ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

Application of a Pickering Emulsified Polymeric Gel System as a Water Blocking Agent

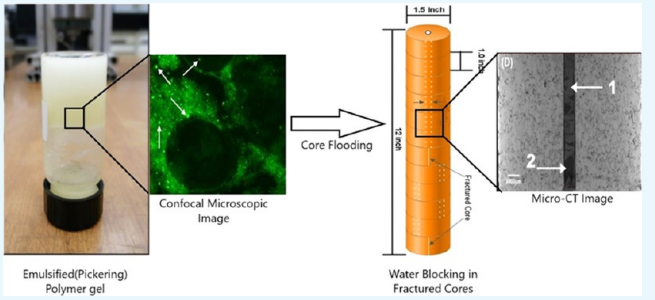
Tinku Saikia,* Abdullah S. Sultan,* Syed R. Hussaini, Assad Barri, Nur Iman Khamidy, Abdulmalek A. Shamsan, Eassa Abdullah, Ammar Al-Ramadhan, Ayman Almohsin, and Mohammed Bataweel

Cite This: *ACS Omega* 2021, 6, 30919−30931

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The conventional methods for controlling excess water production in oil/gas wells can be classified on the basis of the mechanism (pore-blocking mechanism and relative permeability modification) used. Gel systems developed on the basis of a pore-blocking mechanism completely block the pores and stop the flow of both oil and water, whereas a relative permeability modifier (RPM) only restricts the flow of a single phase of the fluid. The gel working on the basis of the pore-blocking mechanism is known as a total blocking gel. An invert emulsified (PAM−PEI) polymer gel is a relative permeability modifier system. The same invert emulsion system is tested as a total blocking gel system in this research work. The dual-injection technique (1st injection and 2nd injection) was used for this purpose. In this research work, the emulsion system was tested at a temperature of 105 °C. The core sections with drilled holes and fractures were used for the core flooding experiments, representing a highly fractured reservoir. The developed emulsified gel system was characterized using a dilution test, an inverted bottle test, microscopic images, and FTIR images. The emulsified polymer gel was tested using a core flooding experiment. After the 2nd injection, the postflood medical CT and micro-CT images of the core sections clearly showed the presence of two different phases in the core section, i.e., the oil phase and the gel phase. The core flooding experiment result indicates that the gel formed after the 2nd injection of the emulsion system can withstand a very high differential pressure, i.e., above 2000 psi. The gel did not allow any oil or water to be produced. Hence, the developed emulsified polymer gel system with the help of a dual-injection technique can be efficiently used as a total blocking gel for high-temperature reservoirs.

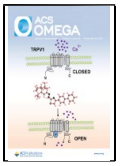


1. INTRODUCTION

The average global oil recovery factor is as low as 34%.[1,2] There are many reasons for this low recovery and one of the prominent reasons is high water cut production. This difficult problem is the most common among the matured wells and becomes more pronounced in the wells with extended reach drilling and multilateral wells.[3] The excess water production not only decreases the oil production rate but also leads to corrosion of a tube, hydrostatic loading, and fine migration. The increase in water production demands a more complex water−oil separation system and results in rapid corrosion of the well equipment.[3] On average, the production of 75 million barrels of oil resulted in the production of 210 million barrels of water, and it is even worse in places such as the North Sea oil field, etc. This makes the production cost of one barrel of oil equal to one barrel of water. Annually, approximately 40 billion dollars worldwide are required for wastewater treatment and disposal.[4] All of these collectively resulted in the early abandonment of mature wells due to uneconomical production.

The most common methods for controlling excess water production can be broadly divided into two groups, i.e., the chemical treatment method and the mechanical method. The mechanical method usually includes isolating or blocking the water-producing zone using cement squeezing, packer, or plug. The success rate with this method is usually only limited to 30% and this method is only effective in the wells with easily identifiable oil- and water-producing zones. It is ineffective in the wells where water and oil coproduced from the same producing zone and in the wells with microlayered formations or in the case of in-depth formation water breakthrough.[5] The most common chemical treatment method includes the gel treatment method. The gel used can be a polymer gel or a silicate gel. The in situ cross-linked polymer gels are

Received: June 16, 2021
Accepted: October 20, 2021
Published: November 8, 2021



conventionally used water shut-off systems. The selection of the type of an in situ polymer gel is based on the type of fracture or matrix. The gels with high gel strength were used in highly fractured zones and the lower gel strength systems were employed in small fractures/matrices with lower productivity. In situ cross-linked polymer gels can withstand a high-pressure difference because of their higher gel strength and can be used in highly fractured zones. The in situ cross-linked polymer gel method did include a few drawbacks, which limit its effectiveness of the water shut-off application in the fields. The uncontrolled gelation time, changes in the gelant composition due to the reservoir fluid and mineral contact, and variation in gelation due to shear degradation are a few of the major drawbacks. Moreover, the in situ cross-linked polymer gel may block the oil-producing zone, which is not a desirable outcome after the water shut-off job.

To avoid these complications, different researchers present different water shut-off/conformance control systems such as polymer microgel flooding[6−9] and an emulsified polymer gel system.[10] Polymer microgels include colloidal dispersion gels (CDGs), preformed particle gels (PPGs), temperature-sensitive microgels (Bright-Water), and pH-sensitive polymer microgels.[6,11−18] However, the mentioned polymer microgel flooding methods also struggled to solve the major drawbacks. The performed particle gel method is limited to reservoirs with extreme permeability contrast and cannot penetrate low-permeability formations due to relatively large particle size. The gelation in the CDG method is affected by the shear and chemical reaction between reservoir rock and fluids; the gel may easily penetrate the oil-producing zones, and the gels' thermal and salt resistance will depend on the polymer properties.[19]

The emulsified polymer gel system is an invert emulsion (w/o emulsion).[10] The aqueous phase (polymer and cross-linker) is emulsified in the diesel oil. The outer layer of diesel provides the desired protection to the aqueous phase from the reservoir rock and the fluids until the gel system penetrates to the desired zone of interest. After that, the emulsion system breaks, and the aqueous phase gels under the reservoir conditions and the diesel oil form the desired conduit for the oil to flow. The water flow will be restricted in the oil conduit because of immiscibility. For the water to flow through the oil conduit, it has to push the oil out from the oil conduit first. Therefore, in the multiphase (oil−water) flow, the oil will be produced from the oil conduit, whereas water will be blocked. This is the proposed postulate.

In this paper, the emulsified polymer gel system is developed using diesel as the continuous phase and gelant (polymer and cross-linker) as the dispersed phase. The organoclay is used for emulsion stabilization. The developed emulsion system was tested via core flooding experiments and found to be an efficient relative permeability modifier during the previous experiments.[10] The core flooding experiments were performed with two different types of cores, i.e., Berea sandstone and an artificially fractured carbonate rock. However, in this research work, we not only studied the working principle of the emulsified gel thoroughly and proved the postulates with the help of tomographic images but also tested the emulsified polymer gel as a total blocking gel system. It was tested that if need arises in the field, then the same system can be used as a total blocking gel or not. The dual-injection technique is tested during the core flooding experiment for the emulsified polymer gel to act as a total blocking gel. In the 1st injection, the emulsion system was injected into the core section. After the gelation time because of the emulsion separation, two different phases existed in the pore space and in the fractures, i.e., a separated diesel phase and a gelled aqueous phase. During the 2nd injection, the same emulsion system was injected again and this emulsion system will displace the separated diesel oil and the unconsolidated gel from the 1st injection emulsion system. This research work is an account of the dual application of a single system as a relative permeability modifier and a total blocking gel system depending upon the requirement. This was achieved with the help of a dual-injection technique. In this work, the core flooding experiment was conducted only to test the system as a total blocking gel. This research work will help to reduce the operational complexities in the oil field. The ability to use a single formulation as a relative permeability modifier and a blocking gel depending upon the requirement provides greater flexibility to the field engineers.

2. MATERIALS

An invert emulsion has a continuous phase of diesel oil and a dispersed aqueous phase of a polymer and a cross-linker mixture. The organic Cloisite 20 is used as an emulsifier, which prevents the coalescence of the aqueous phase. The diesel having a density of 0.832 kg/L and viscosity of 1.6 cP was obtained from the local gas station. The polymer used is polyacrylamide (PAM) and the cross-linker used is polyethylenimine (PEI). The PAM was supplied in a powdered state (M_w 4.5−7.5 MDa) from SNF Floerger, France, and PEI from MPI Biomedicals. PEI is in solution form with a 50% aqueous solution and a molecular weight of 43 kDa (average) and a density of ∼1.07 g/mL. The PEI is a branched-chain polymer with a base structure of $(CH_2CH_2NH)_x$. Cloisite 20 is organically modified phyllosilicate having a particle size of D_{50} < 10 μm and a density (20 °C) of 1.80 g/cm^3; it was supplied by BYK, U.K. The water used for the preparation of PAM and PEI solution is field mixing water supplied by a local operating company. The composition of water is shown in Table 1. The concentration of total dissolved solids in the field mixing water is 922.96.

3. MECHANISM ILLUSTRATION, INSTRUMENTS, AND THE PROCEDURE

3.1. Mechanism Illustration. The developed emulsified gel system is designed to be used in such a way that it will switch its role from a relative permeability modifier to a total

Table 1. Brine Composition

sl. no.	ion	concentration (mg/L)
1.	sodium (Na^+)	185.53
2.	potassium (K^+)	12.40
3.	magnesium (Mg^{2+})	27.00
4.	calcium (Ca^{2+})	59.14
5.	fluoride (F^-)	0.50
6.	chloride (Cl^-)	382.83
7.	bromide (Br^-)	2.01
8.	nitrate (NO_3^-)	3.83
9.	sulfate (SO_4^{2-})	244.20
10.	ammonium (NH_4^+)	5.48
11.	lithium (Li)	0.04
total dissolved solids		922.96

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

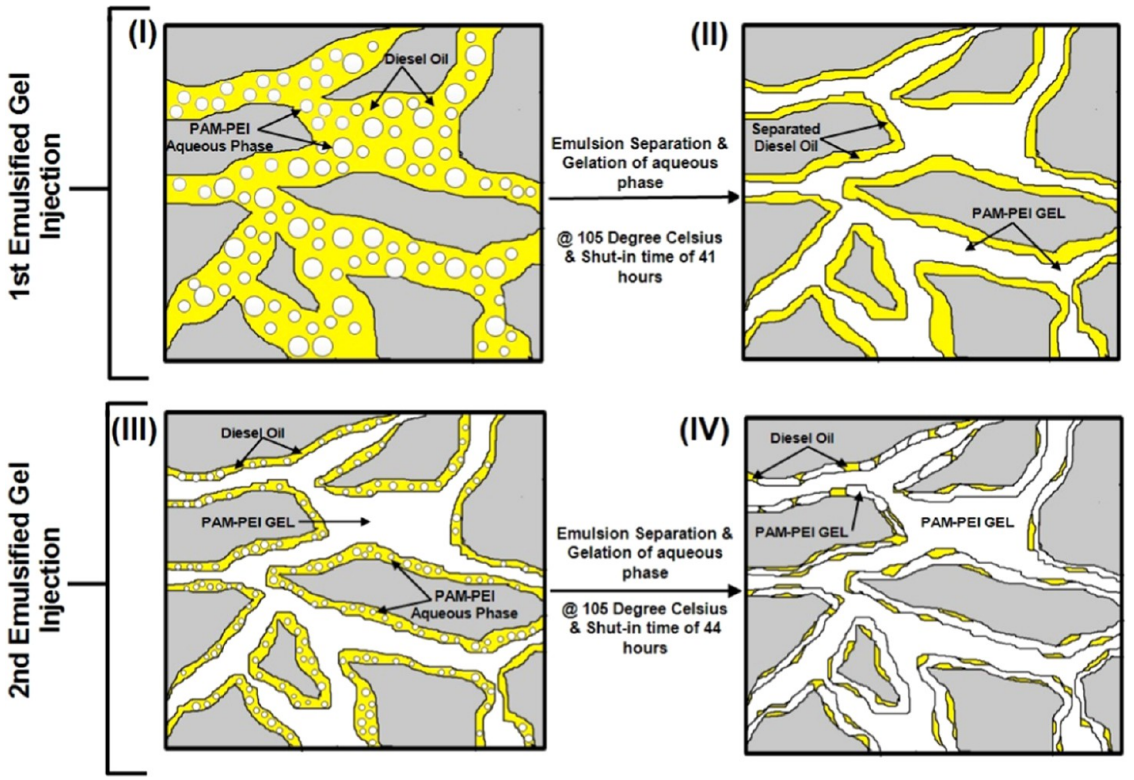


Figure 1. Illustration of the proposed mechanism: (I, II) 1st emulsified gel injection and (III, IV) 2nd emulsified gel injection.

blocking gel system. The application of the developed emulsified gel system as a relative permeability modifier was presented in the previous work.[20] In this research work, the use of a dual-injection technique for switching the role of an emulsified gel system is presented. Figure 1 shows the pictorial illustration of the mechanism responsible for this change. During the 1st emulsified gel injection, the emulsion system was injected into the core section, and the interconnected pore spaces were filled with the emulsion system. The PAM−PEI mixture remains as a dispersed aqueous phase in the continuous diesel oil, as shown in Figure 1I. Due to the higher temperature of 105 °C and with time, the emulsion systems break. The aqueous phase (after shut-in time) becomes a gel due to the cross-linking of PAM and PEI at high temperatures. The oil phase provides a thin channel around the gel phase, as shown in Figure 1II. If the objective is to achieve relative permeability modification, then step I and step II are sufficient. The gel phase will block the water flow, whereas the thin diesel channel will provide the conduit for crude oil to flow due to miscibility. The water will only flow if it will push the entire length of diesel oil from the thin channel because of immiscibility. Hence, during the multiphase flow in the treated zone after treatment, only crude oil flowed and the water flow became highly restricted.

When the same emulsion system is injected again, the emulsion occupies the thin channels previously occupied by the separated diesel oil after 1st injection, as shown in Figure 1III. Again, the required shut-in time is provided, and a temperature of 105 °C is maintained. This resulted in the separation of an injected (2nd injection) emulsion and gelation of a separated aqueous phase, as shown in Figure 1IV. Whereas, the separated diesel oil (2nd injection) was not able to form a continuous diesel channel after the emulsion separation, as the space available is very confined and the diesel channel was blocked in between by the gelled aqueous phase. This allows the same emulsified gel system to act as a total blocking gel after the 2nd injection.

3.2. Emulsion Preparation. The prepared emulsified polymer gel is an invert Pickering emulsion system. The dispersed phase is a mixture of PAM and PEI aqueous solutions. The continuous phase is diesel oil. The aqueous polymer solution is a 3.0 wt % PAM solution and the aqueous cross-linker solution is a 1.0 wt % PEI solution. The Silverson L5M-A mixer was used to prepare the PAM and PEI solutions as well as for the preparation of the emulsified polymer gel system. The Silverson mixer has the highest speed of 10 000 rpm, and the speed is controlled using an infinitely variable electronic speed controller. The double-filtered field mixing water is used in the aqueous phase. The PAM solution was prepared using powdered PAM and mixing the same at a temperature of 40 °C for 8 h at a 700 rpm mixing speed. The PEI solution was prepared in the same manner; only the mixing was carried out for 1 h at 700 rpm and 40 °C. The temperature of the solutions during stirring was maintained using a hot plate. In the diesel oil, Closite 20 was dispersed by stirring at 1600 rpm for 15 min. Closite 20 provides the desired emulsion stability and prevents the coalescence of the aqueous phase.

After the preparation of PAM, PEI, and diesel solution, the emulsion was prepared using mixing method III.[21] In mixing method III, the PAM and PEI solutions were mixed prior to the emulsification in the diesel oil. After PAM and PEI solution mixing, the diesel solution was poured slowly on top of the PAM−PEI mixture. The bulk phase of the PAM−PEI solution and the diesel solution on top was stirred with an intermittent increase in the stirring speed up to 10 000 rpm. The stirring was continued at 10 000 rpm for 15 min.

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

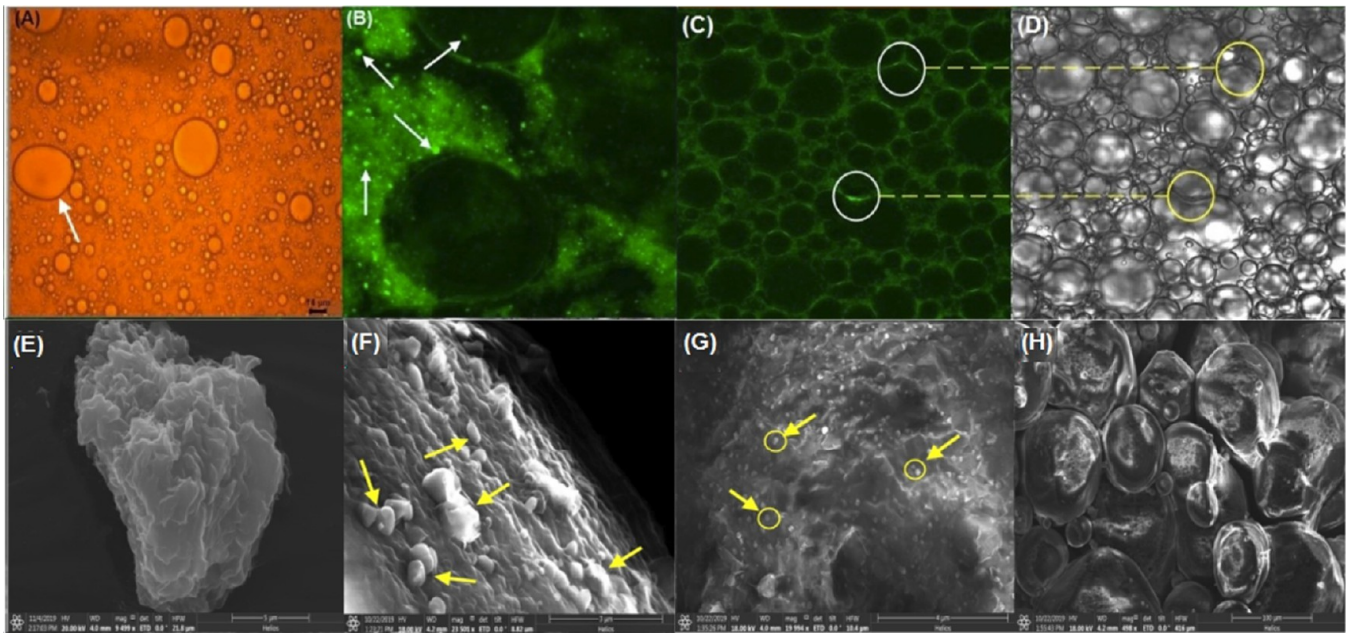


Figure 2. Emulsion droplets. (A) Optical microscopy images, (B) confocal microscopy image (50×) (Cloisite 20 particles shown by white arrows), (C, D) confocal microscopy image (4×) (nonspherical droplets shown by circles), FIB-SEM images, (E) surface morphology of Cloisite 20 particles and (F−H) emulsion topology of Cloisite 20 particles at the interface (yellow arrows).

3.3. Emulsion Characterization. The prepared Pickering emulsified polymer gel system was tested for its state (i.e., direct/invert emulsion) using a dilution test method as well as conductivity measurement. A Thermo Scientific Orion Star A215m was used to measure the emulsion systems' pH and conductivity. The dilution test is one of the simplest methods for the determination of the type of emulsion. The emulsion droplet is exposed to an external water phase in a beaker; if the emulsion system is a direct emulsion, then the emulsion droplet will disintegrate due to a miscible external phase. If the emulsion is an invert emulsion, then the droplet will remain intact due to an immiscible external phase. Also, the conductivity value of the emulsion system supports or validates the dilution test results. The invert emulsion gives zero or negligible emulsion conductivity, which represents an outer nonaqueous phase of the emulsion.

The vial inversion test was performed to have a qualitative analysis of the gel strength. The prepared emulsified gel system was tested at a temperature of 105 °C after 24 h. The Sydnask code was used to grade the gel strength (Table S1). In this test, the emulsified gel was subjected to the test temperature in a vial, and after the desired time interval, the gel strength of the gel was tested by inverting the vial and matching the state of the gel with the Sydnask code gel description. The best match description is the gel strength of the prepared gel system.

To understand more about the emulsion droplets' shape, size, and surface morphology, different microscopic images were obtained and analyzed. A Leica DM2000 microscope with Hi Plan 10× lens was used to obtain the optical images of the emulsion system. An Olympus FV3000 confocal microscope (with a magnification of 50×) was used to understand more about the microstructure of the emulsion droplets. The emulsion droplet was visualized at ambient conditions in a welled slide without a coverslip. An imaging fluorescent agent (Rhodamine 6G) was also used in the emulsion system. The confocal microscope uses laser light and operates on the basis of fluorescence optics. The laser light focuses onto a defined spot in the specimen at a particular depth instead of illuminating the whole sample. This resulted in the emission of fluorescent light exactly at the point of interest.

An FEI Helios NanoLab G3 UC Scanning Electron Microscope (SEM) was used to study the surface morphology of the emulsion droplets. The SEM operates using a focused ion beam (FIB) technique instead of an electron beam technique. The Cloisite 20 particles were placed in a carbon tape-covered aluminum stud. The excess clay particles were blown away using filtered air, which leaves a very fine layer of clay particles on the stud. A Quorum Q150T turbomolecular-pumped cutter was used for carbon coating the clay particles. A high-density amorphous carbon film was coated on the clay surface by repeating the coating process three times.

The used FIB-SEM is not suitable for the analysis of samples at a liquid state; therefore, the emulsion drop at the top of the alumina stud was exposed in a preheated vacuum oven at a temperature of 105 °C. After the drying procedure, the emulsion drop was carbon-coated following the same procedure.

3.4. Core Flooding. The water shut-off system was tested with a core flooding test. An AFS 200 system from CoreLab was used for the core flooding experiment. The schematic of the setup is shown in Figure S1. The core flood system is a high-temperature−high-pressure system. The maximum injection pressure of 7500 psi can be attained with the help of a two Isco syringe pump. The upper-temperature limit of the setup is 200 °C. The back pressure of 1000 psi can be maintained with the help of a back-pressure regulator. The back-pressure regulator releases the gases from the system and helps to retain the injected solutions' liquid state in the system. All of the pressure, temperature, and flow data readings are measured and recorded every second using a highly precise data acquisition system.

3.5. Medical Computed Tomography (CT). The CT scan images of the cores before and after the core flooding were obtained using a Toshiba Alexion TSX-032A medical X-

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

ray CT scanner. The scanner provides the images with a resolution of approximately ≥1 mm. The analysis of the CT scans images helps in the identification of emulsified polymer gel system propagation into the cores and understanding the efficacy of the developed emulsion system to block all of the flow channels. The major fractures and the wormholes present in the core were identified on the CT scan images using PerGeos software.

3.6. Microcomputed Tomography (CT). To assess the injection and gelation of the emulsified polymer gel system in the core at the level of a pore system, a micro-CT scanner was used. A Zeiss Versa XRM-500 X-ray micro-CT scanner was used. It provides a resolution (True Spatial Resolution) of greater than 0.7 μm. The pore system analysis can be done by varying the resolution between 1 and 50 μm.

4. RESULT AND DISCUSSIONS

Many researchers suggested the placement of a mature gel to block the open fractures. The mature gel only occupies the open fractures and its concentration as well as rigidity increases during the injection process. This increase is due to the separation of the solvent from the gel during the leak-off process.[22−24] The occurrence of narrow wormholes in the injected mature gel is common in nature, and these narrow wormholes are the pathways for the water after the gel rupture. However, it seems that the mature gel usually effectively constricts these pathways with a small degree of gel swelling. The matured gel not only has lower initial rupture pressure but also demands intensive pumping in the oil fields. In comparison to the mature gel injection, when the gelant is injected into the open fractures, the solvent does not separate from the gelant and the gel concentration remains the same. The gelant solution not only occupies the fracture but also enters the matrix adjacent to the open fracture. This helps to form a strong bond between the gel in the matrix and the gel present in the fracture during the cross-linking. This bonding helps the gelant to attain an increased initial rupture pressure in comparison to a mature gel.[25] The drawback associated with the gelant is that the rupture paths in the immature gel after gelation are wider in comparison to the mature gel.[26] To fill the comparable section of fracture, it requires a very high degree of swelling. Moreover, polymer adsorption is a common problem associated with gelant injection.[27] However, the injection pumping pressure for gelant injection is less demanding in comparison to the mature gel in the oil fields.

The use of the proposed emulsified gelant in this research work provides a simple solution to the problems associated with the gelant injection. As the gelant is emulsified in diesel oil, the polymer adsorption is prevented easily. During the emulsified polymeric gel (gelant) injection, a back pressure of 1000 psi was maintained, which forced the emulsified gelant to not only fill the open fracture but also to penetrate the core matrix completely. After the emulsion separation when the gelant starts to form the gel, the bond between the gel in the fracture and in the matrix helps to increase the initial rupture pressure. Even the wormholes, where the chances of gel rupture are the maximum, were initially occupied by the separated diesel oil, which restricts the water flow. Moreover, as this research work proposed the use of dual injection, the

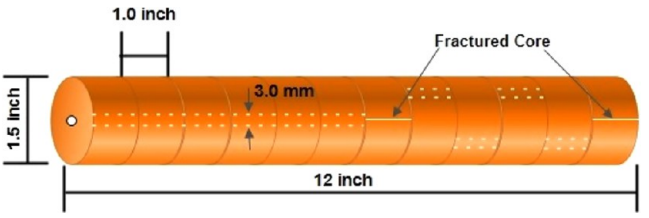


Figure 3. Core section used for core flooding.

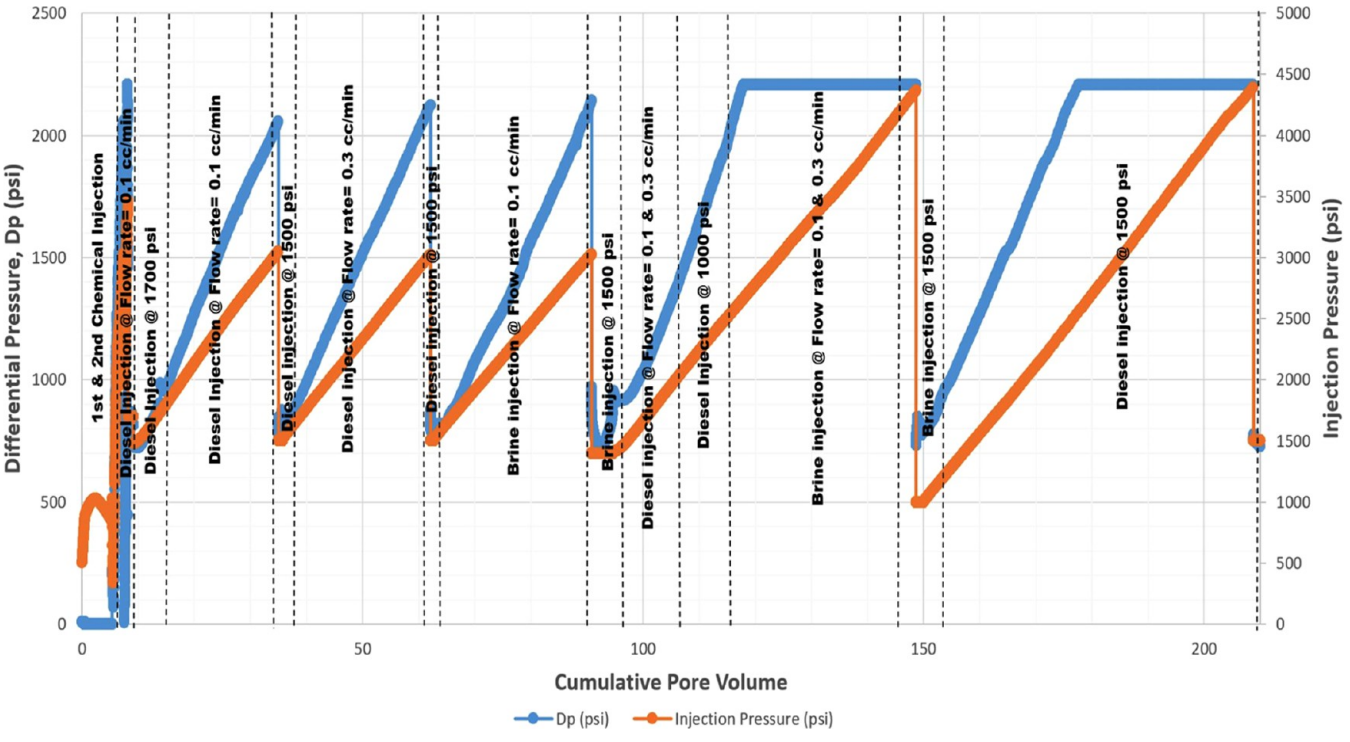


Figure 4. Variation in the differential pressure during the core flooding experiment.

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

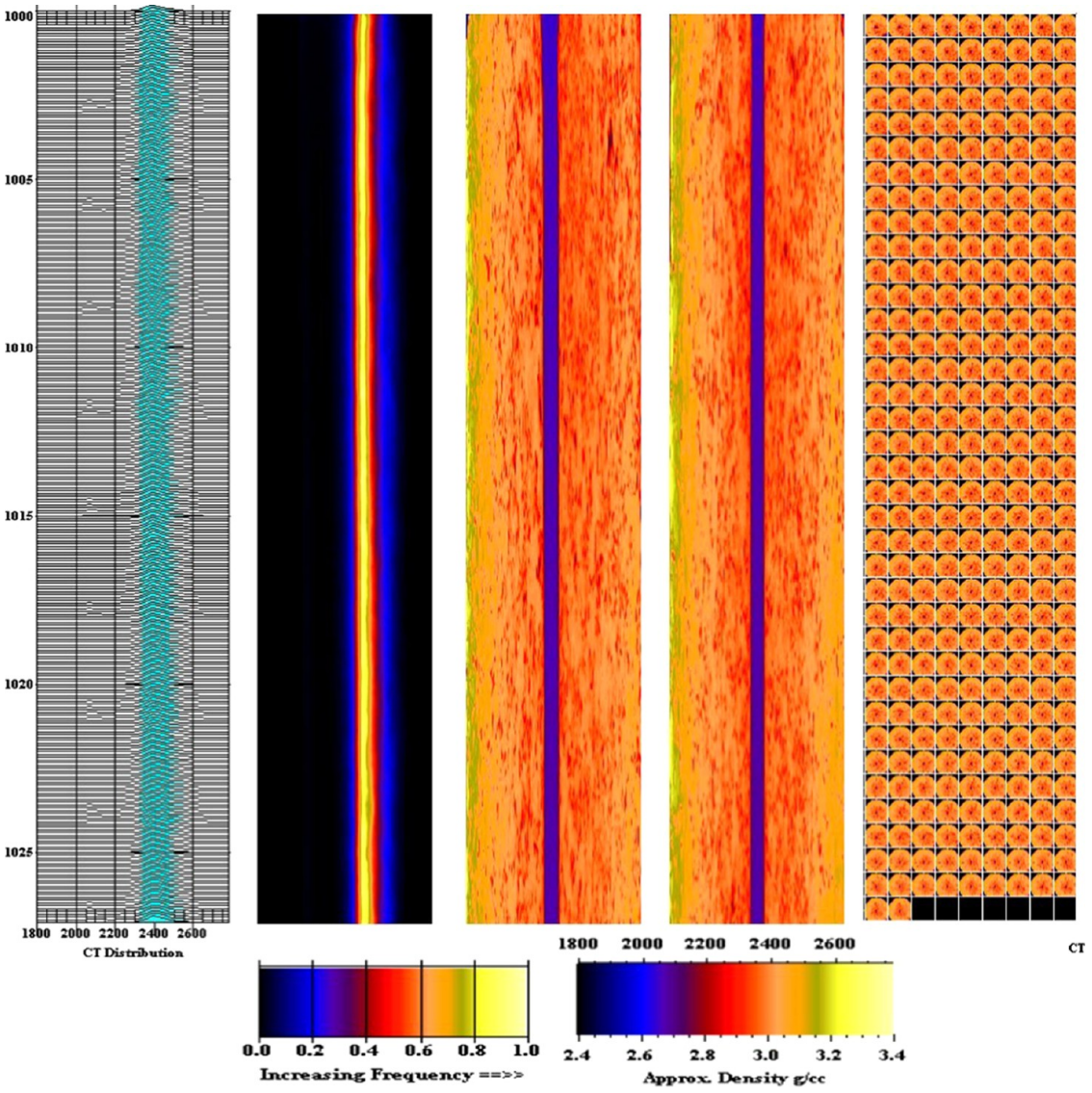


Figure 5. CT distribution of core section 5 (preflooding).

wormholes will be occupied or blocked by the emulsified gel injected during the 2nd injection. This may have even compensated for the effect of the gelant slumping due to gravity. These observations are supported by the core flooding experiment results, where the injected emulsified gel withstands and restricts a very high differential pressure (in the range of 2000 psi) during brine and diesel injection after the shut-in period. During the 1st injection, the emulsified gel system was injected until approximately 50 mL of the emulsified gel was produced from the outlet side. Similarly, in the 2nd injection, the injection was continued until approximately 50 mL of the emulsion was collected from the outlet side. It was seen that during the 2nd injection, initially, diesel and a small amount of a weak gel were dispersed and produced from the outlet side of the core flooding setup.

4.1. Emulsion Characterization. The developed Pickering emulsified polymer gel was found to be an invert (water-in-oil) emulsion system when tested via a dilution test method. The emulsion droplet was exposed to a water phase in a beaker and the emulsion droplet maintained its spherical shape without dispersing in the water phase, as shown in Figure S2. As the external phase of the emulsion is diesel oil, therefore, due to immiscibility with a water phase in the beaker, the emulsion droplet remains nondispersed.

The vial inversion test was also performed to qualitatively study the gel strength and gelation characteristics of the developed Pickering emulsified polymer gel system. For the qualitative quantification of the polymer gel system's gel strength, the Sydansk code was used (Table S1). The emulsified polymer gel was subjected to a temperature of 105 °C for 24 h in an airtight glass bottle. After 24 h, the oil separation took place on the emulsion system due to high temperature, which can be easily seen in Figure S3A. Comparing the state of the gel shown in Figure S3B with the Sydansk code, it was found that the emulsified polymer gel after gelation represents code H. Slight deformation was seen on the gel surface upon inversion but the gel remained as a nonflowing gel.

The presence of nonspherical droplets in the Pickering emulsion is a unique feature of the Pickering emulsion; other emulsions only consist of spherical droplets.[28] In Figure 2A, the nonspherical droplet can be identified in the microscopic image, and is indicated by a white arrow. As shown in Figure 2B, it can be easily identified that the Cloisite 20 particles are

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

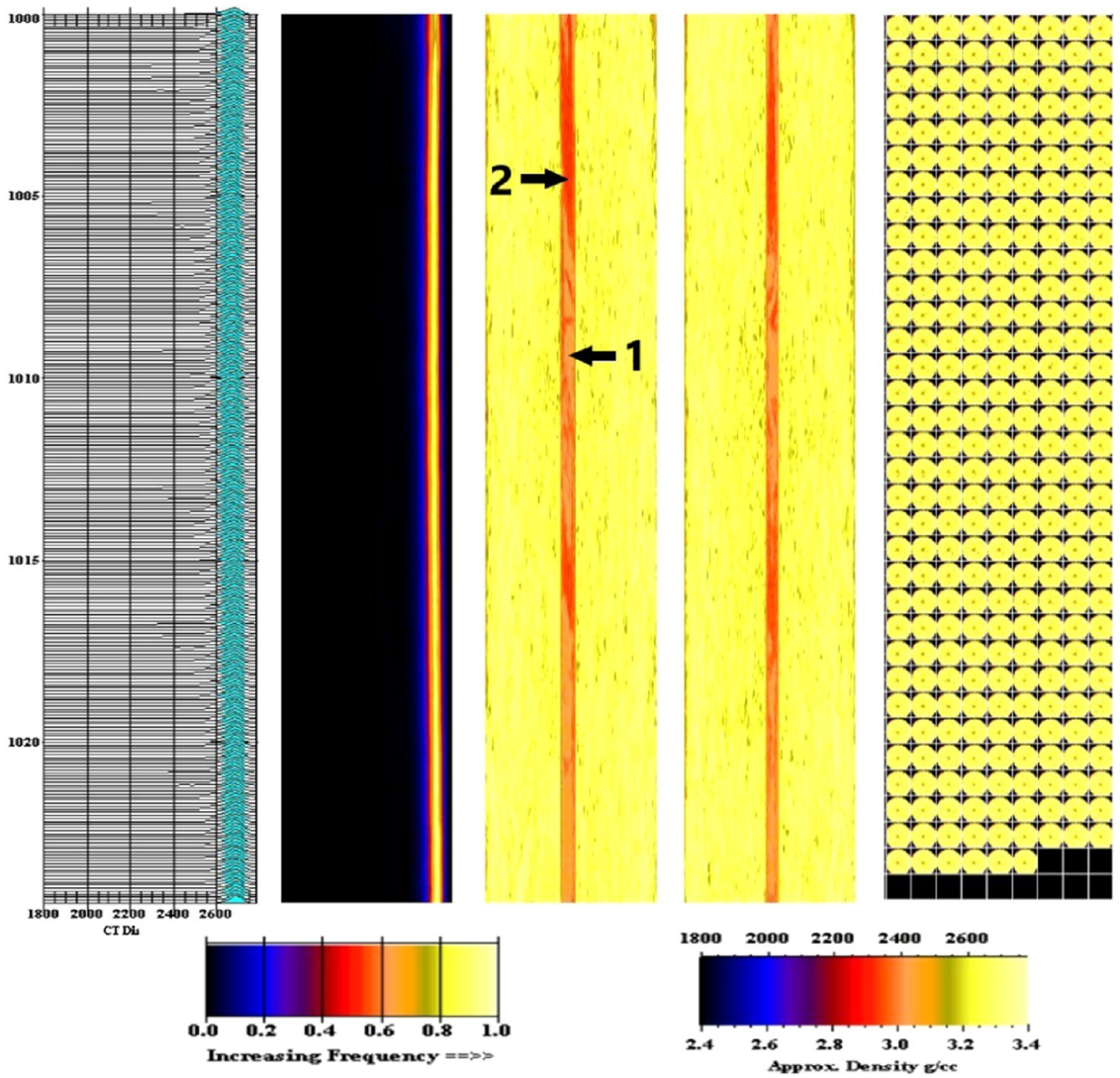


Figure 6. CT distribution of core section 5 (postflooding).

present in the oil phase as aggregated particles, and not all of the particles are at the interface between a continuous oil phase and disperse aqueous droplets. A few of the clay particles are indicated by the white arrows in Figure 2B. In Figure 2C,D the circles indicate the corresponding nonspherical droplets in both the images. It is interesting to see in Figure 2C that the fluorescence at the surface of nonspherical droplets or at the droplet surfaces, which are very close to one another, is higher than the rest of the continuous phase in the emulsion. This is may be because of the presence of a high concentration of Cloisite 20 particles in the form of a particle bridge of the adjacent interface of the two droplets.[29] Further investigation (which is not in the scope of this work) may help to understand the stabilization mechanism (such as network stabilization) utilized by the particles in the emulsion systems.

Pickering stabilization in the emulsion system can be further understood in a better way with the help of FIB-SEM images (Figure 2). The organic particles (Cloisite 20) used as an emulsifier are a type of layered silicates having a nonmetric thickness and a particle size of D_{50} < 10 μm. The layered structure can be clearly seen in Figure 2E. The used Cloisite 20 is organically modified organoclay with an increased interlayer spacing and better interactions with organic polymers.[30] The organoclay particle size further decreases during the emulsion formulation because of the high-speed stirring, and it may reduce to a range of 0.7−3 μm.[31] In Figure 5F, the organoclay particles adsorbed on the surface of the emulsion droplets can be clearly seen, and in Figure 5G, the type of distribution of the organoclay particles on the surface of the droplet can be understood clearly. It can be easily concluded that the particles do not have ordered layer-by-layer deposition (i.e., sequential close packing) or random ballistic deposition, which is usually achieved with platelike solid stabilizers. The Cloisite 20 organoclay provides a kind of imperfect surface coverage to the emulsion droplets, which allows molecular transport through void spaces at the interface. This is a desirable characteristic of the developed emulsion system as it is required for the separation of an oleic phase and an aqueous phase in the reservoir. Figure 5H presents the state of the dried emulsion sample at a 498× magnification.

4.2. Core Flooding. The emulsified polymeric gel system developed is tested in the core flooding experiment. Mixing method III was used for the preparation of an emulsified polymeric gel in this core flooding experiment 5. The carbonate core used in the experiment consisted of 12 core sections. Each core section had a dimension of a 1.5 in.

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

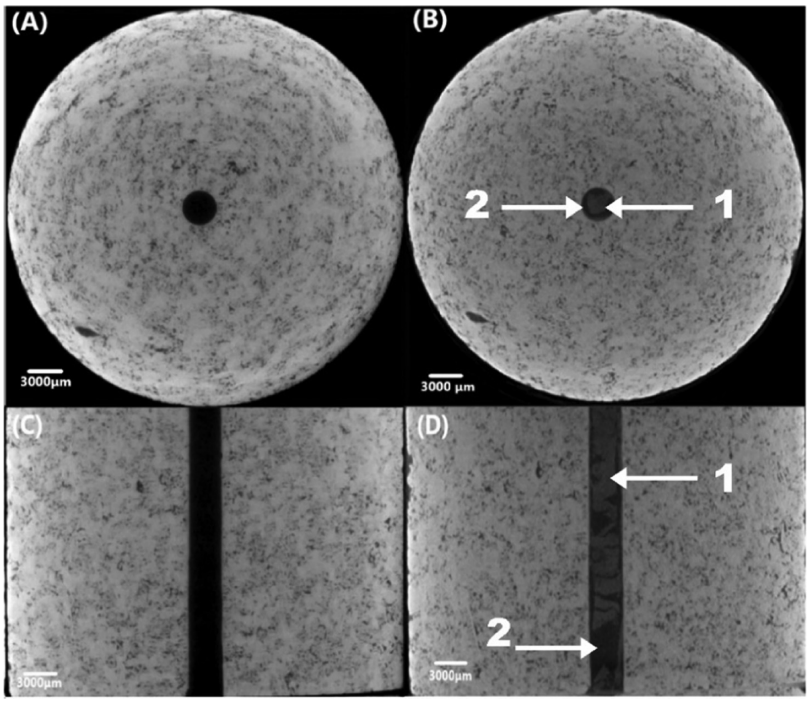


Figure 7. Micro-CT core section 5. (A) Preflooding Z slice, (B) postflooding Z slice, (C) preflooding X slice, and (D) postflooding X slice.

diameter and a 1.0 in. length, as shown in Figure 3. All of the core sections are drilled with a 3.0 mm diameter hole except core sections 7 and 12. The core sections 7 and 12 are fractured lateral. The drilled holes in the core sections 1−6 are concentric holes and drilled holes in sections 8−11 are eccentric holes. The drilled holes and lateral fracture in the core sections were introduced to depict the highly fractured reservoir.

The core holder and pressure lines were pressure tested for any leakages. The experiment was conducted at a constant temperature of 105 °C. A back pressure of 1000 psi and an overburden pressure of 1500 psi were maintained in the core holder during the initiation of the experiment. The overburden pressure was increased to 4300 psi in between the experiment depending upon the differential pressure value and the injection pressure value. Approximately, a time period of 3 h was provided for the homogenization of temperature in the core flooding setup. The initial permeability of the core sections was approximately in a range of 125 md. The emulsified polymeric gel was injected at a constant flow rate of 1 cm^3/min, and approximately, a 5.35 pore volume of the polymeric gel was injected. Although the cross-linking between a PAM and PEI mixture (i.e., gelant) started when they were mixed together, but only when they were subjected to a higher reservoir temperature, the emulsion separation took place and the rapid cross-linking started to change the gelant to form the desired gel. After the injection of the emulsified gel, the gel was aged for approximately 41 h. This aging allowed the emulsion system to separate into an oleic phase and an aqueous phase in the core at 105 °C. The emulsion systems are thermodynamically unstable systems and they are susceptible to separation via sedimentation, creaming, flocculation, and Ostwald ripening.[32] All of these lead to the separation of the oil phase and the aqueous phase in the emulsion system. The aqueous phase turned into a gel and the oleic phase provided the desired channel. After the 1st shut-in period, the emulsified polymeric gel was injected for the 2nd time with a constant flow rate of 1.0 cm^3/min. The increase in the differential pressure during the injection was due to the fact that the 2nd emulsified gel injection was pushing the gel and the oleic phase channel present in the core sections from the 1st emulsified gel injection. The emulsified gel injection during the 2nd gel injection must have taken the path through the flow channel created by the oleic phase after the 1st emulsified gel injection, and in the process, it also displaced some of the loose gel from the core. This observation is supported by the fact that during the 2nd emulsified gel injection, we saw the diesel and a small amount of loose gel coming out from the outlet. Approximately, a 2.35 pore volume of the emulsified gel was injected during the 2nd emulsified gel injection. The 2nd shut-in period of approximately 44 h was provided to the aging of the injected emulsified gel.

After the 2nd shut-in period, the diesel oil was injected into the core section at a flow rate of 0.1 mL/min. After injection of a 0.6 pore volume of diesel oil, it was seen that the differential pressure reading increases to 2135 psi, and then the diesel injection was changed to constant pressure injection at a 1700 psi injection pressure. Approximately, after the injection of a 0.97 pore volume of diesel, the injection was again shifted to constant flow rate injection with a flow rate of 0.1 cm^3/min. The injection was continued till the differential pressure value reached the value of 2056 psi. Again the injection of diesel changed to constant pressure injection with an injection pressure of 1500 psi. The injection of diesel continues alternately in a constant pressure mode and a constant flow rate mode, as shown in Figure 4. Only a few drops of liquid were seen on the outlet side, which is negligible. In a similar manner, the brine was injected into the core sections with a constant pressure mode and a constant flow rate mode. However, after repeated alternate water and diesel injection, no fluid was produced from the outlet. The emulsified polymer gel completely blocked the permeability of the core sections. The

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

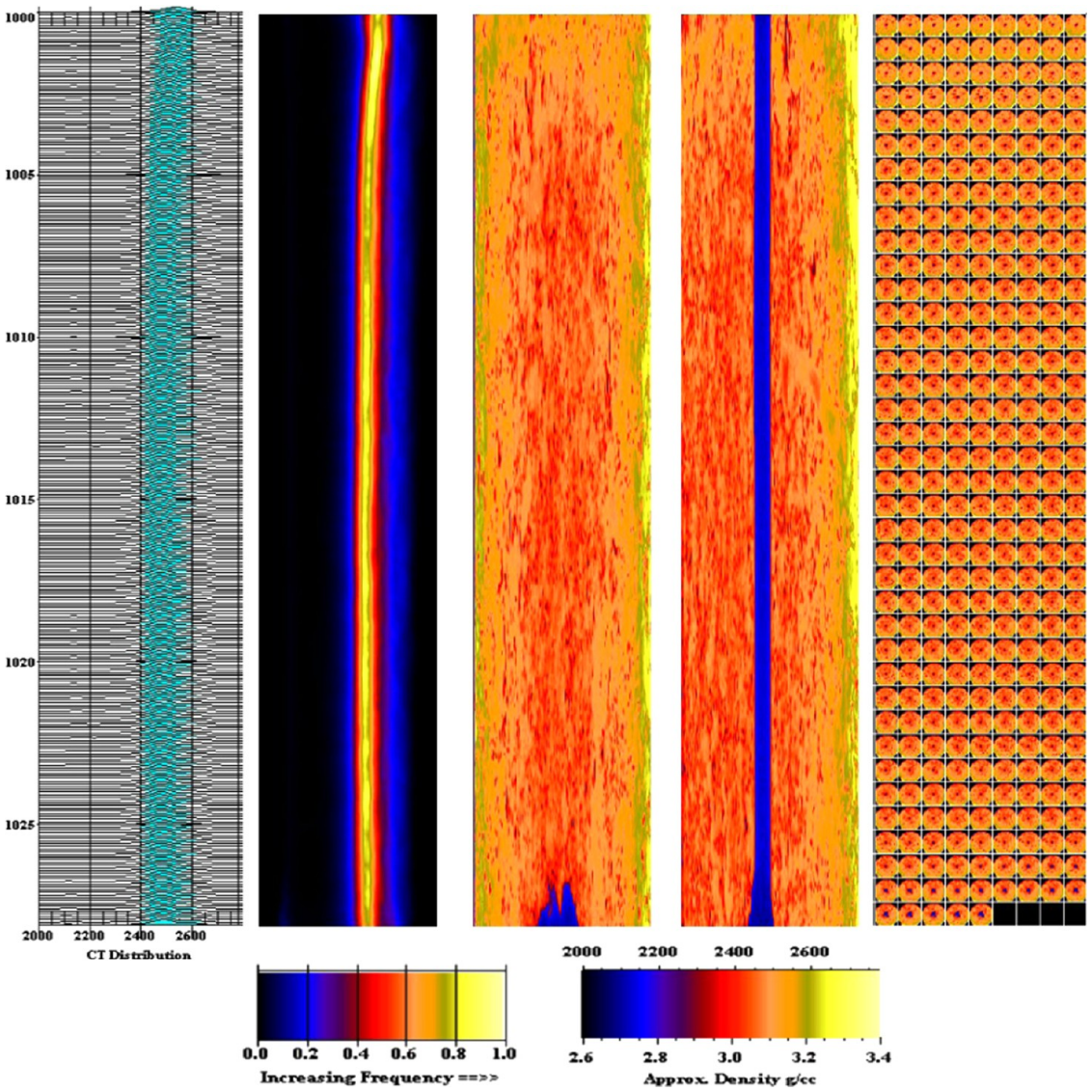


Figure 8. CT distribution of core section 9 (preflooding).

gel was efficient enough to withstand the differential pressure of approximately 2000 psi even in the core sections with drilled holes representing highly fractured reservoir conditions. The emulsified gel system can be used as a total blocking gel using the double injection method.

The developed emulsion system when tested as RPM at higher temperature reservoir conditions was found to be efficient enough to control the excess water production without affecting the oil production.[10] The emulsion system was injected only once in the previous study but the same emulsion system was injected twice in this present study. In this study, the core flooding results showed that the 2nd injection of the emulsion system blocked the water flow as well as oil flow through the core section. Thus, the same system acts as a total blocking gel.

4.3. Medical and Micro-CT Scan Analysis. The medical and micro-CT scan images of the core sections before and after the core flooding provide better insights into the mechanisms and conditions via which the emulsified polymeric gel was successfully tested as a relative permeability modifier that can be utilized as a total blocking gel.

The two core sections were randomly selected for the medical and micro-CT analysis among the core sections. Core sections 5 and 9 were drilled core sections. Comparing Figures 5 and 6, it is clearly seen that the emulsified gel penetrated into the core section properly and filled the drilled hole in core section 5 completely. The CT number distribution of core section 5 before flooding was approximately 2400, which was increased to approximately 2700 after the core flooding. This indicates the penetration and gelation of the injected emulsified gel into core section 5. The medical CT images also indicated the presence of two phases in the drilled hole of core section 5; with the help of a color code, the two phases can be identified. The phases are named as "1" and "2", whereas due to the lower resolution, it was not very clear and the micro-CT image analysis was done.

In Figure 7, the presence of a gel in the drilled section of the core in both the Z slice and the X slice of the core section after flooding can be identified clearly. It can be easily concluded that the drilled hole, as well as the pores in the core section, were completely blocked as neither diesel oil nor brine flowed through the core sections during the core flooding experiment after the 2nd gelation. In the after-flooding core section

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

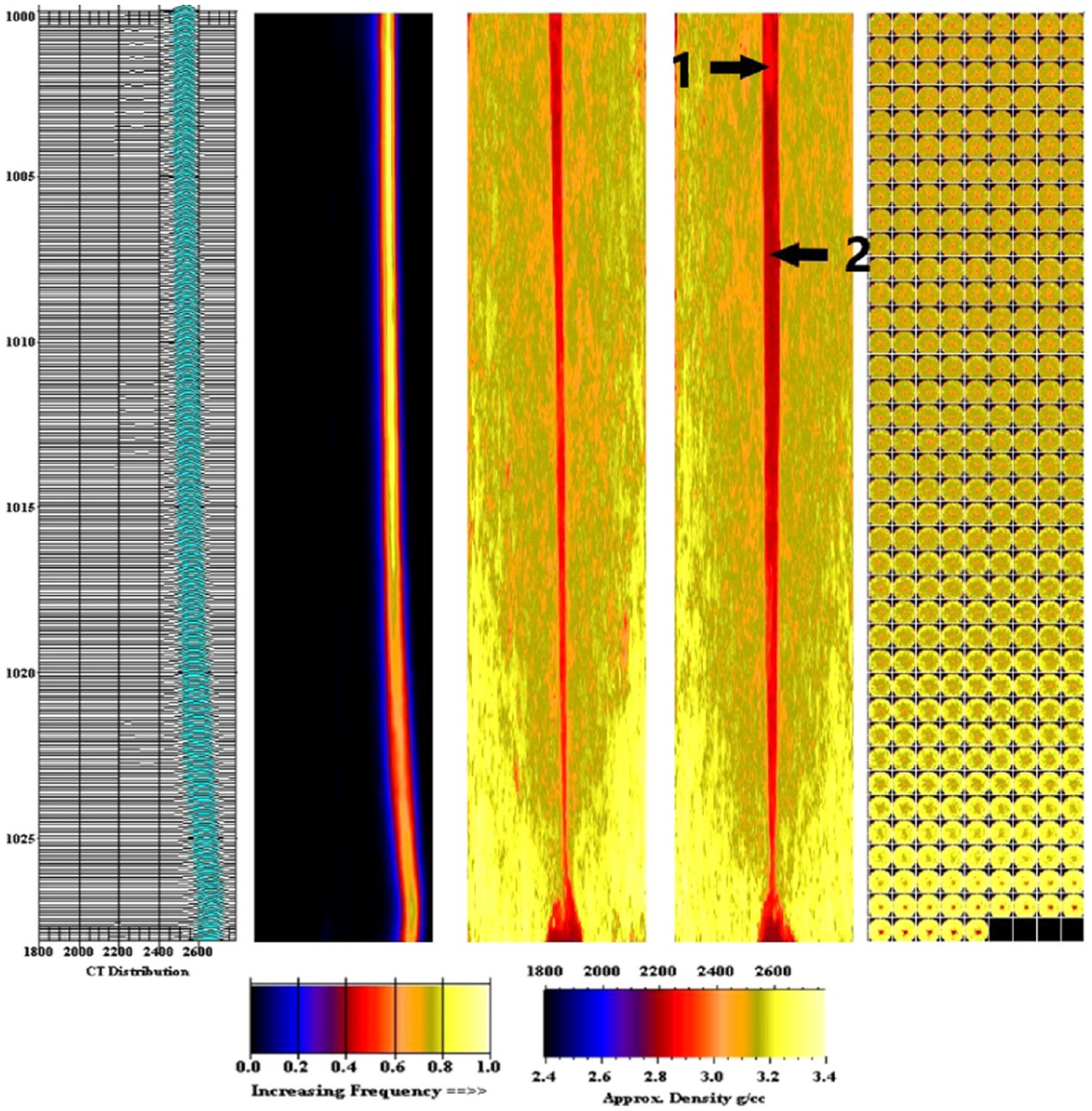


Figure 9. CT distribution of core section 9 (postflooding).

images, the presence of two phases after the gelation can easily be identified. The two phases are shown in Figure 7B,D, and denoted 1 and 2; the denoted phase "1" is the gel in the core section. It is very evident from the micro-CT image that after the emulsion separation, the aqueous phase and the oleic phase separated at reservoir conditions and formed two different phases. The aqueous phase converted into the gel state and the oleic phase was present in the form of a channel in between the gel phase. Without the 2nd emulsified polymer gel injection, the oleic channel would have provided a proper flow channel to the diesel oil and restricted the flow of the brine; similar results were seen in the previous core flooding experiments in this project. In this core flooding experiment, the core sections were subjected to 2nd emulsified polymer gel injection. The 2nd injection pushed the partially gelled aqueous phase and the diesel oil from the core sections. This is evident from the fact that during the 2nd injection, the partially gelled aqueous phase and diesel oil were flowing out from the core sections.

After the 2nd injection, the core contains the rigid gel from the 1st injection and the emulsion injected during 2nd injection. The emulsion injected during the 2nd injection again separated into the oleic phase and the aqueous phase. The aqueous phase was converted into a gel at reservoir conditions, and the oil phase forms flow channels. In the micro-CT images, it is not clear that the phase denoted as 1 is either a gel from 1st injection, 2nd injection, or a combined gel structure resulting after both the injection stages. The 2nd injection, however, completely blocked the pores, the fracture, and the drilled holes in the core section. Hence, it may be suggested that the same emulsion system can be applied as a conformance control system or water shut-off system according to the injection technique. The dual injection will completely block even the highly fractured reservoirs.

Comparing the pre- and postflooding and medical CT and micro-CT images of core section 9, similar conclusions can be made (Figures 8 and 9). The CT number distribution in the preflooding medical CT image was approximately 2500, which was increased to approximately 2700 in the postflooding micro-CT image. This increase in the CT number distribution represents an increase in the density of the core section due to the presence of a gel. However, the CT number distribution was not uniform in the entire length of core section 9. In some

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

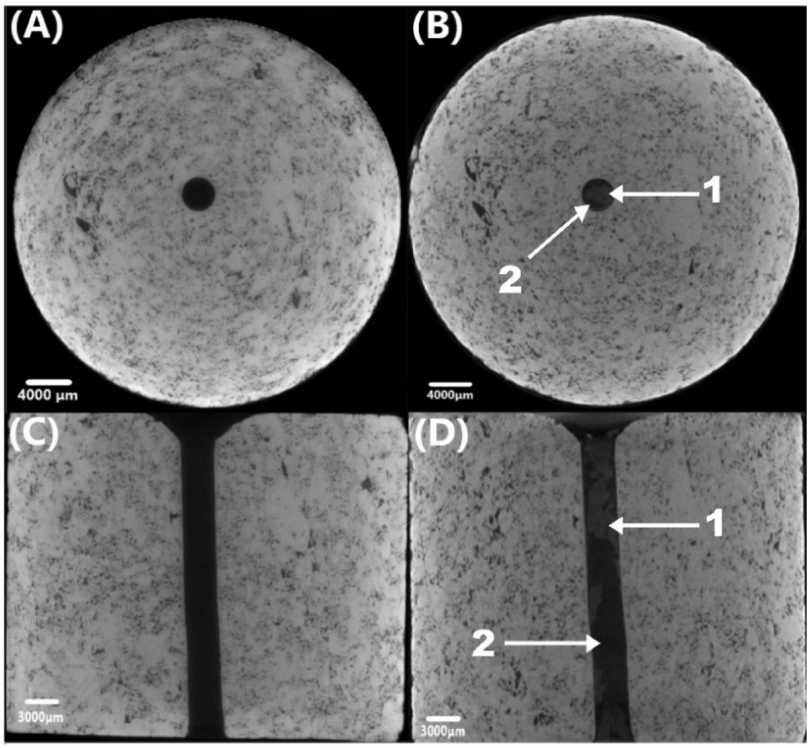


Figure 10. Micro-CT images core section 9. (A) Preflooding Z slice, (B) postflooding Z slice, (C) preflooding Y slice, and (D) postflooding Y slice.

regions, the CT number of core section 9 postflooding is approximately equal to the preflooding, indicating the unoccupied space or the presence of a lighter phase fluid (Figure 9). The micro-CT images of core section 9 also support the CT number distribution. In Figure 10, the presence of two phases can easily be seen indicated by "1" and "2". The gel phase "1" only presents up to half the portion of the drilled hole in core section 9; the rest of the portion is mainly filled with phase 2 (Figure 10D). In the absence of a CT number comparison of the three phases (i.e., diesel, brine, and gel), it is difficult to determine about phase 2. But, it is certain that it is a different phase, and after the 2nd injection, the gel blocked the pores, fractures, and drilled holes in the core sections completely. The same was verified by the core flooding experiment performed in this research work. In the core flooding experiment, neither oil not brine was produced during the injection, which confirms that the cores are blocked in such a way that it was able to withstand a differential pressure of as high as 2000 psi.

5. CONCLUSIONS

This research work proved the proposed postulate on the working principle of an emulsified polymer gel for relative permeability modification. The micro-CT images proved that the emulsion system at higher temperature breaks and forms two distinct regions, i.e., gel and diesel channels. In this research work, the same system was tested for its performance as a total blocking gel. The application of a dual-injection method helped to achieve this objective. During the 2nd injection, the oil from the emulsified gel (1st injection) was pushed out along with the partially gelled gelant. The emulsified gelant not only completely occupied the fracture in the cores but also penetrated the matrix of the core. This helped the gel to achieve a higher initial rupture pressure; even the gel could withstand a differential pressure as high as 2000 psi. This type of dual application system may provide the field engineers greater flexibility to use the same system for different purposes according to their requirements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02956.

Schematic diagram of the AFS 200 (CoreLab) core flooding setup (Figure S1), emulsified polymer gel dilution test to identify the type of emulsion: (A) front view of the invert emulsion and (B) top view of the invert emulsion (Figure S2), emulsified polymer gel inverted bottle test to check the gelation and gel strength: (A) vertical position and (B) inverted position (Figure S3), and Sydnask gel strength code (Table S1) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Tinku Saikia − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0001-7230-6074; Phone: +966 (013) 860-1793; Email: tinku.saikia@kfupm.edu.sa; Fax: +966 (013) 860-4447

Abdullah S. Sultan − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia; Centre for Integrative Petroleum Research, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0001-9617-4678; Phone: +966 (013) 860-2728/2586; Email: sultanas@kfupm.edu.sa; Fax: +966 (013) 860-4447

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931

Authors

Syed R. Hussaini − *Centre for Integrative Petroleum Research, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Assad Barri − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Nur Iman Khamidy − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Abdulmalek A. Shamsan − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Eassa Abdullah − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Ammar Al-Ramadhan − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Ayman Almohsin − *Saudi Aramco, EXPEX ARC, Dhahran 31311, Saudi Arabia*

Mohammed Bataweel − *Saudi Aramco, EXPEX ARC, Dhahran 31311, Saudi Arabia*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02956

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge the King Fahd University of Petroleum and Minerals for providing necessary laboratory facilities and Saudi Aramco for providing the financial support under project CIPR 2323. The authors extend their appreciation for the outstanding support by laboratory technician Jafar Al Hamad and research assistant Nadeem Ahmed Syed.

■ REFERENCES

(1) Saikia, T.; Sultan, A.; Barri, A. A.; Khamidy, N. I.; Shamsan, A. A.; Almohsin, A.; Bataweel, M. Development of Pickering Emulsified Polymeric Gel System for Conformance Control in High Temperature Reservoirs. *J. Pet. Sci. Eng.* **2020**, *184*, No. 106596.

(2) Abdulbaki, M.; Huh, C.; Sepehrnoori, K.; Delshad, M.; Varavei, A. A Critical Review on Use of Polymer Microgels for Conformance Control Purposes. *J. Pet. Sci. Eng.* **2014**, 741−753.

(3) Ghosh, B.; Bemani, A. S.; Wahaibi, Y. M.; Hadrami, H.; Boukadi, F. H. Development of a Novel Chemical Water Shut-off Method for Fractured Reservoirs: Laboratory Development and Verification through Core Flow Experiments. *J. Pet. Sci. Eng.* **2012**, 176−184.

(4) Bailey, B.; Crabtree, M.; Tyrie, J.; Elphick, J.; Kuchuk, F.; Romano, C.; Roodhart, L. Water Control, Oilfield Review, *Schlumberger*, 2000, 30−51.

(5) Bedaiwi, E.; Al-Anazi, B.; Paiaman, A.; Al-Anazi, A. Polymer Injection for Water Production Control through Permeability Alteration in Fractured Reservoir. *Nafta* **2009**, 221−231.

(6) Coste, J.-P.; Liu, Y.; Bai, B.; LI, Y.; Shen, P.; Wang, Z.; Zhu, G. In *In-Depth Fluid Diversion by Pre-Gelled Particles. Laboratory Study and Pilot Testing*, SPE/DOE Improved Oil Recovery Symposium, 2000.

(7) Al-Anazi, H. A.; Sharma, M. M. In *Use of a PH Sensitive Polymer for Conformance Control*, Proceedings - SPE International Symposium on Formation Damage Control, 2002.

(8) Frampton, H.; Morgan, J. C.; Cheung, S. K.; Munson, L.; Chang, K. T.; Williams, D. In *Development of a Novel Waterflood Conformance Control System*, Proceedings - SPE Symposium on Improved Oil Recovery, 2004.

(9) Spildo, K.; Skauge, A.; Aarra, M. G.; Tweheyo, M. T. A New Polymer Application for North Sea Reservoirs. *SPE Reservoir Eval. Eng.* **2009**, 427−432.

(10) Saikia, T.; Sultan, A. S.; Barri, A. A.; Khamidy, N. I.; Shamsham, A. A.; Almohsin, A.; Bataweel, M. Development of Pickering Emulsified Polymeric Gel System for Conformance Control in High Temperature Reservoirs. *J. Pet. Sci. Eng.* **2020**, No. 106596.

(11) Fielding, R. C.; Gibbons, D. H.; Legrand, F. P. In *In-Depth Drive Fluid Diversion Using an Evolution of Colloidal Dispersion Gels and New Bulk Gels: An Operational Case History of North Rainbow Rang Unit*, Proceedings - SPE Symposium on Improved Oil Recovery, 1994.

(12) Mack, J. C.; Smith, J. E. In *In-Depth Colloidal Dispersion Gels Improve Oil Recovery Efficiency*, Proceedings - SPE Symposium on Improved Oil Recovery, 1994.

(13) Sheng, J. J. Status of Surfactant EOR Technology. *Petroleum* **2015**, 97−105.

(14) Bai, B.; Huang, F.; Liu, Y.; Seright, R. S.; Wang, Y. In *Case Study on Preformed Particle Gel for In-Depth Fluid Diversion*, Proceedings - SPE Symposium on Improved Oil Recovery, 2008.

(15) Mustoni, J. L.; Norman, C. A.; Denyer, P. In *Deep Conformance Control by a Novel Thermally Activated Particle System to Improve Sweep Efficiency in Mature Waterfloods of the San Jorge Basin*, Proceedings - SPE Symposium on Improved Oil Recovery, 2010.

(16) Yañez, P. A. P.; Mustoni, J. L.; Relling, M. F.; Chang, K. T.; Hopkinson, P.; Frampton, H. In *New Attempt in Improving Sweep Efficiency at the Mature Koluel Kaike and Piedra Clavada Waterflooding Projects of the S. Jorge Basin in Argentina*, Proceedings of the SPE Latin American and Caribbean Petroleum Engineering Conference, 2007.

(17) Yu, X.; Pu, W.; Chen, D.; Zhang, J.; Zhou, F.; Zhang, R.; Gu, S. Degradable Cross-Linked Polymeric Microsphere for Enhanced Oil Recovery Applications. *RSC Adv.* **2015**, 62752−62762.

(18) Yang, H.; Hu, L.; Chen, C.; Gao, Y.; Tang, X.; Yin, X.; Kang, W. Synthesis and Plugging Behavior of Fluorescent Polymer Microspheres as a Kind of Conformance Control Agent in Reservoirs. *RSC Adv.* **2018**, 10478−10488.

(19) Liu, Y.; Bai, B.; Shuler, P. J. In *Application and Development of Chemical-Based Conformance Control Treatments in China Oil Fields*, Proceedings - SPE Symposium on Improved Oil Recovery, 2006.

(20) Saikia, T.; Sultan, A.; Barri, A. A.; Khamidy, N. I.; Shamsan, A. A.; Almohsin, A.; Bataweel, M. Development of Pickering Emulsified Polymeric Gel System for Conformance Control in High Temperature Reservoirs. *J. Pet. Sci. Eng.* **2020**, *184*, No. 106596.

(21) Saikia, T.; Sultan, A.; Al Hamad, J. S. Effect of Mixing Method on the Rheokinetics of Pickering Emulsified Gel System Used as Disproportionate Permeability Reducer. *Rheol. Acta* **2020**, 875−885.

(22) Seright, R. S. Polymer Gel Dehydration during Extrusion through Fractures. *SPE Prod. Facil.* **1999**, 110−116.

(23) Seright, R. S. Gel Propagation through Fractures. *SPE Prod. Facil.* **2001**, 225−231.

(24) Seright, R. S. An Alternative View of Filter-Cake Formation in Fractures Inspired by Cr(III)-Acetate-HPAM Gel Extrusion. *SPE Prod. Facil.* **2003**, 65−72.

(25) Ganguly, S.; Willhite, G. P.; Green, D. W.; McCool, C. S. In *The Effect of Fluid Leakoff on Gel Placement and Gel Stability in Fractures*, Proceedings - SPE International Symposium on Oilfield Chemistry, 2001.

(26) Brattekas, B.; Graue, A.; Seright, R. S. In *Low Salinity Chase Waterfloods Improve Performance of Cr(III)-Acetate HPAM Gel in Fractured Cores*, Proceedings - SPE International Symposium on Oilfield Chemistry, 2015.

(27) Jia, H.; Pu, W. F.; Zhao, J. Z.; Liao, R. Experimental Investigation of the Novel Phenol-Formaldehyde Cross-Linking HPAM Gel System: Based on the Secondary Cross-Linking Method of Organic Cross-Linkers and Its Gelation Performance Study after Flowing through Porous Media. *Energy Fuels* **2011**, 727−736.

(28) Dickinson, E. Food Emulsions and Foams: Stabilization by Particles. *Curr. Opin. Colloid Interface Sci.* **2010**, 40−49.
(29) French, D. J.; Brown, A. T.; Schofield, A. B.; Fowler, J.; Taylor, P.; Clegg, P. S. The Secret Life of Pickering Emulsions: Particle Exchange Revealed Using Two Colours of Particle. *Sci. Rep.* **2016**, No. 31401.
(30) Hosseini, H.; Shojaee-Aliabadi, S.; Hosseini, S. M.; Mirmoghtadaie, L. Nanoantimicrobials in Food Industry. In *Nanotechnology Applications in Food: Flavor, Stability, Nutrition and Safety*; Elsevier, 2017.
(31) Saikia, T.; Sultan, A. S. Development of Silane-Modified Colloidal Silica Pickering Emulsion Stabilized by Organophilic Micronized Phyllosilicate for Conformance Control. *J. Pet. Sci. Eng.* **2020**, No. 107427.
(32) Gonzalez Ortiz, D.; Pochat-Bohatier, C.; Cambedouzou, J.; Bechelany, M.; Miele, P. Current Trends in Pickering Emulsions: Particle Morphology and Applications. *Engineering* **2020**, 468−482.

https://doi.org/10.1021/acsomega.1c02956
ACS Omega 2021, 6, 30919−30931