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Full Length Article

Comprehensive evaluation of a novel re-crosslinkable preformed particle gel for the water management of reservoir with concentrated divalent ions

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ABSTRACT

As one of the most widely used technology to ameliorate the reservoir's heterogeneity, polymer gels have been applied for more than 60 years. However, how to plug fractured reservoirs with significant abnormal features, high temperature and high salinity, especially the divalent cations, is still a challenging target. This work systematically evaluated a novel salt-resistant re-crosslinkable preformed particle gel (SR-RPPG) designed for fractured reservoirs with excellent salt resistance (up to 5 % CaCl₂). We evaluated the swelling kinetics, thermal stability and plugging efficiency of this SR-RPPG. We assessed the swelling kinetic and re-crosslinking behavior of the SR-RPPG through the bottle test method. High temperature-resistant glass tubes with thermally stable O-rings were employed to evaluate the long-term thermal stability of the SR-RPPG product, and the testing lasted for over 200 days. A fractured model was used to assess the plugging efficiency of the SR-RPPG product. Results showed that the SR-RPPG could swell more than 30 times its original volume in 5 % CaCl₂ and a middle east formation water. Besides, the SR-RPPG gel slurry can re-crosslink to form a rubber-like elastic bulk gel at 80–100 °C, and the elastic modulus of the re-crosslinked bulk gel can reach up to 1350 Pa with a swelling ratio of 10. The SR-RPPG prepared in 1 % NaCl, 2 % KCl, middle east formation water and 5 % CaCl₂ with a swelling ratio of 10 have been stable for over 200 days at 100 °C. The core flooding test demonstrated that the SR-RPPG could efficiently block the open fractures, and the water breakthrough pressure gradient reached 927.30 psi/ft (20.98 MPa/m).

1. Introduction

A large portion of hydrocarbon is located in fractured reservoirs with severe heterogeneity. The abundant natural fractures and void space conduits could significantly deteriorate the sweep efficiency during water, polymer or CO₂ flooding [1,2]. Under such circumstances, gel treatment could be a potential candidate for improving the oil recovery in fractured reservoirs [3,4].

Several gel systems have been developed, and some commonly used gel systems are in-situ polymer gel and preformed particle gels (PPG). In the case of in-situ gel systems, polymer, usually polyacrylamide (PAM) and crosslinker solutions are injected into the reservoir simultaneously or sequentially. The hybrid solution can change to gels at reservoir conditions and divert the post-injected fluid to the un-swept oil-rich zones [5]. On the other hand, PPG treatment involves injecting swelled gel particles. PPG is pre-crosslinked gel particles that can swell but not dissolve in the brine. After being well packed in the fracture, it can form

a mechanical robust gel plug and physically plug the fractures [6].

However, one acute problem that affects the gel treatment efficiency is the high salinity, especially the abundant divalent cations such as Ca²⁺ and Mg²⁺ ions [7]. Most gel systems have a relatively good thermal stability at medium temperatures with a relatively low concentration of divalent cations (10 to several thousand ppm). For example, Sydansk reported that the polymer composed of 5 wt% of low molecular weight PAM and 0.37 wt% of Cr (III) has a lifetime of over 900 days at 124 °C in synthetic seawater with a hardness of 3400 ppm [8]. Moradi reported that by using a phenolic crosslinker and a thermally stable polymer, the crosslinked gel could be stable at 150 °C for over 376 days in a brine containing 437 ppm of Ca²⁺ and 1256 ppm of Mg²⁺ [9]. Bai reported that the PPG could be stable at 120 °C with the NaCl concentration up to 300000 ppm. However, the stability of these gels decreased dramatically with the increase of divalent cations concentration. This is because long-term exposure to high temperatures can alter the polymer structure and crosslinking density [10]. In the case of in-situ gels, after extensive

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hydrolysis, the excessive carboxylate groups could be chelated by the divalent cations and cause severe syneresis [11,12]. For example, even employing AN-125, a polymer containing 25 % (molar ratio) of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), the syneresis ratio of the gel crosslinked by Cr (III) reached 20 % only after 40 days of aging at 95 °C in a synthetic connate brine containing 19099 ppm of Ca^{2+} and 2273 ppm Mg^{2+} [13]. In addition, after replacing Cr (III) with phenol and formaldehyde, the crosslinked AN-125 gel began to syneresis after 30 days of aging at 110 °C in brine containing 8895 ppm of Ca^{2+} and 821 ppm of Mg^{2+} [14]. The hydrolytic stability of in-situ polymer gels can be improved by introducing a complexing agent which can complex the divalent cations and protect the polymer gels from being chelated by these cations [15,16]. These complexing agents can also complex Cr (III) and other metallic crosslinkers, so the compatible crosslinkers can only be organic crosslinkers such as phenol/formaldehyde and polyethyleneimine. However, it should be mentioned that it is hard to maintain gelant integrity due to chromatographic separation during the transportation process. The low solubility of the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ligand complex might precipitate and block the oil-bearing matrix, which raises significant concerns about this technology [17]. Traditional PPG is also acrylamide-based polymer gels, which are vulnerable to syneresis caused by the concentrated divalent cations under high temperatures. The hydrolytic stability of PPG can be significantly improved by copolymerization of acrylamide with other thermal stable and salt-resistant monomers such as AMPS, 1-Vinyl-2-pyrrolidinone (NVP), N, N dimethyl acrylamide (DMAM) and sodium styrene sulfate (SSS), etc [6,18–20]. For example, a crosslinked terpolymer containing acrylamide, AMPS and NVP was reported to have a syneresis ratio of less than 30 % after 90 days of aging at 130 °C in brine containing 49729 ppm of Ca^{2+} and 3183 ppm of Mg^{2+} [18]. Bhushan reported a crosslinked copolymer composed of N, N dimethyl acrylamide and sodium styrene sulfate has a lifetime of over 12 months at 150 °C in 1 wt% CaCl_2 solution [20]. Another severe problem affecting oil recovery in fractured reservoirs is the high conductivity between injection and production wells. Field tests have proved that both in-situ gel and PPG have limited plugging efficiency in reservoirs with large fractures or void space conduits [21–24]. In addition, field test showed that the polymer gels could transport through these high conductivity features and were found in the production well [21,22].

To meet the harsh reservoir conditions of the middle-east fractured oil reservoirs (Ca^{2+} 19000 ppm, Mg^{2+} 2411 ppm, temperature 100 °C), our group has developed a novel high salinity-resistant PPG (SR-RPPG) product that can re-crosslink to form a bulk gel after being placed in the fracture and remain stable at 100 °C for over 200 days in brine containing up to 5 wt% of CaCl_2 . This novel salt-resistant re-crosslinkable PPG comprises acrylamide (60 mol%), 2-acrylamido-2-methylpropane sulfonic acid (40 mol%), xanthan gum (XC), N, N-Methyl-enebisacrylamide, and pre-embed Cr (III)-based crosslinker. Xanthan gum was introduced to enhance the salt-resistance and gel strength [25,26]. This work aims to evaluate whether this SR-RPPG can be applied in high-temperature fractured reservoirs regarding its swelling kinetics, re-crosslinking behavior, gel strength, hydrolytic stability and plugging efficiency. We have studied the effect of polymer composition, additive types, temperature, pH and salinity on the re-crosslinking behaviors, gel strength and thermal stability.

2. Materials

SR-RPPG was fabricated by Daqing New Wantong company and used as received. This novel SR-RPPG is a dry, blueish-green particle. Portland cement (type C) was used to prepare the fracture model. Based on the requirements from ConocoPhillips and Occidental Petroleum, SR-RPPG with a particle size of 1–2 mm and a swelling ratio of 10 was used during the thermal stability and plugging test.

2.1. Swelling kinetics

The dynamic swelling kinetics of the SR-RPPG (1–2 mm) was evaluated in different brine solutions. A vibrating shaker was used to simulate the dynamic swelling process, and the volume of the swelled SR-RPPG was recorded as a function of time. In addition, brines such as 2 wt% KCl, 5 wt% CaCl_2 , and synthetic middle east formation water were implemented to study the effect of salinity on the swelling kinetics. The composition of the synthetic middle east formation water is listed in Table 1.

2.2. Re-crosslinking behavior

The re-crosslinking behavior of SR-RPPG was evaluated using the bottle-test method [27]. SR-RPPG dry gel particles with a size of 1–2 mm and swelling ratio of 10, half swelling (HS), full swelling (FS) and excessive brine (EX) were utilized for the re-crosslinking test. The swelled gel particle slurry was sealed in a high-temperature resistant glass tube, and ultra-high purity argon was sparged into the gel slurry for 30 min during the swelling process before sealing. After absorbing all the free water, the glass tube was put into a pre-heated oven and checked periodically. The crosslinking start time was the time when some weak association occurred between different gel particles, and the ending time was the time when the gel particle slurry changed to a uniform bulk gel without any visible boundaries. The detailed visual testing method can be found in the previous publication [22,28].

2.3. Rheology measurement

The rheology tests were performed on the Haake MARS III rheometer at room temperature. Parallel-plate geometry-P35 Ti L was chosen for the test with a gap of 1 mm. The linear viscoelastic region of the re-crosslinked bulk gel was determined through Strain sweep experiments. In addition, the elastic and viscous modulus of the crosslinked gel was measured through time-dependent oscillation experiments with the strain and frequency controlled at 1 % and 1 Hz, respectively. The gel strength test for each sample was repeated three times.

2.4. Hydrolytic thermal stability evaluations

SR-RPPG samples with different swelling ratios and brine solutions were aged at 100 °C. High-temperature and high-pressure resistant glass tubes were used for the thermal stability test. Gel volume, morphology and code change were monitored during the aging test [27].

2.5. Core-flooding and gel degradation test

Fig. 1 shows the core-flooding experiment setup. A fractured cement core with a fracture width of 1.5 mm was used. The cement core was prepared using Portland cement. The prepared cement slurry was dumped into a cylindrical mold with a diameter of 5.08 cm. Then, a stainless-steel strip with a thickness of 0.15 cm and a height of 2.54 cm was put in the middle of the mold vertically during the curing process. The stainless steel was removed after 6 to 8 h of hydration before the cement was fully set. The experiment procedure involves the following steps. First, the dried gel particles were swelled in the middle east formation water. Then, after absorbing all the free water, the gel slurry was injected into the fracture with a 1 mL/min placement rate till the injection pressure became stable. Different from the filed application, where the gel suspension was injected into the fractures, we decided to

Table 1
Chemical composition of synthetic formation water.

Ions	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-
Concentration/ $\text{mg} \cdot \text{L}^{-1}$	59286	19000	2411	132157	359

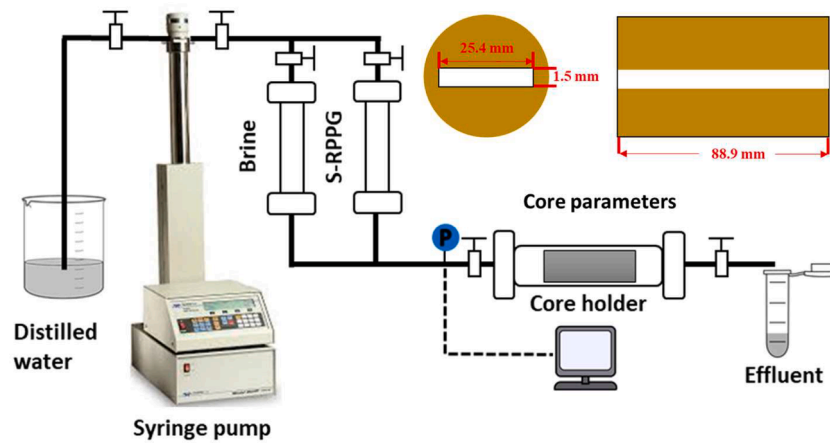


Fig. 1. Core flooding experiment setup.

inject the gel slurry after no free water could be observed. This is because we can better control the swelling ratio of the gels placed in the fracture in this way. Then the core was sealed and aged at 100 °C for three days till fully re-crosslinking. After that, the constant water flow rate method was adopted to get the water breakthrough pressure, and the water injection rate was 1 mL/min. Then, after the water breakthrough, we change the flow rate to 0.1, 0.25, 0.5, 1 and 2 mL/min and use the stable pressure at each flow rate to calculate the residual resistance factor (F_{rr}). The residual resistance factor, F_{rr} , was calculated by the following equations:

$$F_{rr} = \frac{k_{before}}{k_{after}} \quad (1)$$

$$k_{initial} = \frac{b^2}{12} \quad (2)$$

Where k_{before} is the initial fractured cement core permeability, and b is the width of the fracture; k_{after} is the fractured cement permeability after the water breakthrough and is calculated based on Darcy's law.

Based on our previous research, 12wt %NaOH activated 6 wt%

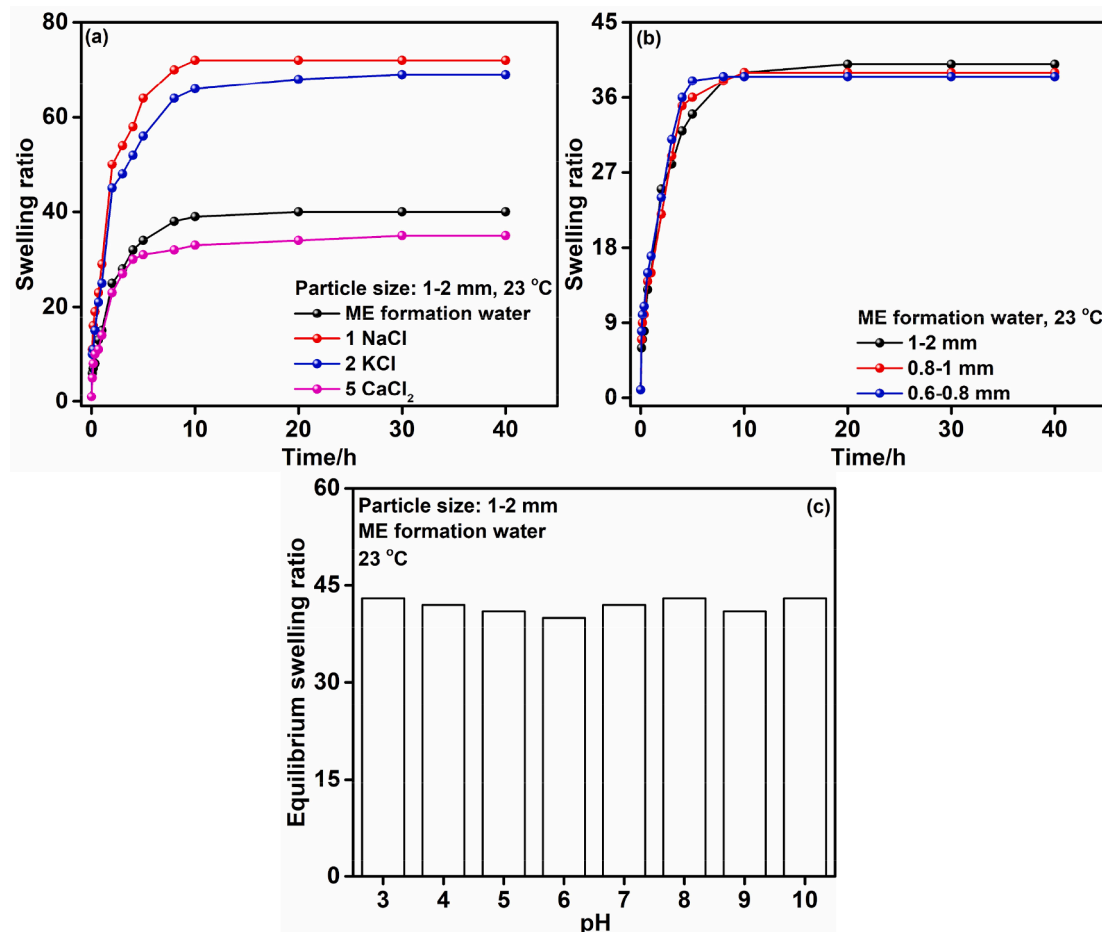


Fig. 2. Effect of (a) brine types, (b) particle size, (c) brine pH on the swelling kinetics of the SR-RPPG.

$\text{Na}_2\text{S}_2\text{O}_8$ has good performance in breaking the bulky gel [29]. Therefore, in this work, we chose NaOH activated $\text{Na}_2\text{S}_2\text{O}_8$ as the breaker solution. The degradation test was carried out at 80 °C. The precise procedures were as follows: 10 g of re-crosslinked SR-RPPG was immersed into 30 mL of breaker solution. Then, the bottle was sealed and heated at 80 °C and the residual weight of the SR-RPPG was recorded every 1 h.

3. Discussion

3.1. Swelling kinetics

The field injection can be better designed after knowing the swelling rate and equilibrium swelling ratio of the SR-RPPG [22]. Fig. 2 (a) shows the swelling kinetics of the SR-RPPG in different brines. The SR-RPPG took around 10 h to reach the equilibrium swelling ratio, and the equilibrium swelling ratio decreased sharply in divalent ion solutions. The equilibrium swelling ratios in 1 % NaCl, 2 % KCl, 5 % CaCl_2 and middle east formation water were 72, 69, 35 and 40, respectively. The SR-RPPG has a relatively low equilibrium swelling ratio in divalent ion solutions due to the strong charge shielding effect [30]. The swelling behavior can be well explained by the osmotic pressure developed because of the unequal distribution of ions in the polymer gel phase and brine solution [31,32]. At the beginning of the swelling, the concentration gradient difference between the gel phase and brine solution results in the fast swelling rate. At the end of the swelling, the polymer gel matrix has saturated with salt ions, and thus the relatively small concentration gradient can not make the gel absorb more water and swell [33]. It should be noted that the osmotic pressure is strongly related to the ionic strength. The existence of multivalent ions such as $\text{Ca}^{2+}/\text{Mg}^{2+}$ could significantly decrease the osmotic pressure compared with the Na^+/Cl^- ions. Besides, the “ionic crosslinking” between the polymer gel and the multivalent ions is another factor that can severely decrease the equilibrium swelling ratio [32]. For example, in Gupta's work, the equilibrium swelling ratio of acrylamide-based hydrogel in 0.1 M NaCl and CaCl_2 solution was 80 ~ 100 and 20 ~ 30, respectively [32].

The effect of particle size on the swelling kinetics was also studied, as shown in Fig. 2 (b). The swelling rate increases with the decrease of particle size, and the equilibrium swelling ratio fluctuates in a small range. For example, SR-RPPG with particle sizes ranging from 0.6 to 0.8 and 1–2 mm reach the equilibrium swelling ratio after 6 and 10 h. We also studied the effect of brine pH on the equilibrium swelling ratio. The brine pH value was adjusted using dilute HCl and NaOH solutions, and the result is shown in Fig. 2 (c). pH has a negligible effect on the equilibrium swelling ratio.

3.2. Re-crosslinking behavior

After swelling, the pre-embedded crosslinker could gradually diffuse out and interact with adjacent particles to generate new crosslinking bonds. A reasonable re-crosslinking time could decrease the well shut-in time and avoid blocking wellbore or injection facilities. In general, the near-wellbore gel treatment requires a re-crosslinking time of 4 ~ 12 h [34]. The Middle East oil field's surface facilities temperature, injection temperature, and reservoir temperature are 45, 80 and 100 °C, respectively. Therefore, we tested the re-crosslinking behavior of the SR-RPPG under these temperatures to guide the field application.

Fig. 3 shows the gel appearance after 30 h of aging at different temperatures, and the gel slurry was prepared in the synthetic middle east formation water with a swelling ratio of 10. There is no re-crosslinking at 45 °C, and the gel particles can be separated easily. However, at 80 and 100 °C, the gel slurry has already formed a bulky gel, and the gel code was Code I. Fig. 4 shows the crosslinking time at 80 and 100 °C.

The re-crosslinking can be accelerated by increasing temperature

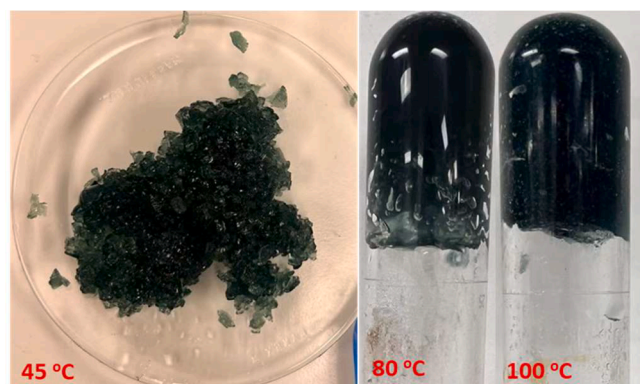


Fig. 3. Gel appearance after 30 h of aging at different temperatures (ME formation water).

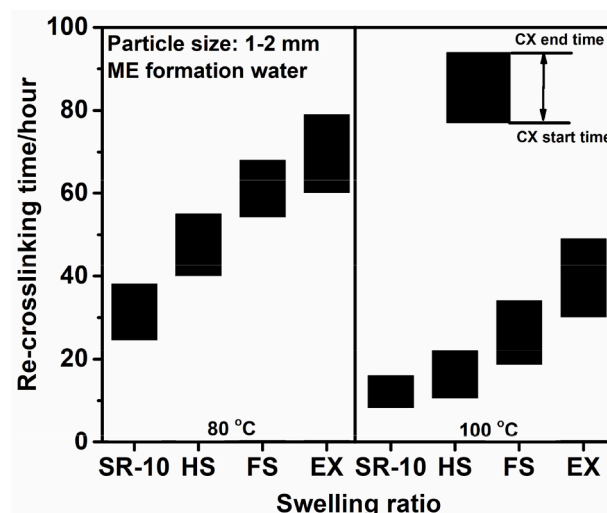


Fig. 4. Effect of swelling ratio and temperature on the re-crosslinking time.

and decreasing the swelling ratio. The re-crosslinking start time of SR-RPPG (SR-10) at 80 and 100 °C were 23 and 8 h, respectively. Besides, the re-crosslinking starting time at 100 °C increased from 8 h to 30 h as the swelling ratio increased from 10 to full swelling with excess brine (free water). Gels with excessive water need more time to form effective re-crosslinking bonds than the fully swelled sample. This is because, at the beginning of the re-crosslinking test (0 ~ 20 h), the weak association between gel particles can be broken during the inspection process by shaking or turning the tube upside down, and the particles can be re-dispersed in the solution. However, with the extension of aging time, some gel aggregates form in the tube bottom and can not be separated by shaking. Gradually, the remaining gel particles interact with the gel aggregates and generate a bulk gel. We also studied the effect of particle size on the re-crosslinking starting time, and the result is shown in Fig. 5 (a). The re-crosslinking time can be significantly shortened by decreasing particle size. For example, the re-crosslinking starting time at 100 °C decreased from 22 h to 4 h as the particle size reduced from 2 to 4 mm to 0.6–0.8 mm. Therefore, more attention should be paid if the gel treatment deploys small gel particles, and pre-flush formation with cold water could be a choice to cool down the formation temperature to place the small gel particle in the target zones.

In addition, we also tested the effect of brine pH on the re-crosslinking starting time, as shown in Fig. 5 (b). The brine pH value has a negligible impact on the re-crosslinking starting time and the starting time increases slightly as the pH increases.

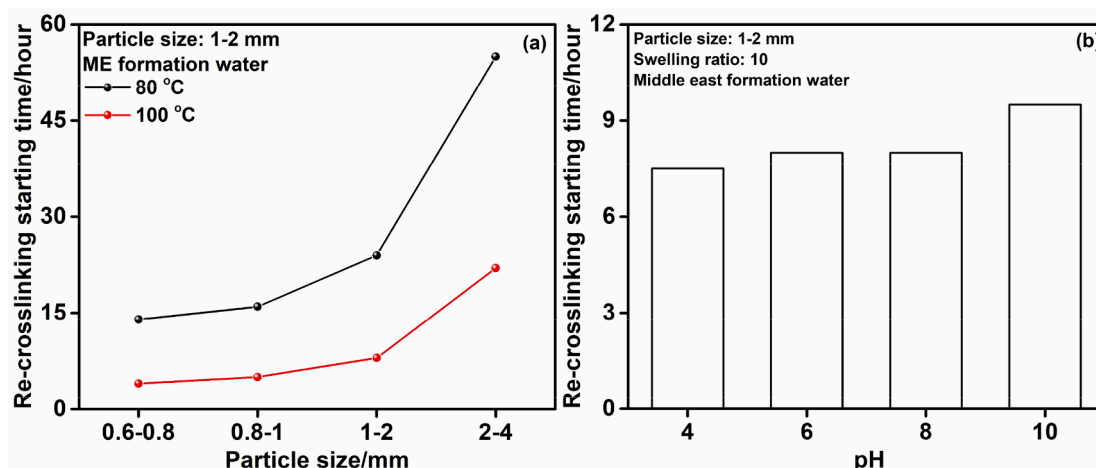


Fig. 5. Effect of (a) particle size, (b) brine pH on the re-crosslinking time.

3.3. Gel strength

The elastic modulus of the re-crosslinked gel was employed to represent the gel strength. The effect of salinity, swelling ratio and dried gel particle size on the gel strength was systematically evaluated. After three days of curing, the re-crosslinked gels are subjected to the rheology test. Fig. 6 (a) shows the effect of the swelling ratio on the gel strength. The gel strength gradually decreases as the swelling ratio increases. For example, the re-crosslinked gel with a swelling ratio of 5 has an elastic modulus of 9205 Pa and the gel strength decreases to 87 Pa as the swelling ratio increases to 40. Besides, the gel strength increases with

the decrease of particle size, as depicted in Fig. 6 (b). This is because small particles have more interaction surface area and are well packed than large particles. In addition, the gel strength decreases with the increase of divalent cation concentration. As shown in Fig. 6 (c), the re-crosslinked gels have higher gel strength in 1 % NaCl, and 2 % KCl brines compared to 5 % CaCl_2 and middle formation water.

3.4. Thermal stability test

During the long-term thermal stability test, the gel volume and gel code were monitored. Fig. 7 shows the long-term thermal stability test

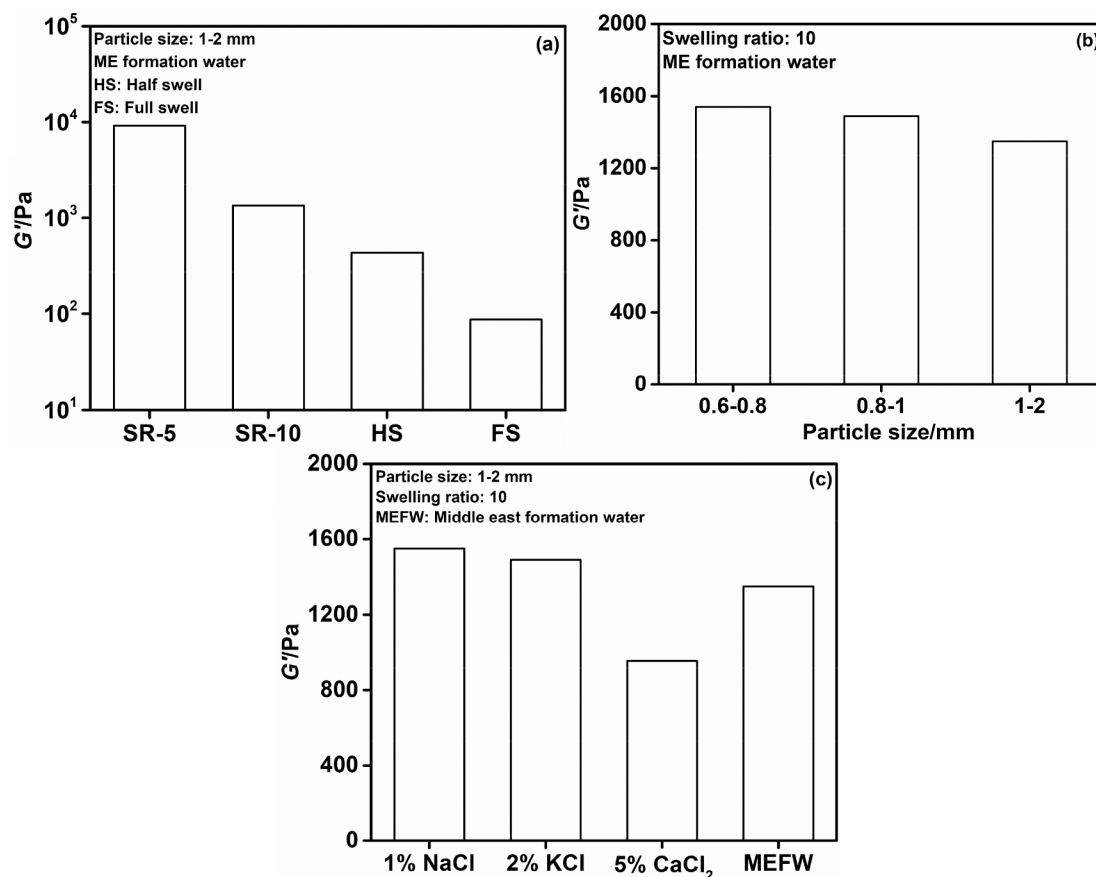


Fig. 6. Effect of (a) the swelling ratio, (b) particle size, (c) salinity on the gel strength.

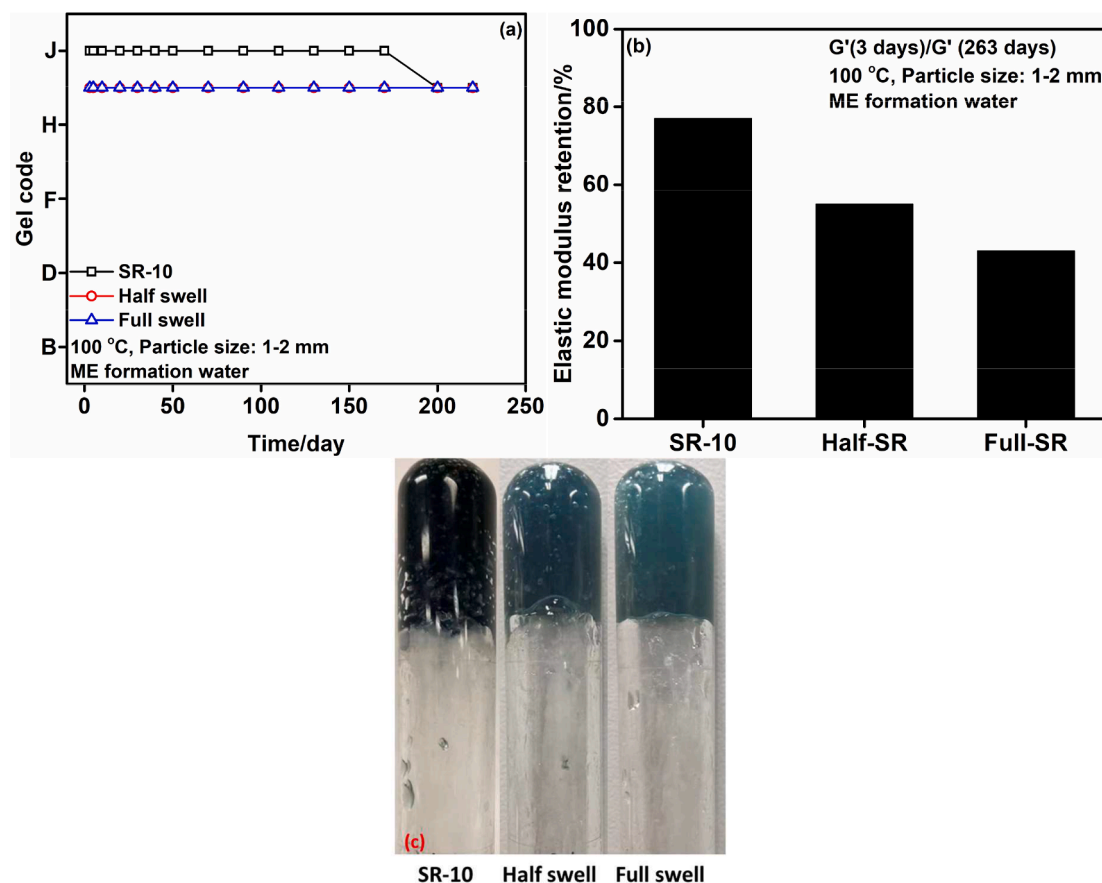


Fig. 7. (a) Gel code changes during the long-term thermal test; (b) elastic modulus retention ratio after 263 days of aging; (c) gel appearance after 200 days of aging.

results of the SR-RPPG with different swelling ratios at 100 °C in the middle east formation water. Gels with different swelling ratios are stable at 100 °C after 220 days of aging, and we did not observe any syneresis and volume loss during the thermal stability test. After 220 days of aging, the gel code was Code I, and the bulky gel still maintains its mechanical integrity, but the gel strength decreased by 23 ~ 57 %. The degradation can not be avoided at high temperatures, but it is not severe enough to degrade the crosslinked gel from Code I (Rigid gel) to Code A ~ E. We think the loss in gel strength could either be caused by the oxygen radical triggered chain scission or the hydrolysis of AM/AMPS followed by the partially over-crosslinking with Cr (III) [19,35]. The oxygen radical could come from the residual oxygen during the

argon sparging process or the oxygen leaking through the thermally stable O-ring because the O-ring as rubber is still permeable to air/oxygen [36]. The SEM test also confirmed the degradation of the polymer network. Fig. 8 shows the microstructure of the re-crosslinked gel after 5 and 200 days of aging. The network collapsed after 200 days of aging, but we can still observe the interconnected network structure.

Fig. 9 shows the thermal stability of the re-crosslinked gels in different brines. The re-crosslinked gels with a swelling ratio of 10 are stable in 1 % NaCl, 2 % KCl and 5 % CaCl₂, and no syneresis was observed during the thermal stability test.

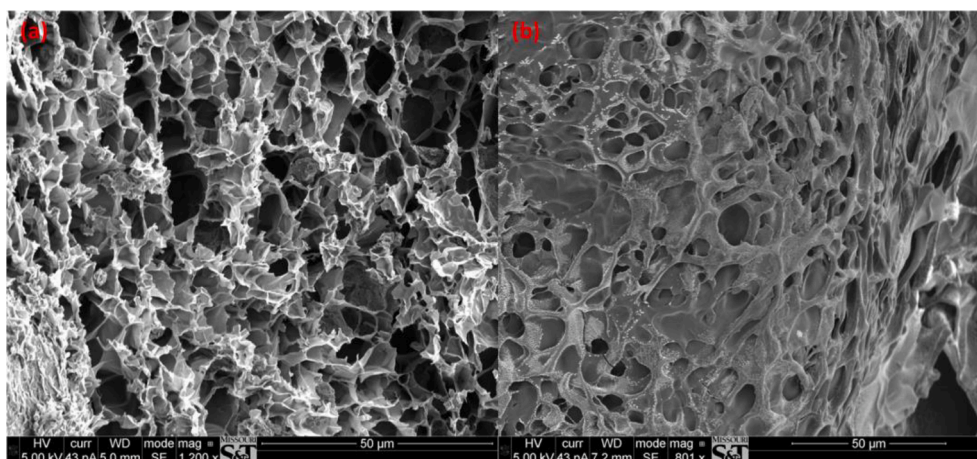


Fig. 8. Microstructure of the SR-RPPG (SR-10, ME formation water) after (a) 3 days, (b) 200 days of aging at 100 °C.

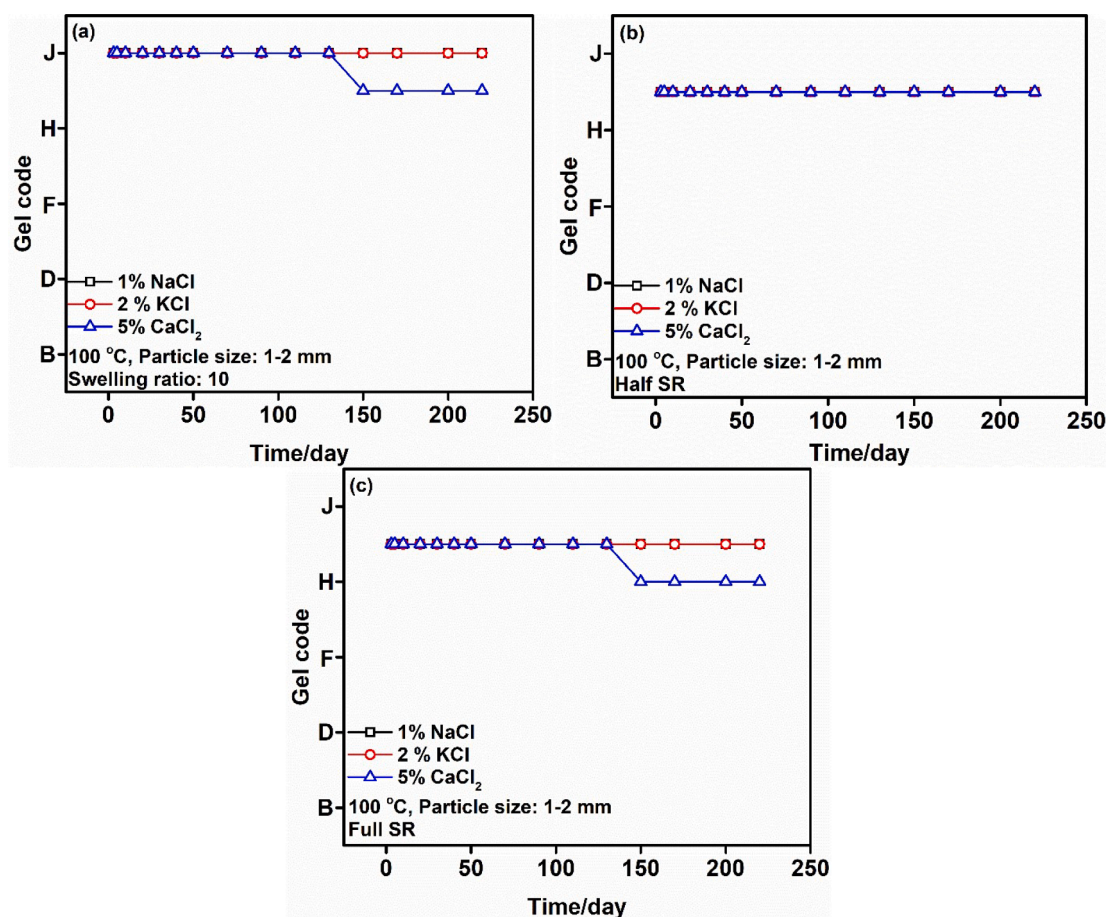


Fig. 9. Effect of swelling ratio on the thermal stability (a) SR-10, (b) half swelled, (c) fully swelled.

3.5. Core flooding and degradation test

Fig. 10 depicts the core-flooding results of the SR-RPPG. We will not start the gel slurry injection until the gel particles absorb all the free water, which differs from the field application, where the gel suspension was injected into the fractures. This is because, in this way, we can better control the swelling ratio of the gels placed in the fracture. The gel injection pressure data is shown in Fig. 10 (a). After over 15.74 FV (fracture volume) of gelant injection, the stable injection pressure was 93 psi. After gel slurry injection, we cleaned the injection inlet and outlet to ensure no gel was left in the tubing that might result in additional pressure resistance during the water breakthrough test.

The breakthrough pressure was achieved through the method of constant flow rate (1 mL/min). The water breakthrough pressure was 261.50 psi (927.30 psi/ft, 20.98 MPa/m), and even after the water breakthrough, the injection pressure can still be maintained at a relatively high-pressure level. In addition, we did not observe any gel particles produced from the fracture during the experiment, which demonstrated the re-crosslinked bulky gel could resist the post-injected fluid efficiently. The effect of injection rate on the residual flow resistance is shown in Fig. 10 (c). The F_{rr} gradually decreases with the increase of flow rate, and the F_{rr} ranges from 1×10^8 to 1×10^9 , which means the fracture permeability can reduce more than 10^8 times.

SR-RPPG might plug undesired zones or injection facilities during the gel treatment. Therefore, we tested whether the SR-RPPG can be degraded easily under the stimulation of breaker solution. Fig. 11 shows the degradation test result. In the beginning, the bulky gel kept absorbing water and swelling. But severe degradation can be observed after 1 h. This is because the osmotic pressure is proportional to absolute temperature [31]. Therefore, the bulky gel kept swelling at high

temperatures, becoming more permeable to the breaker solution. SR-RPPG with swelling ratios of 10 and 20 degraded completely after 7 and 5 h, respectively. The breaker solution comprises 12 % NaOH and 6 % APS, in which both the polymer chains and crosslinking bonds can be readily destroyed [29].

4. Further discussion

Our group has been focused on developing re-crosslinkable/re-associable preformed particle gels for plugging large fractures and void space conduits. Currently, our group has developed a series of RPPG products, including low-temperature applicable RPPG (LT-RPPG) [24,28], and high-temperature resistant RPPG (HT-RPPG) [37]. The LT-RPPG and HT-RPPG were designed for low temperature (20 ~ 80 °C) and high temperature (100 ~ 130 °C) reservoirs, respectively. The field application demonstrated that the RPPG could be readily pumped into the reservoir and has excellent long-term plugging efficiency to open fractures/void space conduits [22]. However, all the RPPGs have limited thermal/phase stability at 100 °C in middle east injection water ($\text{CaCl}_2 + \text{MgCl}_2 = 3\%$). The previous HT-RPPG comprises acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, N, N-Methylenebisacrylamide, polyvinyl alcohol, and polyethyleneimine. The HT-RPPG was synthesized through the surface initiation method, and the swelled gel particles can re-crosslink through the transamidation between PEI and amide groups. The stability of the previously reported HT-RPPG in the middle east formation water can be improved after recipe modification, but the changes in the recipe significantly increase the production cost because the organic crosslinker (PEI) is extremely expensive, and increasing PEI and AMPS content could bring extra cost and making this gel system uneconomic. Therefore, in this work, we developed a novel, cheaper Cr

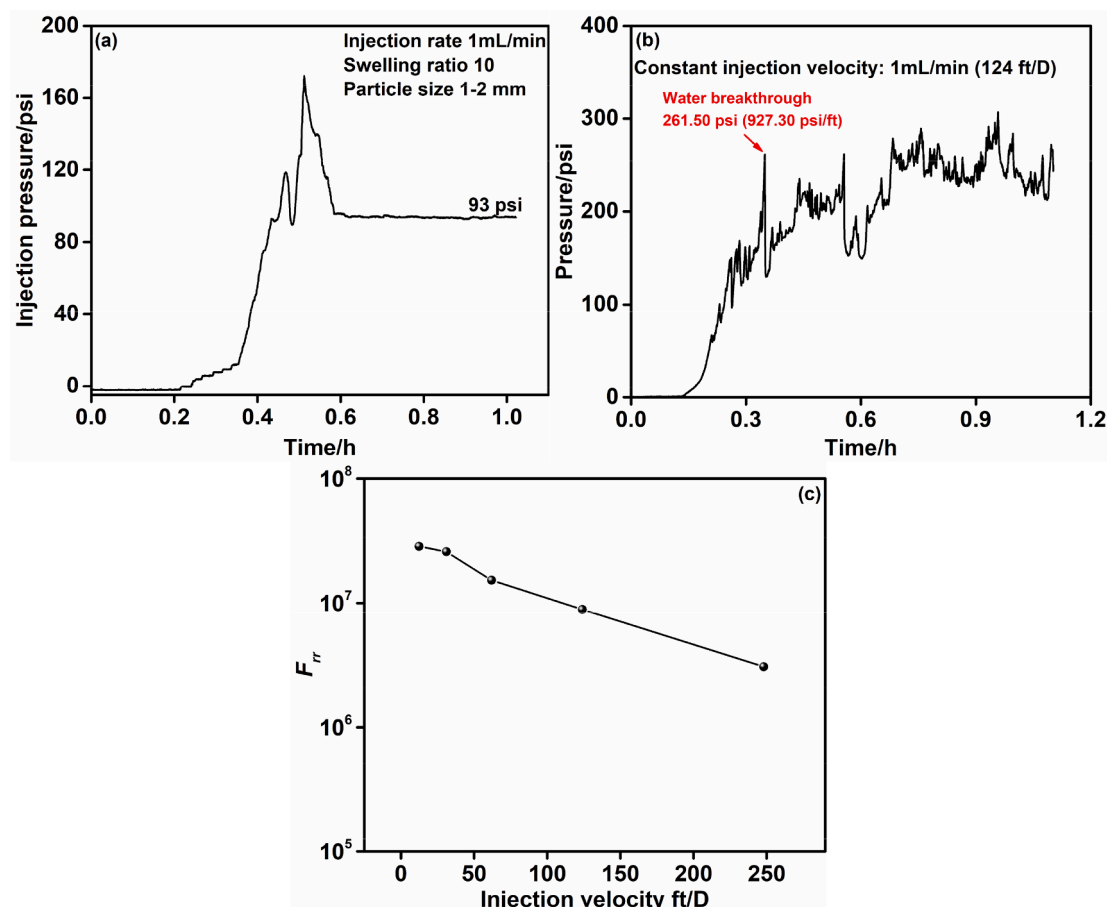


Fig. 10. (a) Gel placement pressure; (b) Water breakthrough test, (c) F_{rr} at various injection rates.

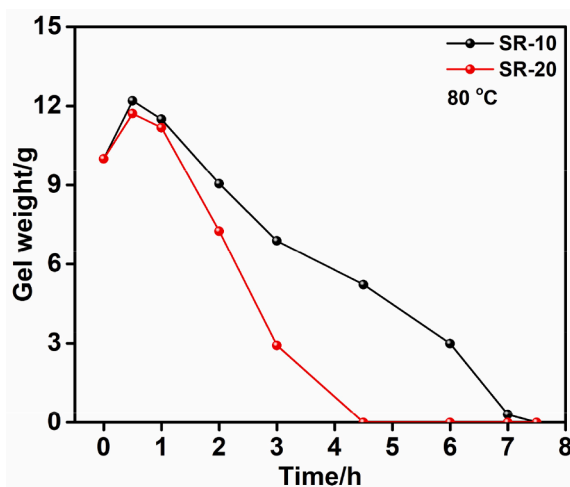


Fig. 11. Degradation behavior of the SR-RPPG.

(III) based RPPG, which can reform a bulky gel and remain stable in the middle east reservoir conditions.

This novel SR-RPPG comprises AM and a high content of AMPS, chromium acetate, and xanthan gum. The increase in AMPS content could significantly enhance the stability of polymer gels in middle east formation water, as shown in Fig. 12. The AMPS unit has been proved to delay the amide group's hydrolysis rate, and the large pendant sulfonic group could also improve the salt resistance of the polymer chains [38–40]. However, the strength/integrity of the primary gel after

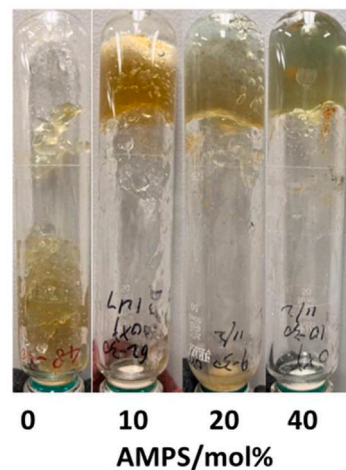


Fig. 12. Gel appearance after 100 days of aging at 100 °C (no MBA and XC, swelling ratio 30, ME formation water).

polymerization decreases significantly with the increasing AMPS content. This is because the strong repulsion between sulfonic groups reduces the polymer chain entanglement. Getting a bulky primary gel with a fixed shape/good integrity in the lab with high AMPS content (60 mol %) is easy. But for the pilot production, it is hard to get a bulky gel with more than 40 mol% of AMPS because the factory can not remove the oxygen to the same level as we did in the lab, and the factory is more likely to get a sticky, viscous flowing gel after polymerization. It is difficult for the factory to handle the flowing gel because the cost to dry

and grind the flowing gel is exceptionally high compared with handling bulky gels with a fixed shape.

One easy way to enhance the strength/integrity of the primary gel is to add more crosslinker I (MBA) to improve the crosslinking density, but the rigidity also increases with the MBA feeding amount, which has a negative effect on the strength/integrity of the re-crosslinked gel and gel injectivity. Particle gels with a high crosslinking density are very rigid and lack the flexibility to interact with other gel particles to re-form a uniform bulky gel. Furthermore, the robust gel particles can not readily propagate through the fracture due to poor transformability/elasticity. Therefore, we can not use a high concentration of MBA to facilitate the pilot production. Innovated by Jianping Gong's work [41], we successfully improved the integrity of the primary gel by using a double network structure. We screened a series of polymers, including polyacrylamide, polyvinyl alcohol, polyvinylpyrrolidone, methylcellulose, and xanthan gum (XC), to see whether they can enhance the integrity/strength of the primary bulky gel. Fortunately, both methylcellulose and XC can significantly improve the strength/integrity of the primary bulky gel. However, methylcellulose can stabilize the bubbles generated during the argon sparging process during the synthesis, resulting in monomer solution leakage from the reactor. Therefore, XC was used to enhance the strength/integrity of the primary gel during the pilot production process. The result showed that the elasticity/integrity of the primary bulky gel is greatly enhanced after adding 1 % of XC (Fig. 13 (a)). Furthermore, adding XC could also significantly improve the strength of the re-crosslinked gel. The re-crosslinked gel strength was almost doubled after adding 1 % of XC, as shown in Fig. 13 (b).

We think one possible reason for the significant gel strength/integrity increase is that adding XC/Cr (III) together could form a double network structure. Gong has pointed out that the essential feature of a

mechanical robust double network gel is that it has to contain two polymers with a strong asymmetric structure [42]. More precisely, the primary polymer network should be rigid or brittle and tightly cross-linked, while the second network is loosely crosslinked high molecular weight polymer. As shown in Fig. 14, in the case of SR-RPPG, the primary network is the rigid covalently crosslinked poly (AM-co-AMPS), and the secondary network is the loosely Cr (III) crosslinked XC network. Furthermore, the additional physical entanglement between XC and

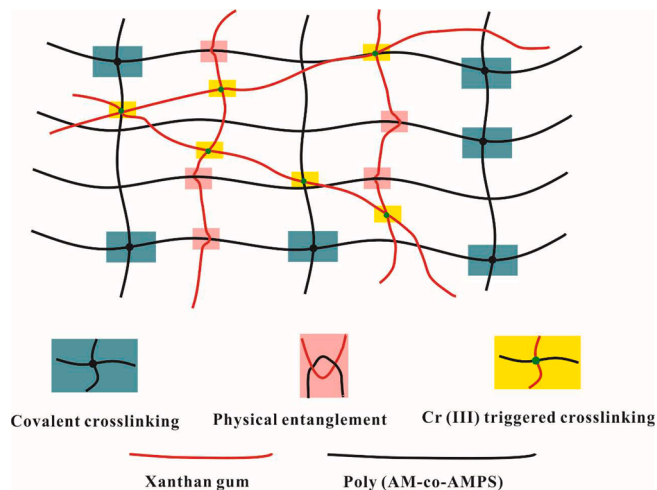


Fig. 14. Schematics of hydrogels with covalently crosslinking, physical entanglement and Cr (III) triggered crosslinking.

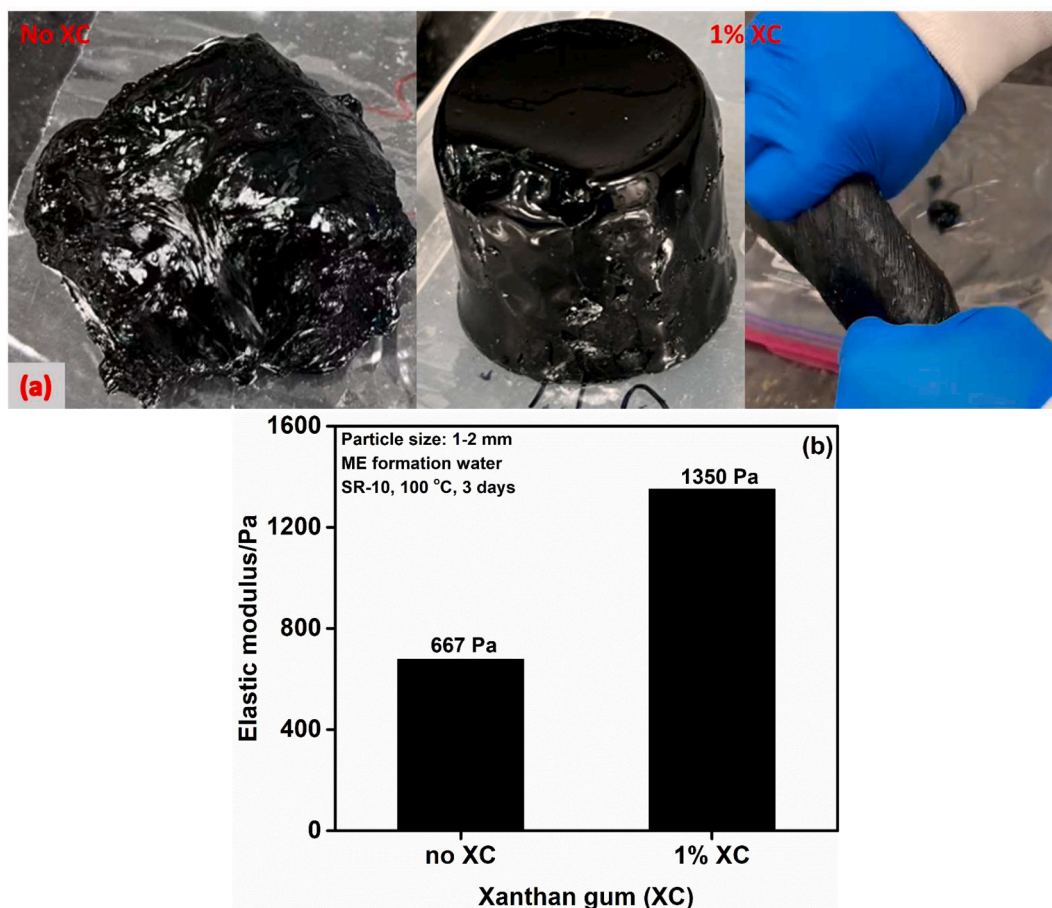


Fig. 13. (a) Primary gel appearance after polymerization (MBA 20 ppm), (b) elastic modulus of the re-crosslinked gel with and without XC.

poly (AM-co-AMPS) could make the primary/re-crosslinked gel less brittle and tougher [43]. It has been demonstrated that the toughness of hydrogel increases considerably with the percentage of physical entanglement [43]. In addition, the crosslinking between Cr (III) polymer chains is not based on covalent bonds. Therefore, the interaction between Cr (III) and XC/ poly (AM-co-AMPS) further enhances the chain entanglement.

Jia also found that adding XC/Cr (III) could significantly improve the gel strength [26]. He did one experiment without adding Cr (III) during the synthesis process, and he found that XC can not significantly enhance the strength of the covalently crosslinked acrylamide-based hydrogel.

More work will be done to study whether the maximum application temperature of this SR-RPPG can be extended to 120 °C or higher by increasing the AMPS content. Besides, we will also optimize the polymerization process and study the effect of Cr ligand type, such as malonate and lactate, on the re-crosslinking time and gel strength.

5. Conclusions

A novel salt-resistant re-crosslinkable preformed particle gel designed for high salinity reservoirs with large fractures or void space conduits was systematically evaluated in this work. This novel SR-RPPG has excellent mechanical strength, thermal/phase stability, and plugging efficiency and could be a promising candidate to improve the conformance of fractured reservoirs.

- (1) The equilibrium swelling ratio decreases with the increase of salinity. The SR-RPPG can swell more than 30 times its original volume in the middle east formation water and the half swelling and full swelling time were 6 and 10 h (1–2 mm).
- (2) The re-crosslinking starting time increases with particle size and salinity but decreases as the temperature increases.
- (3) The elastic modulus of the re-crosslinked gel with a swelling ratio of 10 ranges from 956 to 1550 Pa depending on the salinity. The divalent cation has a negative effect on the gel strength.
- (4) The re-crosslinked bulk gels have excellent thermal and phase stability in middle east formation water and 5 % CaCl₂ solution. In addition, we did not observe any syneresis and volume loss during the 200-day aging test at 100 °C.
- (5) Core-flooding test demonstrates that the SR-RPPG has excellent plugging efficiency to opening fractures and the water breakthrough pressure gradient reaches to 927.30 psi/ft (20.98 MPa/m) for a given fracture being tested.
- (6) Adding XC and Cr (III) together during the synthesis process could significantly enhance the toughness/strength of both the primary and re-crosslinked gels.

CRedit authorship contribution statement

Tao Song: Conceptualization, Methodology, Investigation, Software, Writing – original draft. **Mohamed Ahdaya:** Investigation. **Zhanmiao Zhai:** Investigation. **Thomas Schuman:** Supervision. **Baojun Bai:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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