

## A Study on Environment-Friendly Polymer Gel for Water Shut-Off Treatments in Low-Temperature Reservoirs

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**ABSTRACT:** In this study, the zirconium acetate crosslinked gel systems are studied owing to their environment-friendly and gelation performance in low-temperature reservoirs through rheological measurements, environmental scanning electron microscopy, and scanning electron microscopy. The effects of various parameters on the gelation properties, stability, and microstructure in bottle test and porous media were addressed. With the increase of concentrations and temperature, gelation time is reduced and gel strength is increased. In addition, the gel systems show salt tolerance and shearing resistance. The environment-friendly gel systems have a high stability in both injection water and formation water. A three-dimensional network structure was formed in the gel and confirmed by environmental scanning electron microscopy. The three-dimensional gel network was also formed in porous media, which bridges across the pore throats and reduced the water permeability in the formation. This study suggests that environment-friendly polymer gels can be used for water shut-off treatments in low-temperature reservoirs. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40154.

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### INTRODUCTION

Oil recovery occurs through three main processes: primary recovery, secondary recovery, and tertiary recovery. Primary recovery refers to the volume of oil produced by the natural energy available in the reservoirs. Once the natural reservoir energy has been depleted and the well oil production rates decline during primary recovery, it is necessary to provide additional energy to maintain the formation pressure. Generally, water is injected into oil reservoirs to complement or increase the original energy within the reservoir. This process is named secondary recovery or water flooding injection. However, long-term water flooding during the development of oilfield has resulted in aggravated heterogeneity of reservoirs, the injection water breakthroughs into producing wells along the high permeability channels or fractures which leads to water production from producing wells, then reduces oil production. To improve formation heterogeneity and minimize water production, the chemical methods, including injection gelling systems, particle systems, resin systems, foams, and so on, have been widely used for water shutoff treatments in worldwide field trials.<sup>1–3</sup> Among

them, the most commonly used chemical methods for controlling water production treatments are to inject gelling systems for the advantages of cost-effective, controllable gelation time, and adjustable strength.

The gelling systems used for water shut-off treatment are mainly composed of synthetic polymer or biopolymer and metallic or organic crosslinkers. Biopolymers such as guar, lignin, and cellulose have been used in oil industry for many years. But the field tests indicate that biopolymers are susceptible to free-radical attack, which leads to the degradation of macromolecules. As a result, the gel systems based on the biopolymers are instable which cannot meet the requirements for a long-term water shut-off treatment. In addition, the high price of biopolymers also limits their broad application in oilfield. Hence, the gel systems based on the synthetic polymers have been widely used to control excess water production for their long-term stability and low cost. Although polymer-based gels have enjoyed a very high success rate in worldwide field trials, few studies have been done on the gel systems for water shut-off treatments in low-temperature (<35°C) reservoir.<sup>4</sup> Generally, gel-based organical

**Table I.** Chemical Analysis of Injection Water and Formation Water

Ion composition (mg/L)	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	Salinity
Injection water	31.86	8.46	161.46	243.24	46.98	0.08	492.08
Formation water	65.18	16.77	5162.93	7465.29	6.78	1121.54	13,838.49

crosslinker, such as polyethylenimine, phenol–formaldehyde, and so on, are usually used for high-temperature (60–150°C) reservoirs.<sup>5</sup> In low-temperature reservoirs, the crosslinking reaction cannot proceed. Another concern with gel-based metallic crosslinkers such as chromium and inorganic zirconium is their short gelation time and gel strength at temperatures lower than 35°C. However, the chromium crosslinkers, especially those based on Cr<sup>6+</sup>, are toxic and cannot meet the current environmental regulations.<sup>6,7</sup> Moreover, the chromium-based gel systems can be crosslinked in several hours, which further reduces the propagation of chromium ions into the formation. The addition of retarding agents, such as glycolates, salicylates, and malonates, increases the gelation time of gel systems, which also results in the formation of weaker gels.<sup>8</sup>

Inorganic zirconium (ZrOCl<sub>2</sub>) crosslinked gels are known to have strong gel strength in low temperature. The crosslinking mechanism and effects of various parameters on the gel systems have been described previously by our group.<sup>9</sup> However, the crosslinking reaction can be completed within only a few dozen seconds, thereby bringing difficulties for in-depth placement into reservoir formation and restricting its application in low-temperature reservoirs. To overcome the issues of short gelation time and environmental pollution, an environment-friendly polymer gel based on zirconium acetate is proposed. The gelation process of crosslinking based on zirconium acetate under constant shearing rate was only studied.<sup>10</sup> However, no systematic study has been done for the gelation performance and microstructure of gel systems at low temperature. Hence in this study, we focused on the gels based on zirconium acetate. The objectives of this study include three points: (1) to determine the effects of polymer and crosslinker concentrations, salinity, temperature, and shearing on the gelation time and gel strength; (2) to study the stability of gels prepared in injection water and formation water, and (3) to investigate the microstructure of gels.

**Table II.** Gel Strength Code

Gel strength code	Gel description
A	No detectable gel formed
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	Highly deformable nonflowing gel
G	Moderately deformable nonflowing gel
H	Slightly deformable nonflowing gel
I	Rigid gel

## MATERIALS AND METHODS

### Materials

Hydrolyzed polyacrylamide (HPAM) with degree of hydrolysis of 20.1% and average molecular weight of 10,000,000 g/mol was provided by Yabang, China. Zirconium acetate was used as the crosslinking agent and purchased from Zibo, China, and the original concentration used in all experiments was 23%. Chemical analyses of the injection water and formation water from Xinjiang oilfield in China are summarized in Table I.

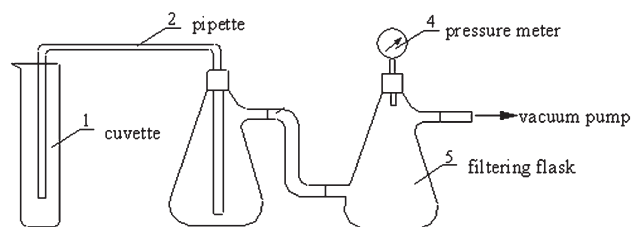
### Preparation of Gels

The polymer (1.0 g) was first added into injection water (200 g) and stirred to produce a polymer solution with concentration of 0.5% at room temperature. Then, polymer solution was diluted to the required concentration (0.2, 0.3, and 0.4%) using injection water. Sequentially, the zirconium acetate crosslinker was dropped slowly into the abovementioned polymer solution and stirred to produce a uniform gelling solution. Finally, the gelling solution (volume, 25 mL) was injected into an ampoule bottle through tygon tubing and the ampoule was sealed at neck. The crosslinking reaction is initiated by heating the gelling solution up to 28°C (reservoir temperature) in an oven.

### Measurement and Analysis

**Determination of Gelation Time.** To study the effect of various parameters on the gelation time of polymer gel, the bottle testing method as an experimental technique provides a semi-quantitative measurement of gelation rate and gel strength.<sup>11</sup> The gel strength during the gelation progress was expressed as an alphabetic code of A through I which is summarized in Table II. The bottle is inverted at frequent intervals to observe gel formation. Through this method, the gelation time was noted as the time at which the gels were highly deformable but not flowing (Code: F).

**Determination of Gel Strength.** The breakthrough vacuum method was carried out to determine the gel strength. The experimental flow chart is shown in Figure 1. The gel strength was determined as follows. The device was connected and the gel was placed into a cuvette. The vacuum pump was then opened and the pipette was placed downward until the end of determination. Finally, the maximum pressure (gel strength) during the process was recorded.

**Figure 1.** The experiment flow chart.

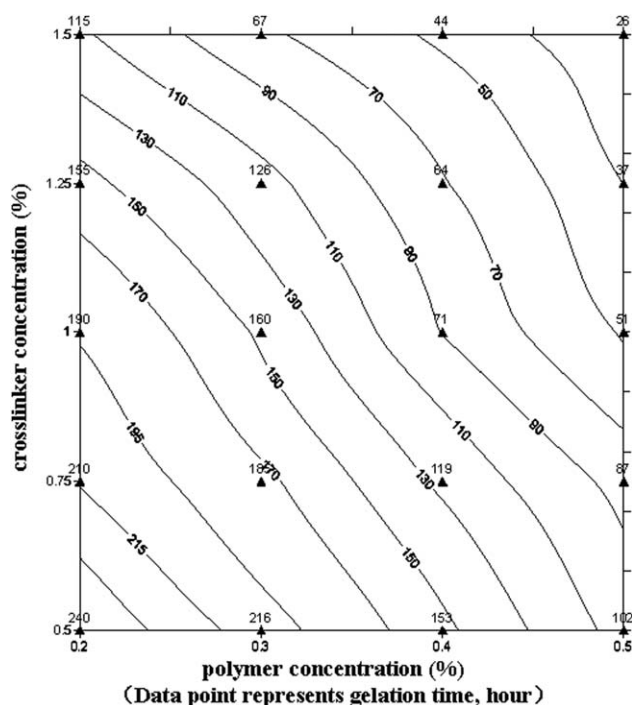


Figure 2. The contour map of gelation time of zirconium acetate gels.

**Rheological Measurements.** The stability of gel system was investigated using a Haake Rheostree RS75 rheometer with a concentric cylinder system at 28°C (reservoir temperature). The oscillatory shear frequency was varied from 0.01 to 10 Hz.

**Microstructure Characterization.** Environmental scanning electron microscopy (ESEM, Quanta 200 FEG, FEI, Hillsboro, OR) was employed to observe the gelation microstructure. During the experiment, a drop of gel was directly placed on a covered ESEM grid at 28°C. The pressure of the system initially ranged from 313 to 455 Pa and the temperature was set to 0°C. Determinations were conducted at a voltage of 15 kV and a working distance in the range of 5–10 mm.

To compare the performance of gels before and after injection into the core, scanning electronic microscope (SEM) was used to observe the microstructure of gel in the core. One pore volume of gelling solution (0.4% polymer + 1.0% zirconium acetate) was injected into a core ( $\varnothing$  25 mm  $\times$  80 mm). Then, the core was placed at 28°C for 2 days. Next, the core was quickly transferred to a vacuum cup of liquid nitrogen and frozen at  $-80^{\circ}\text{C}$  for 2 h. Subsequently, the core was put into lyophilizer for 24 h with a vacuum pressure ranging from 7 to 8 Pa. After freeze-drying, the core was crushed 30 mm to 40 away from the inlet, and then the gel was investigated using a SEM (Hitachi S-4800) with an accelerating voltage of 3.0 kV.

## RESULTS AND DISCUSSION

### Gelation Performance

**Effect of Polymer and Crosslinker Concentration.** The concentrations of polymer and crosslinker were critical for the structure and properties of gel systems. The concentration of polymer was varied from 0.2 to 0.5%, whereas the crosslinker

was varied from 0.5 to 1.5%. Figures 2 and 3 show the contour map of gelation time and gel strength.

As shown in Figures 2 and 3, the gelation time can be controlled within 26–240 h by varying the polymer or crosslinker concentration, whereas the gel strength can be adjusted in the range of 0.032–0.081 MPa. The gels with higher polymer or crosslinker concentrations can be formed more rapidly and become stronger. Higher crosslinking densities can result from higher number of crosslinking sites that in turn result from higher concentrations.<sup>12,13</sup> Thus, the gel formation rate increased, leading to a decrease in the gelation time and an increase in gel strength. The gelation time and gel strength can be adjusted by varying the polymer or crosslinker concentrations. As a result, an appropriate formula for oilfield applications based on the reservoir conditions can be selected from the contour maps as shown in Figures 2 and 3.

**Effect of Salinity.** The water's salinity on the gelation time and gel strength was significant. The effects of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> on the gelation performance (formula: 0.4% HPAM + 1.0% crosslinker) were examined at 28°C. Table III summarizes the effect of ionic concentration on the gelation time and gel strength. To these three different salts, all the gelation time and gel strength decreases when ions were added to the gelling solution. This behavior can be explained as follows: through adding inorganic salts, these inorganic salts compress the electric double layers of polymers, and thus decreasing repulsion forces between the charged groups and allowing the reactions to occur more easily.<sup>14</sup> However, monovalent cations and divalent cations have a slightly negative effect on gel strength. It seems that hydrophilic carboxylate groups from the polymer interact with divalent cations in high ionic concentration condition.<sup>15</sup> As a result, excessive crosslinking may occur and negative sites, which decrease the gel strength, may form in the gel systems.

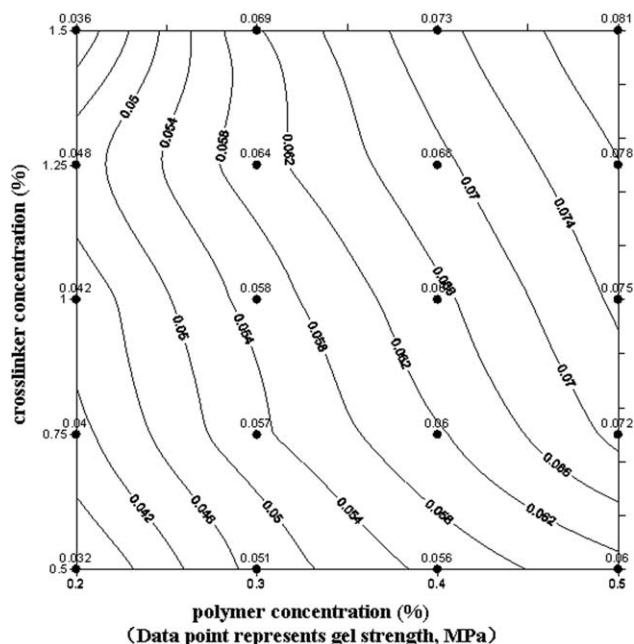


Figure 3. The contour map of gel strength of zirconium acetate gels.

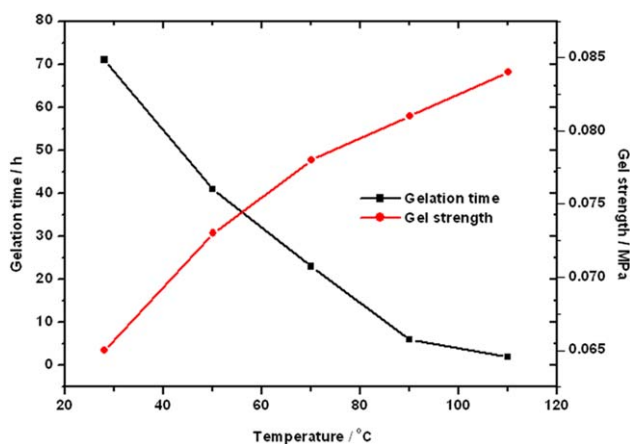
**Table III.** Effect of Salinity on Gelation Time and Gel Strength

Salt	Concentration (%)	Gelation time (h)	Gel strength (MPa)
NaCl	0.5	43	0.063
	1.0	32	0.062
	2.0	24	0.059
	3.0	10	0.058
CaCl <sub>2</sub>	0.1	65	0.065
	0.2	49	0.064
	0.3	37	0.062
MgCl <sub>2</sub>	0.1	61	0.064
	0.2	44	0.063
	0.3	33	0.062

**Effect of Temperature.** Temperature plays a key role in determining the performance of gel systems. The effect of temperature on the gel performance of a gelling solution containing 0.4% of HPAM and 1.0% of crosslinker prepared in injection water was determined.

Figure 4 shows the gelation time and gel strength of gel system at various temperatures (28–110°C). The gel strength increases with the temperature, whereas the gelation time decreases. At 28°C, the initial gelation time was 71 h and sharply decreased to 2 h at 110°C, indicating that the increase in temperature accelerated the gelation process and produced stronger gels over a shorter gelation time. This finding can be attributed to the thermal motion of molecules. The thermal motion of the molecules in the solution accelerates the intertwining reaction between polymer molecules and zirconium ions when increasing the temperature, and increases their opportunity to agglomerate.<sup>16</sup> As a consequence, the gelation process is accelerated and the gels become stronger at higher temperatures.

**Effect of Shearing.** Shearing degradation takes place when a gelling solution is transported through injection equipment or flows during formation. Thus, it is important to investigate the effect of shearing on the gelation time and strength of a gel sys-

**Figure 4.** Effect of temperature on gelation performance. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

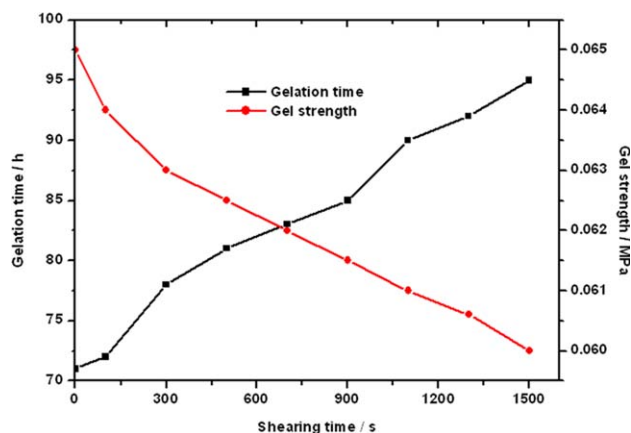
tem. To simulate shearing degradation under field conditions, waring agitator method was used at a shearing rate of 2000 rpm. Figure 5 shows the effect of shearing on the gel systems (formula: 0.4% HPAM + 1.0% crosslinker) at 28°C.

The results shown in Figure 5 indicate that an increase in shearing time increases the gelation time and decreases the gel strength. The effect of shearing degradation was evident during the gelation process but the gel strength retention rate remained above 90% after shearing for 1500 s. Based on these results, we conclude that shearing disrupts the molecular aggregates that give rise to reactions with the crosslinker, resulting in an increase in gelation time and a decrease in gel strength. However, the disrupted molecules reaggregate when shearing is ceased, and the molecules joined together yet again to form the gel. In addition, the introduction of acrylate groups to the polymer chain also provides significant chain rigidity to the gel, and thus allowing the polymer to exhibit better shearing stability.<sup>17,18</sup>

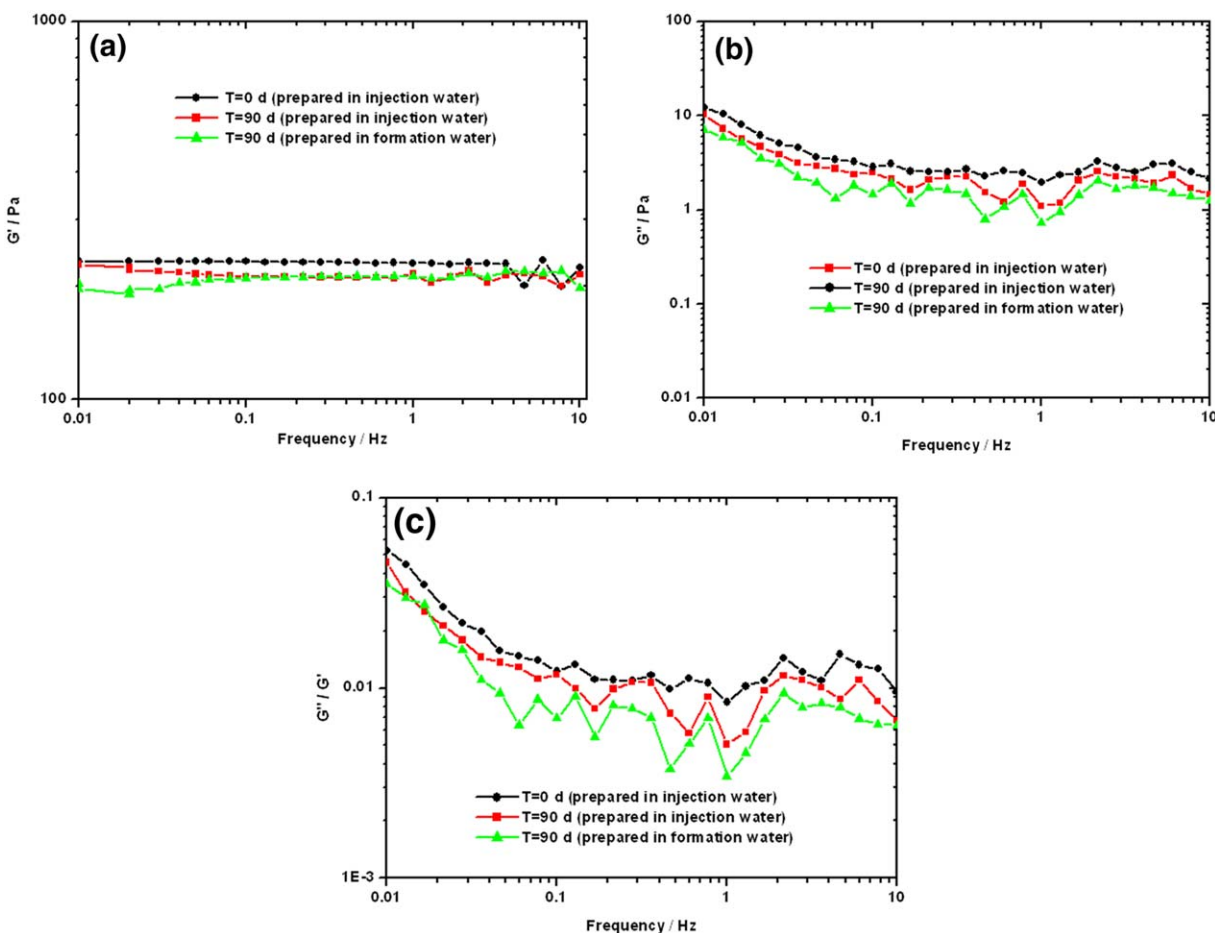
### Stability of Gel Systems

Gels can be prepared using either injection water or formation water. These water solutions contain various ions that can affect the gelation stability. Therefore, a study on the stability of gels prepared from either injection water or formation water is of great interest. Two gelling solutions were prepared, one using injection water and the other using formation water. Then, the gels were put into oven for 90 days at 28°C. Figure 6 shows the rheological properties of gels containing 0.4% HPAM + 1.0% crosslinker.

Figure 6 shows the rheological curves of gels under three different conditions. All of the storage moduli  $G'$  and loss moduli  $G''$  decreased with the frequency [Figure 6(a,b)]. Both  $G'$  and  $G''$  of the gel systems prepared in injection water and formation water have a just slight decrease when these gels aged for 90 days at 28°C, indicating that the gel systems remain strong even after 90 days. In addition, the loss factor ( $G''/G'$ ) is also a function of gel stability.<sup>19,20</sup> But it is not as well behaved as the storage modulus and loss modulus: as the frequency increases the loss factor decreases gradually [Figure 6(c)]. The loss factor of the gel prepared in injection water ( $T=0$  days) decreases from 0.0528 at 0.01 Hz to 0.0095 at 10 Hz. However, the loss factor

**Figure 5.** Effect of shearing on gelation performance. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





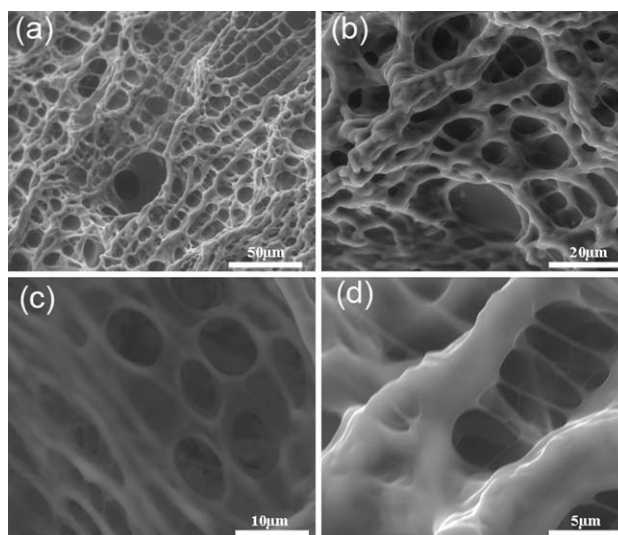
**Figure 6.** Rheological of the gel systems containing 0.4% HPAM + 1.0% crosslinker. (a) Storage moduli  $G'$  for gel systems under three different conditions; (b) loss moduli  $G''$  for gel systems under three different conditions; (c) loss factors ( $G''/G'$ ) versus frequency for gel systems under three different conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the gel prepared in injection water ( $T = 90$  days) and formation water ( $T = 90$  days) remained almost unchanged, which may be attributed to the stable structure of the gels. This finding demonstrates that the gel systems have a high stability.

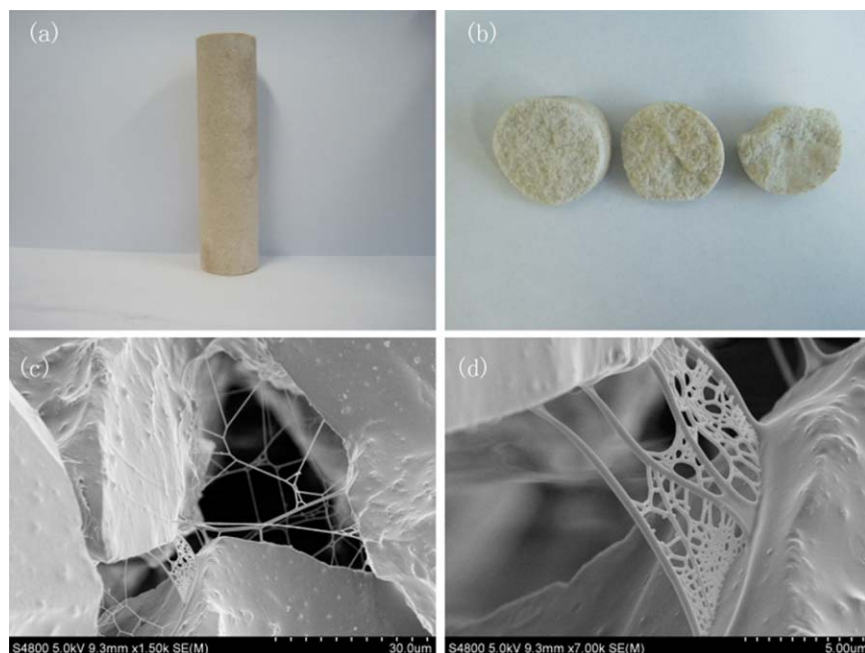
#### Microstructure of Gels

The structure of a gel is an important determinant of its rheological and functional properties, including water holding capacity, stability, and plugging capacity. The microstructures of the gels were studied in bottle test and porous media as follows.

**In Bottle Test.** To obtain a better understanding of zirconium gels, ESEM was used to investigate the microstructures of the gels subjected to bottle tests. Figure 7 shows the ESEM images of the gels in hydrated conditions. In this case, the gels are composed of a three-dimensional network structure [Figure 7(a,b)]. The gel systems retain their gelled state and mechanical consistency throughout the ESEM imaging procedure, revealing a uniformly porous mesh-like network structure. The pore sizes range from several micrometers up to about  $10\ \mu\text{m}$ . Surrounding the pores [Figure 7(c)], chain bunch structures appear as a



**Figure 7.** ESEM images of gels with 0.4% HPAM + 1.0% crosslinker in bottle test. (a)–(d) Microstructure of the bulk gel at magnifications of 1000, 2000, 4000, and 8000 $\times$ , respectively.



**Figure 8.** SEM images of gels with 0.4% HPAM + 1.0% crosslinker in porous media. (a) and (b) The core for the experiment; (c) and (d) SEM images of gels in porous media at magnifications of 1500 and 7000 $\times$ , respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

continuous network a few micrometers thick, together with node, composed of three-dimensional gel network structure. This structure with numerous small pores may result in lower syneresis and great water holding capacity, which can increase the stability of gels.<sup>21</sup> In the gel structure, carboxylate group ( $-\text{COO}^-$ ) of polymer is converted to Zr(IV) complexation through crosslinking reaction, incorporating hydrophilic groups into the chain bunch. It can be attributed to the clusters of water-filled mesh structures, which promotes the stability of gel systems during oil well treatment.

**In Porous Media.** Although the microstructure of gel in bottle test shows a three-dimensional network structure, the microstructure of gel in porous media, the interaction existed between gel and porous media remain unclear. Figure 8 shows SEM images of the microstructures of the gels in porous media. Figure 8 shows an obvious “skeleton structure” of gels in porous media. A three-dimensional network structure of gel was formed. In the small pore throats [Figure 8(d)], the skeleton structure is rather thick and solid, such that the branched chain can be tightly locked together to form a compact and continuous network. When the gels are formed in the formation, the three-dimensional gel network bridges across the pore throats and restricts the flow of water. When produced water is injected and contacted with the gel systems, the gel network inflates and increases water flow resistance, thus reducing the water permeability in the formation.<sup>22</sup> However, the gel skeleton was sparse and the branched chain showed fragmentary distribution in large pore throats [Figure 8(a–c)]. This is because the viscoelastic gels were previously stretched under elongational forces with increasing distance between pore throats. Although the network is not too compact and bridging became more difficult

in pore throats under this condition, it also increases water flow resistance and reduces permeability of reservoir cores.

## CONCLUSIONS

In this study, an environment-friendly polymer gel composed of polyacrylamides and zirconium acetate used for water shut-off treatments in low-temperature reservoirs was systematically analyzed. The following conclusions were obtained:

1. The gelation time of the gel systems can be controlled within the range of 26–240 h and the gel strength can be adjusted from 0.032 to 0.081 MPa at 28°C.
2. The environment-friendly gel systems have strong salt tolerance and shearing resistance. The gel strength retention rate remained above 90% after shearing for 1500 s at 2000 rpm.
3. The gel systems have high stability in both injection and formation water at 28°C, which means that they can be preferred in low-temperature reservoirs for water shut-off treatments.
4. In the bottle test, a three-dimensional network structure is formed in the gels and confirmed by ESEM, which promotes the stability of gel systems.
5. A three-dimensional gel network is also formed in porous media. This network bridges across the pore throats and reduces the water permeability in the formation.

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