

---

01 Feb 2022

## Comprehensive Evaluation of a High-Temperature Resistant Re-Crosslinkable Preformed Particle Gel for Water Management

Bowen Yu

Shuda Zhao

Yifu Long

Baojun Bai

Missouri University of Science and Technology, baib@mst.edu

*et. al.* For a complete list of authors, see [https://scholarsmine.mst.edu/geosci\\_geo\\_peteng\\_facwork/2077](https://scholarsmine.mst.edu/geosci_geo_peteng_facwork/2077)

Follow this and additional works at: [https://scholarsmine.mst.edu/geosci\\_geo\\_peteng\\_facwork](https://scholarsmine.mst.edu/geosci_geo_peteng_facwork)



Part of the [Chemistry Commons](#), and the [Geological Engineering Commons](#)

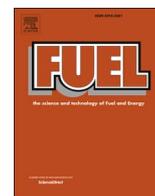
---

### Recommended Citation

B. Yu et al., "Comprehensive Evaluation of a High-Temperature Resistant Re-Crosslinkable Preformed Particle Gel for Water Management," *Fuel*, vol. 309, article no. 122086, Elsevier, Feb 2022.

The definitive version is available at <https://doi.org/10.1016/j.fuel.2021.122086>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Geosciences and Geological and Petroleum Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).



# Comprehensive evaluation of a high-temperature resistant re-crosslinkable preformed particle gel for water management

Bowen Yu, Shuda Zhao, Yifu Long, Baojun Bai\*, Thomas Schuman

Missouri University of Science and Technology, United States

## ARTICLE INFO

### Keywords:

Water management  
Conformance improvement  
High-temperature reservoir  
Thermostable  
Re-crosslinkable preformed particle gel  
Void-space conduit

## ABSTRACT

Gel treatment has been widely applied to control conformance for improving oil recovery and control water production in mature oil fields. However, most of the hydrogel systems are limited when being applied in the harsh environments of high temperatures. A systematic evaluation was conducted in this study to evaluate a modified PPG product, the high temperature resistant re-crosslinkable preformed particle gel (HT-RPPG) which can re-crosslink to form a bulky material and keep thermostable in the large-opening features after placement. This material was developed to overcome the limitations of conventional PPGs in the reservoirs with large-opening features such as open fractures, void conduits, wormholes, and so on. The HT-RPPG can swell up to 18 times of its original size at room temperature (23°C), and the swelling ratio is independent of brine concentration and types. We conducted a series of experiments to evaluate the effect of particle size, temperatures, swelling ratios, brine types on re-crosslinking time, as well as the gel strength, blocking performance and thermostability after re-crosslinking. Smaller particle sizes result in the HT-RPPGs swell and re-crosslink much faster. Higher temperatures increase the swelling and re-crosslinking rate, while the larger swelling ratios (more feeding brine) can slow down the re-crosslinking time. HT-RPPG re-crosslinking process can be delayed when the particles contact with  $\text{Ca}^{2+}$ . Additionally, the re-crosslinking of HT-RPPG is a temperature-responsive reaction which can only start after reaching the target temperature of 100 °C or above. The HT-RPPG has kept its volume and strength stable at 100 to 130 °C for over 10 months so far. A blocking performance test was conducted by using the tubing model to simulate void-space conduit (VSC), and breakthrough pressure reached to 427 psi/ft.

## 1. Introduction

With the development of oil fields, extra energy was required to maintain reservoir pressure after the depletion of natural energy for primary recovery. Water flooding, which was considered as the most practical operation approach as secondary oil recovery, has been widely used to maintain the reservoir pressure and displace the remaining oil. However, excessive water production has become the major problem because it leads to an increased load on fluid-handling facilities, increases the corrosion and scale problems, and raises environmental concerns. To correct the heterogeneity and control excessive water production problems, water management materials such as polymers, crosslinked polymer gels, and so on, can be injected into the wells to totally or partially block the high permeable zones/areas or reduce water production [7,39]. Polymer gels have been considered as one of the most economic materials to be injected for the purpose.

Two categories of gels are commonly applied for conformance

control: in-situ-crosslinking polymer gels and preformed particle gels (PPGs). Due to the controllable gelation time, adjustable strength, and good injectivity, in-situ gels have been most commonly used in oilfields traditionally [20,32]. Zhu et al. [42] described a terpolymer-gel system crosslinked by Polyethylenimine (PEI), the gelation time can be adjusted by controlling the PEI molecular weight and terpolymer concentration [42]. The gelation time can be controlled in few hours at 150 °C/302 °F and keep thermostable with less than 5% syneresis for 60 days. Not only in the conformance control area, Jia et al. [45] developed an in-situ foaming agent which was enhanced by double crosslinking by  $\text{Cr}^{3+}$  and PEI as a well-killing fluid [45]. This polymer gel system was designed for the low-pressure oil/gas reservoir.

However, some drawbacks such as unpredictable shear degradation, gelant compositional changes caused by the contact with reservoir minerals and fluids, bring uncertainties to the application of such gels, especially when a large amount of gel is used in oilfields. Moreover, same as the profile modification mechanism of polymer flooding, the

\* Corresponding author.

E-mail address: [baib@mst.edu](mailto:baib@mst.edu) (B. Bai).

<https://doi.org/10.1016/j.fuel.2021.122086>

Received 30 July 2021; Received in revised form 10 September 2021; Accepted 22 September 2021

Available online 30 September 2021

0016-2361/© 2021 Elsevier Ltd. All rights reserved.

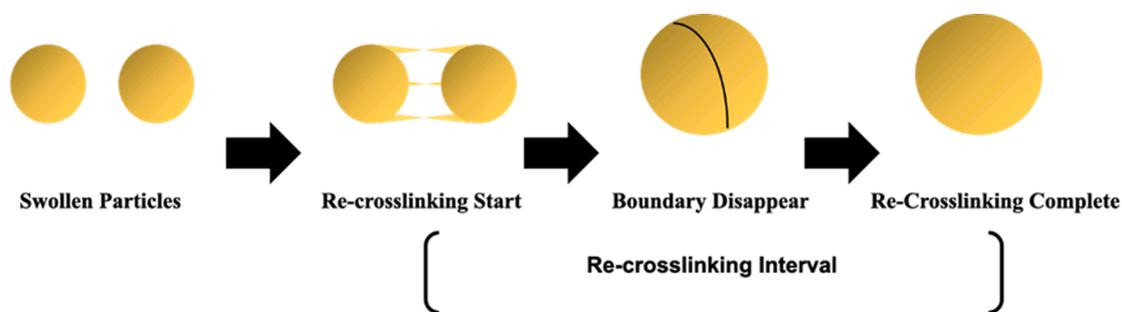


Fig. 1. Re-crosslinking Stages Classification of HT-RPPG.

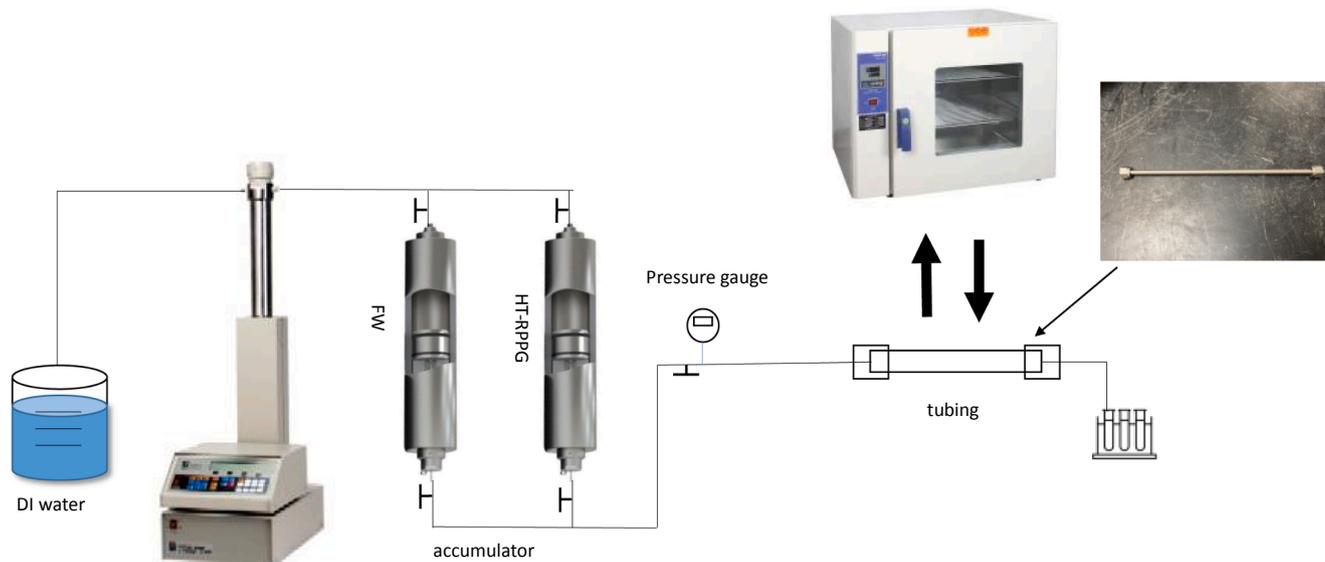


Fig. 2. RPPG-injection Apparatus.

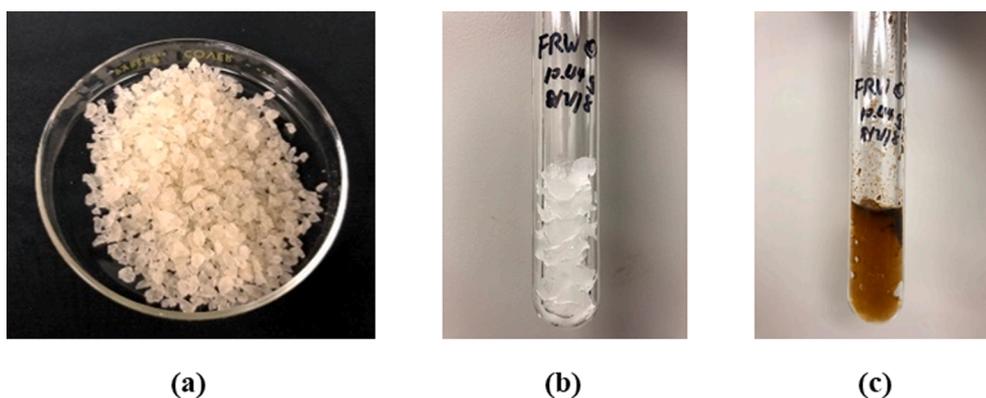


Fig. 3. HT-RPPG (a) Dry Particles (b) Before Re-crosslink (c) After re-crosslink.

gelant which has the same rheology viscosity property as polymer before crosslinking tends to enter and damage the un-swept oil-rich zones and areas. PPG is a kind of superabsorbent with polymeric 3D networks, which is formed at surface facilities and is able to swell a few to hundred times of its initial volume in water [6,8]. Because PPGs are easily prepared and pumped in oilfields, PPG treatments have been widely applied recently in many oilfields [2,33]. Due to the relatively larger size compared with the pore size of conventional porous media, strength-and size-controllable PPGs prefer to enter the fractures and fracture-like channels Bai et al. [3]. Therefore, particle treatments can minimize the risk of formation damage on low-permeability un-swept zones or

areas. Many positive results of PPG treatments have been reported in last two decades for their applications in mature reservoirs. However, some field applications show that PPGs cannot effectively plug the super high flow openings, such as large opening fractures, voids or conduits because these individual particles can flow through these large channels and cannot form effective plugging [4,15]. Lab experiments have demonstrated that PPGs can be partially washed out from the fracture, which significantly reduce the PPG plugging efficiency to fracture and conduits [35]. Sun et al. [31] proposed a method to combine resin-coated particles with PPG to overcome the performance of PPG in the fractures [31].

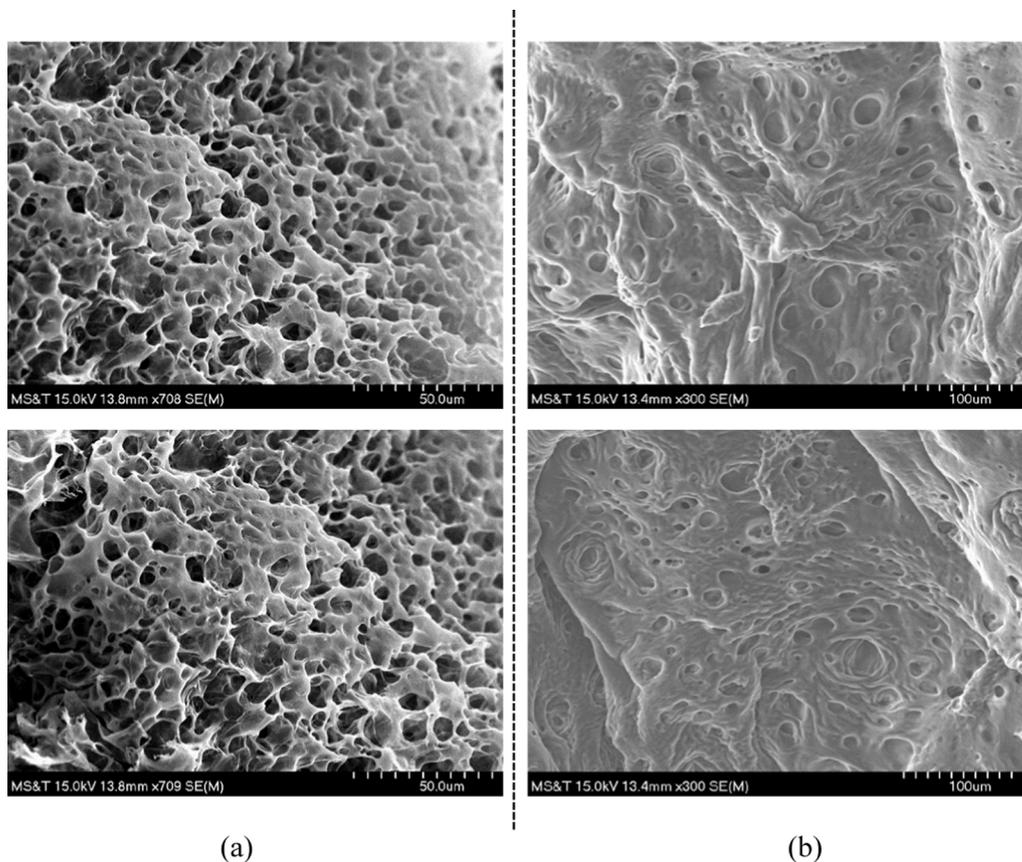


Fig. 4. SEM Characterization of HT-RPPG (a) Before Re-crosslink (b) After Re-crosslink.

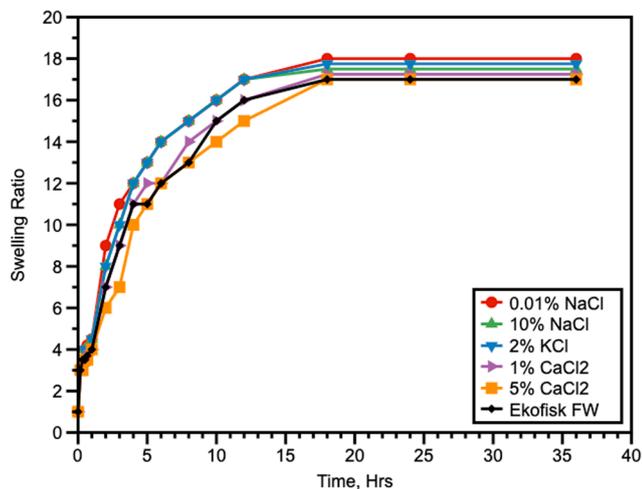


Fig. 5. Effect of brine concentration and types on rppg swelling kinetic and equilibrium.

Re-crosslinkable preformed particle gel (RPPG) has been developed which has a better performance to block such abnormal fractures in mature oil reservoirs [34]. RPPG can re-form to bulky material from the relatively smaller individual PPG particles. Pu et al. [28] evaluated a commercial product of RPPG that can be used in the reservoirs with temperatures from 20 to 80 °C.

Nowadays, with the continuous development of conventional reservoirs, the reservoirs with high-temperatures have been widely developed [14,44]. Even though there is no uniform understanding of the concept of “high-temperature reservoir”, in most conformance control

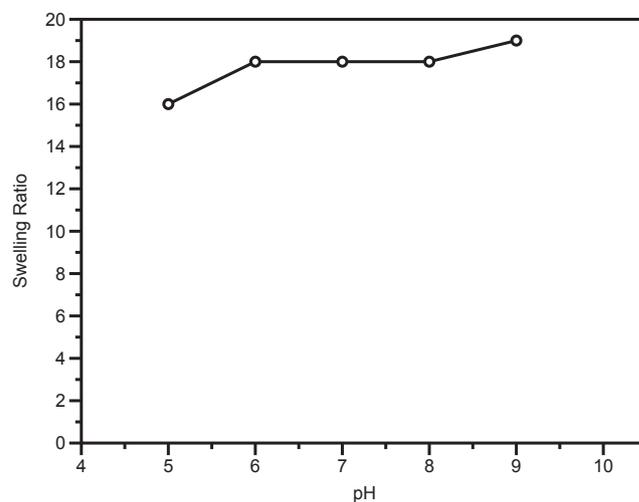


Fig. 6. Effect of pH on swelling kinetics and equilibrium.

cases, a reservoir can be considered as a “high temperature” reservoir if its temperature is higher than 80 °C, and an “extremely high-temperature” reservoir if its temperature is no less than 120 °C [5,42,43]. To increase the thermostability of the PPGs, Durán-Valencia et al. (2014) developed PPG enhanced with modified bentonite, this product exhibited a good thermostability at 130 °C/266 F [11]. Saghafi et al. [30] reported another nanocomposite system involving N,N-dimethylacrylamide (DA) as a new temperature-tolerant monomer. Researchers reported this product can keep thermostable at 145 °C/293 F [30]. Beyond the alteration of the monomers, Zhang et al. [38] developed a new crosslinker, tetraalkylammonium chloride (TAAC),

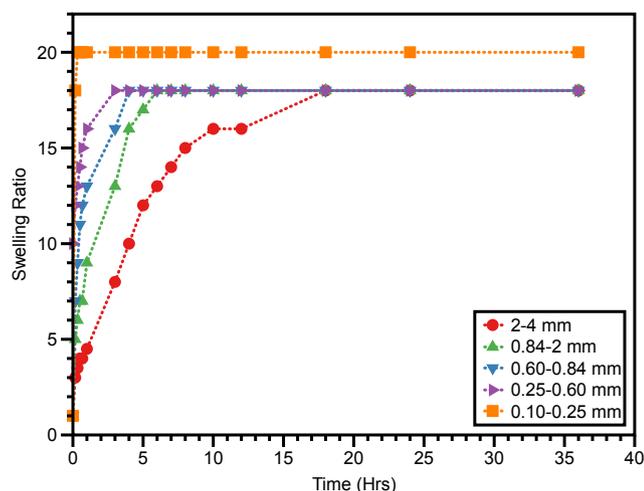


Fig. 7. Effect of particle size on swelling kinetics and equilibrium.

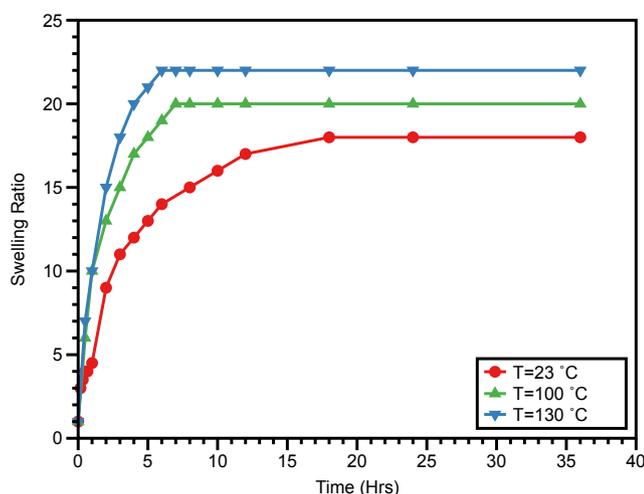


Fig. 8. Effect of temperature on swelling kinetic and equilibrium.

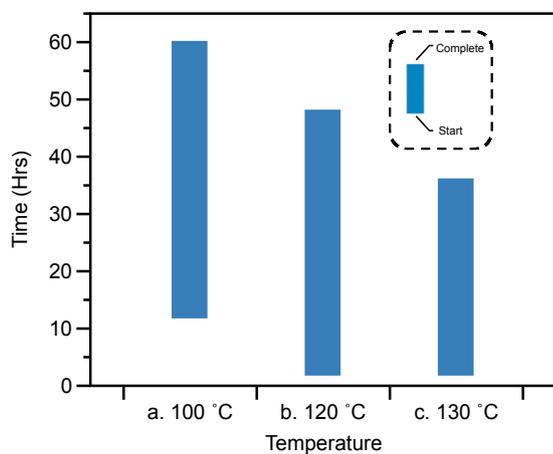


Fig. 9. Effect of temperature on HT-RPPG Re-crosslinking time.

which can significantly improve the structural strength and thermostability of the hydrogels, researchers reported that this product could keep thermostable at 250 °C [38]. Amiri et al. (2018) developed an Acrylamide-based nanocomposite hydrogel, cobalt acetyl acetone (Co

(acac)<sub>2</sub>) was applied in the gel system to enhance the thermostability [1].

A novel kind of RPPG (HT-RPPG) is developed and scaled-up in the pilot for conformance control treatments for high and extremely high-temperature reservoirs. The objective of this paper is to provide a comprehensive study for the HT-RPPG as conformance control agent for large opening conduits or fracture problems. After being mixed with brine and placed at the target temperature (100–130 °C), the HT-RPPG can swell and re-crosslink to form a new bulk gel. Thus, the HT-RPPG takes advantage of both the in-situ crosslinked gel system and the PPG system. The HT-RPPG can be dispersed with brine and pumped into the formation. After the gel placement, re-crosslinking occurs to form a new bulk gel in large opening features in a reservoir. In this study, the swelling kinetic, re-crosslinking behaviors, thermostabilities, as well as rheological strength of the HT-RPPG are quantified in variety of conditions.

## 2. Experimental methods

### 2.1. Materials

HT-RPPG (high temperature resistant re-crosslinkable preformed particle gel), provided by Daqing Xinwantong Technology Developing Company, is used for experiments. The HT-RPPG is a kind of dried, yellow particles (Fig. 3(a)) mainly composed of crosslinked poly (acrylamide-co- N-vinyl-2-pyrrolidone). Its apparent bulk density is 1.37–1.45 g/cm<sup>3</sup>, with a moisture content of less than 5%.

### 2.2. Swelling capacity measurement

Swelling kinetics and equilibrium swelling ratio of HT-RPPG were determined by monitoring the volume changes in a variety of solvents (0.01%, 5%, 10% NaCl; 2% KCl (pH from 5 to 9, adjusted by HCl and NaOH); 1% CaCl<sub>2</sub>) and Ekofisk Formation Water (FW). 2% KCl was selected because this brine is often used to prepare injection fluids in oilfields. The weight of particles before swelling,  $W_i$  was then measured and mixed with brine for hydration. The test tubes were sealed at room temperature (23 °C). The particles' volume ( $V_f$ ) was observed after hydration, and we define the swelling ratio (SR) using the following Eq. (1).

$$SR = \frac{V_f}{W_i} \quad (1)$$

where  $W_i$  is the weight (g), and  $V_f$  is the volume (ml). This definition about swelling ratio is different from traditional one which either uses the volume-volume ratio or weight-weight ratio but it is more convenient for field applications. The equilibrium swelling ratio, ESR, could be achieved when the SR of swollen particulates became constant, which is the maximum amount of brine that the particles can absorb [10].

### 2.3. Re-crosslinking time test

The bottle-test method [32] was used to qualitatively analyze the re-crosslinking time. HT-RPPG particles were swollen by deoxygenated brine and controlled the swelling ratio by the volume of feeding brine from 1:5 to 1:20 (with free water), and then sealed before being placed into the ovens with target temperatures (100–130 °C). The re-crosslinking process was separately defined by two parameters as the starting time and the interval period, shown in Fig. 1. The starting time of the re-crosslinking process is defined as the time that weak associations occur among particles, and the interval period refers to the duration between the starting time and the time that the boundaries of the particles disappear [28,37]. The morphology of the samples was checked hourly to determine the re-crosslinking stage during the bottle-test.

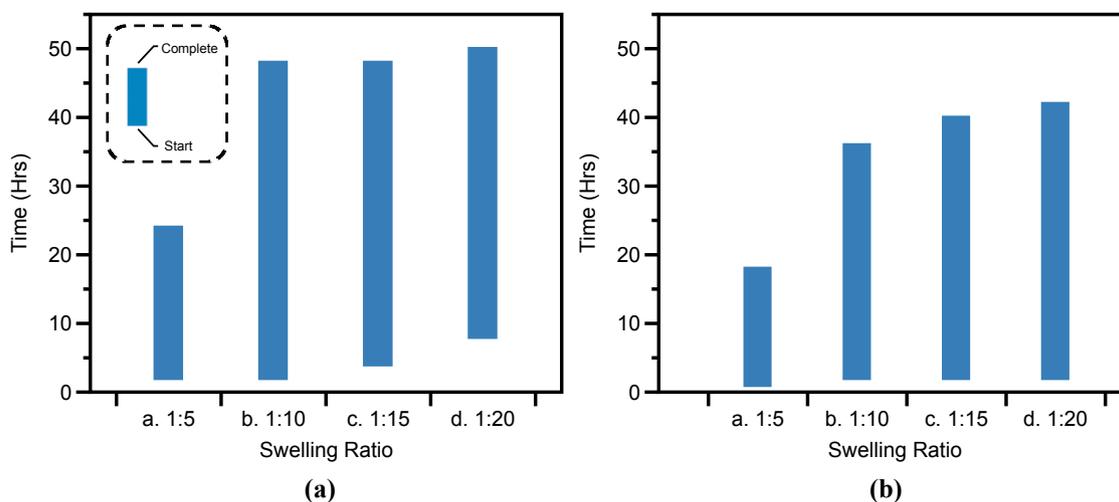


Fig. 10. Effect of swelling ratio on HT-RPPG Re-crosslinking Time at (a) 120C and (b) 130C.

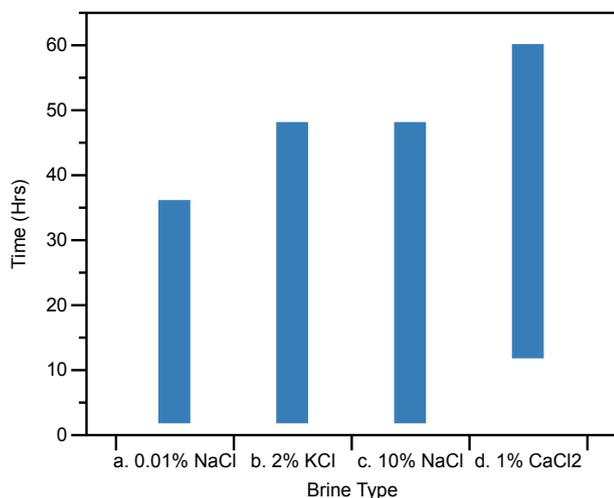


Fig. 11. Effect of brine concentration and type on HT-RPPG Re-crosslinking time.

#### 2.4. Scanning electron microscopy (SEM) characterization

Morphology (3-D networks) of HT-RPPG before and after re-crosslinking were characterized using Hitachi S-4700 Field Emission Scanning Electron Microscope (SEM). To prepare the samples, HT-RPPG before and after re-crosslinking were frozen with liquid nitrogen at the beginning, which was followed by the 12 h freezing-dry process. Networks of HT-RPPG were placed on a conductive tape which was attached to the stainless-steel stub and then sprayed with Au/Pd nanoparticles.

#### 2.5. Rheology property

HAAKE Rheometer (Germany) with a PP35 Ti (plate-plate geometry) was used to measure the rheology properties of the HT-RPPG. The testing was subjected to oscillatory shearing for modulus measurement. The measurements were carried out at room temperature (23 °C) and set the rheometer as oscillation time-dependent experiment model at a fixed frequency of 1 Hz and strain ( $\gamma$ ) of 1% to perform shear elastic modulus as a function of time. To determine the linear viscoelastic region, the oscillation strain-dependent measurement was conducted the experiment model at a fixed frequency of 1 Hz to study the  $G'$  of the gel as a function of strain.

#### 2.6. Thermostability evaluation

The thermostability evaluation was conducted by monitoring the volume and morphology changes of re-crosslinked HT-RPPG under varying solvents and temperatures according to Eq. (1). The effects of swelling ratio and solvents were investigated. For the effects of swelling ratio, samples were controlled at the HT-RPPG to brine ratio of 1:5–1:20 (with free water) by using the different volume of feeding brine (2% KCl). To study the influence of the solvents, pre-weighted HT-RPPG particles were mixed with the varying types of brine (0.01% NaCl, 10% NaCl, 1% CaCl<sub>2</sub>). To avoid gel degradation caused by oxidation at high-temperature conditions, argon was purged in the vessels before HT-RPPG was sealed in the target temperatures (100 to 130 °C).

#### 2.7. Blocking performance evaluations

The test was carried out to evaluate the blocking performance of HT-RPPG. Fluid flow through conduits has many similarities with pipeline/tube flow [16,21,23], so a single stainless-steel tubing with an inner diameter of 0.15 in. and a length of 0.82 ft was used to represent void/conduits in reservoirs. The apparatus used for the core-flooding test is shown in Fig. 2.

The HT-RPPG with the swelling ratio of 10 was prepared by immersing the HT-RPPG particles in synthetic North Sea Ekofisk formation water, which has a total dissolved solid (TDS) of 70,000 ppm. As an example of the test process, the pump was set at a constant-flow-rate mode of 0.1 cc/min to flush the tube with the swollen HT-RPPG until the pressure became stable. After that, the tube was sealed and placed in the 130C oven for 48 h to re-crosslink.

The gel breakthrough pressure was tested using a step-wise method in which brine was initially injected at a low injection pressure and then increased to high injection pressures in steps to monitor the pressure that the gel or injection fluid starts to come out from the outlet of the model. The breakthrough moment is often accompanied with a sudden pressure drop. In this experiment, we started with the initial pressure of 20 psi, and the injection pressure was increased by 10 psi every time and maintained for 5 min. The initial permeability of the tubing was calculated based on the following equation [12]:

$$k_{\text{initial}} = \frac{d^2}{32} \quad (2)$$

where  $d$  is the inner diameter of the tube.

After the breakthrough was observed, the brine injection flow rate was changed to 0.5 cc/min until the pressure became stable again. The residual resistance factor,  $F_{rr}$ , was calculated by the following equation:

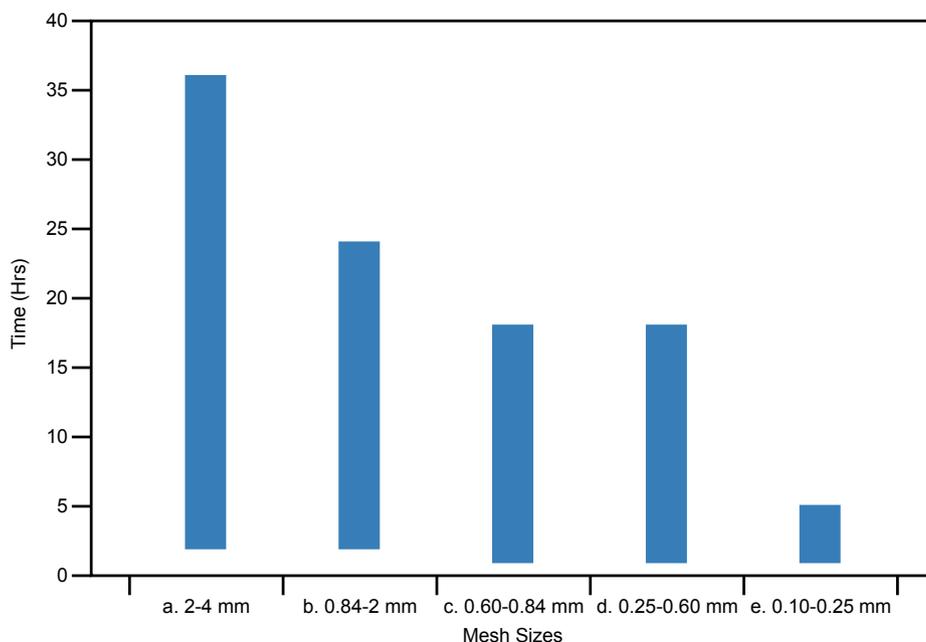


Fig. 12. Effect of particle sizes on HT-RPPG Re-crosslinking Time.

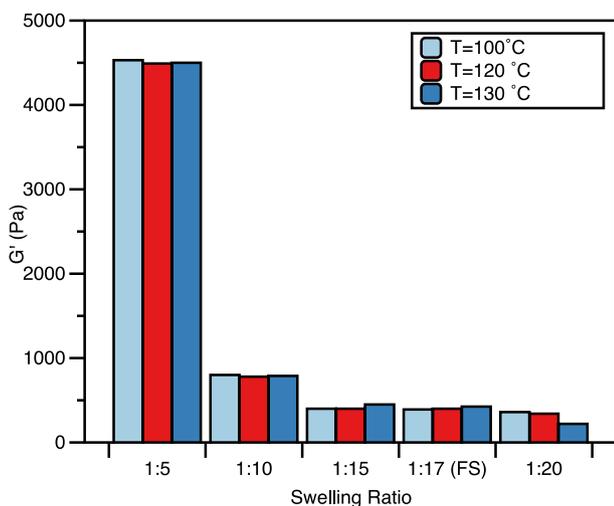


Fig. 13. Effect of swelling ratio on HT-RPPG elastic modulus (Time-Sweep).

$$F_{rr} = \left( \frac{k_{initial}}{k_{post}} \right)_q \quad (3)$$

where  $k_{initial}$  is the initial permeability and  $k_{post}$  is permeability after the treatment, both of them were calculated by using the following Darcy's law [9]:

$$k = \frac{q\mu L}{A\Delta P} \quad (4)$$

where  $q$  and  $\mu$  were the flow rate (cc/s) and viscosity of the liquid (cP).  $L$  and  $A$  were the length (cm) and cross-sectional area (cm<sup>2</sup>) of the plugged fractures.  $\Delta P$  was the pressure change (atm).

To better describe the blocking performance of HT-RPPG, blocking efficiency of HT-RPPG was calculated with the following equation [17]:

$$\text{BlockingEfficiency} = \left( 1 - \frac{1}{F_{rr}} \right) \times 100\% \quad (5)$$

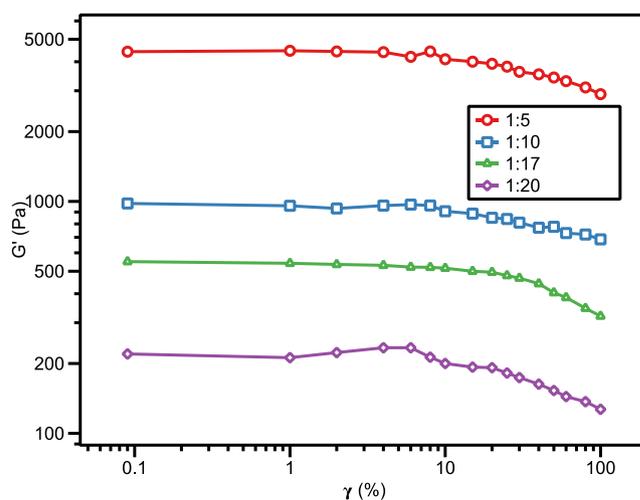


Fig. 14. Effect of swelling ratio on HT-RPPG elastic modulus (Strain-Sweep).

### 3. Results and discussion

#### 3.1. HT-RPPG re-crosslinking behavior and microstructure

To observe the re-crosslinking process of HT-RPPG, dry HT-RPPG samples (shown in Fig. 3(a), size 2–4 mm) were swollen in brine, then they were sealed in the pressure tubes (shown in Fig. 3(b)) and placed at 130 °C. After 48 h aging, the swollen HT-RPPG formed a bulk gel (shown in Fig. 3(c)) and no obvious interface can be observed in this newly formed bulk gel. The microstructures of HT-RPPG before and after re-crosslinking are shown in Fig. 4, new 3-D networks formed after the re-crosslinking process, the scale was changed from 50  $\mu$ m before re-crosslink to 100  $\mu$ m after re-crosslink to present a clear view of the 3-D network.

Swelling Kinetic and Equilibrium Characterization. In general, superabsorbent polymers (SAPs) can swell several times to hundreds in brine, and the swelling ratio and swelling kinetics are affected brine types, concentration, and pH [22]. Therefore, we evaluate the effect of

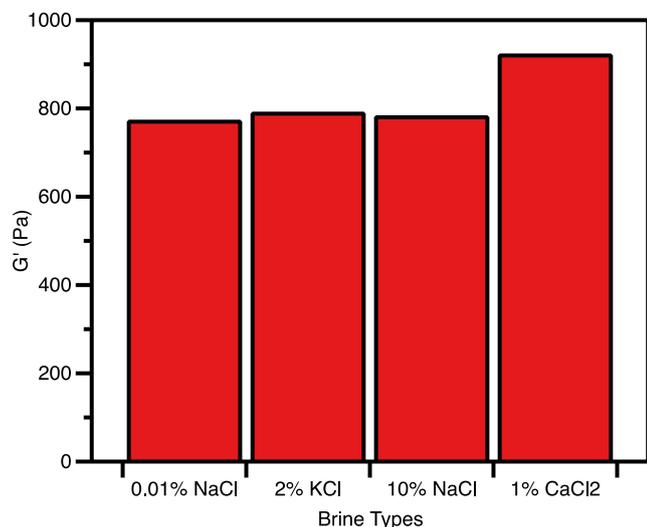


Fig. 15. Effect of brine types on HT-RPPG elastic modulus.

the brine salinity, brine pH as well as particle sizes on swelling kinetic and swelling ratio, and the results are shown in Figs. 5 to 8.

Fig. 5 illustrates the salinity effect on swelling kinetic and equilibrium swelling ratio of HT-RPPG at room temperature (23 °C). A power-law behavior, Voight-based equation was obtained by the swelling kinetic [26].

$$SR_t = SR_c(1 - e^{-t/\tau}) \tag{6}$$

where  $SR_t$  is the swelling ratio at time  $t$  (mL/mL),  $SR_c$  is the equilibrium swelling ratio (“power parameter,” mL/mL),  $t$  is the time (hours) for swelling ratio and  $\tau$  is the “rate parameter” that is related to the  $SR$  at time. The value of  $\tau$  for hydrolyzed and non-hydrolyzed polymer gels are found between 1.3 and 2.5[27]. The result shows that the salinity doesn’t show a significant effect on the swelling kinetic and equilibrium swelling ratio of the HT-RPPG particles. It was because the HT-RPPG is a non-hydrolyzed polymer gel, which means less hydrophilic groups ( $-COO^-$ ) present in its structures, therefore, the monovalent and divalent ions can only have limited effect on the swelling kinetic and equilibrium swelling ratio. Moreover, low polymer hydrolyzed ratio

results in a higher  $\tau$  value for HT-RPPG, according to the Eq. (6), the swelling rate of HT-RPPG was limited. From the results, HT-RPPG took around 18 h to reach 17 times of equilibrium swelling ratio, which was much slower than the other PPGs used in high-temperature reservoirs [18]. This swelling delayed phenomenon which is caused by the screening effect [25] is the favorable property for gel placement [8].

Fig. 6 shows the swelling ratio of HT-RPPG particles in varying pH solutions (pH = 5–9). The pH solutions were prepared by acidified 2% KCl with HCl and alkalinized 2% KCl with NaOH. The swelling ratio was stabilized at 17 times in the range of pH from 6 to 8. The swelling ratio increased with the pH while the pH value was from 5 to 6; and the swelling ratio increased with the pH while the pH value was from 8 to 9 as well. This phenomenon can be explained by the cooperative relation between  $-COOH$  and  $-COO^-$  groups [38]. When the pH of the solution is 5–6,  $-COO^-$  groups turn into  $-COOH$  groups, this will decrease the negative charge repulsion and increase the association between  $-COOH$  groups due to the formation of the hydrogen bond. Thus, the water absorption will decrease because of the larger crosslinking density with the decrease of pH value [19]. However, when the pH is higher than 8,  $-COOH$  groups transfer to  $-COO^-$ , the polymers are hydrolyzed, which causes the resistance of polymer to water permeation decrease and leads to the increase of water absorption [27].

When dealing with the reservoir heterogeneity problems with PPG or RPPG, it’s of importance to select a proper size of particles, because the oversized particles could lead to injectivity problems while the block capacity of undersized particles may not be enough to plug the channels or be flooded out of fluid channels [36]. Several sizes of particles were investigated in this research. Fig. 7 illustrates the particle sizes effect on the swelling behaviors of HT-RPPG particles. The swelling rate increases with the decrease of particle size. The smallest HT-RPPG particles with 0.10–0.25 mm-size have the highest swelling rate and takes less than 5 min to reach the equilibrium swelling ratio of 20 times. For the other size particles, it took about 3, 4, 6, and 18 h to reach the equilibrium swelling ratio of 18 times. Interestingly, with the fastest swelling rate, the smallest size HT-RPPG also has the largest swelling ratio. The possible explanation is the 3-D structure of crosslinked polymers were damaged during the shearing and cutting processes, and this damage might lead to a lower crosslinking density of the RPPG and thus results in a higher swelling ratio. The particles of other sizes have the same equilibrium swelling ratio but different swelling rates. The smaller particles which have larger specific areas make brine diffuse into the polymer gel 3D

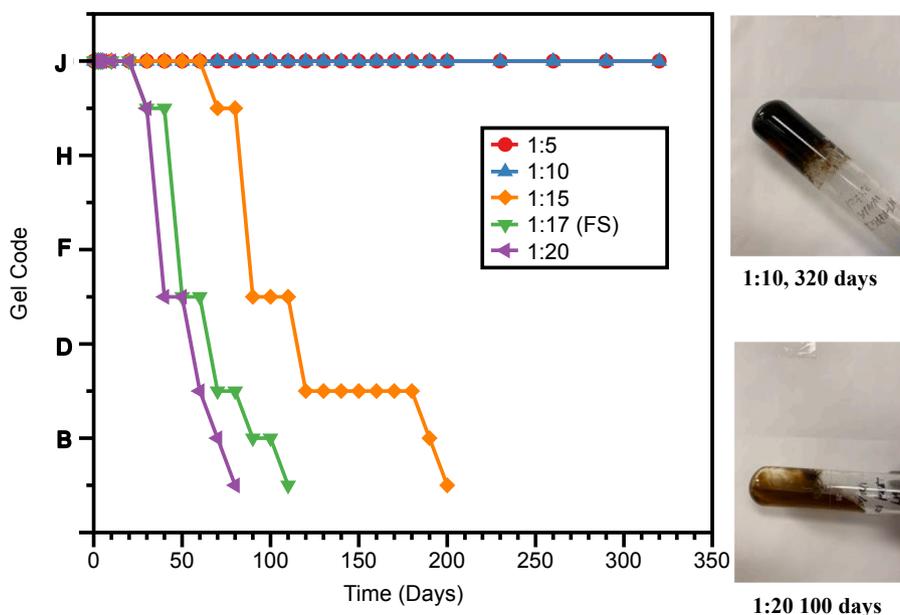


Fig. 16. Durability of HT-RPPG with different swelling ratio in 2% KCl at 120 °C.

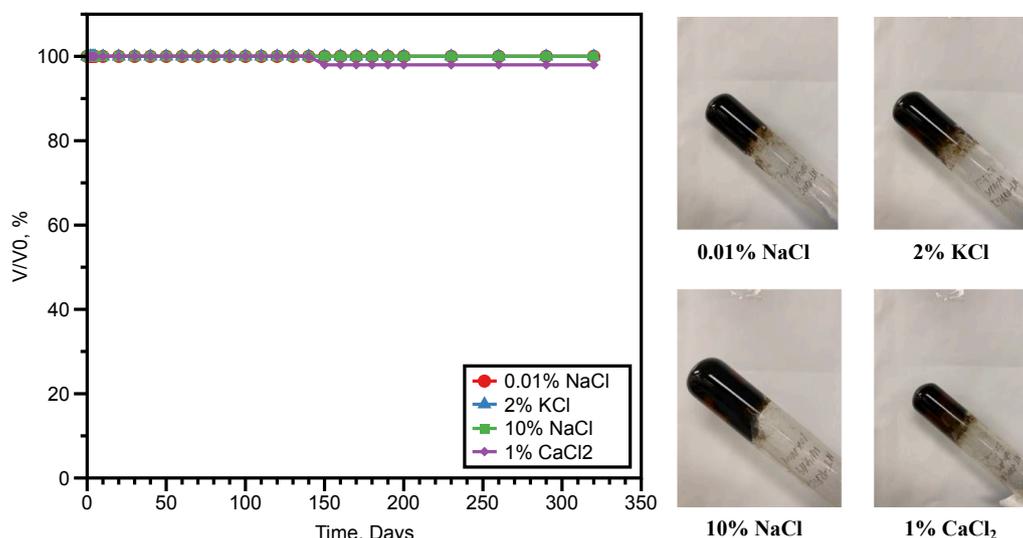


Fig. 17. Durability of HT-RPPG with 1:10 swelling ratio in different brines at 120 °C.

Table 1

Bottle test gel strength code.

Gel Code	Descriptions
A (1)	No Detectable Gel Formed
B (2)	Highly Flowing Gel
C (3)	Flowing Gel
D (4)	Moderately Flowing Gel
E (5)	Barely Flowing Gel
F (6)	Highly Deformable Gel
G (7)	Moderately Deformable Non-flowing Gel
H (8)	Slightly Deformable Non-flowing Gel
I (9)	Rigid Gel
J (10)	Ringling Rigid Gel

network much faster and therefore can swell faster.

Illustrated in Fig. 8, environment temperature shows a strong effect on the swelling kinetic and swelling ratio of HT-RPPG. It takes 18 h for 2–4 mm-sized HT-RPPG particles to reach the equilibrium swelling state at room temperature (23 °C). With a reservoir temperature increases,

both the swelling rate and ratio of HT-RPPG increase.

### 3.2. Re-crosslinking time characterization

The effects of temperatures, swelling ratios (ml/g), feeding brines, and particle sizes were investigated to study the re-crosslinking behaviors of HT-RPPG. Fig. 9 shows the re-crosslinking time of HT-RPPG affected by temperatures. 2% KCl was used to prepare the 2–4 mm sized HT-RPPG particles with a swelling ratio (particle-brine ratio) of 1:10. With the temperature increase, the re-crosslinking rate tends to be increased due to the reaction stimulated by high temperatures.

Fig. 10 shows the swelling ratio (2% KCl, 2–4 mm particles) effect on re-crosslinking time at (a) 120 and (b) 130 °C. The swelling ratio was controlled from 1:5 to 1:20. In each temperature, with the swelling ratio increase, the start time of re-crosslinking tends to be delayed. However, there was a different story when excessive water presented (swelling ratio 1:20), polymer diffusion/relaxation during swelling [29] would affect the swelling start and interval time, which means the particles can swell to enlarge the contact interface and re-crosslinking process can be

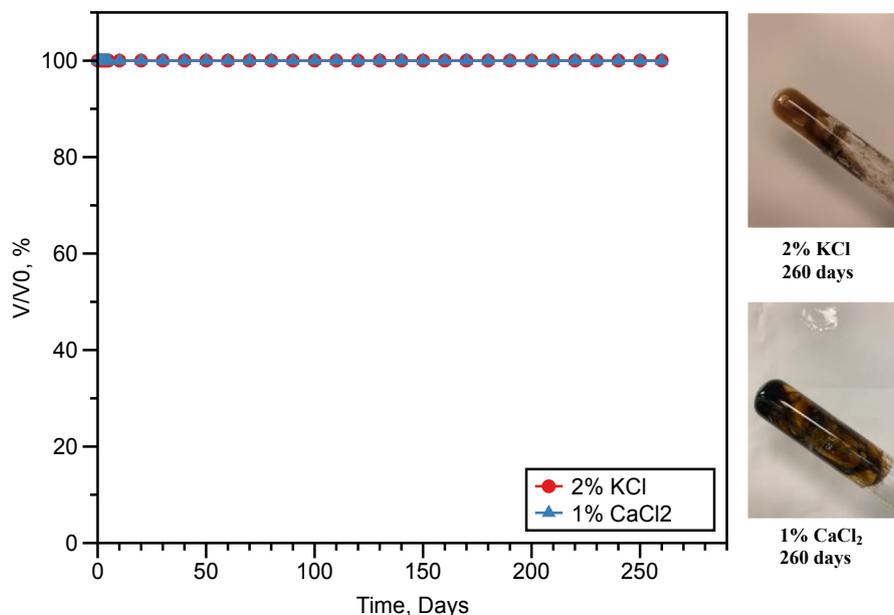


Fig. 18. Durability of HT-RPPG with 1:10 swelling ratio in different brines at 130 °C.

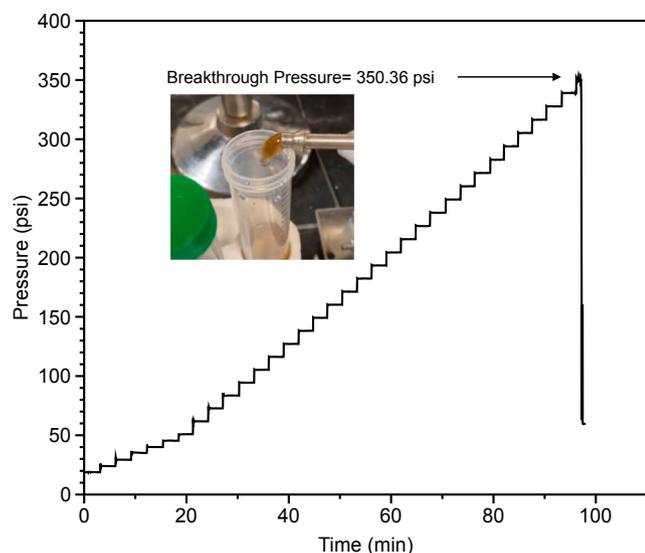


Fig. 19. Breakthrough pressure measurements for the gel-treated tubing.

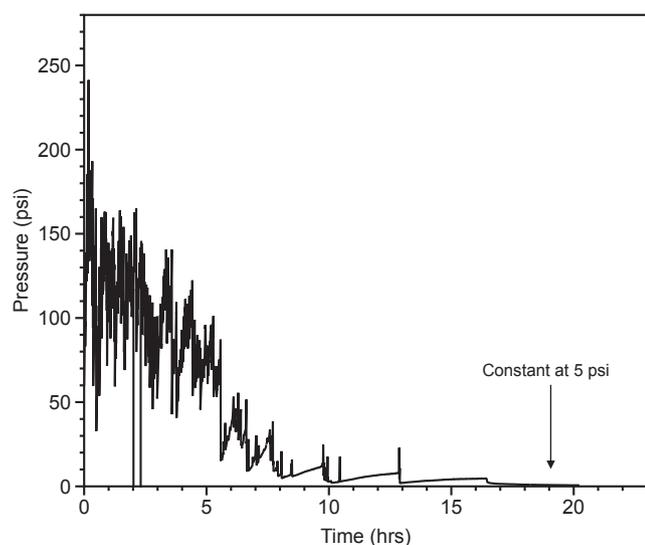


Fig. 20. Pressure measurements for post water flooding of gel-treated tubing after breakthrough.

speeded up with larger contact interface. Compared with the re-crosslinking time of 1:20 swelling ratio in 120 °C, HT-RPPG particles in 130 °C not only have a higher diffusion / swelling rate to enlarge the contact interface but also a higher re-crosslinking reaction rate stimulated by higher temperature. These lead to an earlier re-crosslinking start time and a shorter interval.

Fig. 11 shows the effect of brine types on re-crosslinking time. The testing temperature was set at 120 °C and the HT-RPPG swelling ratio was set at 1:10. The HT-RPPG fed by 0.01% NaCl was the earliest to start the re-crosslinking process among the samples and has the shortest reaction interval. While an obvious delay of re-crosslinking reaction is detected on particles prepared with 1% CaCl<sub>2</sub>. This is because the sodium alginate was preloaded in the HT-RPPG particles to enhance the gel strength by forming “eggshell” crosslinked structures with ionic bonding of divalent or trivalent ions (e.g. Ca<sup>2+</sup>) [13,41]. Therefore, the re-crosslinking can be delayed.

Fig. 12 illustrates the effect of particle sizes on the swelling behavior of HT-RPPG. The HT-RPPG particles were swollen in 2% KCl with a 1:10 swelling ratio and sealed at 130 °C. With the decrease of the particle

sizes, HT-RPPG tends to start re-crosslinking reaction earlier and the interval tends to be shorter due to the relatively larger contact area among smaller particles. Thus, the particle sizes show a strong effect on the re-crosslinking behavior of HT-RPPG.

**Rheological Strength Evaluation.** The effect of swelling ratios of HT-RPPG particles and re-crosslinking temperatures on elastic modulus ( $G'$ ) of re-crosslinked gel is illustrated in Fig. 13 (Time-Sweep) and Fig. 14 (Strain Sweep). As temperature increases from 100 to 130 °C, there are no obvious changes of  $G'$ . However, with the swelling ratio increase from 1:5 to 1:20,  $G'$  decreases dramatically from around 4470 Pa to 320 Pa. In Fig. 14, the increase swelling ratio doesn't show the significant effect on the linear viscoelastic region, the linear viscoelastic region can be considered up to 10% of shear strain.

Fig. 15 demonstrates the relationship between feeding brine types and the  $G'$  of HT-RPPG. The swelling ratio was fixed at 1:10 and the re-crosslinking temperature was 120 °C. The  $G'$  of re-crosslinked HT-RPPG particles is higher when fed with 1% CaCl<sub>2</sub>. As mentioned earlier, sodium alginate embedded in the particles can crosslink with divalent or trivalent to increase the crosslink density [40]. Therefore, the strength of HT-RPPG is enhanced when in contact with Ca<sup>2+</sup>.

### 3.3. Thermostability test

Crosslinked poly (acrylamide-co- n-vinyl-2-pyrrolidone) was used as the backbone of HT-RPPG to improve the thermostability. As the comonomer, NVP (n-vinyl-2-pyrrolidone) can protect AM (acrylamide) groups against extensive thermal hydrolysis [24]. Gel strength code and volume changes were recorded during the aging and used to determine the stability of HT-RPPG. As a water management agent, decreasing in strength or volume (caused by dehydration or degradation) can result in the water breakthrough, which can be considered as unstable. Shown in Figs. 16 and 17, at 120 °C, HT-RPPG samples swollen by 2% KCl with 1:5 and 1:10 swelling ratio kept their initial volume without any strength loss and were considered as “ringing gel” after aged for more than 320 days. The oxygen that remained in the tube caused HT-RPPG to become darker in color. With the swelling ratios higher than 1:15, re-crosslinked HT-RPPGs became “flowable gel” after aged for 30–60 days according to the Bottle Test Gel Strength Code shown in Table 1, [32]. However, the RPPG with the swelling ratio of 10 have been stable for more than 320 days so far, and the thermostability is not affected by the brine types. The thermostability of HT-RPPG at 130 °C was shown in Fig. 18, with the swelling ratio of 10, HT-RPPG can keep thermostable for more than 260 days and so far.

### 3.4. HT-RPPG blocking performance evaluation in conduit model

The HT-RPPG with the swelling ratio of 10 was first injected into the tube at a flow rate of 0.1 cc/min until the injection pressure was stabilized, less than 5 wt% of dehydration was detected during this process. And then, the tube filled with the RPPG was sealed and placed into a 130 °C oven for 48 h to allow the swollen gel particles being re-crosslinked. After that, the tube was mounted to the experimental apparatus again for the breakthrough pressure and blocking efficiency tests.

The breakthrough pressure was tested using step-wise pressure increasing method. A strong bulk gel was observed from the outlet of the tube as shown in Fig. 19 when the pressure was increased to 350.36 psi, which could be converted to a pressure gradient of 427.26 psi/ft.

After the breakthrough was observed, the brine-injection flow rate was changed to 0.5 cc/min. Shown in Fig. 20, the stabilized injection pressure finally reached 5 psi after being flooded for 16.5 h, the calculated residual resistance factor  $F_{rr}$  is about 115,914, which is equivalent to the blocking efficiency of 99.999%.

#### 4. Conclusions

A novel high temperature resistant re-crosslinkable preformed particle gel (HT-RPPG) was systemically evaluated as a conformance control agent for the reservoirs with abnormal fluid channels such as opening fractures, voids, conduits, and so on. Swollen particles of HT-RPPG can re-crosslink to form a robust bulky gel after being placed in the target location. The swelling behaviors including equilibrium swelling ratio and swelling kinetics of HT-RPPG are not significantly affected by the brine types. The re-crosslinking behaviors of HT-RPPG were affected by temperatures, swelling ratios, brine types as well as particles sizes. At 100, 120, and 130 °C, HT-RPPGs re-crosslinked from the particles with a smaller swelling ratio exhibit a higher rheological strength. The long-term thermostability test shows no observed volume or strength loss detected on HT-RPPG with 1:5 and 1:10 swelling ratio for at least 320 days at 120 °C and 260 days at 130 °C. Plus, the re-crosslinked HT-RPPG can provide excellent blocking performance for a conduit model and the breakthrough pressure can reach to 427 psi/ft.

#### CRedit authorship contribution statement

**Bowen Yu:** Writing-Original draft; Investigation. **Shuda Zhao:** investigation. **Yifu Long:** Investigation. **Baojun Bai:** Supervision, Project administration. **Thomas Schuman:** Supervision.

#### 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.

#### References

- Amiri S. Synthesis and characterization of acrylamide/(3-acrylamidopropyl) trimethyl ammonium chloride solution and acrylamide/Na-montmorillonite hydrogels via controlled radical polymerization for use as high-temperature and high-salinity oil reservoirs. *Polym Bull* 2018;1–17. <https://doi.org/10.1007/s00289-018-2394-y>.
- Bai B, Li L, Liu Y, Liu H, Wang Z, You C. Preformed particle gel for conformance control: factors affecting its properties and applications. *SPE Reserv Eval Eng* 2007; 10:415–22. <https://doi.org/10.2118/89389-PA>.
- Bai B, Liu Y, Coste JP, Li L. Preformed particle gel for conformance control: transport mechanism through porous media. *SPE Reserv Eval Eng* 2007;10:176–84.
- Bai B, Zhang H. Preformed-particle-gel transport through open fractures and its effect on water flow. *SPE J* 2011;16:388–400. <https://doi.org/10.2118/129908-pa>.
- Bryant SL, Bartosek M, Lockhart TP, Giacca D. Polymer gels for high temperature water shutoff applications. *SPE J* 1997;2:447–54. <https://doi.org/10.2118/36911-PA>.
- Chauveteau G, Omari a, Tabary R., 2001. New size-controlled microgels for oil production. *SPE Int. Symp. Oilf. Chem.* 1–8. <https://doi.org/10.2118/64988-MS>.
- Chu H, Liao X, Dong P, Chen Z, Zhao X, Zou J. An automatic classification method of well testing plot based on convolutional neural network (CNN). *Energies* 2019; 12. <https://doi.org/10.3390/en12152846>.
- Coste, J.-P., Liu, Y., Bai, B., Li, Y., Shen, P., Wang, Z., Zhu, G., 2000. In-Depth Fluid Diversion by Pre-Gelled Particles. Laboratory Study and Pilot Testing. Society of Petroleum Engineers (SPE). <https://doi.org/10.2118/59362-ms>.
- Darcy, H., 1856. Les fontaines publiques de la ville de Dijon: exposition et application: Victor Dalmont.
- De KS, Aluru NR, Johnson B, Crone WC, Beebe DJ, Moore J. Equilibrium swelling and kinetics of pH-responsive hydrogels: models, experiments, and simulations. *J Microelectromechanical Syst* 2002;11:544–55. <https://doi.org/10.1109/JMEMS.2002.803281>.
- Durán-Valencia C, Bai B, Reyes H, Fajardo-López R, Barragán-Aroche F, López-Ramírez S. Development of enhanced nanocomposite preformed particle gels for conformance control in high-temperature and high-salinity oil reservoirs. *Polym J* 2014;46:277–84. <https://doi.org/10.1038/pj.2013.99>.
- Formulas and Calculations for Petroleum Engineering, 2019. , Formulas and Calculations for Petroleum Engineering. <https://doi.org/10.1016/c2018-0-00117-6>.
- George M, Abraham TE. Polyionic hydrocolloids for the intestinal delivery of protein drugs: Alginate and chitosan - a review. *J Control Release* 2006. <https://doi.org/10.1016/j.jconrel.2006.04.017>.
- Huang, S., Huang, C., Cheng, L., Liu, T., Chen, Z., Mao, W., 2015. Experiment Investigation of Steam Flooding of Horizontal Wells for Thin and Heterogeneous Heavy Oil Reservoirs 1–10. <https://doi.org/10.2118/177030-ms>.
- Imqam A, Bai B, Al Ramadan M, Wei M, Delshad M, Sepehrmoori K. Preformed-particle-gel extrusion through open conduits during conformance-control treatments. *SPE J* 2015;20:1083–93. <https://doi.org/10.2118/169107-PA>.
- Imqam A, Wang Z, Bai B. Preformed-particle-gel transport through heterogeneous void-space conduits. *SPE J* 2017;22:1437–47. <https://doi.org/10.2118/179705-pa>.
- Li, D.-X., Hou, J.-R., 2009. Research on Profile Control and Water Shut-off Performance of Pre-crosslinked Gel Particles and Matching Relationship between Particle and Pore Size 1 SONG Xin-wang 2 CAO Xu-long 3 CHI Qing-sheng 4 The 3rd Oil production Area of Huanxiling Oil Production Factory, Huanxiling Liaohe Oilfield, Canadian Research & Development Center of Sciences and Cultures. <https://doi.org/10.3968/j.ans.1715787020090202.004>.
- Long, Y., Yu, B., Zhu, C., 2019. Conformance improvement for ultra-high-temperature reservoir: A comparative study between hydrostable and conventional preformed particle gel. *Soc. Pet. Eng. - Abu Dhabi Int. Pet. Exhib. Conf.* 2018, ADIPEC 2018 1–10. <https://doi.org/10.2118/192738-ms>.
- Mahdavinia GR, Zohuriaan-Mehr MJ, Pourjavadi A. Modified chitosan III, superabsorbency, salt- and pH-sensitivity of smart ampholytic hydrogels from chitosan-g-PAN. *Polym Adv Technol* 2004;15:173–80. <https://doi.org/10.1002/pat.408>.
- Makwana SB, Patel VA, Parmar SJ. Development and characterization of in-situ gel for ophthalmic formulation containing ciprofloxacin hydrochloride. *Results Pharma Sci* 2016;6:1–6. <https://doi.org/10.1016/j.rinphs.2015.06.001>.
- McCool S, Li X, Willhite GP. Flow of a polyacrylamide/chromium acetate system in a long conduit. *SPE J* 2009;14:54–66. <https://doi.org/10.2118/106059-pa>.
- Mirdarivande S, Sadeghi H, Godarzi A, Alahyari M, Shasavari H, Khani F. Effect of pH, and salinity onto swelling properties of hydrogels based on H-alginate-g-poly (AMPS). *Biosci Biotechnol Res Asia* 2014;11:205–9. <https://doi.org/10.13005/bbra/1256>.
- Mishra, A., Abbas, S., Braden, J., Hazen, M., Li, G., Peirce, J., Smith, D.D., Lantz, M., 2016. Comprehensive review of fracture control for conformance improvement in the Kuparuk River Unit - Alaska, in: *Proceedings - SPE Symposium on Improved Oil Recovery. Society of Petroleum Engineers (SPE)*, pp. 11–13. <https://doi.org/10.2118/179649-ms>.
- Moradi-Araghi, A., Cleveland, D.H., Westerman, I.J., 1987. DEVELOPMENT AND EVALUATION OF EOR POLYMERS SUITABLE FOR HOSTILE ENVIRONMENTS: II - COPOLYMERS OF ACRYLAMIDE AND SODIUM AMPS., in: *Society of Petroleum Engineers of AIME, (Paper) SPE*, pp. 319–326. <https://doi.org/10.2118/16273-ms>.
- Muthukumar M. Screening effect on viscoelasticity near the gel point. *Macromolecules* 1989;22:4656–8. <https://doi.org/10.1021/ma00202a050>.
- Omidian H, Hashemi SA, Sammes PG, Meldrum I. A model for the swelling of superabsorbent polymers. *Polymer (Guildf)* 1998;39:6697–704. [https://doi.org/10.1016/S0032-3861\(98\)00095-0](https://doi.org/10.1016/S0032-3861(98)00095-0).
- Pourjavadi A, Mahdavinia GR. Superabsorbency, pH-sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-poly(acrylamide) hydrogels. *Turkish J Chem* 2006;30:595–608.
- Pu, J., Bai, B., Alhuraishawy, A., Schuman, T., Chen, Y., Sun, X., 2018. A novel re-crosslinkable preformed particle gel for conformance control in extreme heterogeneous reservoirs. *Proc. - SPE Annu. Tech. Conf. Exhib.* 2018-Sept. <https://doi.org/10.2118/191697-ms>.
- Pu J, Zhou J, Chen Y, Bai B. Development of thermotransformable controlled hydrogel for enhancing oil recovery. *Energy Fuels* 2017;31:13600–9. <https://doi.org/10.1021/acs.energyfuels.7b03202>.
- Saghafi HR, Naderifar A, Gerami S, Emadi MA. Improvement in thermo-chemical swelling of nanocomposite preformed particle gels for conformance control in harsh oil reservoir conditions. *Can J Chem Eng* 2016;94:1880–90. <https://doi.org/10.1002/cjce.22577>.
- Sun L, Li D, Pu W, Li L, Bai B, Han Q, et al. Combining preformed particle gel and curable resin-coated particles to control water production from high-temperature and high-salinity fractured producers. *SPE J* 2020;25:938–50. <https://doi.org/10.2118/198887-PA>.
- Sydansk, R.D., 1988. A New Conformance-Improvement-Treatment Chromium(III) Gel Technology. *SPE Enhanc. Oil Recover. Symp.*
- Targac, G., Gallo, C., Smith, D., Huang, C.K., Autry, S., Peirce, J., Baohong, L., 2020. Case history of conformance solutions for west sak wormhole/void space conduit with a new reassembling pre-formed particle gel RPPG, in: *Proceedings - SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers (SPE)*. <https://doi.org/10.2118/201302-ms>.
- Wang L, Long Y, Ding H, Geng J, Bai B. Mechanically robust re-crosslinkable polymeric hydrogels for water management of void space conduits containing reservoirs. *Chem Eng J* 2017;317:952–60. <https://doi.org/10.1016/j.cej.2017.02.140>.
- Wang Z, Bai B. Preformed-particle-gel placement and plugging performance in fractures with TIPS. *SPE J* 2018;23:2316–26. <https://doi.org/10.2118/193997-PA>.
- Wu, D., Zhou, K., An, Z., Hou, J., 2018. Experimental study on the matching relationship between PPG Size and reservoir heterogeneity, in: *Society of Petroleum Engineers - SPE International Heavy Oil Conference and Exhibition 2018, HOCE 2018. Society of Petroleum Engineers*. <https://doi.org/10.2118/193709-MS>.
- Wu DY, Meure S, Solomon D. Self-healing polymeric materials: A review of recent developments. *Prog Polym Sci* 2008;33:479–522. <https://doi.org/10.1016/j.progpolymsci.2008.02.001>.
- Zhang X, Wang X, Li L, Zhang S, Wu R. Preparation and swelling behaviors of a high temperature resistant superabsorbent using tetraallylammonium chloride as crosslinking agent. *React Funct Polym* 2015;87:15–21. <https://doi.org/10.1016/j.reactfunctpolym.2014.12.006>.

- [39] Zhao H, Zhao P, Bai B, Xiao L, Liu X. Using associated polymer gels to control conformance for high temperature and high salinity reservoirs. *J Can Pet Technol* 2006;45:49–54. <https://doi.org/10.2118/06-05-04>.
- [40] Zheng Q, Zhao L, Wang J, Wang S, Liu Y, Liu X. High-strength and high-toughness sodium alginate/polyacrylamide double physically crosslinked network hydrogel with superior self-healing and self-recovery properties prepared by a one-pot method. *Colloids Surfaces A Physicochem Eng Asp* 2020;589:124402. <https://doi.org/10.1016/j.colsurfa.2019.124402>.
- [41] Zhou Q, Kang H, Bielec M, Wu X, Cheng Q, Wei W, et al. Influence of different divalent ions cross-linking sodium alginate-polyacrylamide hydrogels on antibacterial properties and wound healing. *Carbohydr Polym* 2018;197:292–304. <https://doi.org/10.1016/j.carbpol.2018.05.078>.
- [42] Zhu D, Hou J, Chen Y, Wei Q, Zhao S, Bai B. Evaluation of terpolymer-gel systems crosslinked by polyethylenimine for conformance improvement in high-temperature reservoirs. *SPE J* 2019;24:1726–40. <https://doi.org/10.2118/194004-PA>.
- [43] Zhu, D., Hou, J., Wei, Q., Chen, Y., Peng, K., 2017. Development of a High-Temperature Resistant Polymer Gel System for Conformance Control in Jidong Oilfield.
- [44] Ziegler, R., Technology, W., International, W., 2017. High-Pressure/High-Temperature Challenges 179184.
- [45] Jia H, Yang XY, Zhao JZ. Development of a novel in-situ-generated foamed gel as temporary plugging agent used for well workover: Affecting factors and working performance. *SPE J*. 2019;24:1757–76. <https://doi.org/10.2118/194215-PA>.