

# Delayed-Crosslink Hydrogel for Improving Oil Recovery in Differential Heterogeneous Reservoirs

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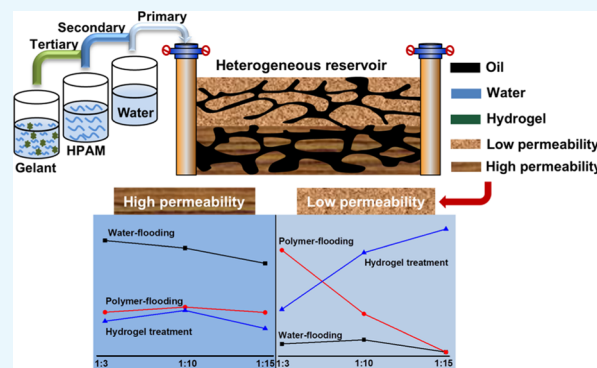
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**ABSTRACT:** Premature water production is an inevitable issue that results in loss of quantities of reserves in heterogeneous oilfields especially with large permeability ratios. Hydrogel treatments, preferentially plugging large channels, are efficient techniques to reduce excessive water circulation. In this work, a moderate delayed polyacrylamide hydrogel was fabricated applying in-depth plugging to promote oil production. Suitability tests of delayed hydrogel in the presence of quartz sand confirmed its mature delay over 10 days, providing the low-viscosity gelant sufficient time for entering the deep layer. Single sand-pack displacement tests demonstrated the excellent plugging ability in differential permeability layers to strongly promote the follow-up oil production. Aiming at heterogeneous reservoirs with three different permeability ratios, conventional displacements and hydrogel treatments were sequentially conducted. In comparison with water- and polymer-flooding that mainly performed exploitation at low-permeability-contrast layers ( $K_{\text{high}}/K_{\text{low}} = 3$ ), the delayed hydrogel technique after polymer-flooding was capable of improving the oil recovery efficiency of unswept zones at high-permeability-contrast zones ( $K_{\text{high}}/K_{\text{low}} \geq 10$ ). Recovery in heterogeneous layers with permeability ratios ( $K_{\text{high}}/K_{\text{low}}$ ) of 10 and 15 was enhanced to 48 and 59%, respectively from 18 and 0%. In addition, rheological behaviors and morphologies elucidated the delayed hydrogel with extruding deformation and high yield strength, facilitating water shutoff and improvement of oil production.



## INTRODUCTION

Excessive water production earlier in heterogeneous reservoirs often led to unproductive cycling of injected enhanced oil recovery (EOR) chemicals, whereas large amounts of residual oil remained in subterranean region.<sup>1–5</sup> Long-term chase flooding always enters large permeability layers, leaving otherwise low permeability zones unswept or poorly swept.<sup>6–8</sup> Most oilfields were discovered in continental sedimentary basins, which were characterized by complicated oilfield geologies having high-permeability contrasts.<sup>9</sup> To enlarge the sweeping area, plugging agents were required to be injected into the depth of the formation to block large channels so that the subsequent fluids get diverted to the previously unswept oil-rich layers.<sup>10,11</sup> Gel treatment is one of the most cost-effective techniques for water shutoff and sweeping improvement.

Varieties of hydrogels have been studied for oil recovery.<sup>12–22</sup> Many studies enhanced recovery through particle gel<sup>16,18,19,21</sup> or microgel<sup>20</sup> technology corresponding to the oilfield geometry. Surfactants combining with gels<sup>12,16</sup> were utilized for improving the recovery efficiency. Even the porous medium was controlled by promoting the sealant strength to reduce heterogeneity<sup>13,14,17</sup> or by treating special geological

configurations.<sup>15</sup> Among these technologies, polyacrylamide gels were extensively used for managing the water yield.<sup>23–31</sup> Nano particles such as clay,<sup>23</sup> montmorillonite,<sup>24</sup> and cellulose<sup>32</sup> were chosen to improve the strength of hydrogels for EOR. Particle gels,<sup>33,34</sup> directly or through re-cross-linking, were injected into the large channels acting as plugging agents. Active microorganisms were immobilized into the polymer gels, which help to improve oil recovery through metabolizing carbonate and bioactive components of surfactants or ammonium.<sup>31,32</sup> However, most of these hydrogels were hardly applied in displacement practice or in oil recovery. Although a few of them were evaluated in simple core-flooding operations,<sup>25,27–34</sup> conventional gels always formed plugging in the immediate vicinity of the wellbore, leading to chase water detouring to the far untreated high permeability zones.<sup>35–37</sup> Therefore, delayed hydrogel treatment was further prompted for deep plugging. Delayed cross-linking can be adjusted through cross-linkers, ligands that form complexes with host cross-linkers, or slow-release synthesis. One possible way was

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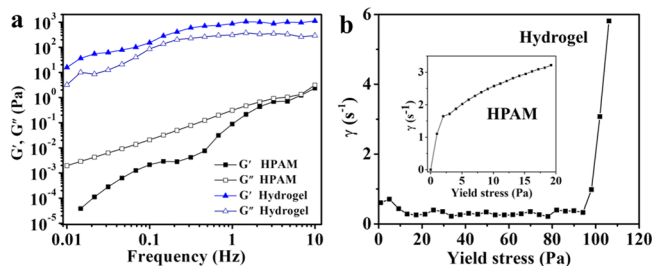
reported<sup>38</sup> using strong ligands such as malonate or glycolate to associate with Cr(III), and a delay occurred till the binding construction of the ligand with the crosslinker. Cordova et al.<sup>39</sup> used polyethylenimine (PEI) and dextran sulfate (DS) to entrap and control the release of Cr(III) in polymer–Cr(III) fabrication, however, the delay strongly relied on the pH, ionic strength, and temperature. As a primary release-controlled agent, DS was too expensive to be widely used in oilfields. Jayakumar and Lane<sup>40</sup> chose 2-acrylamido-2-methylpropane sulfonic acid<sup>41</sup> as a high-temperature delayed source substituting DS to combine with PEI achieving several days delay at 100 °C. However, the gelation at low temperature is uncertain because PEI was mainly applied at medium and high temperatures.<sup>42–44</sup> Xu<sup>45</sup> designed a delayed gel based on the slow release of methenamine, phenol, and citric acid crosslinkers from the cavity of  $\beta$ -cyclodextrin, and the release highly depended on the hydrophobicity of the competitive long-chain fatty alcohol in hydrolyzed polyacrylamide (HPAM) solutions. Thus, a cost-effective and easily fabricated delayed hydrogel was extremely needed for deep plugging.

In this study, partially hydrolyzed PAM (HPAM) with a moderate hydrolysis degree of 5% was utilized to form coordination cross-linking with Cr(III) acetate through intermediate complexes<sup>46</sup> to prolong gelation, and the resulting system exhibited over 10 days delay, which is beneficial to function in-depth plugging. The viscosity, yield stress, and morphology of the delayed hydrogel were studied to examine the deformation, migration, and extruding behaviors. Suitability and corresponding plugging performance in quartz sand were verified through static gelling and single-sand-pack displacement tests. Furthermore, double-core tests displayed how to increase the sweeping efficiency of the delayed hydrogel and HPAM in heterogeneous layers with low-, medium-, and high-permeability ratios ( $\geq 10$ ). The distinctions and advantages of the delayed hydrogel treatment at differential heterogeneity were presented.

## RESULTS AND DISCUSSION

### Rheological Behaviors of Polymer Hydrogels.

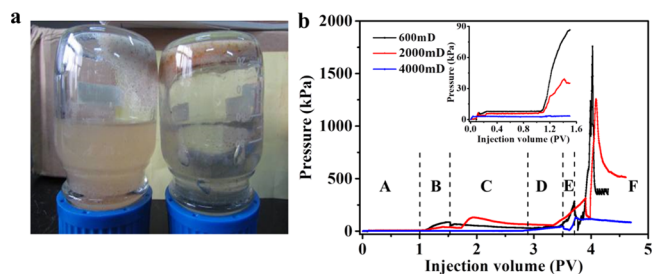
The rheological behaviors of HPAM and hydrogels were analyzed to inspect the viscoelastic extrusion during oil extraction. For HPAM, both elastic ( $G'$ ) and viscous moduli ( $G''$ ) increased with an increasing shear frequency, as shown in Figure 1a.  $G''$  increased from  $10^{-3}$  to 3.1 Pa as the shear frequency increased to 10 Hz.  $G''$  was always larger than  $G'$ , revealing a viscous shear-thickening fluid. Exhibiting a low yield stress of 1.1 Pa (Figure 1b), HPAM was easily induced to flow once the external stress was above 1.1 Pa, which would effectively



**Figure 1.** (a) Elastic ( $G'$ ) and viscous ( $G''$ ) moduli of both HPAM and hydrogels as a function of frequency and (b) comparison of the yield stress for HPAM and hydrogels.

decrease the mobility ratio between oil and water for polymer-flooding because of its high mobility. As a result, polymer-flooding enlarged the sweeping area of the targeted reservoir after suffering from unproductive cycling of water displacements. As for hydrogels,  $G'$  and  $G''$  were  $10^3$  to  $10^5$  times larger than those of HPAM, and  $G'$  was always larger than  $G''$ , indicating an elastic fluid of hydrogels, which showed distinct differences from HPAM (Figure 1a). As shear frequency increased,  $G'$  increased to 1100 Pa, demonstrating the extraordinary elasticity of the hydrogel. While suffering from shear, hydrogels sustained a high elastic deformation. Besides displaying a high yield stress of 101.9 Pa, the hydrogel cannot be driven until the stress was increased above 101.9 Pa (Figure 1b). Once the hydrogel is formed in the porous channel, it is too difficult to be extruded out. The behaviors indicated that the hydrogel is a reliable plugging agent for reducing excessive water production.

**Suitability of a PAM Hydrogel to a Heterogeneous Permeability Layer.** To evaluate suitability of the as-prepared gelant with quartz sand, static gelation blending with 100 mesh quartz sand in a ratio of 3:1 was conducted at 45 °C. Figure 2a compares the states of quartz sand before and



**Figure 2.** (a) Comparison of quartz sand before and after gelling (left: no gelling; right: gelling), (b) pressure curves of three different single sand-pack model tests during the entire displacement phrase (A: first water flooding, B: polymer flooding, C: second water flooding, D: delayed hydrogel treatment, E: third water flooding; and F: fourth water flooding).

after gelling. Before that, all the quartz sand that dispersed in the low-viscous gelant dropped off because of gravity once the beaker was inverted (on the left in Figure 2a). After 10 days of gelling under 45 °C, the gelant gelatinized. No quartz sand dropped but was suspended stably at the bottom (on the right in Figure 2a). Unlike the complete dispersion initially, the sand was binding together with the viscous hydrogel. Also, the gelation time almost kept constant even though blending with sand, suggesting little static adsorption quartz sand with the gelant. Additionally, mixing with quartz sand, the hydrogel maintained thermal stability at 45 °C for several months and even longer. The results illustrated the excellent suitability of the hydrogel with quartz sand that constituted the sand-pack models.

Figure 2b compares the displacement pressures of three different permeability sand-pack models. After the first water-flooding for permeability measurement, 0.5 PV slug of 1000 mg/L polymer acting as a profile control agent was injected. The injection pressures during polymer-flooding increased and varied distinctly among the three sand packs. For a low permeability model of  $0.6 \mu m^2$ , the pressure increased to 275 kPa from 11.3 kPa. The pressure of the permeability model of  $2 \mu m^2$  increased to 38 kPa. With regard to the high

permeability of  $4 \mu\text{m}^2$ , the pressure was merely 3.5 kPa during the polymer injection of 0.5 PV slug. This comparison indicated that the polymer performed an excellent profile modification in the low permeability model. After the second water-flooding, a slug gelant of 0.7 PV was injected, respectively. The third water-flooding was run to drive the gelant to the depth of the models. Following that, the models were under  $45 \text{ }^\circ\text{C}$  for gelling. Until complete gelation, the fourth water-flooding was conducted to investigate the plugging effect in different permeability models. Figure 2b shows that three curves increased sharply to maximum pressures, suggesting the block of large channels. Through hydrogel treatment, as shown in Table 1, the residual

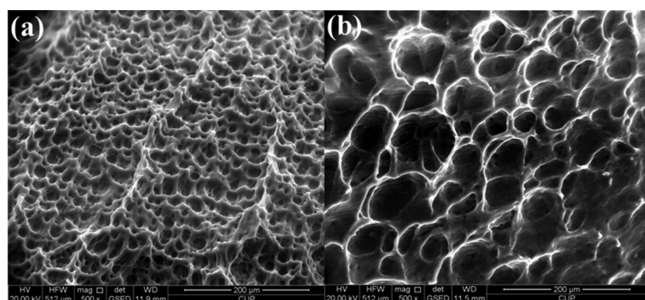
**Table 1. Results of Plugging Tests in Single Sand-Pack Models<sup>a</sup>**

parameter	test 1	test 2	test 3
permeability $k_1$ ( $\times 10^3 \mu\text{m}^2$ ) before injecting	600	2000	4000
permeability $k_2$ ( $\times 10^3 \mu\text{m}^2$ ) after injecting	1.5	25	125
RRF	400	80	32

<sup>a</sup>Note: RRF, residual resistance factor,  $\text{RRF} = k_1/k_2$ .

resistance factor (RRF) of low, medium, and high permeability models were 400, 80, and 32, respectively; this is why the peak pressure of three different permeability models during water-flooding achieved 1759, 1257, and 130 kPa. Obviously, the larger the RRF, the higher the maximum displacement pressure. The chase water was repelled to enter small unswept channels after high permeability zones were plugged. Correspondingly, the permeability of the plugged models decreased to 1.5, 25, and  $125 \mu\text{m}^2$  from the initial 600, 2000, and 4000, indicating favorable plugging. The single sand-pack displacement results strongly supported that the gelant can well-adapt to achieve efficient plugging in differential permeability models.

**Morphology of HPAM and Hydrogels.** PAM polymer acting as profile modification agent could increase the mobility ratio between chase water and crude oil, thus to enlarge the sweeping area, but it seldom exerts positive control in high permeability zone. Fortunately, the robust delayed hydrogel could block large paths to improve sweeping efficiency. These two distinct effects may be closely related to their morphology. As shown in Figure 3, HPAM revealed a regular sparse framework which overlapped layer by layer. It seems that the framework was interwoven by means of the entangled polymer that was mainly responsible for the network. A large amount of transparent pores appeared with sizes ranging between 10 and  $20 \mu\text{m}$ . The pores were nearly filled with flowing water



**Figure 3.** Morphology of both (a) HPAM and (b) hydrogels.

together with a loose framework and may determine the polymer having high mobility for migration during polymer displacement. Also, the polymer would be propelled easily by the chase fluid. By contrast, the morphology of hydrogels exhibited solid frameworks, and no apparent pores appeared. The structure beneath the surface was invisible owing to the dense network. It appeared that the pores (Figure 3b in black) were filled with aggregated bundles, which formed a robust structure, resulting in higher strength than the polymer. The hydrogel could still hold the function of plugging in the reservoir, though the chase water-flooding was continuously carried out.

**Enhanced Oil Recovery in Double-Core Displacement Tests.** To investigate oil recovery efficiency of delayed hydrogel treatment after polymer-flooding in heterogeneous reservoirs, double-core experiments with three different permeability contrasts of 1:3, 1:10, and 1:15 were conducted to study the flooding pressure, fractional flows, and enhanced oil recovery during displacement. The parameters of core samples and oil recoveries at different stages are summarized in Table 2.

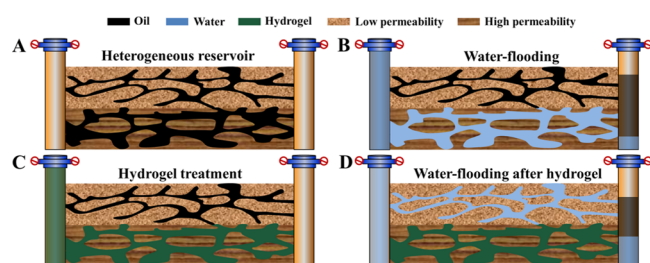
**Permeability Ratio of 1:3.** Parallel cores with a permeability ratio of  $0.3:0.9 \mu\text{m}^2$  were saturated with oil, the viscosity of which was  $9.8 \text{ mPa}\cdot\text{s}$ , as simulated in Figure 4A. Initial oil saturation ( $S_o$ ) values of high and low permeability cores were 74.45 and 77.5%, respectively (Table 2). Displacement experiments underwent water-, polymer-, second water-flooding, gelant-injection, and last water-flooding, and the results are presented in Table 2 and Figure 5. The pressure curve fluctuated with various injecting fluids and pore volumes, and it kept a low pressure of approximately 30 kPa during the first water-flooding (Figure 5a). Fractional flow curves (black in Figure 5b) revealed that over 95% water flowed into the high permeability core for sweeping (Figure 4B), and the oil recovery through water-flooding ( $R_w$ ) was 52.42% (Table 2 and red in Figure 5c). Less than 5% of chase water entered the low permeability channel (red in Figure 5b), and the resulted  $R_w$  was merely 4%. As a result, for heterogeneous reservoirs with a low permeability ratio, sole water-flooding played a significant part in the high permeability zone but resulted in extremely low  $R_w$  on the low permeability layer because of high flowing resistance. Water cut during the first water-flooding was up to 95% (red in Figure 5b). The 0.5 PV polymer of 1000 mg/L was injected, followed by the second water-flooding. Up to 40% polymer flowed into the low permeability core for displacing the residual oil because of the increase in the mobility ratio. Therefore, Table 2 shows that  $R_{pw}$  in the low permeability core increased to 49.64%, compared to  $R_{pw}$  of 18.6% in the high zone. The comparison indicated that polymer functioned excellent as profile modification in heterogeneous reservoirs with a low contrast coefficient of 1:3. Later, the chase water gradually detoured to the high permeability zone. When the water cutting increased, a gelant slug of 0.5 PV was injected. The parallel core was kept gelling under  $45 \text{ }^\circ\text{C}$  for 12 days. Following this, third water-flooding was conducted for oil recovery after hydrogel treatment (Figure 4C). Figure 5a shows that the pressure sharply increased to 2500 kPa during the process of gelant injection, and the subsequent sweeping pressure also increased to 2300 kPa, suggesting the reasonable injection of gelant and formation of the hydrogel. As shown in the fractional flow curves, more than 90% of the chase water entered the low permeability core (red in Figure 5b), confirming the plugging



Table 2. Key Parameters of Heterogeneous Double-Core Models during Displacement<sup>a</sup>

parameter	permeability contrast coefficient for core					
	1:3		1:10		1:15	
	high	low	high	low	high	low
permeability $k$ ( $\mu\text{m}^2$ )	900	300	3000	300	4500	300
porosity $\phi$ (%)	28.89	26.62	31.09	27.1	30.68	26.16
initial oil saturation $S_o$ (%)	77.5	75.45	75.8	75.0	70.82	70.6
$R_w$ (%)	52.42	4	48.91	6.01	41.71	0
$R_{pw}$ (%)	18.6	49.64	21.02	18.62	18.48	0
$R_{Gw}$ (%)	14.34	20.82	19.44	48.42	10.9	59.9
EOR (%)	17.4		33.19		33.42	
total oil recovery (%)	78.36		81.20		75.25	

<sup>a</sup>Note:  $R_w$ , oil recovery of water-flooding;  $R_{pw}$ , oil recovery of polymer-flooding;  $R_{Gw}$ , oil recovery after hydrogel treatment; EOR, enhanced oil recovery.

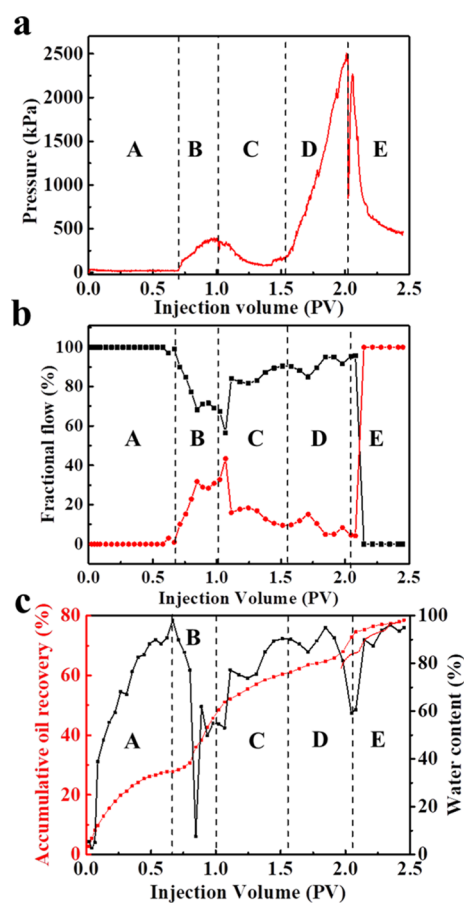


**Figure 4.** Schematic of different displacement stages in a heterogeneous reservoir. (A) Oil-rich heterogeneous layers, (B) initial water-flooding, (C) hydrogel treatment for plugging high permeability zone, and (D) water-flooding after hydrogel treatment.

of the delayed hydrogel in the high permeability zone. As a result, partial residual oil left in the low and high permeability zones were further recovered, and  $R_{Gw}$  was 20.82 and 14.34%, respectively. Undoubtedly, owing to low resistance, the injected gelant preferentially entered and plugged the high permeability core, so that the chase water was able to displace the abundant residual oil in low permeability (Figure 4D). The water cutting decreased by 35% because of the hydrogel technique (Figure 5c).

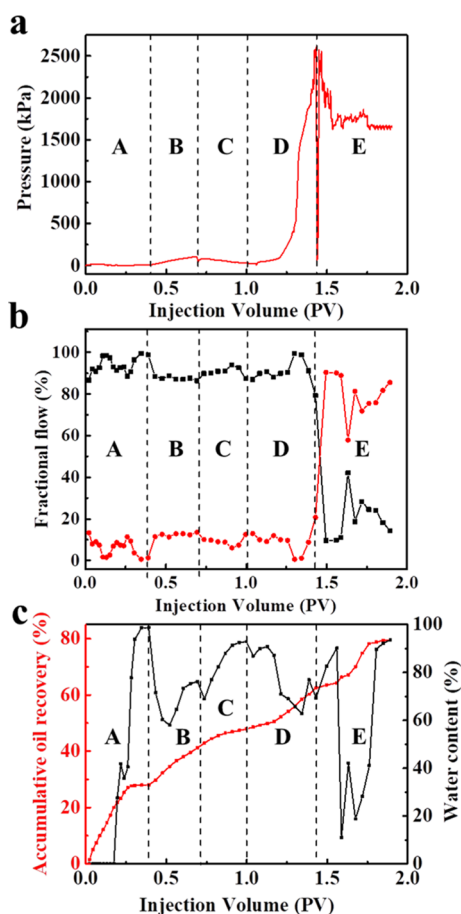
**Permeability Contrast of 1:10.** To further investigate the plugging capacity of the hydrogel especially after polymer-flooding, a parallel core with a medium permeability ratio of 0.3:3.0  $\mu\text{m}^2$  was utilized for displacement tests. Oil recovery of the first water-flooding ( $R_w$ ) in the low permeability core was 6.01% compared to high  $R_w$  of 48.91% in the high permeability core. Evidently, large amounts of chase water entered large channels of 3.0  $\mu\text{m}^2$  (Figure 6b). For the following injection of the polymer, the pressure increased to 107 kPa (Figure 6a), much higher than that of water-flooding, but lower than that of the same procedure (378 kPa) in the low permeability ratio of 1:3 (Figure 5a). Fractional flowing improved little compared to the initial water-flooding, and the chase water still kept flowing into the large channels, which is significantly different from the improvement after polymer injection in the low permeability ratio layer of 1:3 where more water entered the low permeability layer (Figure 5b).

As a result,  $R_{pw}$  in the low permeability core increased to 18.62% from 6.01% ( $R_w$ ), which is much lower than the high efficiency of 49.64%, operated in the low permeability ratio of 1:3. Contributing a higher oil recovery than water-flooding, polymer-flooding functioned better at the low-permeability-ratio layers of 1:3 over the medium of 1:10. To increase the recovery efficiency in the low permeability core, hydrogel



**Figure 5.** (a) Pressure curve as the function of injection volume in the low-permeability-ratio double-core, (b) relationship between fractional flow and the injection volume, (c) accumulative oil recovery and water cut versus the injection volume. (A: first water-flooding, B: polymer injection, C: second water-flooding, D: gelant injection and gelation, and E: third water-flooding).

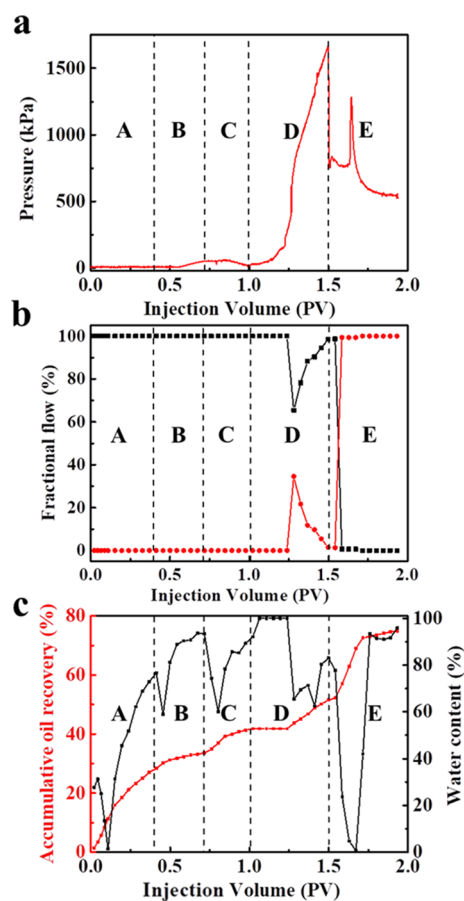
treatment was implemented. A high water-flooding pressure of 2500 kPa after the hydrogel-treatment is displayed in Figure 6a, and it is concluded that the hydrogel slug formed and plugged the large channel. As observed from the fractional flow curve, 80% chase water rapidly diverted the orientation to the low permeability core (Figure 6b). Water content significantly dropped to approximately 10% (Figure 6c), and oil recovery ( $R_{Gw}$ ) in the low permeability core increased to 48.42%, compared to  $R_{pw}$  of 18.62%. Unlike 17.4% in the low



**Figure 6.** (a) Pressure curve as the function of injection volume in the medium-permeability-ratio double-core, (b) relationship between fractional flow and the injection volume, (c) water cut and accumulative oil recovery vs the injection volume. (A: first water-flooding, B: polymer-injection, C: second water-flooding, D: gelant-injection and gelation, and E: third water-flooding).

permeability contrast of 1:3, the total EOR in the medium permeability ratio of 1:10 was 33.19% (Table 2). The comparison distinctly indicated that the delayed hydrogel technique conducted in the medium-permeability-ratio heterogeneous layer had evident superiority over the zones with a low-permeability-contrast, whereas polymer-flooding would improve recovery efficiency at the low permeability ratio heterogeneous zone.

**Permeability Contrast of 1:15.** Parallel cores with a large permeability ratio of 0.3:4.5  $\mu\text{m}^2$  were utilized to inspect the EOR efficiency of the delayed hydrogel treatment. Similar to those at the low and medium permeability ratio cores, the pressure in Figure 7a showed an apparent increase in both processes of gelant injection and the subsequent water-flooding. Clearly, 100% chase water entered into the high permeability core before hydrogel-treatment (Figure 7b) with no chase fluid sweeping the low permeability zone.  $R_w$  and  $R_{pw}$  in low permeability layers in Table 2 were both zero. Conventional polymer-flooding was capable of improving the sweeping area, but it did not function at all. Also, severe water circulation occurred, and the water cut even reached 99% (Figure 7c). Because of the hydrogel treatment, the fractional flow curve showed that over 90% chase water diverted to the low permeability core, where the previously unswept residual oil was displaced. Therefore,  $R_{Gw}$  in the low permeability core



**Figure 7.** (a) Pressure curve as the function of injection volume in the high-permeability-ratio double-core, (b) relationship between fractional flow and the injection volume, (c) water cutting and accumulative oil recovery versus the injection volume. (A: first water-flooding, B: polymer-injection, C: second water-flooding, D: gelant-injection and gelation, E: third water-flooding).

increased to 59.9% (Table 2) compared to 10.9% in the high permeability zone. Meanwhile, during the third water-flooding stage, the water cut significantly decreased from 80 to 0% (Figure 7c), illustrating that the enriched oil left in the low permeability zone was swept out. For the heterogeneous zone with a large permeability ratio of 1:15, the oil recovery was enhanced by 33.42% (Table 2) owing to the follow-up hydrogel treatment after polymer-flooding.

Further,  $R_{Gw}$  of the low permeability core with a ratio of 1:3 was much lower than that in both medium and high contrasts of 1:10 and 1:15, confirming the outstanding profile control and water shutoff of the delayed hydrogel in heterogeneous reservoirs having medium and high permeability ratios.

## CONCLUSIONS

In conclusion, the delayed cross-linked PAM hydrogel technique after polymer flooding displayed distinct advantages while applied in heterogeneous reservoirs with large permeability ratios for EOR. Based on the study, the major summaries can be drawn: (i) Cr(III) established coordination cross-linking with HPAM resulting in delayed gelation over 10 days, exhibiting excellent in-depth plugging to avoid the detouring of the follow-up chase water. Suitability tests and single sand-pack models proved the well-adaptation of the gelant to achieve efficient profile modification for differential

Table 3. Formula of Simulated Water

ions	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
content (mg/L)	1686.89	0.72	0.83	1214.37	96.79	2196.00	0.68

permeability layers. (ii) PAM-delayed hydrogels possessed high viscoelasticity and yield stress, being capable of sustaining shear and extrusion deformation during migration for sweeping. Exhibiting a dense structural framework, hydrogels provided a favorable elastic intensity for steady plugging large channels. (iii) Parallel-core displacing tests supported the fact that polymer-flooding functioned better as a profile modification and oil-displacing agent for heterogeneous layers having low permeability ratios, whereas for medium-permeability-contrast and large-permeability-contrast ( $\geq 10$ ) zones, delayed hydrogel treatment extracted far more residual oil. The displacement models provided favorable guidance for in situ industrial production in heterogeneous oilfields.

## EXPERIMENTAL SECTION

**Materials.** Partially hydrolyzed polyacrylamide (HPAM) AN905 with a molecular weight of  $8 \times 10^6$  to  $10^7$  and a hydrolysis degree of 5% was purchased from SNF flocculant (France), and chromium(III) acetate was purchased from Laize Chemicals (China). Thiourea was provided from Oriental Chemicals (China). Crude oil was obtained from Daqing Oilfield, China, with a viscosity of 9.8 mPa·s at 45 °C. The simulated aqueous solution with a salinity of 5196.28 mg/L for gelant preparation was supplied from Daqing Oilfield, and its general formula is given in Table 3.

**Preparation of Polymer Hydrogel.** PAM powder (0.5 g) was slowly dissolved in the simulated aqueous solution under stirring for 4 h to obtain a homogenous solution, and 0.5 mL of 10 wt % chromium(III) acetate cross-linker and 0.4 mL of 5 wt % thiourea were added dropwise into the previous suspension by stirring again for 30 min. The gelant was well-prepared and further placed under 45 °C for gelling. The polymer and cross-linker concentration was kept at 0.5 and 0.05 wt %, respectively.

**Rheological Measurements.** Rheological properties of the hydrogels were performed using a German HAAKE RS600 rheometer. Rheological behaviors of polymers and hydrogels were characterized using a Z41-Ti coaxial cylinder and PP20 plate-to-plate geometry sensors, respectively. The tests were first set in a stress oscillation scanning model with a stress range of 1–100 Pa and a shear rate of 1 Hz to obtain a linear viscoelastic region, in which a fixed stress of 4 Pa was ascertained. The subsequent viscoelasticity and yield tests were executed as a function of frequency ranging from 0.01 to 10 Hz. The tests were all carried out at 45 °C.

**Environmental Scanning Electron Microscopy.** Environmental scanning electron microscopy was performed using a quanta 200F microscope (American FEI) to observe morphologies of both HPAM and the hydrogel. An annular gaseous secondary electron detector was subjected to a vacuum degree of 267 Pa. Samples of 0.10 mL fluid or soybean-size hydrogels were initially placed into the three cylindrical grooves of a copper cylinder, which were further frozen to -60 °C using liquid nitrogen. The copper cylinder loading samples were put into the sample cell for vacuuming. Observations were performed along with the slow sublimation of the icy samples.

**Flow and Displacement Experiment. Single Sand-pack Plugging Tests.** The single sand-pack tests were conducted under a constant flow rate of 0.40 mL/min at 45 °C, while the water-flooding, polymer-flooding, and gelant injection were operated in turns. During the entire operation, water-flooding was initially completed to achieve a stable pressure, followed by the injections of 0.5 PV polymer, the second chase water, 0.7 PV gelant, and the third follow-up water. The final water injection was not performed until the gelant completely gelatinized.

**Double-Core Displacement Tests.** Figure 8 shows the schematic device of the parallel core flow tests as given in ref 9.

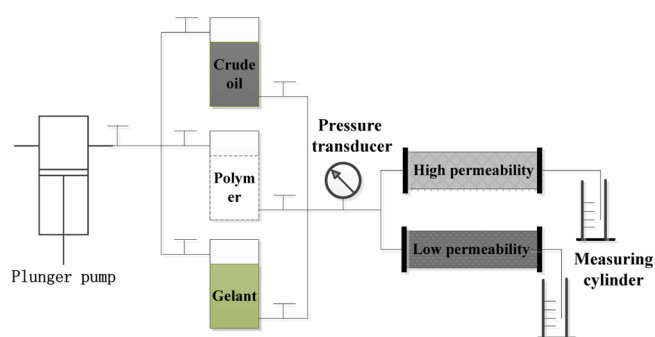


Figure 8. Schematic of parallel sand-pack tests.

The experiments were carried out at a constant flow rate of 0.40 mL/min under 45 °C. Water-flooding was performed to measure the permeability of the cores, and the cores were both saturated with crude oil, followed by polymer, second water-flooding, gelant injection, third water driven, and fourth water-flooding. The process of water driven was run to impel the gelant to the depth of the cores. The fourth water-flooding was conducted for oil recovery after hydrogel treatment.

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### Notes

The authors declare no competing financial interest.

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