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Lessons Learned from Laboratory Study and Field Application of Re-Crosslinkable Preformed Particle Gels RPPG for Conformance Control in Mature Oilfields with Conduits/Fractures/Fracture-Like Channels

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Abstract

This paper surveys the role of re-crosslinkable preformed particle gels (RPPG) in addressing conformance challenges within mature oilfields. Despite widespread preformed particle gel (PPG) application in 15,000+ wells, their limitations in sealing fractures and conduits prevalent in mature reservoirs have driven the development of RPPG formulations. Synthesized in various sizes from micrometer to millimeter levels, these environmentally friendly RPPGs are tailored for diverse reservoir conditions. Findings showcase the successful laboratory-scale creation and upscaling of RPPG products, offering adaptability to temperatures from 20 to 175°C, customizable sizes, swelling ratios (5 to 40 times), and re-crosslinking times spanning minutes to days. Field applications, notably in Alaska's West Sak field, demonstrate the efficacy of RPPG in resolving Wormhole/Void Space Conduit issues. The paper outlines preferred functionality, properties, evaluation methods, application conditions, and field outcomes, emphasizing RPPG's amalgamation of PPG advantages and in-situ gels into a singular composition, mitigating uncertainties while markedly improving plugging efficiency in fractures and conduits through a rubber-like bulk gel formation. This comprehensive review presents RPPG as a pivotal innovation, poised to revolutionize conformance strategies in many mature oilfields, offering a promising solution to prevailing reservoir challenges

Introduction

Reservoir heterogeneity is one significant issue leading to early excess water production in water flooding reservoirs or early gas production in gas flooding reservoirs. Gel treatments have been widely implemented as a cost-effective method to reduce the reservoir heterogeneity by reducing the permeability of high permeability zones/streaks/fractures/voids during hydrocarbon production, from which more oil can be swept from reservoirs and excess water/gas production can be reduced. Traditionally, in-situ gels have been widely used to control reservoir conformance. The mixture of polymers and crosslinkers and other chemical additives, called gelant, is injected into the target formation and form a gel to fully or partially seal the formation at the reservoir temperature (Sydansk et al. 1992). However, some uncertainties in gelation seriously impact the results of in-situ gel treatments, including:

- The polymer in a gelant is susceptible to degradation from the shears generated by pumps, wellbores, and the porous media in reservoirs, significantly impacting both gelation time and gel quality.
- Chromatographic phenomena arise as a gelant transports through porous media. Typically composed of polymer, crosslinker, and additives, the diverse compositions exhibit varying transport abilities and adsorption rates in porous media. This leads to changes in the gelant composition from near wellbore to the in-depth of a reservoir, thereby challenging the control of gel quality as initially designed.
- During its propagation in formations, a gelant undergoes dilution by formation water, resulting in a shift in the ratio of different components. Consequently, controlling the gel quality becomes challenging.

Another area of interest in gel treatments emerged with the introduction of preformed particle gels in 1996 (Bai et al. 2007). These particle gels are synthesized at surface facilities before injection, eliminating gelation in the reservoir. As a result, they can effectively overcome the distinct drawbacks inherent in in-situ gelation systems mentioned above. A variety of preformed particle gels have been successfully developed, including preformed particle gels (PPGs) (Bai et al. 2007, Schuman et al. 2022), microgels (Chauveteau et al. 2000, Rousseau et al. 2005, Zaitoun et al. 2007), pH-sensitive gels (Al-Anazi et al. 2002, Huh et al. 2005), and temperature-sensitive submicron-sized polymers (bright water) (Pritchett et al. 2003, Frampton et al. 2004). These particles primarily differ in size (Bai et al. 2013). Various publications have highlighted the economic implementation of PPGs, microgels, and submicron-sized particles to reduce water production and increase oil production in mature oil fields. For instance, it was reported that PPGs have been successfully applied in more than 10,000 injection wells by 2013 (Bai et al. 2013), and their application has continued to grow since then. Nevertheless, recent research has identified some limitations of particle gels, as listed below:

- Millimeter-sized particles can notably decrease the permeability of high zones such as streaks, fractures, and fracture-like features, including voids and conduits, resulting from water and CO_2 flooding. However, their ability to completely obstruct these high-permeability features, particularly in the presence of open fractures, is constrained (Zhang et al. 2011, Imqam et al. 2015). Some field applications have also illustrated that these particles may not effectively seal formations as expected, potentially due to being flushed out. Therefore, there is a necessity to innovate new types of millimeter-sized particles capable of forming associations or recrosslinking after placement in extremely high conductive features, thus augmenting their blocking efficiency.
- Injecting swelling-retarding nano- or micrometer particles for in-depth fluid flow control and large volume of gel treatments is a plausible idea for many people in the industry. People believe that (1) particles can be easily injected into a reservoir before swelling because of their smaller size; (2) the particles can better block the channels after travelling to the in-depth of a formation and swell there because of its bigger size. However, the fact is that particles will become much weaker if they swell more, which raises the question as to which type of particles can flow mostly easily through porous media: small, strong particles or large, weak particles. Our experimental results indicate that large, fully swollen particles transport much more easily through both open fractures and porous media than small, partially swollen particles (Zhang et al. 2011, Almohsin et al. 2014). Our results also showed that the fully swollen particles have less resistant to water that partially

swollen particles even the former has a larger size. These results indicate the idea of delaying swelling rate might not favorable for improving particle propagation into the in-depth of a reservoir and enhancing blocking efficiency. Therefore, it is important to develop a new type of nano- or micrometer-sized particles that can re-associate or recrosslinking together after transporting into the in-depth in a reservoir, where the associated/recrosslinked particles can significantly reduce the rock permeability.

To overcome the major drawbacks of current particle gels and in-situ gels mentioned above, we develop a new type of particle gels, called re-associate or re-crosslinked preformed particle gel (RPPG). This type of particles is synthesized by multiple compositions of chemicals, including monomer/polymer, crosslinkers and additives. When the particles are injected into formation, the multiple compositions that are in cooperated into a single particle can transport through formation in the form of single particle, which can avoid the major problems of shear degradation, chromatographic and dilution inherent in in-situ gels. For the reservoir conformance problems caused by fractures or fracture-like features, such as voids, conduits, the new type of millimeter or micrometer particles will be injected into the high conductive features, where they will re-crosslink together under reservoir temperatures to form bulk gels to block fluid flow. For the reservoir conformance problems caused by matrix (no extremely high permeability streaks or channels or fractures exist in formation), the new type of nano- or micro-particle will be injected into reservoirs. After the particles move into the in-depth of a formation, the particles can re-crosslink to increase fluid flow resistance. Several types of RPPG which are suitable for different reservoir situations have been successfully developed. The novel RPPGs can be used for conformance control, fluid loss control or kick kill treatment in a drilling process, or leakage blocking underground.

In this paper, we outline the preferred functionality for all VSF (Void Space Filler) products, and briefly introduce the RPPG properties, evaluation methods, conditions needed for application, and provide field execution conditions and results. Finally, we discuss where and how the novel products can be best applied in oilfields.

Preferred Functionality for all VSF (Void Space Filler) Products

When conformance control problems are evaluated, the types of problems must be carefully defined. The primary flow conduit or flow path that creates the problem must be clearly understood. This problem analysis and its importance to developing an effective solution was well described in a recent JPT article (Smith 2023). In many cases the primary problem flow path is through some VSC (Void Space Conduit). Some like to call these features "Super-K" flow paths. However, it should be clear that these problems have nothing to do with permeability. These are purely liquid filled open flow paths that can vary significantly in size and shape. Their character can be developed in many ways. Some are sand production wormholes as identified and characterized in SPE papers (Peirce et al. 2014, Targac et al. 2020). Some are fractured (either induced or natural) systems that have commonly been enhanced through dissolution or erosion of rock. See SPE-103044 (Smith et al. 2006) and SPE-190209 (Aamodt et al. 2018) as examples of very large systems. Others can be tighter or narrower fractures which have been identified and characterized in a multitude of papers. The point remains that these VSC flow path systems, however they are developed, become very dominant in their influence on damaging the volumetric sweep efficiency or conformance control of any flood process. Because of the extreme nature of these problems the only options are to shut in the well or wells that are involved or attempt to resolve the problem by a variety of methods to fill the VSC to some level with a VSF (Void Space Filler) product. Many of these VSC systems penetrate deep into the producing formation. Thus, they cannot be effectively resolved with a near wellbore shutoff solution. Because of these characteristics the development of effective VSF products has become very important.

When outlining the basic needs for solving these VSC problems, the following desired VSF product characteristics can be stated:

1. The VSF product is desired to have low in-place cost – (Desired due to volume of VSF needed)
2. The VSF product should be easy to mix and pump.
3. The VSF product should be effective in uniformly displacing and filing a VSC (Limited or no gravity segregation-Top to bottom and moderate viscosity for complete coverage etc.)
4. The VSF product should have the ability to be pumped over a large rate range: (1 to 10 BPM.)
5. The VSF product should enter and occupy only void space (limited/no formation rock matrix permeable entry)
6. The VSF product should have properties that prevent, limit or control contamination with reservoir fluids.
7. After placement, the VSF product needs to rapidly develop enhanced mechanical strength or ability to resist redistribution or removal.
8. After placement, the VSF product should have very limited or no inherent permeability (needs to be significantly << formation permeability)
9. Finally, the VSF product needs chemical, biological, mechanical, and thermal stability; (resists breakdown by acid, bugs, & pressure and thermal cycles)

Historically it has been very difficult to achieve all these properties with a single product. For example, cement systems achieve the strength requirements for desired VSC control products, but they have several failings including cost, ease of mixing, ability to control contamination, and uniform VSC displacement due to gravity segregation. Some of these limitations can be improved by using N2 and surfactant to create nitrified cement blends with higher viscosity and lower density. However, the cost and volume limitations are often significant enough to make the solution with nitrified cement uneconomic.

Since all the older products have a variety of limitations and difficulties it was decided that a new product might be possible which could resolve many of the older product limitations. This led to the idea of developing a PPG type of product but with enhanced properties that would allow bonding of the product which eliminates a key failure of current PPG products, which is its ability to resist redistribution or removal of the product.

RPPG Development Process and Products being developed

Considering the drawbacks of in-situ gel and PPG in treating open fractures or void space conduits, in early 2014, our group initiated to develop a new product termed re-crosslinkable PPG (RPPG) that combines the advantages of both in-situ gel and PPG (Targac et al. 2020, Pu et al. 2019). RPPG offers us a new way to plug void space conduits where a concentrated mechanical robust gel plug is needed. RPPG can be recognized as a new type of void space filler that can only enter the void space and it can be hardly moved after re-crosslinking. By balancing the mixing/swelling time and pumping rate/time, we can place a concentrated gel in fracture, and after fully re-crosslinking the gel pack is almost impermeable to both water or gas. Besides, RPPG can attach firmly to the rock surface owing to its potent adhesion properties.

RPPG belongs to PPG capable of swelling but not dissolving in brine. It comprises two main components, which are acrylamide-based polymers and a re-crosslinking agent. The re-crosslinking ability was achieved by adding a non-reacted crosslinker during the polymer synthesis. Inspired by the self-healing materials, we successfully synthesized several re-crosslinkable gel systems through dynamic metal-ligand interactions (Pu et al. 2019). Metal ions which can interact with the polymer chains through electrostatic interaction were added during the hydrogel synthesis to endow the hydrogel with self-healing properties (Mozhdehi et al. 2014, Song et al. 2023, Song, Zhai, et al. 2022). Depending on the requirements on re-crosslinking time, hydrolytic thermal stability, and environmental regulations, the re-crosslinking agent can also be organic materials. The polymer backbone can also be manipulated to reach the goal of CO_2 and high-temperature resistance. The polymer composition significantly affects the swelling kinetics, thermal stability, and gel strength. For example, with the increasingly stringent environmental regulations in offshore oil reservoirs such as the North Sea Ekofisk region, our group developed several environmentally friendly RPPGs by using environmentally friendly re-crosslinking agents and thermally stable monomers. These HT-RPPGs are nontoxic to terrestrial and aquatic creatures (Yu et al. 2022). RPPG, depending on the particle size, can be synthesized through aqueous free radical polymerization, inverse emulsion polymerization, and precipitation polymerization. The particle size can be controlled from nanometer to millimeter, depending on the needs of field applications.

The pristine RPPG is synthesized through the commonly used free radical polymerization. While we are not satisfied with the gel strength and swelling kinetics that we initially designed. Therefore, we further polish the RPPG through polymer backbone structure modification or using additives. We proved that the strength of the re-crosslinked gel can be significantly improved by switching the polymer backbone from linear to branched structure. The strength of both primary and secondary gel and the maximum swelling ratio can be controlled by adopting an interpenetrating network structure.

Figure 1 illustrates the developmental history of RPPG. Since the beginning of the JIP, our group has developed 10 PPG/RPPG products that can be used for water and CO_2 plugging as shown in Table 1, including one ultra-high temperature resistant PPG (HT-PPG), two low-temperature applicable RPPG (LT-RPPG), two medium-temperature salt-resistant RPPG (MT-RPPG), two CO_2-resistant RPPG (CO_2-RPPG), and three high-temperature resistant RPPG (HT-RPPG). LT/CO_2/MT-RPPGs are metallic crosslinker-based RPPG, which can re-crosslink through electrostatic interaction, and the re-crosslinking mechanism of HT-RPPG was based on transamidation. In the case of conformance control in water flooding reservoirs: RPPG products can be applied to treat reservoirs with temperatures ranging from 23 °C to 130 °C, and the HT-PPG can be applied to reservoirs with temperatures up to 150 °C. Besides, RPPG can also be developed to improve the CO_2 sweep efficiency in CO_2 flooding reservoirs. We tested their stability at the temperature ranging of 20-80 °C, and more tests are on-going to see if they can be used in higher temperatures. Table 2 summarizes the stability of different RPPGs.

Table 1—Applicable temperatures of developed products

		Low		Medium				High			
Temperature	°F	68	104	140	149	176	230	248	266	284	302
	°C	20	40	60	65	80	110	120	130	140	150
LT-RPPG*1											
LT-BRPPG*1&2											
MT-RPPG-I*1											
MT-RPPG-II*2											
HT-RPPG-I*1											
HT-RPPG-II*1&2											
HT-BRPPG*1&2											
HT-PPG*1											
CO_2-RPPG*1											
CO_2-BRPPG*1&2											

Commercial product

Lab product

Note*1: Filed patent

Note*2: Lab product with improved gel strength, salt-resistance and thermal stability

Table 2—Evaluation result of current products

Salinity	1~10% NaCl	2~4% KCl	1% $CaCl_2$	Ekofisk FW	OXY SW	OXY IW	TLM FW
LT-RPPG	√	√	√				
LT-BRPPG*1	√	√	√				
MT-RPPG	√	√	√			x	
MT-RPPG*1	√	√	√			√	
HT-RPPG-I	√	√	√	√			√
HT-RPPG-II*1	√	√	√	√			
HT-BRPPG*1	√	√	√	√			
HT-PPG	√	√	√	√			
CO_2-RPPG	√	√	√		√		
CO_2-BRPPG*1	√	√	√		√		

Note*1: Lab product with improved gel strength, salt-resistance and thermal stability
Ekofisk FW: Ekofisk formation water
OXY SW: OXY seawater
OXY IW: OXY Oman injection water
Testing temperature and duration:
LT-RPPG: 20-80 °C, 1 year
CO_2-RPPG: 20-65 °C, 2 months, CO_2 pressure 700-2900 psi
MT-RPPG: 80-110 °C, 1.5 year
HT-RPPG: 80-130 °C, 1.5 year

Commercial product
Lab product

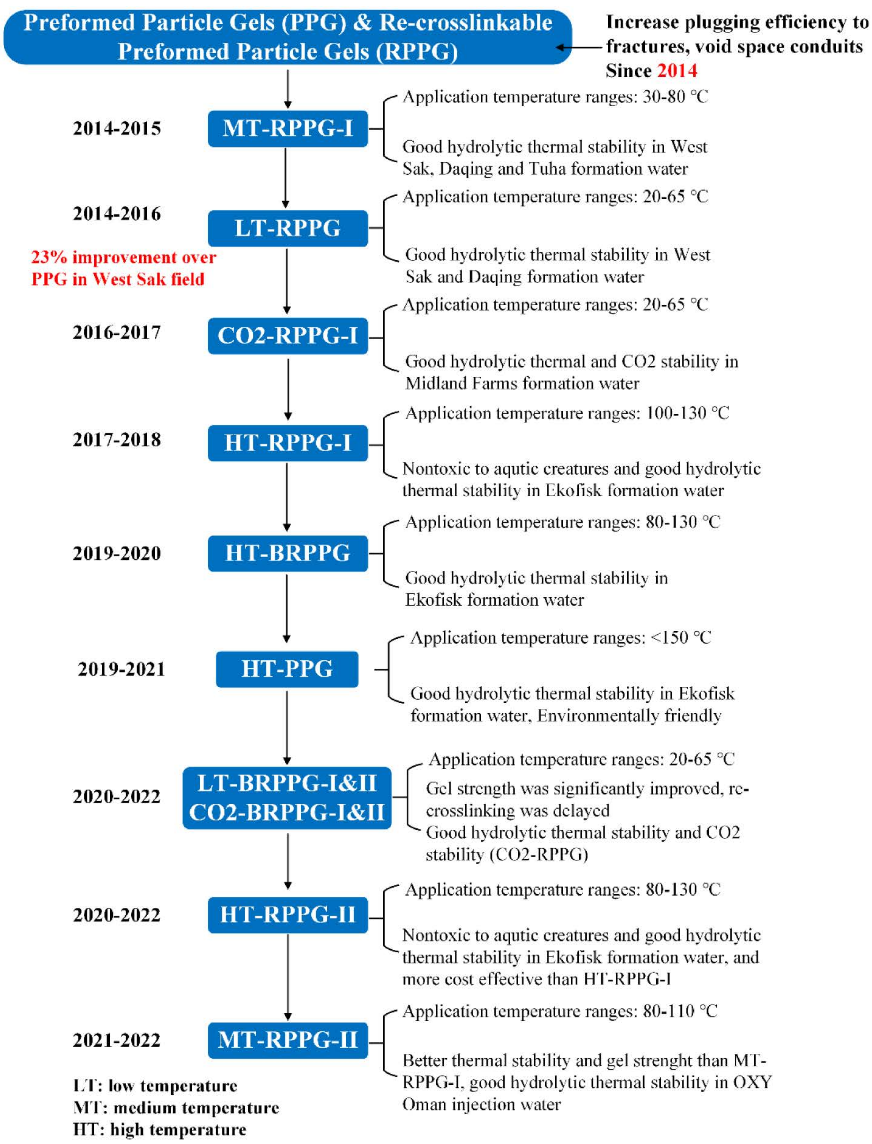

Figure 1—RPPG development history

The following definitions were deployed in this work to reflect the applicable temperature ranges of current PPG/RPPG products.

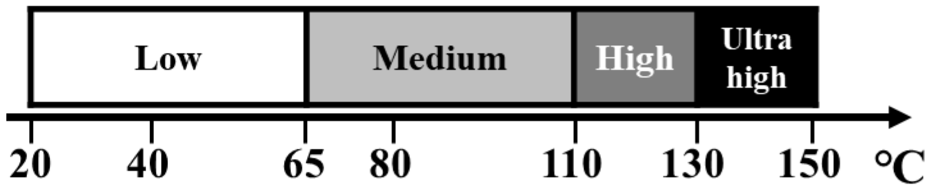

Figure 2—Temperature classification scheme

Major Properties to Be Evaluated and their Evaluation Methods

These products are usually required to be evaluated in the following aspects as shown in Figure 3.

- Swelling kinetics and equilibrium
- Re-crosslinking time
- Gel strength after re-crosslinking
- Hydrolytic thermal stability, or/and CO_2 stability if it is used for CO_2 flooding reservoirs
- Plugging performance

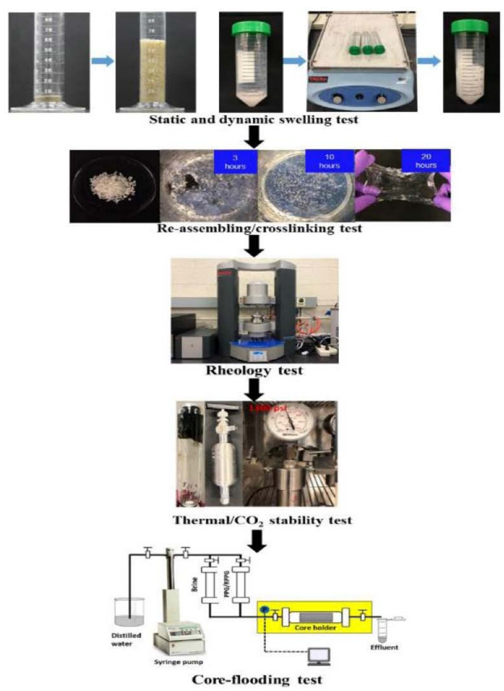

Figure 3—RPPG properties to be evaluated.

Swelling kinetics

Swelling behavior plays an essential role during field treatment design. The two most important parameters that need careful consideration during the field treatment design are swelling rate and ultimate swelling ratio or called equilibrium swelling ratio, which are significantly influenced by temperature and salinity. The swelling kinetics results can help better design the field injection rate to ensure that the gel slurry can reach the target zones with a desired swelling ratio within the transit time (Targac et al. 2020). The transit time is determined by calculating the injection rate and wellbore volume from the surface to the target areas. In addition, we can manipulate the final re-crosslinked gel strength by controlling the amount of water exposed to the gel particles.

The swelling kinetics can be assessed by immersing gel particles in various brines. A typical static swelling kinetics test is shown as follows, 2 g of dry particles with a diameter of 2-4 mm were placed into a scaled cylinder containing 200 mL of 2% KCl. The volume of the hydrated RPPG is recorded periodically, and swelling is considered complete when the volume remains constant for over 24 hours. To simulate the dynamic swelling process, a vibrating shaker is employed. A typical dynamic swelling kinetics test is shown as follows, 1 g of dry particles with a diameter of 2-4 mm was placed into a scaled centrifuge tube containing 100 mL of 2% KCl. The tube was placed on the shaker and the volume of hydrated RPPG was recorded periodically. The swelling ratio is calculated using equation (1), where Vt is the volume of RPPG at different time, Mo is the weight of the dried RPPG. The reason that we use dry RPPG weight rather than the RPPG volume is that weight is much easier to measure during field applications.

$$SR = V_t / M_o \qquad \text{Equation 1}$$

Re-crosslinking time

A bottle test method was deployed to test the re-crosslinking time. Contrary to instantaneous re-crosslinking, this process is characterized by two distinct parameters: the starting time and the interval of the re-crosslinking process. Both time parameters were recorded referring to the phase transition of the swollen particles that had been used for evaluating self-healing materials. The starting time signifies when weak associations first emerge among the particles, while the interval denotes the time span between the starting time and when the particle boundaries vanish. During the bottle test, the morphology of samples was recorded hourly to obtain the re-crosslinking starting time and completing time.

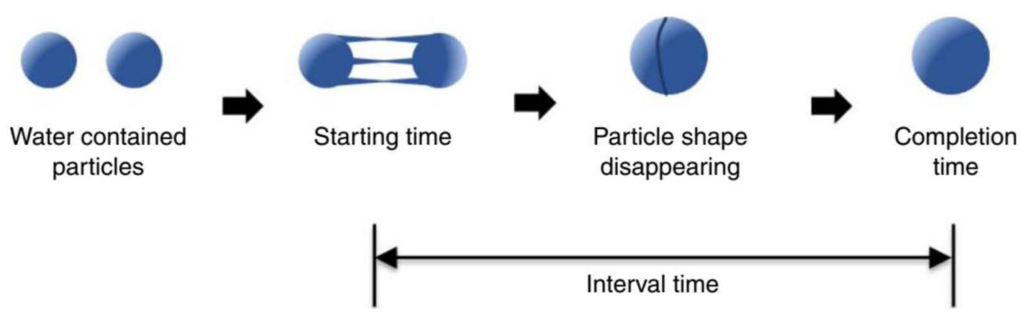

Figure 4—RPPG re-crosslinking process (Pu et al. 2019)

Rheology test

The rheological properties of the RPPG were tested using a rheometer, e.g. Haake MARS III from Thermo Scientific Inc. Strain sweep experiments were conducted to determine the linear strain regime. Samples with size of 2 cm±0.1 cm in diameter and 1.5 mm ± 0.1 mm in height, were measured using the rheometer at ambient temperature (23 °C). The spindle used in this process is P35Ti L, and the gap was set at 1 mm. The test was selected as the oscillation time-dependent experiments model with a fixed frequency of 1 Hz and a controlled strain of 1% to obtain elastic modulus (G') and viscous modulus (G"). G' was used to evaluate the strength of the gel.

Hydrolytic thermal stability tests

A bottle test method was deployed to test the stability of different RPPGs. A typical thermal stability test process is outlined as follows: 2 g of gel particles are added into a high-pressure glass tube containing a certain amount of brine, followed by sparging argon for 20 min before sealing. After that, the high-pressure glass tube was put into the preheated oven. The gel strength was evaluated using the Sydansk code method, and both gel strength and gel volume were monitored during the aging test (Sydansk 1988). High-pressure glass tubes with temperature-resistant O-rings (USA Sealing, size 110, Material: 80 Shore A AFLAS, BATCH No: 180806003) were deployed to prevent leakage during long-term thermal stability tests. It should be noted that oxygen plays a crucial role in the thermal stability of RPPGs at high temperatures, and oxygen can accelerate the degradation of polymer gels. Therefore, the oxygen should be removed as cleanly as possible.

In the case of the CO_2 stability test, high-temperature and high-pressure resistant stainless steel vessels were deployed. After placing the gel slurry, CO_2 was injected into the chamber till reached the designed pressure. A pump and an accumulator were utilized to fill the vessel with CO_2. A typical CO_2 exposure experiment was as follows: 15.0 g of fully reassembled gel was placed in the vessel. Then the vessel was connected to an accumulator pre-filled with CO_2. Subsequently, CO_2 was pumped from the accumulator to the vessel until the vessel pressure attains the designated level. The vessels were sealed, and the gel was extracted at specific intervals to measure the remaining weight and elastic modulus, providing insights into the stability of the gels under CO_2 conditions.

Plugging efficiency test

Man-made sandstone, carbonate or cement fracture models have been deployed to test the plugging performance. Gel slurry is injected into the fracture and after fully re-crosslinking, water and CO_2 breakthrough tests are performed to get the plugging performance and residual resistance factor. The water or CO_2 breakthrough test can be performed through constant pressure or constant flow rate method. Here we show the procedure of constant flow rate method and the detailed procedure of constant pressure method can be found in our previous publication (Song, Ahdaya, et al. 2022). A typical plugging test of RPPG, evaluated using a man-made cement fracture as one example, is shown as follows. The fractured core is prepared using Portland cement. The prepared cement slurry is 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 is put in the middle of the mold vertically during the curing process. The stainless steel is removed after 6 to 8 hours of hydration before the cement was fully set. The experiment procedure involves the following steps. First, the dried gel particles are swelled in the formation water. Then, after absorbing all the free water, the gel slurry is injected into the fracture with a 1 mL/min placement rate till the injection pressure becomes stable. Different from the filed application, where the gel suspension is injected into the fractures, we decide to 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 is sealed and aged at reservoir temperature for three days till fully re-crosslinking. After that, water is injected at a constant flow rate (same as RPPG injection rate) to obtain water breakthrough pressure which is the maximum pressure when the first drop of water is found from outlet. After the water breakthrough, we change the flow rates to 0.1, 0.25, 0.5, 1 and 2 mL/min to get stable pressures at each flow rate. The stable pressure at each flow rate is used to calculate the residual resistance factor (F_{rr}). The residual resistance factor, F_{rr}, is calculated by the following equations:

$$F_{rr} = \frac{k_{before}}{k_{after}} \tag{1}$$

$$k_{initial} = \frac{b^2}{12} \tag{2}$$

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

Brief Summary of Major Products

Currently, a series of PPG and RPPGs have been developed and tailored to reservoirs with diverse temperature and salinity profiles, as illustrated in Figure 1, Table 1 and Table 2. These products are designed to perform effectively across a temperature range from room temperature up to 150°C as shown in Figure 2, accommodating particle sizes ranging from nano-meters to millimeters. Additionally, certain particles have been specifically engineered to enhance CO_2 sweep efficiency by exhibiting resistance to low pH CO_2 conditions. Below, the follow provides concise introductions to some key products that have been documented in literatures.

Low-Temperature RPPG: LT-RPPG (Pu et al. 2019)

At the outset, an RPPG designed for application in temperatures ranging from 40 to 80 °C was developed, exhibiting controllable crosslinking time and robust gel strength upon recrosslinking. However, ConocoPhillips shifted its focus to WestSack in Alaska, characterized by a reservoir temperature around room temperature. Consequently, a Low-Temperature RPPG (LT-RPPG) tailored for such reservoir conditions was formulated and subsequently manufactured. Figure 5 illustrates key properties of the LT-RPPG, encompassing swelling kinetics, re-crosslinking time, and gel strength. The dried gel particle demonstrates the ability to swell and reform into an elastic bulk gel, with a maximum swelling ratio reaching approximately 38. The re-crosslinking time spans from 30 minutes to 35 hours, contingent on the temperature and swelling ratio. The elastic modulus of the fully crosslinked gel can attain levels up to around 11,000 Pa when the swelling ratio is 5.

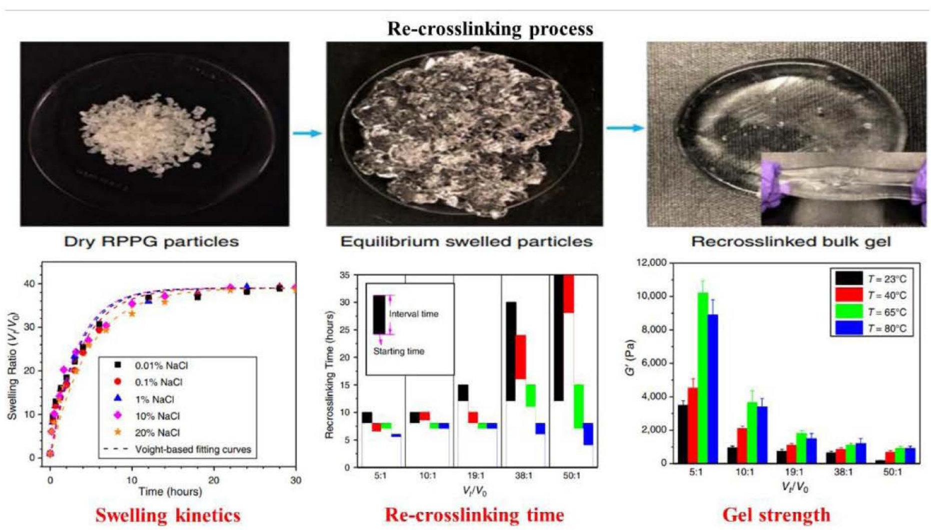

Figure 5—Re-crosslinking, swelling kinetics and rheology of LT-RPPG

Figure 6 shows the thermal stability and plugging performance of LT-RPPG. LT-RPPG has excellent hydrolytic thermal stability, and no free water was found in the sealed ampoules for over 300 days at 80 °C. Besides, the plugging performance of LT-RPPG is much better than conventional PPG in terms of water breakthrough pressure and residual resistance factor. The water breakthrough pressure of LT-RPPG and PPG were 238 and 48.5 psi, respectively. The residual resistance factor of LT-RPPG is around 200 times higher than the traditional PPG (40 K in the Figure) and a large portion of PPG was flushed out from the fracture while LT-RPPG maintained good integrity in the fracture.

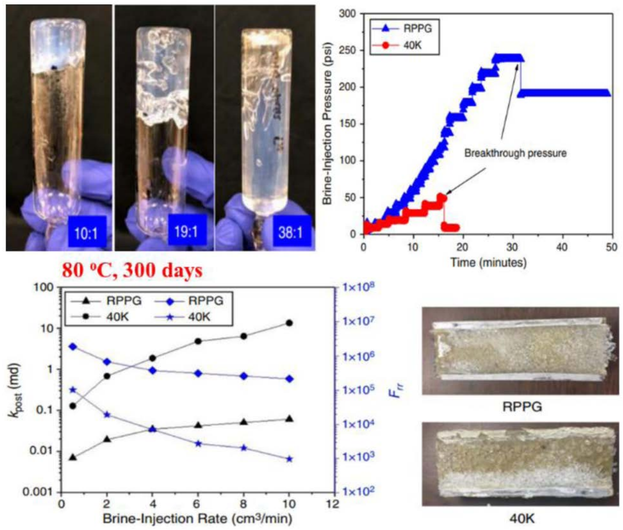

Figure 6—Thermal stability and core flooding results

CO_2 Resistant RPPG: CO_2-RPPG (Song, Zhai, et al. 2022)

The CO_2-RPPG was specifically engineered to seal fractures or void spaces in reservoirs undergoing CO_2 flooding. This strategic design arises from the fact that CO_2 has the ability to dissolve in brine, creating an acidic environment. Traditional polyacrylamide gels like Cr crosslinked polyacrylamide and conventional PPG tend to be unstable in acidic conditions, leading to pronounced syneresis after prolonged exposure to liquid or supercritical CO_2 (Sun et al. 2017, Sun et al. 2020). Consequently, the development of a CO_2-resistant RPPG became imperative.

CO_2 resistance was achieved through incorporating specific monomers, such as sodium styrene sulfonate, known for their insensitivity to acidic conditions. The developed CO_2-RPPG exhibits a maximum swelling ratio ranging from 30 to 44, diminishing with increasing salinity. Figure 7 illustrates that the re-crosslinking time varies between 2 and 10 hours. While the gel strength surpasses that of the LT-RPPG, the re-crosslinking time is notably shorter. Notably, the CO_2-RPPG demonstrates robust adhesion strength to both sandstone and carbonate cores, with adhesion strength ranging from 0.2 to 1.2 psi. Figure 8 provides insight into the gel strength and microstructure of the CO_2-RPPG before and after exposure to CO_2. Remarkably, the gel strength increases by nearly 20% after 60 days of exposure to 2900 psi CO_2. During the degassing process, the polymer gels expand and transform into a porous foam gel. Although the polymer gel network structure experiences a slight collapse after exposure, it maintains overall integrity, affirming the exceptional CO_2 stability of the CO_2-RPPG.

The supercritical CO_2 breakthrough pressure was 265 psi/feet (5.48 MPa/m). After the breakthrough of supercritical CO_2, as the injection rate increased from 1 to 100 ft/day, the Frr decreased from 107 to 105, and the plugging efficiency reached over 99.99%, as shown in Figure 9. Besides, during the core flooding test, we did not observe any gel production, and a tacky gel cake was observed when we opened the fracture.

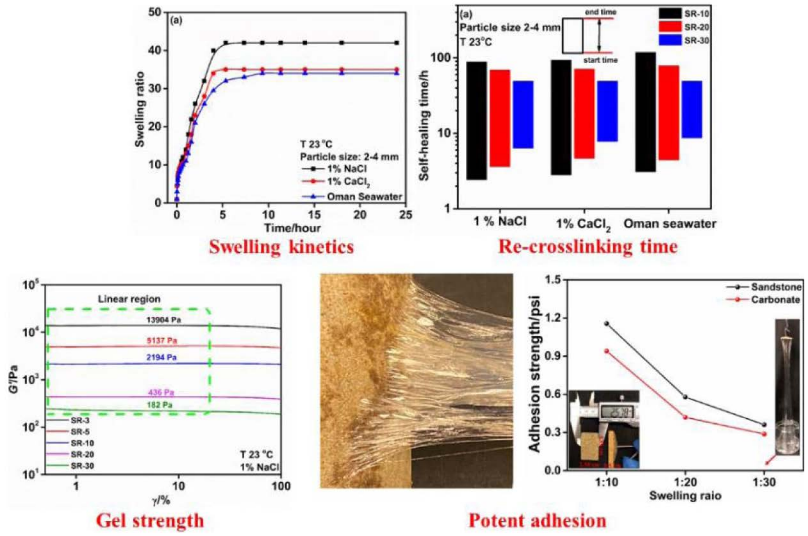

Figure 7—Swelling kinetics, rheology and adhesion behavior of CO_2-RPPG

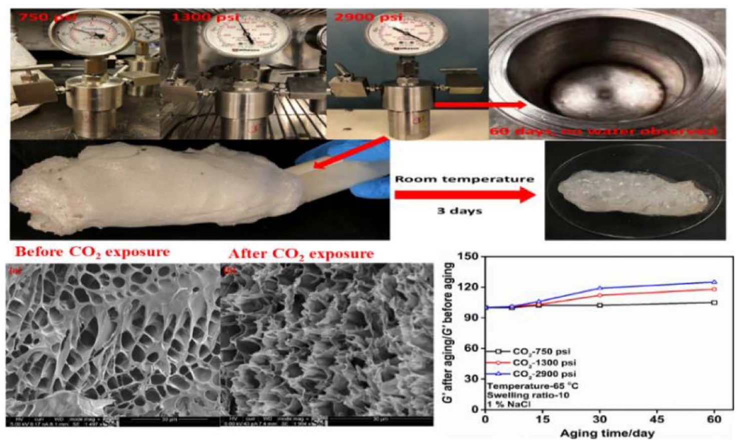

Figure 8—CO_2 stability test results

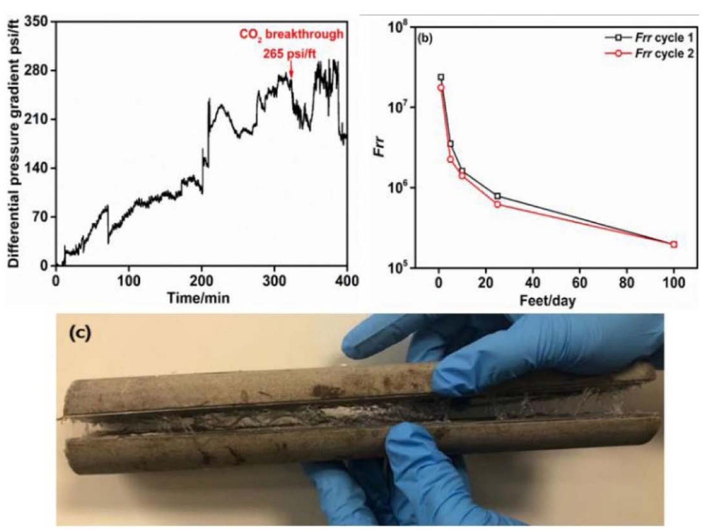

Figure 9—Supercritical CO_2 plugging test

MT-RPPG (Song et al. 2023)

MT-RPPG was designed for high-temperature and high-salinity reservoirs. It contains a large portion of salt-resistant monomers which can also be used to plug the large fractures in high-temperature CO_2 flooding reservoirs. Figure 10 shows the swelling kinetic, re-crosslinking time, and gel strength of MT-RPPG. The maximum swelling ratio and gel strength decrease as the salinity increases, and the gel strength (SR-10) ranges from 800-1500 Pa. We did not observe any syneresis or volume loss during the thermal stability test. After 220 days of aging, all the bulky gels still maintained good mechanical integrity, as shown in Figure 11. The microstructure collapsed a little bit after 200 days of aging, but we can still observe the interconnected network structure. 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, as shown in Figure 12. 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. Besides, the Frr ranges from 1×108 to 1×109, which means the fracture permeability can be reduced more than 108 times.

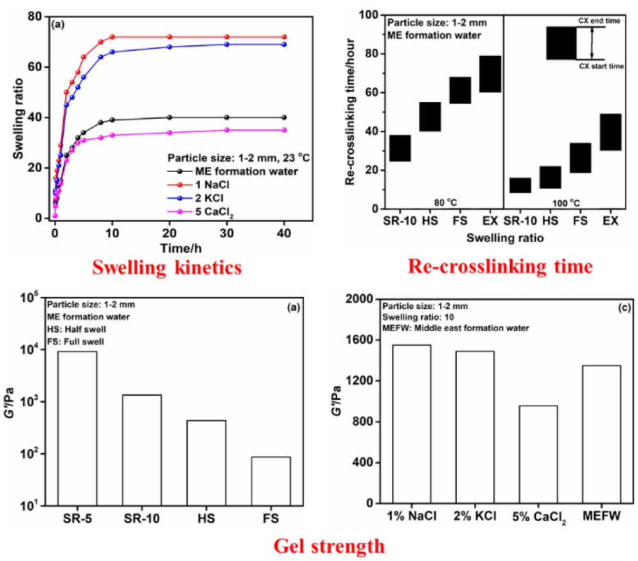

Figure 10—Swelling kinetics, re-crosslinking time and rheology behavior of MT-RPPG

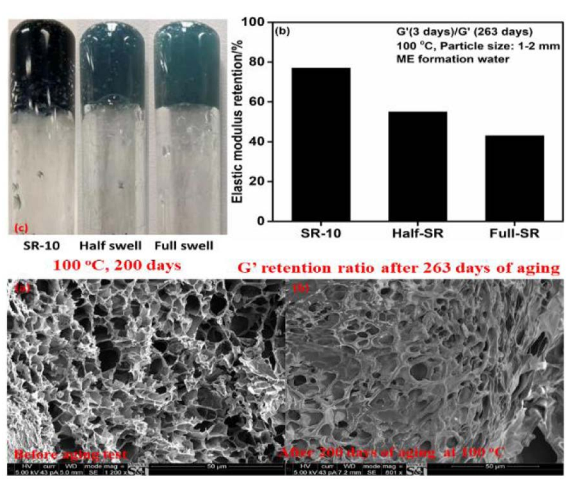

Figure 11—Thermal stability of MT-RPPG

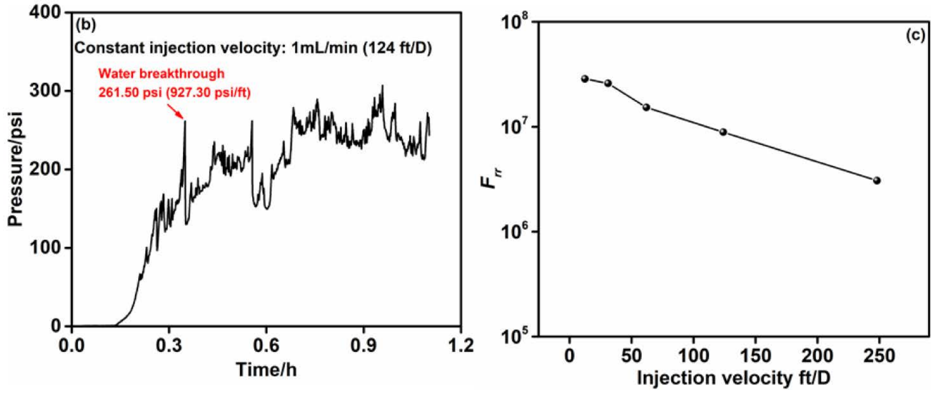

Figure 12—Plugging test of MT-RPPG

High Temerature Resistant RPPG: HT-RPPG (Yu et al. 2022)

HT-RPPG was designed for high-temperature and high-salinity reservoirs with stringent environmental regulations, as shown in Figure 13. The maximum swelling ratio of HT-RPPG is lower than the previous LT/CO_2/MT-RPPG because the polymer backbone is composed of non-ionic monomers, and the maximum swelling ratio is around 18. The recrosslinking time ranges from 4-12 hours, and the elastic modulus of the re-crosslinked gel with a swelling ratio of 10 is around 850 Pa.

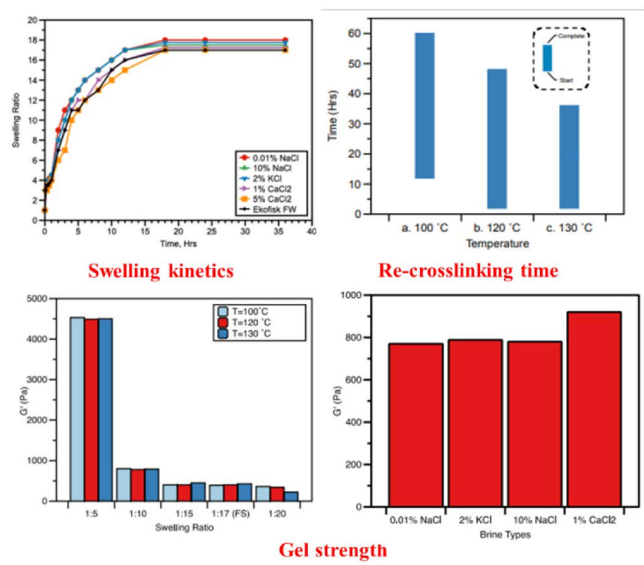

Figure 13—Swelling kinetics, re-crosslinking time and rheology behavior of HT-RPPG

HT-RPPG has excellent thermal stability at 130 °C, when the swelling ratio is 5 and 10, as shown in Figure 14. The water breakthrough pressure gradient can reach up to 427 psi/ft, and the F_{rr} was 115,914.

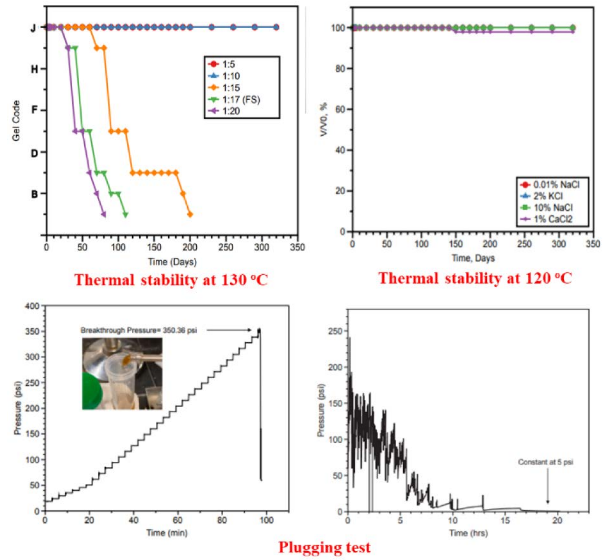

Figure 14—Thermal stability and plugging performance of HT-PPG

Experience Learned from Field Tests (Smith)

Once commercial quantities (>> 2000 lbs) of RPPG product were available to place into large VSC systems, it became necessary to develop detailed field procedures which would utilize the RPPG properties to effectively fill and plug off a VSC problem. A primary member of the JIP desired to solve VSC problems that resulted from sand production wormholes that destroy sweep efficiency in the West Sak field. These problems are well described in SPE papers (SPE-169073, (Peirce et al. 2014), and SPE-201302, (Targac et al. 2020). The first article deals with the utilization of PPG to resolve these problems and the second article focuses on the use of RPPG and the resulting improvements. The second article also provides a nice description of the treatment design characteristic and how the RPPG products properties were utilized to achieve an effective solution. This article will highlight some treatment options and concerns that were discussed and some that were not discussed in the earlier article.

Although filling the entire VSC would provide the best overall solution, it is difficult to achieve without risking filling major portions of either the injector or producer wellbores. Treating both the injector and producer wells would be the best way to achieve full control of the VSC, but several operational concerns around treating the producer have prevented execution of producer side treatments. A primary aspect of this concern is the ability to place product into the VSC from the producer side once the injection side has been isolated. The reverse would also be true that if we place RPPG into the producer first, then achieving placement of RPPG into the injector might be limited causing us to fill the injection wellbore with RPPG. Thus, it was deemed best to continue with injector side placement of the RPPG product which had already seen some success with PPG where concerns over producing back the PPG had already prevented producer side treatments. Some still believe that a producer side treatment may be more effective than injection side treatments but to date none have been attempted.

To create an effective plug in this VSC, the displacement and coverage of the RPPG within the VSC was deemed to be very important. It was recognized that to do this the RPPG product must be placed into the VSC with limited free water in the slurry. This was defined as the fully swollen stage. That is the RPPG product has basically absorbed almost all the free water, with only a limited amount of water left to allow for slurry conditions to support pumpability. This condition allows the greatest viscosity and the least density differential due to the large amount of water already absorbed by the product. To achieve this condition requires a careful balance of product swell rate and product concentration with pumping transit time from surface to placement into the VSC feature. The first two RPPG treatments utilized CT to control the placement of the product at or very near the VSC intersection with the wellbore as established by profile logs. Although CT assisted in balancing the pump rate and transit time, it also had two major concerns. The first concern was having a situation where the RPPG product reached an un-pumpable condition prior to existing the CT resulting in plugging the CT. The second concern was about the product flowing up the backside of the CT during placement of the RPPG and potentially sticking the CT. Due to these risks the practice of using CT during placement was eliminated for the safer and cheaper process of simply pumping the product full-bore. The desire remained to try and balance pumping time with swell rate, but so long as the dynamic pumping condition existed during placement it is believed that gravity segregation will be minimal within the VSC. This resulted in a modification to the procedures that allowed the leading edge of the treatment to be pumped into the VSC in a condition slightly less than fully swollen. Since we continue to keep the product moving into the VSC the leading edge will at some point reach a fully swollen state before pumping is shut down. This maintains the objective of reaching the preferred product conditions within the VSC for the most effective displacement and allows the product to bridge within the VSC and provide significant pressure resistance.

Some members of the operations team were concerned that this pressure resistance would exceed frac pressure causing the need to shut down pumping operation early which would result in filling a portion of the injector. As experience with pumping was gained this concern diminished which allowed the jobs to go to higher pump pressure before going to flush. As noted in the second article this also resulted in more effective longer lasting solutions. Although some RPPG treatments still result in continued conduit flow or failures after several months of control, it is believed that these failures are due to continued sand production and not production of the RPPG. So far very small quantities of the RPPG product as being identified at the production facilities. This is unlike the traditional PPG product where some significant volumes of PPG have been observed at the production facilities. The continued production of sand and what is believed to be the primary reason for continued failures may eventually justify production well treatments, but this is still under consideration.

Bottom-line the new RPPG product has increased the success rate and the longevity of the treatments which has clearly justified the effort. This work has shown that these VSC features can effectively reduce flow during placement from initial rates of 5 BPM on vacuum to ~1 BPM at over 1000 psi. This also results in the offset producers WC reducing from 100% to something around 60 % WC or less.

Discussion

We are continuing to look for field opportunities to utilize the new RPPG products that have been developed. These products include a CO_2 stable RPPG, which swells even more in the presence of CO_2, higher strength branched RPPG and HT (high temperature) stable RPPG. Some HT-RPPG versions are even designed for fracture VSC control in an the environmentally sensitive region of the North Sea. The belief is that many problems originally reserved for only cement or nitrified cement can be properly solved with these new RPPG products. Although we have only utilized the larger 1mm to 4mm products which require rather large VSC problems for placement. The continued use of similar PPG products in fluid loss control during drilling and other field conformance problems indicates the potential these superior RPPG products can bring to solving these VSC problems.

At this point the full potential and overall limitations of these RPPG products have not been completely field tested, but it remains true that these products have the desired properties needed to solve many VSC problems. As stated in the desired treatment conditions outlined in the introduction, this new RPPG product fits all the desired properties better than any other VSF product with only a few minor limitations which the research group continues to address.

We have systematically evaluated the transport and plugging performance of millimeter-sized RPPG (>50 um) and clearly know the RPPGs can be successfully used to plug open fractures or VSC. Therefore, they can be not be only used to control reservoir conformance for those reservoir with such features, but they can also should also be applicable to However, current experiments results do not support whether RPPG can be used to solve the high permeability channels with pore-net work structure, such as proppant filled fracture.

We are actively seeking field opportunities to deploy newly developed RPPG products. These encompass a CO_2-stable RPPG, known for its heightened swelling in the presence of CO_2, a higher-strength branched RPPG, and an HT (high temperature) stable RPPG. Certain versions of the HT-RPPG are tailored for fracture VSC control in the environmentally sensitive North Sea region. We believe that many challenges traditionally addressed by cement or nitrified cement can be effectively tackled with these innovative RPPG products.

Currently, our utilization has primarily focused on larger 1mm to 4mm products, necessitating substantial VSC problems for placement. The continued application of similar PPG products in fluid loss control during drilling and addressing other field conformance issues underscores the potential of these superior RPPG products in solving VSC problems.

While the full potential and limitations of these RPPG products have not been entirely field-tested, their possession of desired properties necessary for solving many VSC problems is evident. As outlined in the desired treatment conditions outlined in the introduction, this new RPPG product aligns with all the desired properties better than any other VSF product, with only a few minor limitations that our research group continues to address.

We have systematically evaluated the transport and plugging performance of millimeter-sized RPPG (>50 um) and have demonstrated their successful use in plugging open fractures or VSC. Consequently, they can be utilized not only to control reservoir conformance in reservoirs with such features but also to address high permeability channels with pore network structures. However, current experimental results do not support the use of RPPG in solving high permeability channels with pore network structures, such as proppant-filled fractures.

Ongoing Research Efforts and Prospects for Future Research

Re-crosslinking time controllable nano- or micro-gels

While our research group continues to prioritize the ongoing improvement of RPPG products to enhance VSC system control, there is growing interest among certain companies in developing RPPGs capable of penetrating deep into rock matrix permeability to plug or regulate high-permeability systems. It is well know that selectively managing higher permeability intervals in highly heterogeneous reservoirs has long posed a challenging problem. Recent efforts have focused on developing swelling-delay particles to address this challenge. However, as noted in the Introduction of this paper, while the delayed swelling properties may enhance plugging efficiency when there is a perfect match with pore throat size, accurately determining pore size distribution in real reservoirs, especially in mature oilfields subjected to prolonged flooding, remains difficult. Alternatively, the potential solution could lie in developing micro- or nano-gels with low adsorption capabilities and the ability to re-crosslink after being delivered deep into a reservoir. This characteristic transforms them into robust products, enhancing their ability to effectively seal the formation.

High-temperature re-crosslinking delayed CO_2-RPPG

We presently assess the re-crosslinking time and stability of our current CO_2-RPPGs solely at temperatures up to 80°C. However, it has come to our attention that certain CO_2 flooding reservoirs exhibit temperatures reaching 120°C. Consequently, it is imperative to scrutinize our existing products to determine their suitability for these reservoirs in terms of both re-crosslinking time and thermal stability. If they fall short of meeting the requirements, the development of novel products becomes necessary. Nevertheless, evaluating such products under the demanding conditions of high temperature and pressure, especially over prolonged periods of several months, poses ongoing challenges.

Ultra-high temperature resistant PPG/RPPG

Our research team has developed a new PPG system that stays stable at 150°C for almost 2 years (Salunkhe et al. 2021, Schuman et al. 2022). Using this gel technology as a base, we've modified the system and tested its stability at 200°C. The adjusted HT-PPG remains stable at 200°C for over 6 months (Tao 2023). Moreover, adding a specific clay during synthesis gives the HT-PPG self-healing abilities. The bulk gel crosslinked by clay shows good thermal stability and mechanical strength. The re-crosslinked bulk gel also stays stable at 200°C for over 6 months. Currently, our focus is on extending the temperature upper limit to 275°C for the preferential fluid flow control in geothermal reservoirs.

Potential Application of RPPG in other Areas

The assessment of millimeter-sized (>100 um) RPPGs for plugging fractures has been conducted, revealing their successful utilization in controlling fluid flow during the flooding of mature oilfields and in fluid loss control during drilling. Nevertheless, their potential applications in sand control, carbonate reservoir conformance control, re-fracking, conformance while drilling, wellbore leakage control, plugging and abandonment (P&A), remain unexplored. The unique characteristics of RPPGs suggest their promising candidacy for these areas.

Conclusion

- Millimeter-size (>10 um) PPGs have been widely applied to various reservoirs (temperature up to 150 °C) for conformance control due to their easy-operation, good gel quality control and low costs.
- Novel Environmental-friendly RPPG has been synthesized with controllable re-crosslinking time (30 minutes to days). The RPPGs can efficiently plug large opening fractures/conduits/wormhole in the reservoirs (room temperature to 150°C). It can be used in both injection wells and production wells.
- RPPGs is available with the varied size from 100 nm to 5 mm; All components are uniformly distributed in RPPG (all-in-one).
- Stable CR-PPGs and CR-RPPGs can increase CO_2 and natural gas miscible injection sweep efficiency improvement.
- PPG and RPPG products can be applied to natural gas reservoirs to control water production or natural gas injection wells for injection profile control.

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