

High-Temperature-Resistant, Low-Concentration Water-Controlling Composite Cross-Linked Polyacrylamide Weak Gel System Prepared from Oilfield Sewage

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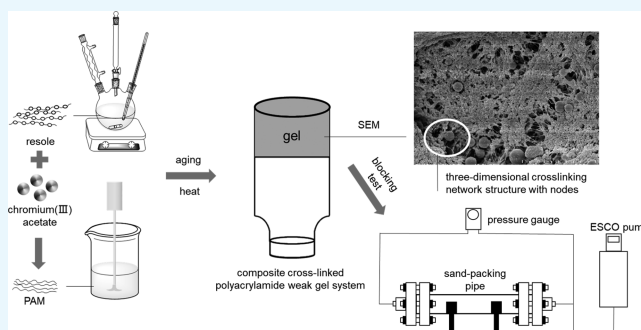
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ABSTRACT: The polyacrylamide weak gel is an effective system to block a high-permeability layer, realize water control, and enhance oil recovery. However, its application is limited by poor temperature resistance and high polymer dosage. In this paper, an inorganic–organic composite cross-linking agent was synthesized by using Cr(III) and phenolic resin. The composite cross-linking agent can cross-link low concentrations of polyacrylamide to obtain a high-temperature-resistant weak gel system in oilfield sewage. By adjusting the ratio of Cr(III), phenolic resin, and polyacrylamide, an optimum formula MF-7 can be obtained according to the gel strength. Results from evaluation experiments show that the strength of MF-7 can reach H grade even at polyacrylamide concentrations as low as 0.3%. The temperature resistance of the weak gel system is up to 100 °C, and no syneresis occurs after 330 h at 95 °C. Scanning electron microscopy (SEM) results show that MF-7 has a three-dimensional network structure with spherical nodes. The spherical node is composed of polyacrylamide, and its structure size is completely matched with the hydrodynamic radius of the used polyacrylamide. When combined with the network structure formed by Cr(III), the dense cross-linking network structure with nodes can greatly improve the strength and thermal stability of the gel system. The higher the molecular weight of the polyacrylamide used, the higher the strength of the gel obtained. Overall, the composite cross-linking agent can synergistically improve the mechanical properties of the gel, and this weak gel system formed by oilfield sewage is more economical and tolerant.



1. INTRODUCTION

After a long period of water injection in the oilfield, reservoirs generally face the problem of increased heterogeneity, which leads to the injected water preferentially advancing along the high-permeability channels or superior channels, resulting in ineffective water injection.^{1–3} Ineffective water injection not only reduces the recovery rate but also causes water wastage, pollutes the groundwater, and aggravates the aging of equipment.^{4–6} Therefore, it is necessary to achieve the water control by means of profile control. At present, it is widely recognized to form a gel system through cross-linking polymers such as polyacrylamide to isolate the hyperpermeable layer. The gel system will expand the swept area of the injected water, improve the mobility ratio, and thereby enhance oil recovery.^{7,8} Based on this, it is of great significance to carry out profile control operations economically and effectively, especially under the background of unstable international oil prices. Recycling the produced water is a good way to minimize costs and helps environmental protection.

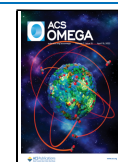
In the process of oil exploitation, the output of oilfield sewage is huge. The broad sense of oilfield sewage includes

oilfield produced water, sewage after washing crude oil, well washing sewage, and sewage produced by enhancing oil recovery. Meanwhile, the narrow sense of oilfield sewage mainly refers to oilfield produced water.⁹ Oilfield sewage usually has high salinity, high bacterial content, alkaline water quality, and some residual chemical agents. In the field applications, oilfield sewage can be used to prepare fracturing fluid, drilling fluid, oil-displacement agents, and so on. They are re-injected into the production well for recycling, realizing the effective utilization of the resources.^{10–12} However, polyacrylamide polymers usually have poor salt resistance. The use of high-salinity water to prepare polymer solutions, especially for medium and low molecular weight polymers, usually significantly reduces their performance. However, if

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organic cross-linking systems, such as phenolic resins, are used in an alkaline environment, it is also a challenge for cross-linking.^{13–15}

To maintain a certain gel strength of the polymer gel system, the polymer concentration in the polyacrylamide weak gel system is of great importance, generally between 0.1 and 3.0 wt %. At these concentrations, the gels can not only play a plugging effect but also exhibit good flowability to enter a deeper formation.^{16–18} To reduce polymer concentrations, such as less than 0.5 wt %, some nanoparticles must be added to enhance the gel strength. Liu et al. added 2–5 wt % silicate to the phenolic resin cross-linking polyacrylamide to increase the cross-linking density and heat resistance.^{19,20} The system formed abundant silicon–oxygen bonds, thereby reducing the polymer concentration to an economical amount of 0.1–0.3 wt %.²¹ Developing new types of cross-linking agents or selecting multiple cross-linking agents is another way to reduce the amount of the polymer. Jin et al. proved the feasibility of a composite cross-linked gel system, but the temperature resistance strength usually did not exceed 90 °C.²² Zhang et al. used a mixed cross-linking system of Cr(III) and phenolic resin. The interaction of covalent bonds and coordination bonds can increase the cross-linking strength of the gel system. The temperature resistance of the gel was up to 140 °C and much higher than the gel by a single cross-linking agent.²³

In summary, the conventional systems have limited temperature resistance and usually use a relatively high concentration of polymers. Moreover, the use of nanoparticles leads to higher costs and more complex formulations. Nanoparticles are also easy to agglomerate and damage the reservoir. The objective of this study is to prepare a low-concentration polyacrylamide weak gel system using oilfield wastewater for water control in high-temperature reservoirs. An organic–inorganic composite cross-linking agent was synthesized, and the relationship between molecular weight and gel strength was studied. Then, a set of gel systems with high strength and good thermal stability was obtained. Rheological tests, differential scanning calorimetry, and thermogravimetric analysis (TG-DSC) were further used for characterizing the strength and thermal stability of the gels. SEM was used to observe the gel microstructure and analyze its high temperature resistance mechanism. Finally, the water plugging ability of the gel system was tested.

2. EXPERIMENTAL SECTION

2.1. Experimental Materials and Equipment. Water-soluble polyacrylamides of different molecular weights (average molecular weights 2.5×10^7 g/mol, 2.2×10^7 g/mol, 2.0×10^7 g/mol, 1.8×10^7 g/mol, 1.5×10^7 g/mol, and 1.2×10^7 g/mol; the degree of hydrolysis is between 30 and 40%), were purchased from Aisen (China) Flocculant Co., Ltd. Chromium acetate (analytical grade), formaldehyde solution (36%), potassium bichromate (analysis of standard solution), phenol (analytical grade), and thiourea (analytical grade) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. NaOH (purity $\geq 96\%$) was purchased from Xilong Science Co., Ltd. The phenolic resin was self-made in the lab. The oilfield sewage was taken from Jidong Oil Field, China. The relevant experimental equipments are shown in Table 1.

2.2. Water Analysis of Oilfield Sewage. The densimeter method, dichromate method, 1,10-phenanthroline spectrophotometry, pH indicator titration, gravimetry, silver nitrate titration, and atomic absorption spectrometry were used to

Table 1. Experimental Equipment

instrument name	instrument manufacturer/model
rheometer	HAAKE RS600
constant temperature heating stirrer	HJ Type
cold field emission scanning electron microscope	Carl Zeiss Gemini SEM 300
temperature control magnetic stirrer	IKA SZCL-2
circulating water multipurpose vacuum pump	SHB-III
thermal analyzer	METTLER TOLEDO TGA/DSC 1
sand-packing pipe displacement device	Self-made
freeze dryer	Kawaichi FD-1-50
digital acidity meter	Shanghai Dapu Instrument PHS-25

measure the concentration of relevant ions (Fe^{3+} , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^-), which may affect the preparation of gel solution and the final strength, chemical oxygen demand (COD), and suspended solids in oilfield sewage.²⁴ All the tests were carried out at 20 °C, and the final result was the average of the two measurements.

2.3. Synthesis of Phenolic Resin and Gel Preparation.

Water-soluble phenolic resin is the first-stage product of thermosetting phenolic resin or resole. Resole, with a large number of highly active hydroxymethyl groups, is suitable to be a cross-linking agent of polyacrylamide. The synthetic process is as follows: a 250 mL three-neck flask equipped with a thermometer, agitator, and reflux condenser was fixed on a constant temperature stirrer through an iron stand. The designed amount of phenol was added into the flask and melted into liquid by heating it to 50 °C. The designed amounts of NaOH solid particles and water were added, stirred, and reacted at a set temperature for 20 min. Formaldehyde solution (36 wt %) was weighed according to the molar ratio of phenol to formaldehyde at 1:3. Formaldehyde solution (80%) was added into the flask and then heated up to 60 °C. The reaction was carried out at constant temperature for 50 min. After adding the designed amount of NaOH, the temperature was increased to 70 °C. The reaction was kept at the set temperature for 20 min. Then, the remaining 20% formaldehyde solution was added and heated up to 90 °C. The reaction was carried out at constant temperature for 30 min. After cooling to room temperature, a brown-red water-soluble phenolic resin was obtained.

The formulations of the gel solution were as follows: 0.3 wt % polyacrylamide solution, 0.1 wt % thiourea (as an antioxidant), and different concentrations of cross-linking agents chromium acetate and phenolic resin. The typical preparation process is as follows (unless otherwise specified, all operations shall be carried out at room temperature):

- (1) Polyacrylamide (1.98 g) was dissolved in 660 mL of oilfield sewage and stirred. The sample was allowed to sit for 24 h without light.
- (2) The solution (60 mL) was added into a 100 mL sample bottle. Also, 0.1 wt % thiourea and different concentrations of cross-linking agent were added and stirred for 25 min to obtain a homogeneous gel solution.
- (3) The gel solution was kept standing for 30 min to remove air bubbles. Then, the sample bottle was put into a 95 °C oven to initiate a cross-linking reaction. The reaction time was 24 to 72 h.

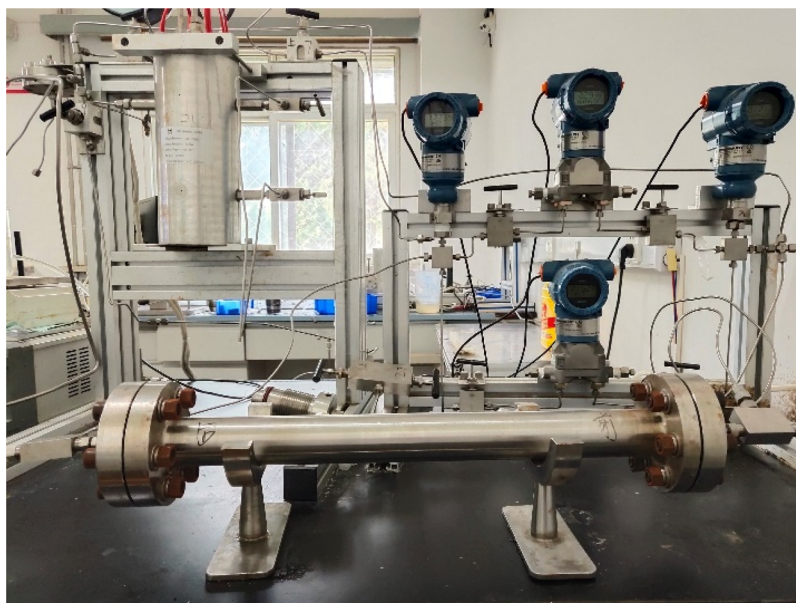


Figure 1. Sand-packing pipe water flooding device.

2.4. Gel Performance Measurement and Formulation Screening. In order to study the strength and stability of the gel with different concentrations of cross-linking agent, the gel strength was tested at different times. The test interval was 30 min, and the time for the gel formation was recorded. Through the inverted bottle experiments, a gel system with good stability and high strength can be screened out.

After placing the optimized system in an oven at 95 °C for 72 h, a HAAKE RS600 rheometer was used to measure the elastic modulus and viscous modulus of the sample.²⁵ A coaxial cylinder Z41Ti system was chosen, and the test temperature was 90 °C. In order to reduce the experimental error, each experiment was repeated 2 times, and their average values were taken as the experimental results. The error of each result must be less than 10%, otherwise it needs to be re-measured. The same approach can be used to prepare gel base fluids of different molecular weights, and the qualities of gels of different molecular weights were evaluated.

2.5. Microstructure Observation. A cold-field scanning electron microscope (SEM) was used to observe the microstructure of the gel. A small amount of gel sample was frozen (−18 °C) to solid for sample shaping. The sample was freeze-dried with liquid nitrogen in a vacuum state, and then the anhydrous sample was placed in a copper plate for sputtering gold treatment to enhance the conductivity of the sample.^{26,27} Among them, the SEM was set to observe at a voltage of 10 kV.

2.6. Thermogravimetric-Differential Scanning Calorimetry Analysis (TG-DSC). A thermal analyzer (TGA/DSC 1) was used to conduct TG-DSC measurement on the gel system. In this experiment, 5–8 mg of sample was heated from 40 to 300 °C in the air atmosphere, and the scanning frequency was 5 °C/min. The relationship between the heat difference and temperature input to the sample and the reference was measured, while the heating environment was detected at the same time. The quality of the test sample changed with temperature or time in order to determine the temperature resistance of the gel system.^{28–30}

2.7. Water Shut-off Test. The water shut-off effect of the gel system was tested by the blocking experiment with a sand-packing tube. Quartz sands (40–50 mesh and 100–120 mesh) were filled into the sand-filling pipe (diameter $d = 25$ mm, effective length $L = 50$ mm), and their volume ratio was set to 1:4 to simulate the permeability of the target block at 350–500 mD. The water flooding device was connected, as shown in Figure 1. First, clean water was injected at a certain flow rate, and permeability k_1 was recorded when the inlet and outlet pressure was stable. Subsequently, the gel solution was pumped until a stable gel solution flows out at the outlet. Then, the sand-filled tube was put in an oven (95 °C) to form a gel, and clean water was continuously injected. After the pressure was stable again, the permeability k_2 was recorded. By comparing and calculating the permeability change of the sand-packed pipe before and after gel injection, the water shut-off effect of the gel system can be obtained.

3. RESULTS AND ANALYSIS

3.1. Oilfield Sewage Water Analysis Results. The oilfield sewage used in the gel is shown in Figure 2, and the water analysis results are shown in Table 2. It can be concluded that the water sample is nearly neutral. The main cations are Na^+ and Ca^{2+} , the anions are HCO_3^- and SO_4^{2-} , and the total salinity is 2152 mg/L. According to the Surin classification method, the water sample is a sodium sulfate type. According to the analysis of the literature and field data, Na^+ will basically not affect the composition of the system at weakly alkaline conditions. However, the Ca^{2+} ions will aggravate the hydrolysis of the system, and the amide group in the polyacrylamide is slowly hydrolyzed to a carboxyl group. Excessive hydrolysis will reduce the stability of the gel at high temperatures.³¹ The chemical oxygen demand (COD) results show that the reducing substance in the sample water is 70 mg/L, and its main components are organic compounds such as crude oil and a small amount of BTEX, PAH, and other substances.³²

3.2. Gel Performance Analysis. By changing the ratio of the two cross-linking agents, the gel strength and stabilization

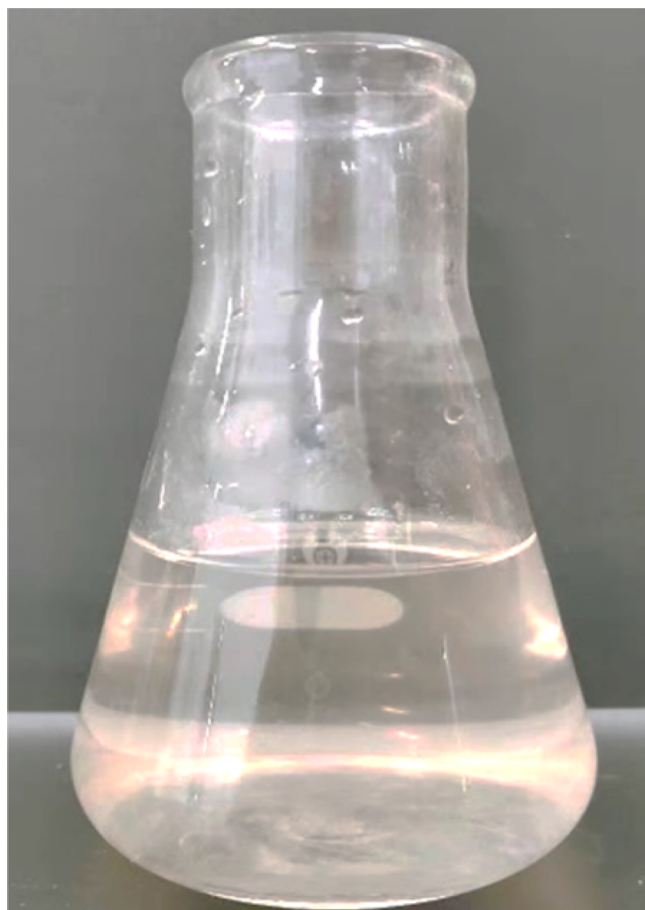


Figure 2. Oilfield sewage for gel preparation.

Table 2. Water Analysis Results

no.	item	unit	value
1	COD	mg/L	70
2	Ph		7.6
3	density	g/cm ³	1.1
4	Fe ³⁺	mg/L	1.14
5	K ⁺	mg/L	3.6
6	Na ⁺	mg/L	810.0
7	Ca ²⁺	mg/L	52.2
8	Mg ²⁺	mg/L	4.9
9	Cl ⁻	mg/L	38.1
10	SO ₄ ²⁻	mg/L	127
11	HCO ₃ ⁻	mg/L	1.07 × 10 ³
12	salinity	mg/L	2152

time at different polyacrylamide concentrations can be obtained. Higher strength grades and longer stabilization times mean that the cross-link of polyacrylamide is better. Also, the corresponding formula has better water control, temperature resistance, and delayed cross-linking properties. As for the standard of gel strength judgment, the internationally accepted gel coding method (GSC classification method) is adopted, in which strength is divided into A–J grades.³³ The specific strength is presented in Table 3 below.

In order to explore the gel-forming properties of polyacrylamide at low concentrations, a series of evaluation experiments were carried out with a fixed polymer concentration of 0.3 wt % and a reducing agent (thiourea)

concentration of 0.1 wt %. The composition and performance of each formula of the gel systems are shown in Table 4. When the concentration of the phenolic resin is less than 0.45 wt % (entries #1–#3), these gels can be stable within 24 h. However, all have been dehydrated after 3 days, and the strengths are lower than grade E. Similarly, when the phenolic resin concentration is higher than 0.45 wt %, the gelling solution is still prone to dehydration, and the strength is substandard. This is because a lower resin concentration means fewer cross-linking sites and smaller cross-linking density, and it is difficult for the gelling solution to achieve strength requirements. In addition, when the resin concentration is too high, the speed of cross-linking reaction is too fast, and a uniform and stable gel structure cannot be formed, which will also cause the thermal stability of the gel to deteriorate.³⁴ As for the chromium acetate, when its concentration is 0.03 wt %, the highest strength of gel is the grade D, which cannot meet the strength requirements as well. Furthermore, when the concentration of chromium acetate is 0.06 wt %, the gel exhibits a high degree of syneresis and even fails to form a gel.³⁵ Therefore, only a gel system with an appropriate concentration and ratio of cross-linking agent can achieve both a higher gel strength and good thermal stability for water lock. Specifically, the optimum concentrations of phenolic resin and chromium acetate are 0.45 and 0.045 wt %, respectively, and the final strength grade is H grade. This optimal formula is sample #5, which is named as MF-7, and further testing and analysis will be carried out.

First, extended time was used to verify the ultimate stability of MF-7, and its appearance after 330 h was observed and recorded at 95 °C. The results showed that there was no significant dehydration in MF-7, and the strength level slightly decreased to G. Then, two control samples were formulated according to the MF-7 ratio, and the effect of a single cross-linking agent on the gel performance was explored. The test results are shown in Table 5. Samples #10 and #11 used phenolic resin and chromium acetate, respectively, and their gel strengths are D and B, respectively. They also have defects such as short stability and easy dehydration (Figure 3).

3.3. Analysis of Rheological Results. The strength and toughness of the gel can be evaluated by its viscoelastic properties, and the measurement accuracy can be determined by the relative standard deviation (RSD).³⁶ The dynamic modulus that characterizes the viscoelasticity of the gel has two types, namely, the elastic modulus (G') and the viscous modulus (G''). The elastic modulus (G') represents the energy stored in the gel during deformation. Viscous modulus (G'') represents the viscosity of the gel. The larger the value of the two is, the greater the strength of the gel is, which is conducive to water control operations.³⁷ There is a criterion for a good gel, in which G' is greater than 4 Pa and G'' is greater than 1 Pa at a frequency of 0.1 Hz.²⁷ For samples MF-7, #10, and #11, G' , G'' , and the inverted picture of gels are shown in Figures 4–6. It can be seen from the above figure that the elastic modulus of MF-7 reaches 21.92 Pa, whose RSD is 5.3%, and the viscous modulus reaches 4.72 Pa at 0.1 Hz, whose RSD is 4.9%. The gel strength of MF-7 is far better than the criterion. The elastic modulus and viscous modulus of sample #10 are only 0.118 Pa and 0.166 Pa at 0.1 Hz, which is far from the criterion. Similarly, the sample #11 has an elastic modulus of 0.511 Pa and a viscous modulus of 0.537 Pa at 0.1 Hz, which also cannot meet the criterion. Therefore, according to the

Table 3. GSC Classification

strength code	gel name	corresponding intensity description
A	nondetecting gel	The viscosity of the system is equivalent to the viscosity of the polymer, and the formation of gel cannot be observed with the naked eye.
B	high flow gel	The viscosity of the gel system is slightly higher than the viscosity of the polymer.
C	flowable gel	The viscosity of the gel system is slightly higher than the viscosity of the polymer.
D	medium flow gel	When the glass bottle is turned over, a small amount of gel (mass fraction < 15%) cannot flow to the other end, often in the shape of a tongue.
E	hardly flowing gel	When the glass bottle is turned over, a few gels can slowly flow to the other end, and most of them (mass fraction > 15%) are not fluid.
F	high deformation nonflowing gel	The gel cannot flow to the mouth of the bottle when the glass bottle is turned over.
G	medium deformation nonflowing gel	When turned over, it can only flow to the middle of the glass bottle.
H	slightly deformed nonflowing gel	When flipped, only the surface of the gel is deformed.
I	rigid gel	When turned over, the surface of the gel does not deform.
J	ringing gel	When shaking the glass bottle, you can feel the mechanical vibration like a tuning fork.

Table 4. Concentration Optimization of Various Additives in the Composite Gel System

entry	polyacrylamide concentration (wt %)	chromium acetate concentration (wt %)	phenolic resin concentration (wt %)	thiourea concentration (wt %)	performance and stability of the gel		
					gel grade (72 h)	stabilization time (h)	syneresis (72 h)
#1	0.3	0.03	0.3	0.1	C	24	yes
#2			0.45		D	24	yes
#3			0.6		B	<24	yes
#4		0.045	0.3		E	24	yes
#5			0.45		H	96	no
#6			0.6		D	<24	yes
#7		0.06	0.3		not glued		yes
#8			0.45		not glued		yes
#9			0.6		not glued		yes

Table 5. Performance Test Results of the Two Gel Systems with a Single Cross-Linked Agent

entry	polyacrylamide concentration (wt %)	chromium acetate concentration (wt %)	phenolic resin concentration (wt %)	thiourea concentration (wt %)	performance and stability of the gel		
					gel grade (72 h)	stabilization time (h)	dehydrated or not (72 h)
#10	0.3		0.45	0.1	D	24	yes
#11		0.045			B	24	yes

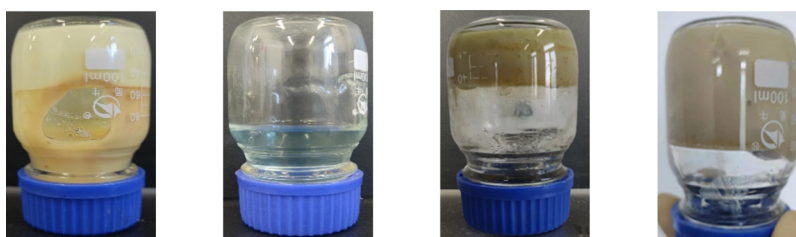


Figure 3. Inverted bottle pictures of selected gel samples after heating (from left to right, they are #10, #11, MF-7 (72 h), and MF-7 (330 h)).

rheological data, the strength of MF-7 with composite cross-linking agents will be significantly improved.

Furthermore, the relationship between molecular weight and gel strength was studied. According to Figures 7 and 8, when the molecular weight of polyacrylamide increases, the G' and G'' of the resulting gel also increase. At the same concentration of polymer and cross-linking agent, the higher the polymer molecular weight is, the better the strength of the gel system is. Meanwhile, the dehydrated phenomenon of the gel is minimized as the molecular weight increases. It could be

analyzed that the larger molecular weight means the larger molecular chain length, which enhances the intermolecular entanglement and forms intensive intramolecular cage space. Thus, the viscosity and elasticity of the polymer solution increase. After cross-linking, large molecular sizes tend to form a denser network structure. As a result, the strength of the gel system is enhanced. The macroscopic viscosity index (MVI) and elasticity index (EI) of the polymer increase, which is consistent with a larger G' and G'' .³⁸

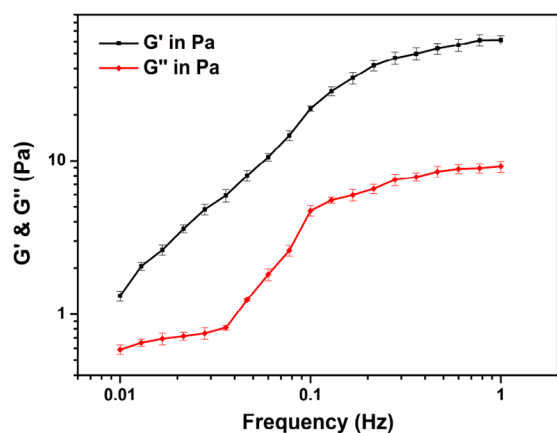


Figure 4. Viscous modulus and elastic modulus of the MF-7 sample at different frequencies.

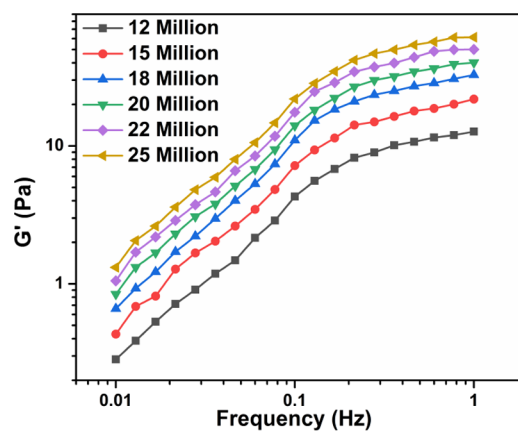


Figure 7. Elastic modulus of the gel samples with different molecular weights at different frequencies.

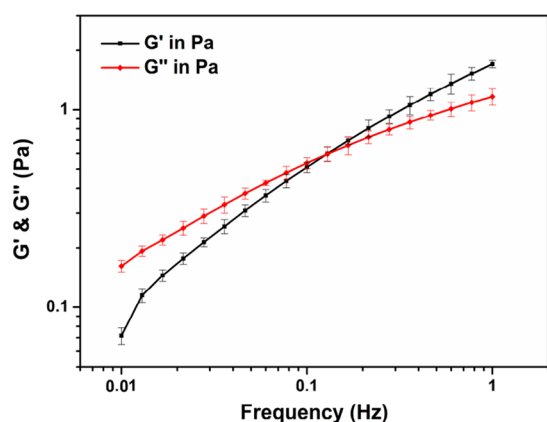


Figure 5. Viscous modulus and elastic modulus of #10 at different frequencies.

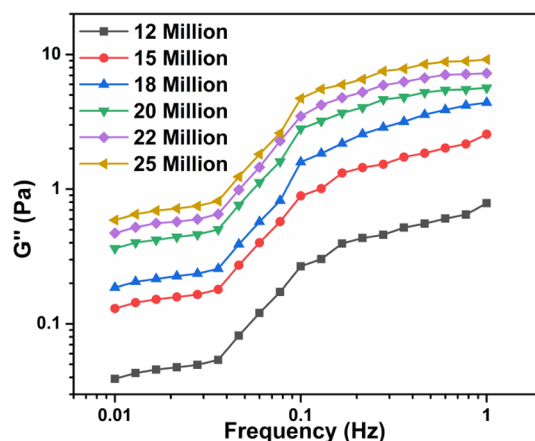


Figure 8. Viscous modulus of the gel samples with different molecular weights at different frequencies.

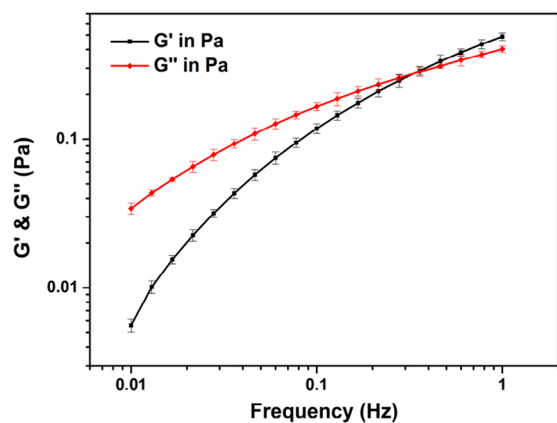


Figure 6. Viscous modulus and elastic modulus of #11 at different frequencies.

3.4. Gel Thermal Stability. TG-DSC measurement can determine a variety of thermodynamic or kinetic parameters and analyze the enthalpy change of the sample through the peak shape of the thermal effect curve so that the thermal stability of the composite gel system can be analyzed.³⁹ The DSC test results of MF-7 are shown in Figure 9. From the TG curve in the figure, it can be seen that it first drops rapidly (35–155 °C) and then tends to be flat (155–300 °C). For the rapid decline of the curve, the reason is presumed to the

evaporation of bound water, and similar results were observed by Zhang et al.²³ After complete dehydration, the mass loss decreases slowly with the increase in temperature. In the DCS curve, an obvious exothermic peak appears at 115 °C, and its peak point is 155.7 °C. Combining with the TG curve, the exothermic peak in the DSC can be regarded as the rupture of the chemical bond. During this transfer, the structure of the gel system is gradually destroyed. That is to say, this temperature is the temperature resistance limit of sample MF-7.⁴⁰ Therefore, the maximum withstand temperature of the gel system is presumed as 155.7 °C. In order to ensure the integrity of the gel structure, its operating temperature should not exceed 115 °C.⁴¹

3.5. Gel Microstructure. The strength and water-locking properties of the gel system are inseparable from the microstructure of the gel. Therefore, in order to study the effect of different cross-linking agents on the microstructure of the gel system, samples MF-7, #10, and #11 were selected for SEM scanning tests. The scanning results are shown in Figure 10.

Sample #10 only uses phenolic resin as the cross-linking agent, and its concentration is consistent with the amount of phenolic resin in MF-7. Figure 10a shows that a large number of spherical structures were formed. This is the cross-linking of covalent bonds formed by dehydration condensation of the amide group in polyacrylamide and the hydroxyl group in the

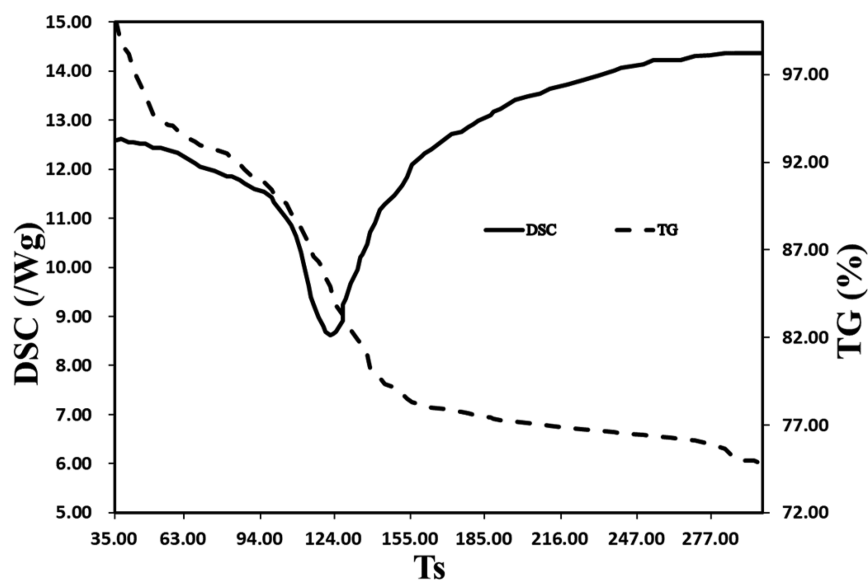


Figure 9. TG-DSC curve of the sample MF-7.

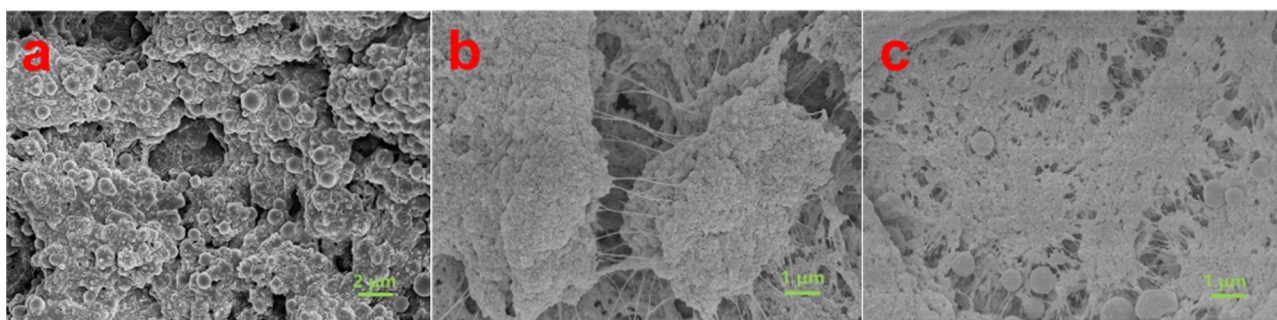


Figure 10. SEM images of the gel system: (a) #10 cross-linking by 0.45 wt % phenolic resin, (b) #11 cross-linking by 0.045 wt % chromium acetate, and (c) MF-7 cross-linking by 0.45 wt % phenolic resin and 0.045 wt % chromium acetate.

phenolic resin. Therefore, the gel system has good thermal stability and strength, which is more suitable for deep well operations.⁶ At the same time, sample #11 uses the same concentration of chromium acetate cross-linker as in the MF-7 sample, while Cr(III) and polyacrylamide are connected through coordination bonds. It can be seen from Figure 10b that the filamentous structure is formed between the polyacrylamide after the coordination. Also, water molecules enter the network through the pores, thereby achieving water lock and water control.³⁴ However, the filament structure is prone to shrinkage and deformation after the temperature increases. It can cause serious dehydration, destroy its microstructure, and thus reduce its strength.⁴² The microstructure of MF-7 cross-linked with phenolic resin and chromium acetate is shown in Figure 10c. It is obvious that there is a three-dimensional network structure with spherical nodes, which is like a dendritic structure, and the mechanical stability will have a positive effect on its elastic modulus.⁴³ The composite cross-linking effect is similar to combining the cross-linking structure of a single cross-linking agent and makes the pore structure even denser. The spherical nodes can greatly enhance the strength and toughness of the network structure, while the existence of the network structure can improve the water lock of the spherical nodes. The effect helps to empower the overall strength and thermal stability of the gel system.

As we know, with the increase in the molecular weight of polyacrylamide, its hydrodynamic radius gradually increases at the same concentration. The hydrodynamic radius of polyacrylamide with a molecular weight of 25 million is mainly in the range of 500–1200 nm, and the distribution is relatively uniform.^{44,45} For the spherical structure of the phenolic resin cross-linked in Figure 10a, 40 sample points are selected for particle size statistics. The statistical results are shown in Figure 11, and the radius is distributed in the range of 500–1300 nm. It is highly coincident with the hydro-

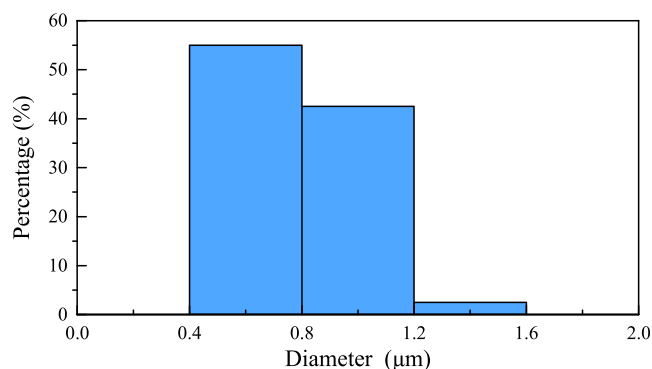


Figure 11. #10 phenolic resin spherical particle size and its distribution statistics from Figure 10a.

dynamic radius of 25 million molecular weight polyacrylamide. It indicated that there was a large amount of intramolecular cross-linking in the phenolic resin cross-linked gel. A stable spherical structure helps the polymer to lock water and improve the affinity between water and the polymer. By comparison, the composite cross-linking system MF-7 can have the structural characteristics of organic/inorganic cross-linking agents and form a dense network structure with nodes. As before, the particle size of the spherical structure of the gel has a high matching of the hydrodynamic radius of the polyacrylamide. Combining the rheological results in Section 3.3, it can be inferred that intramolecular organic cross-linking facilitates water lock, and intermolecular inorganic cross-linking is beneficial to structural stability. Thereby, a composite cross-linking gel can improve the strength of the system at high temperatures.

3.6. Evaluation of Water Shut-off Effect. As is known to us, due to the heterogeneity of the sand-packed pipe after flooding, it is inevitable that there will be dominant channels.⁴⁶ Water automatically chose some preferred channels to flow in the sand-packed pipe, which can represent the water flooding patterns in reservoirs. In the water shut-off experiment, the permeability of the sand-packed pipe can be calculated by Darcy's formula. The calculation is based on the pressure difference between the inlet and outlet, and the formula is

$$k = \frac{Q\mu L}{A\Delta P} \quad (1)$$

Among them, Q is the flow rate of the injected liquid, mL·s⁻¹; μ is the viscosity of the liquid, MPa·s; L is the length of the sand-filled pipe, cm; A is the cross-sectional area of the sand-filled pipe, cm²; and ΔP is the injection pressure difference before and after water flooding, 0.1 MPa.

The calculation formula of the blocking rate is

$$\eta = \frac{k_1 - k_2}{k_1} \times 100\% \quad (2)$$

Among them, η is the blocking rate, %, and k_1 and k_2 are the permeability before and after gel injection, mD, respectively.

The water shut-off effect of sample MF-7 was evaluated with two indicators, namely, the blocking rate and breakthrough pressure.⁴⁷ The results are shown in Table 6. The blocking rate

Table 6. MF-7 Sample Plugging Rate and Breakthrough Pressure Results

sample number	permeability before gel injection (mD)	permeability after gel injection (mD)	breakthrough pressure (MPa)	blocking rate (%)
MF-7	421	42	5.6	90.02

of MF-7 is 90.02%. After the sand-packed pipe being flooded with excessive water, a high-permeability channel appears in the pipe. It can be speculated that the gel system forms a network structure in the high-permeability channel to cut off the water and block the large channels.

4. CONCLUSIONS

1. Through the composite cross-linking system, it is feasible to use oilfield sewage to prepare a high-temperature-resistant, low-concentration weak gel system without adding expensive nanoadditives, which can

greatly reduce the cost of water shut-off operations in high-temperature reservoirs.

2. The optimal formula of the composite cross-linked gel system is MF-7: 0.3 wt % polyacrylamide + 0.045 wt % chromium acetate + 0.45% phenolic resin + 0.1 wt % thiourea. The system can be stable at 95 °C for 330 h without dehydration. The gel strength reaches the H level for the first 96 h.
3. Performance evaluation in TG-DSC tests shows that the maximum temperature tolerance of the composite gel is 155.7 °C. In a water shut-off test of a sand-filled pipe, the MF-7 composite cross-linked gel system can achieve a blocking rate of 90.02%.
4. SEM results show that the gel easily forms a spherical structure after phenolic resin cross-linking. The size of the small balls is distributed in 500–1200 nm, which highly matches with the hydrodynamic radius of the used polyacrylamide. When combined with the network structure formed by Cr(III), the three-dimensional network structure with nodes can greatly improve the strength and thermal stability of the gel system. It also explains the phenomenon that the higher the molecular weight of the polyacrylamide used, the higher the strength of the gel obtained.

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Notes

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