factor affecting the dynamic adsorption capacity. The small size of the pore throat increases the entanglement force between the SRP molecules in the pores, which leads to the thickening of the adsorption layer.

The polymer solution retention varies with the rock permeability, polymer type, concentration, and displacement rate. Manichand and Seright reported that polymer retention values exceeding 0.2 mg/g may influence the oil displacement rate and economics of the polymer flooding process. Therefore, this experiment demonstrated that the use of SRP was not economical.

**Analysis of the Mechanism of Decrease in the Polymer Injection–Production Capacity.** The degree of matching between the polymer molecular size and the core pore size is a key factor influencing the polymer injection capacity.

![Figure 7. Temporal variation in the adsorption capacity of polymers with different molecular weights and concentration of 900 mg/L.](https://DOI.org/10.1021/acsomega.2c00296)

![Figure 8. Polymer adsorption capacity at different liquid–solid ratios.](https://DOI.org/10.1021/acsomega.2c00296)

| polymer            | initial concentration (mg/L) | absorbance | concentration loss (mg/L) | adsorption quality (mg) | sand quality (g) | adsorption capacity (mg/g) |
|--------------------|-----------------------------|------------|----------------------------|-------------------------|------------------|----------------------------|
| medium-molecular SRP| 300.00                      | 0.23       | 131.25                     | 5.25                    | 4.00             | 1.31                       |
|                    | 600.00                      | 0.30       | 204.17                     | 8.17                    | 4.00             | 2.04                       |
|                    | 900.00                      | 0.35       | 328.13                     | 13.13                   | 4.00             | 3.28                       |
|                    | 1200.00                     | 0.43       | 350.00                     | 14.00                   | 4.00             | 3.50                       |
|                    | 1500.00                     | 0.51       | 357.29                     | 14.29                   | 4.00             | 3.57                       |
| high-molecular PHPAM| 300.00                      | 0.22       | 138.95                     | 5.56                    | 4.00             | 1.39                       |
|                    | 600.00                      | 0.34       | 173.68                     | 6.95                    | 4.00             | 1.74                       |
|                    | 900.00                      | 0.45       | 260.53                     | 10.42                   | 4.00             | 2.61                       |
|                    | 1200.00                     | 0.57       | 295.26                     | 11.81                   | 4.00             | 2.95                       |
|                    | 1500.00                     | 0.69       | 303.95                     | 12.16                   | 4.00             | 3.04                       |
| ultrahigh-molecular PHPAM| 300.00                      | 0.19       | 47.14                      | 1.89                    | 4.00             | 0.47                       |
|                    | 600.00                      | 0.29       | 157.14                     | 6.29                    | 4.00             | 1.57                       |
|                    | 900.00                      | 0.39       | 267.14                     | 10.69                   | 4.00             | 2.67                       |
|                    | 1200.00                     | 0.51       | 298.57                     | 11.94                   | 4.00             | 2.99                       |
|                    | 1500.00                     | 0.65       | 314.29                     | 12.57                   | 4.00             | 3.14                       |
injectivity. According to Flory’s theory of polymer solutions, the cyclotron radius (or hydraulic radius) of polymer molecules in the polymer solution can be calculated using the following formula:

\[ r_0 = 0.62 \times 10^{-4} ([\eta]M)^{1/3} \]  

(4)

where \([\eta]\) is the characteristic viscosity of the polymer in an aqueous solution, mL/g; \(M\) is the molecular mass of the polymer, \(\times 10^4\); and \(\alpha\) is a constant, \(\alpha = (10/3)\pi N_s^3\), which is approximately \(4.22 \times 10^{24}\).

The characteristic parameters of several polymers used in the experiment are listed in Table 10. The medium-molecular SRP exhibited a large molecular cyclotron radius of 0.19 \(\mu\)m, and the core permeability decreased when the thickness of the polymer hydration adsorption layer increased. For high platform cores with an average permeability of 100 mD, the permeability decreased by 43.7%. Moreover, the same thickness of the polymer adsorption layer had different effects on the decrease in the core permeability with different permeabilities, especially for low permeability cores (permeability less than 50–100 mD).

### Table 9. Dynamic Adsorption Capacity of Medium-Molecular SRP (\(C_p = 900\) mg/L)

| polymer          | permeability \((10^{-3} \mu m^2)\) | polymer concentration \((mg/L)\) | injection polymer volume \((mL)\) | core quality \((g)\) | adsorption capacity \((mg/g)\) |
|------------------|-----------------------------------|----------------------------------|----------------------------------|---------------------|---------------------------|
| medium-molecular SRP | 107.9                             | 900                               | 462.42                           | 238.2               | 87.1                      | 1.20                       |
|                  | 328.6                             | 900                               | 562.50                           | 186.0               | 73.9                      | 0.99                       |
|                  | 507.9                             | 900                               | 562.50                           | 166.7               | 72.7                      | 0.77                       |

### Table 10. Characteristic Parameters of the Experimental Polymer

| polymer                  | molecular mass \((\times 10^4)\) | intrinsic viscosity \((dL/g)\) | molecular cyclotron radius \((\mu m)\) | decrease in the permeability |
|--------------------------|----------------------------------|--------------------------------|----------------------------------------|-----------------------------|
| medium-molecular SRP      | 700                              | 40.4                           | 0.19                                   | 56.8%                       |
| high-molecular PHPAM      | 1400                             | 33.6                           | 0.22                                   | 59.2%                       |
| ultrahigh-molecular PHPAM | 2500                             | 48.0                           | 0.31                                   | 70.5%                       |

The polymers are characterized by a high molecular weight and long chain morphology. These chains contain many polar groups that attach the rock surface through van der Waals forces and hydrogen bonding available on the pole. This phenomenon decreases the number of polymer molecules in the polymer solution, which decreases the polymer solution concentration and increases the entropy of the polymer solution. Conversely, the entropy reduction is due to the loss of polymer freedom upon adsorption on the surface. Essentially, polymers...
occupy adsorption sites on the rock surface. Consequently, a larger amount of surface area is available for polymer molecules, corresponding to a higher level of adsorption.

The adsorption of polymers in the porous media of hydrophilic rocks can decrease the selectivity of rock permeability. The decrease in permeability caused by polymer adsorption can be explained by the “geometric” effect, that is, the decrease in the pore and throat size caused by the polymer adsorption layer changing the size of the porous medium (restricting the pore throat). When the core permeability is lower than 20 mD and the thickness of the polymer adsorption layer is greater than 0.5 μm, the core is completely blocked. Because polymer adsorption is irreversible, severe adsorption can occur. If the adsorbed polymer occupies a large pore volume, it is difficult to recover a substantial amount of oil. In addition, the formation permeability decreases, resulting in lower recovery.

Figure 11a shows the original state of the surface of the natural core, and Figure 11b shows the surface state of the natural core after polymer flooding. SRP is a highly viscous fluid. When SRP

Figure 10. Effect of shearing on polymer morphology. (a) Initial sample of SRP; (b) Sample of SRP after shearing; (c) Initial sample of PHPAM; (d) Sample of PHPAM after shearing.

Figure 11. Physical drawing of the polymer adsorption plug. (a) Original state of the surface of the natural core; (b) surface state of the natural core after polymer flooding.
passes through the natural core, the polymer is not only adsorbed on the pore surface of the rock but also connects the two sides of the pore. Consequently, a polymer molecular network is formed in the pore, and the pore space is divided into smaller intervals. Moreover, because of the loose cementation of the core, the fine sand particles formed after the broken core are carried by the polymer until they block the middle or outlet end of the core, resulting in a significant decrease in the size of the hole roar. Figure 12 schematically illustrates the adsorption, bridging, and sand-carrying effects of the polymer blockage.

CONCLUSIONS

1. According to the polymer flooding experiments, the lower limit of permeability of the cores displaced by the medium-molecular SRP solution is 20–40 mD. SRP exhibits higher injectability and adsorption retention than those of the PHPAM.

2. The resistance coefficient and the residual resistance coefficient in the natural core flooding experiment are approximately two and three times those of the artificial core for a given permeability.

3. For cores with permeabilities greater than 100 mD, the SRP concentration can be more than 900 mg/L. However, for cores with low permeabilities of approximately 50 mD, the SRP concentration must be less than 900 mg/L.

4. According to polymer adsorption experiments, the static adsorption amounts of the three polymers are steady when the standing time exceeds 36 h. The liquid–solid ratio is a key factor that influences the upper limit of the static adsorption capacity of the SRP. When the SRP concentration is 900 mg/L, the static adsorption amount (3.56 mg/g) is high and approximately 2–5 times the dynamic adsorption amount.

5. The injection capacity of the SRP decreases owing to the following reasons: the molecular gyration radius of the SRP is 0.19 μm, and the permeability can be decreased by 43.7% for Daqing Oilfield with an average permeability of 100 mD. Moreover, considerable aggregation occurs, and the size of the aggregated polymer group can reach 5–10 μm, considerably exceeding the pore radius of the rock. The SRP exhibits a high shear resistance, maintains a high bonding strength, and is not easily damaged. Moreover, the polymer carries fine sand particles, which block the middle or outlet end of the core, resulting in a significant decrease in the size of the pore roar.

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Notes
The authors declare no competing financial interest.

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