INTRODUCTION

The successful exploitation of shale gas in the U.S. has opened a new pattern of global energy. According to the statistics of U.S. Energy Intelligence Agency, shale oil and gas resources in the United States are ranked second in the world. It is reported that the production of shale gas will increase from $1.4 \times 10^{11} \text{ m}^3$ in 2010 to $4.3 \times 10^{11} \text{ m}^3$ in 2035. Shale gas will become the largest source of the total natural gas consumption. The percentage of shale gas will grow from 23% to 45% in the U.S.\(^1\)

It is necessary to conduct hydraulic fracturing for shale reservoirs with characteristics of low porosity and low permeability.\(^2\)-\(^4\) However, conventional fracturing cannot meet the requirements of shale gas production. Shale reservoirs need more irregular network fractures to

Abstract

Hydraulic fracturing is generally necessary to achieve economically viable production rates during exploitation of shale reservoirs. Polyacrylamide-based fracturing fluid is commonly used in shale fracturing. Polyacrylamide (PAM) becomes adsorbed in the shale micro-fractures, decreasing the permeability of the reservoir. For improving the production of shale after being stimulated, the adsorption behavior and adsorption mechanism between the PAM and shale are studied. An ultraviolet spectrophotometer is used to obtain the amount of adsorption. To observe the adsorption morphology, a scanning electron microscope is employed. The action force between the PAM and shale rock is analyzed through Fourier transform infrared spectroscopy, zeta potential instrument, and X-ray photoelectron spectroscopy. The results indicate that hydrogen bonding is the key force between the PAM and shale. A kind of shale micro-fractures model is designed to determine the recovery of permeability. Urea breaks the hydrogen bonding and keeps the molecular of HPG stretch which can decrease the amount of adsorption on the shale surface and effectively recover the permeability of shale micro-fractures up to 72.46% after being damaged. In conclusion, it is believed that the competitive adsorption is a new approach for remediation of the permeability damage by PAM-based fracturing fluid and has great potential in oil field application.

KEYWORDS

competitive adsorption, hydrogen bonding, polyacrylamide, shale micro-fractures, urea
form more percolation passages.\textsuperscript{5-7} To create more network fractures and save economic cost, slick-water fracturing is proved to be the most effective measure in shale reservoirs.\textsuperscript{8,9}

However, slick-water fracturing only provides a small amount of proppant owing to the low viscosity of the fracturing fluid.\textsuperscript{10} To enhance the carrying capacity of proppant and increase the effective volume of reservoir stimulation, high pump rates exceeding 20 m\textsuperscript{3}/min are required to transport the proppant during the hydraulic fracturing process. A significant amount of energy loss occurs owing to the turbulence of the slick-water.\textsuperscript{11-16} One of the primary additives is a drag reduction agent in slick-water which is used to reduce the fluid friction due to the high pump rates.\textsuperscript{17}

Presently, the most common drag reduction agent is a kind of polyacrylamide (PAM) polymer which is usually anionic, nonionic, or cationic.\textsuperscript{18,19} A large amount of slick-water is injected into the shale reservoir for more network fractures. It leads to a large volume of PAM remaining in the shale reservoirs after hydraulic fracturing. Classically, only 5%-55% of slick-water is subsequently recovered as flow-back.\textsuperscript{20-22} The slick-water adsorbed in the fractures or rock matrix seriously limits the production rate of oil/gas (Figure 1). The slick-water damage directly influences the exploitation of shale reservoirs. Therefore, the overall operation tendency of shale fracturing is to reduce the slick-water damage to the reservoirs.\textsuperscript{23-25}

The current practice is to reduce the molecular weight of PAM before flowing back. It is believed that a low molecular weight chain is fit to recover the permeability of shale reservoirs.\textsuperscript{26-28} As a matter of fact, after being flowed back, there will be a large amount of PAM remaining in the micro-fractures in the shale reservoirs which decreases the reservoir permeability. Many works have been designed to reduce reservoir permeability damage before the damage occurs.\textsuperscript{29,30} There is no report that focuses on how to resolve the reservoir damage. It is important to establish a method to assess the behavior of PAM in the micro-fractures of shale reservoirs and to obtain a way to eliminate the damage that has occurred.

Several research works have been conducted to prove that PAM molecules on matrix pore-fracture surfaces can change flow properties and cut back the reservoir permeability.\textsuperscript{31-35} It is clear that the fractures or micro-fractures are the flow route of shale reservoirs. It is different from conventional carbonate and sandstone reservoirs of networked pore spaces and throats. The results of current adsorption-entanglement and blocking theory in the conventional carbonate and sandstone cores are not fit for shale reservoirs without further experimental research and system testing.

Urea can break the interaction between PAM and shale rock which provides an environmentally sustainable, highly efficient, and cost-effective alternative to conventional treatment methods for fracturing fluid damage. Urea has very good environmental protection performance and the degradation products have no pollution to the environment.\textsuperscript{36,37} Hydrogen bonds are easily destroyed by urea because of its strong electronegativity.\textsuperscript{38}

In this novel method, urea is employed to reduce the damage to the pore spaces and throats of shale during hydraulic fracturing. The adsorption-entanglement of the fracturing fluid and the adsorption-blocking in the shale caused by slick-water will be solved by the urea. The urea will decrease the fracturing fluid adsorption and retention in the pore-fracture media. The conductivity of the fracture and the permeability of the rock matrix will be recovered, while the production rate of gas will be improved.

The results will benefit the recovery of the permeability of shale reservoirs after being stimulated and improve the production of gas.

\textbf{FIGURE 1} Diagrams showing the adsorption damage and adsorption process: (A) fracture adsorption, (B) fracture desorption, (C) proppant adsorption, and (D) proppant desorption
2 | EXPERIMENTAL AND METHODS

2.1 | Materials

Cylindrical shale micro-fractures model with a diameter of 2.54 cm and a length of 5.08 cm is used to fill the shale particles with a particle size of 96-120 μm from the Long Ma Xi layer, Sichuan basin to simulate micro-fractures (Table 1). The fracture size distribution of the cylindrical shale micro-fractures model is shown in Figure 2. (First, the micro-fractures structure at different sections of the shale filling layer was photographed by an ultra-long focal length continuous zoom video microscope. Second, according to K-means clustering, the rock skeleton and pore space in the filling layer were segmented, and the pores in the binary map were calibrated by minimum exterior quadrilateral. Finally, the pore size distribution of shale filling was calculated by Matlab programming.) The friction reducer of slick-water is PAM polymer. Anionic polyacrylamide (APAM), non-ionic polyacrylamide (NPAM), or cationic polyacrylamide (CPAM) from Changzheng Chemical Company is used to prepare a high molecular weight 0.1 wt% PAM solution. The molecular weight distribution and the charge density are shown in Table 2. Analytically pure urea is obtained from Changzheng Chemical Company.

2.2 | Experimental setup

Figure 3 presents the flow experimental equipment which is composed of a power driving system, a shale micro-fractures model, a data measurement system, and a data acquisition system. The syringe pump (2PB-1040) is made in Beijing satellite manufacturing factory. The flow rate range is 0.01–9.99 mL/min and the maximum working pressure is 40 MPa. The shale pack is an independent experimental equipment design, which is made of 316 L steel with a length of 5.08 cm and an inner diameter of 2.54 cm. The maximum working pressure is 25 MPa. An ultraviolet spectrophotometer from Shimadzu Corporation is used to study the adsorption capacity.

The Fourier transform infrared spectroscopy (FT-IR) spectra of the specimen were recorded on a FT-IR spectrometer (Equinox 55, Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany). Zeta potential was measured using a zeta meter (Malvern, Zetasizer 2000). The composition of shale rock before and after contacting with slick-water was assessed by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Theta Probe).

3 | EXPERIMENTAL PROCEDURE

The adsorption capacity is determined using an ultraviolet spectrophotometer. The absorbance is measured at a wavelength of 578 nm. The concentration of different PAM in the solution is determined before and after the adsorption process by using previously obtained calibration curves, according to Equation (1).39

\[ \eta = \frac{(C_0 - C_t) \times V}{W} \]  

(1)

\( C_0 \) is the initial concentration of PAM (mg/L), \( C_t \) is the concentration of PAM at a given time (mg/L), \( V \) is the volume of liquid (L), and \( W \) is the mass of adsorbent (g).

The damage degree of PAM solution to the shale particles is characterized by comparing the permeability before and after their contacting.28 Permeability is calculated according to Darcy formula40:

![TABLE 1 X-ray diffraction data for the shale rock used (%)]

| Clay Minerals | Barite | Quartz | Normal Feldspar | Plagioclase | Calcite | Dolomite | Pyrite |
|---------------|-------|--------|-----------------|------------|--------|---------|-------|
| 13.97         | 0.00  | 63.54  | 0.00            | 2.83       | 14.72  | 4.93    | 0.00  |

![FIGURE 2 Fracture size distribution of cylindrical shale micro-fractures model]
where $K$, $A$, and $L$ are the permeability (mD), sectional area (cm$^2$), and length (cm) of shale micro-fractures column. $\mu$ and $Q$ indicate the viscosity (mPa·s) and flow rate (cm$^3$/s) of DI water; and $\Delta P$ (1 × 10$^5$ Pa) is the differential pressure of shale micro-fractures model.

$$K = \frac{\mu \times Q \times L}{A \times \Delta P} \times 10^3$$ (2)

$D_k$ is the damage degree. $K_{max}$ is the permeability of shale pack before contacting with PAM. $K_{min}$ is the permeability of shale particles after contacting with PAM solution.

After the initial permeability of shale particles in the shale particle filled pipe is tested by Equation (2), the PAM solutions with different conditions are injected into the same pipe. The residual solution is blown out by nitrogen gas. Similarly, the permeability of rock to PAM can be measured. The damage degree can be obtained by Equation (3).

$$D_k = \frac{K_{max} - K_{min}}{K_{max}} \times 100\%$$ (3)

Different amounts of urea were mixed with PAM solution, and a series of PAM solutions containing 0-2000 mg/L urea were prepared. Then, the solutions were injected into the shale particle filled pack, respectively, and the optimal dosage of urea can be obtained. To determine the desorption effect of urea under the optimal dosage, clear water was injected into the shale particle filled pack to eliminate water phase damage; then, PAM solution was injected into the same shale pack to obtain the maximum damage degree. Finally, PAM solution containing urea under the optimal dosage was injected to obtain the recovery degree of permeability damage.

4 | RESULTS AND DISCUSSION

4.1 | Adsorption behaviors

The adsorption isotherms and the law of permeability variation of APAM, CPAM, and (NPAM) onto shale are depicted in Figure 4. It is easy to find that the adsorption amounts surged with the increase of the displacement...
time. As the displacement time increased to 120 minute, adsorption amount is no longer changed with the increase of displacement time as shown in Figure 4A. The results show that CPAM has the largest adsorption capacity, while under the same conditions, NPAM comes second. The adsorption capacity of APAM is minimal, only approximately one-third of the CPAM. Figure 4B shows the relationship between damage degree and displacement time. The greater the adsorption amount, the greater the permeability damage. Moreover, there is a general quantitative relationship between the amount of adsorption and the permeability damage (Table 3). It means that APAM is the best friction reducer of slick-water without considering the economic cost.

To observe the change of shale after contacting with PAM, a scanning electron microscope is used. It is seen that due to the existence of mainly layered and plate-like structures of shale bedding, the inside part contains many small debris in Figure 5A. After adsorbing with APAM, the surface of shale seems to be wrapped up by a layer of film as shown in Figure 5B. Small debris particles disappeared, and the layered structure is not clear.

On the other hand, the PAM molecules in the water solution are arranged in a close order and the linear structure is obvious as shown in Figure 6A. After contacting with shale rock, the linear structure of APAM cannot be found in the visual range in Figure 6B because the PAM molecules are coiled and intertwined.

Based on the new approach, the adsorption amount is fitted well as a function of the damage degree of the permeability in Table 3. The damage degree of the permeability can be calculated by using these correlation coefficients after the PAM treatment. Since there is a strong correlation between the adsorption amount and permeability damage, the permeability of shale micro-fractures will be restored accordingly if there is a method to reduce the amount of PAM adsorbed onto shale.

| Type  | Sampling time \( t \) (min) | Adsorption amount \( \eta \) (mg/g) | Damage degree \( D_k \) (%) | Correlation coefficient \( \eta/D_k \) (mg/g) |
|-------|-----------------------------|-----------------------------------|-----------------------------|-----------------------------------------------|
| APAM  | 20                          | 2.23                              | 9.85                        | 0.226                                         |
|       | 60                          | 5.21                              | 23.42                       | 0.222                                         |
|       | 120                         | 9.47                              | 42.76                       | 0.221                                         |
| NPAM  | 20                          | 2.91                              | 10.55                       | 0.276                                         |
|       | 60                          | 8.23                              | 29.84                       | 0.276                                         |
|       | 120                         | 14.85                             | 54.58                       | 0.272                                         |
| CPAM  | 20                          | 3.54                              | 9.97                        | 0.355                                         |
|       | 60                          | 11.62                             | 33.17                       | 0.350                                         |
|       | 120                         | 25.41                             | 72.33                       | 0.351                                         |

APAM, anionic polyacrylamide; NPAM, nonionic polyacrylamide; CPAM, cationic polyacrylamide.
4.2 Adsorption mechanism

The adsorption characteristic of PAM onto shale is studied by infrared spectroscopic method in Figure 7. The amino groups and carbonyl groups of amides of the APAM show strong stretching vibration peaks at 3432 and 1611 cm\(^{-1}\), respectively. Furthermore, the vibration peaks of C=C are not observed, and C-H stretch at 2861 and 2858 cm\(^{-1}\) of the alkyl is obvious in the spectra. It is evident that shale rock will adsorb APAM from slick-water. The results show that after being adsorbed in 1000 mg/L APAM, new bond and conformation are observed on the shale particles surface. It can be confirmed that there is no a chemical reaction between APAM and the shale surface. The force between adsorbed APAM and shale is not as strong as a chemical bond, and the adsorption process may be reversible to a certain extent.

Figure 8 shows that the zeta potential of shale particles with and without PAM. From pH 1 to 12, the zeta potential of shale particles is negative. With the increase of pH, the zeta potential shows a downward trend. After adsorption of PAM, the zeta potential value of shale particles decreases stably. These results suggest that the presence of PAM can lead to the decrease of...
the charge density of the shale surface. It is easy to find that the zeta potential values of APAM, NPAM, and CPAM are different after adsorption. The trend of zeta potential value of PAM is the same basically. However, NPAM and CPAM zeta potential value is reversed. It indicates that the electrostatic force plays an important role in the adsorption of NPAM and CPAM on shale. On the other hand, it also proves that no electrostatic force exists between APAM and the surface of shale particles.

Figure 9A shows the wide-scan XPS spectra of shale particles after being contacted with APAM. As expected, carbon, nitrogen, and oxygen are the major components. The presence of C1s and O1s comes from the original shale particles surface, while N1s in the interacted sample proves the surface process of APAM on the surface of shale particles. High-resolution spectra of XPS, especially C1s spectra and O1s spectra, are needed to identify the chemical bonding between each component.

The high-resolution C1s spectra for shale after interacting with 1000 mg/L of APAM are shown in Figure 9B. The high binding energy shoulders of C1s can be resolved via peak-differentiation analysis into two peaks at binding energies of C-C/C-H (284.8 eV), C-O/C-N (286.0 eV), and O=C-N (287.9 eV). Figure 9C shows the high-resolution XPS O1s spectra. The high binding energy shoulders can be deconvoluted. These deconvoluted peaks belong to N-C=O (531.1 eV), O-C=O/C=O (531.6 eV), and C-O (532.7 eV). It is obvious that a new peak appeared despite APAM or shale not having a peak at 532.0 eV. However, a distinctive characteristic peak can be found in the high-resolution adsorption spectra of XPS. It shows that there is another bonding of O1s besides C=O/C=O/C=O/N=O/C=O, which is the hydrogen bonding energy of 532.0 eV (M-O--H).

**FIGURE 9** Wide-scan spectra of X-ray photoelectron spectroscopy (XPS) for shale particles after reacting with 1000 mg/L of anionic polyacrylamide (APAM) at pH 7.0 for 2 h as (A); High-resolution XPS C1s spectra of shale particles loaded with APAM at pH 7.0 for 2 h as (B); High-resolution XPS O1s spectra of shale particles loaded with APAM at pH 7.0 for 2 h as (C); High-resolution XPS N1s spectra of shale particles loaded with APAM at pH 7.0 for 2 h as (D)
High-resolution N1s spectra of XPS can be performed for shale reacted with 1000 mg/L of APAM (Figure 9D). It clearly shows that the peak of N1s for shale is not found because a narrow scan will yield too much noise. The character of N-C=O/C-N is also indicated by the peak at 399.5 eV in the N1s spectrum at 1000 mg/L of APAM.

Since as mentioned above, the driving force for the adsorption of PAM on shale rock is hydrogen bonding, it is suggested that hydrogen bonding plays a similar important role in the adsorption of polymer on rock.

4.3 | Reduction of adsorption damage by urea

Urea can replace the sites on the shale occupied by PAM molecules and form hydrogen bonding between the shale and the PAM. The adsorption isotherms for PAM on shale with and without urea at pH 7 are shown in Figure 10. When urea is added into the system, the amount of adsorption decreased sharply. It proves that the action force between PAM and shale is hydrogen bonding.

The adsorption behavior of different urea concentrations on the shale surface is investigated. With the PAM concentration fixed, the addition of urea can greatly restrain the adsorption of PAM on shale rock. The saturated adsorption amount of APAM/NPAM/CPAM solution without urea is 8.8/14.3/26.4 mg/g respectively, which clearly decreases with the increase of urea concentration. When the concentration of urea is 400 mg/L, the adsorption amount of APAM/NPAM/CPAM is 4.9/10.8/23.2 mg/g. The values are 3.3/10.6/22.3 mg/g when the concentration of urea increases to 1200 mg/L as shown in Figure 10. The decrease in the amount of adsorption is significant. On the other hand, the dynamic adsorption amount of PAM on the shale is investigated by core-flooding tests with different urea concentrations from 0 to 2000 mg/L. The pore volume and permeability of the shale micro-fractures model are approximately 9.87 cm³ and 0.835 μm², respectively. The dynamic adsorption results are shown in Figure 10. It is found that there is a complete dynamic adsorption and desorption process on the shale. When the concentration of the urea exceeds 1200 mg/L, the dynamic desorption reaches the minimum point. It is indicated that the urea can completely occupy the shale surface. Some PAM molecules will peel off from the shale particle surface. At the same time, the urea will break the intramolecular and intermolecular hydrogen bonding of the PAM and keep the molecular chain from being curly. This will decrease the PAM adsorption and increase the permeability of the shale micro-fractures.

There is a critical urea concentration for breaking the hydrogen bonding. The PAM’s adsorption capacity reduces slightly when the urea concentration is increased to 2000 mg/L. At this concentration, the surface of the shale particle is occupied by the urea molecules and there are no more sites for the urea molecules. Taking economic cost into consideration, the optimal urea concentration is considered to be 800-1200 mg/L.

To accurately represent the obtained data, the adsorption law of PAM and urea in shale has been analyzed by the Langmuir adsorption model. The Langmuir equation can be expressed as follows:

$$ \eta = \frac{a_n C}{1 + aC} $$

According to the original equation of Langmuir adsorption model, it can be deformed into:
$\eta$ is the adsorption capacity (mg/g), $\eta_s$ is the saturated adsorption capacity (mg/g), $C$ is the initial concentration of PAM (mg/L), and $a$ is the adsorption constant.

As shown in Figure 11, the Langmuir isotherm fits quite well with the experimental data ($R^2 > 0.99$). It is proved that the adsorption of PAM on shale belongs to an ideal behavior, and the adsorption film is monomolecular. Langmuir-type isotherm of adsorption is usually detected in these systems.

\[
\frac{1}{\eta} = \frac{1}{a\eta_s} \cdot \frac{1}{C} + \frac{1}{\eta_s}
\]  (5)

**TABLE 4** The saturated adsorption capacity and adsorption constant of anionic polyacrylamide (APAM), nonionic polyacrylamide (NPAM), and cationic polyacrylamide (CPAM)

| Adsorbate                  | $\eta_s$ (mg/g) | $1/a\eta_s$ (g/L) |
|----------------------------|-----------------|-------------------|
| APAM                       | 20.66           | 144.4             |
| APAM with 1200 mg/L urea   | 4.64            | 215.3             |
| NPAM                       | 28.01           | 51.34             |
| NPAM with 1200 mg/L urea   | 12.82           | 73.9              |
| CPAM                       | 38.46           | 33.7              |
| CPAM with 1200 mg/L urea   | 28.65           | 51.7              |

**FIGURE 11** Langmuir adsorption isotherm of (A) anionic polyacrylamide (APAM), (B) nonionic polyacrylamide (NPAM), and (C) cationic polyacrylamide (CPAM)

**FIGURE 12** Changes of permeability of the shale micro-fractures in the competitive adsorption experiments. The change of permeability of the shale micro-fractures by (A) anionic polyacrylamide (APAM), (B) nonionic polyacrylamide (NPAM), and (C) cationic polyacrylamide (CPAM)
The polar functional group on the molecular chain of PAM should attach to the adsorption sites on the shale.\textsuperscript{44} When the adsorption sites of the shale rock are fully occupied, the adsorption reaches a balance. In addition, it is obvious that the slope and intercept of the curve increase after adding urea. It proves that the addition of urea not only reduces the amount of saturated adsorption of PAM on shale but also weakens the adsorption capacity of PAM.

The saturated adsorption capacity and adsorption constant are shown in Table 4. \( \eta_s \) is an important parameter to evaluate the adsorption behavior between adsorbate and adsorbent, which can characterize the number of adsorption sites occupied by PAM on the shale surface. \( \ln \eta_s \) is a reflection of the adsorption energy, and with the increase of \( \ln \eta_s \), the adsorption force between shale and PAM is weakened. It is further proved that urea reduces reservoir damage by competing adsorption with PAM.

Figure 12 shows that the permeability of three shale micro-fractures are all improved. The damage rate (\( D_r, \% \)) of PAM ranges from 60.17\% to 84.55\%, while the restoration rate (\( D_r, \% \)) is from 40.20\% to 72.46\%. Although competitive adsorption of fracturing fluid damage has not been reported previously, the mechanism can be speculated according to the experimental results of this paper. The retained urea in the shale micro-fractures can shield the shale wall. Some PAM molecules will collide on the urea surface instead of on the shale wall. Therefore, the competitive adsorption directly removes the PAM damage and the permeability is recovered.

5 | CONCLUSIONS

PAM molecular applied to shale stimulation will adsorb on the surface of the shale which leads to damage the micro-fracture formed by stimulation. The adsorption capacity is more, the damage is more serious. XPS test confirms that it is hydrogen bonding which links PAM and shale. Urea can play an efficacious role to reduce the hydrogen bonding between the PAM and shale. A novel remediation method: “competitive adsorption of fracturing fluid damage” is proposed. This can be attributed to the decrease of the adsorption area due to the occupation of urea on the shale surface. Taking economic cost into consideration, the optimal urea concentration is considered to be 800–1200 mg/L. The urea also presents good capability to recover permeability up to 72.46\% in the shale micro-fractures displacing assay. These experiments validate the feasibility and validity of competitive adsorption of fracturing fluid damage.

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