

Performance of PAM/PEI gel system for water shut-off in high temperature reservoirs: Laboratory study

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ABSTRACT: A polymer gel is one of the common remediate methods to either reduce or totally block excessive water production in oilfields. Some systems demonstrated an excellent performance in treating the problem like polyacrylamide tert-butyl acrylate (PAtBA)/polyethylenimine (PEI). In this study, polyacrylamide (PAM) was introduced as a cheap alternative to PAtBA that can tolerate high salinity reservoirs. The thermal stability of the PAM/PEI polymeric gel in saline water was examined at 150°C (302F). Samples prepared in sea water showed better stability compared with distilled and field water. Dynamic rheology and core-flooding experiments were used to evaluate the PAM / PEI gel system at high temperatures. NaCl and NH₄Cl were evaluated as a possible retarders for delaying the gelation time in order to achieve a successful placement. NH₄Cl was found to be more effective retarder. Core-flooding tests were conducted in sandstone and carbonate cores. The subject polymer gel was injected at rates typical of those in field applications. The injectivity of PAM/PEI was tested in Berea sandstone cores with initial permeability of ~45 mD. The post-treatment of the system showed a permeability reduction of ~94% for a period of two weeks. The injectivity in low permeability carbonate cores required more retardation compared with the injectivity in sandstone cores. The gel reduced the permeability to brine in Indiana limestone core by 99.8% for more than 5 months. Rheology of cured gel samples indicated that the gel strength needs about one day of curing in the core for the strength to stabilize. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41869.

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INTRODUCTION

One of the serious issues that face the petroleum industry is the production of huge amounts of water. This occurs as a result of the maturity of the oil/ and or gas wells. Different technical, economical, and environmental problems are associated with the increase in water production.¹ The water produced may cause corrosion and scale in the operation tools. In addition, this water needs to be lifted, separated from oil, and re-injected which require special plants which will add more costs. Consequently, excessive water production reduces profitability. Some environmental concerns exist if the produced water is disposed by a large amount without treatment. This water may contain toxic elements such as mercury and arsenic.² Eventually, this may lead to the early end of the economic life of the well if the problem is not treated.

Different mechanical and chemical methods were used in the oil-field to deal with the unwanted water production. The use of poly-

mer gels was considered as one of the remediated chemical techniques to overcome the problem. The application of polymer gels for water control is referred to as conformance improvement treatments (CITs).³ The technology of polymer gels is based on a low viscous flowable mixture of a polymer and a cross-linker referred to as gelant.⁴ Both, the polymer and the cross-linker are water soluble. The gelant is prepared on the surface and then injected into the target zone. Then, with time and temperature the gelant is converted into 3-dimensional (3-D) network structure via a cross-linking reaction between the polymer and the cross-linker. Polymer gels are categorized into two main groups; inorganic and organic, depending on the nature of the cross-linker. In inorganic gels, a metal ion is used to cross-link the polymer through a bonding believed to be coordination covalent bond. The most common element is the trivalent chromium ion (Cr⁺³). An example of inorganic cross-linked gels is the partially hydrolyzed polyacrylamide (PHPA)/Cr⁺³.⁵ On the other hand, organically cross-linked gels

Table I. Specifications of the Cores Used for Polymer Gel Evaluation

Core type	Diameter (cm)	Length (cm)	Pore volume (cm ³)	Porosity (%)	Initial permeability to Brine (mD)
Berea sandstone	3.8 (1.49 in)	7.48 (2.5 in)	13	15	44.45
Indiana limestone	3.76 (1.48)	7.67 (3.03 in)	7.5	8.9	2.98
Indiana limestone	3.59 (1.41)	7.55 (2.97 in)	11	13.89	6.5

are based on a polyacrylamide-based polymer and an organic cross-linker such as polyacrylamide tert-butyl acrylate (PATBA)/polyethylenimine (PEI) gel system.^{6–17} A detailed review of the chemistry and field applications of PATBA/PEI gel system can be found elsewhere.¹⁸

The application of chromium cross-linked gels was limited to low temperature reservoirs. This is due to their low gelation times at high temperatures. Moreover, different technical concerns were associated with chromium cross-linked gels such as thermal stability, propagation into the target zone as well as chromium toxicity.⁷

The widely used organically cross-linked gel is PATBA/PEI. It was applied in different parts around the globe. Although it exhibited high performance for water control at high temperatures but it showed some compatibility problems with some field mixing water when a retarder is used for delaying gelation time.¹⁶ At the same time, recent research indicated that low cost homo polymers of PAM can be used instead of PATBA to form polymeric gels.¹⁹ PAM/PEI showed a permeability reduction of 100% using Berea sandstone cores at 90°C for 1 month. But some reservoirs have a temperature higher than 90°C. Hence, evaluation of PAM/PEI gel system at higher temperatures is needed to recommend the system for higher temperature applications. Hence, the objectives of this study are to study the thermal stability of PAM/PEI polymer gel system in bulk at 150°C (302F) using different salinities (distilled, field, and sea water), optimize a formulation of PAM/PEI with a compatible retarder to delay the gelation time such as NaCl and NH₄Cl for safe system injectivity, evaluate the long-term water shut-off effectiveness of the system at high temperatures (150°C) in sandstone and carbonate lithologies, and examine the effect of aging on gel strength of cured gels to estimate the proper time for gel curing inside the cores.

EXPERIMENTAL

Materials

Two polymer solutions were used in this study. Polyacrylamide (PAM) was provided by SNF Floriger as an aqueous solution and used without further treatment. PAM solution was 20 wt % active and has a molecular weight within the range 250–500 kg/mol (as disclosed by the supplier). PEI was used as a cross-linker in a solution form. Its activity and molecular weight were 30 wt % and 70 kg/mol, respectively. Salts used in this study include Sodium chloride (NaCl), ammonium chloride (NH₄Cl), and potassium chloride (KCl). All these salts were ACS grade.

Berea sandstone and Indiana limestone cores were used to assess the core-flooding experiments. Their properties are given in

Table I. XRD analysis revealed that Berea sandstone core contains 99 wt % Quartz and the balance is Kaolinite (1 wt %), whereas, Indiana limestone core contains 99 wt % Calcite and 0.8 wt % Coasite. The elemental analysis was performed by XRF and the results are shown in Table II. Two Indiana limestone cores were tested to evaluate the polymer gel system in carbonate lithology.

Procedure

The thermal stability was assessed through bulk testing and a wide range of concentrations was used for PAM and PEI. The gelling solutions were prepared at room temperature. The amount of PAM, PEI, or water was added depending on the concentrations of the polymers and the sample volume. For a sample volume of 30 mL with PAM/PEI of (9/1) wt %, 13.5 mL of PAM was added to 15.5 mL water first and stirred for about one minute, then 1 mL of PEI was added and the mixture was stirred for 10 more minutes. The polymer solutions which are referred to as gels were transferred into the Screw-Thread GL 18 Schott-type high thermal resistance glass tubes. Nitrogen gas was circulated through the gelling solutions. Finally, all samples were put in an oven at 150°C (302F).

For the dynamic rheology measurements samples of PAM/PEI (9/1) wt % were prepared at room temperature. A specified amount of salt (retarder) was mixed with field water first, then the two polymers (PAM & PEI) were added in the same way describe above. Then, the sample was loaded to the pressure cell mounted on the rheometer. All tests were done at a temperature of 116°C (240.8F), a pressure of 500 psi (34.47 bar), a frequency of 1 Hz, and a strain of 10%. The selection of the temperature (116°C) was based on a previous study.¹⁶ The down-hole temperature (150°C) of the reservoir was expected to drop by 30.1°C during the pre-flush (2 wt % KCl) injection. Hence, all

Table II. Elemental Analysis of Berea Sandstone and Indiana Limestone Cores

Element	Content (wt %)	
	Berea sandstone	Indiana limestone
Si	49.73	0.1772
Al	4.103	0.616
P	0.3871	0.7011
K	1.443	0.08895
Ti	0.379	0.00674
Fe	1.447	0.1486
Ca	1.185	57.91

Table III. Chemical Analysis of the Formation Brine

Ion	Concentration (mg/L)
Na	59,300
Ca	23,400
Mg	1510
SO ₄	110
Cl	137,000
HCO ₃	353
Total dissolved solids (TDS)	221,673

rheology and injectivity of the polymer gel system were done at 116°C. The formation brine was prepared according to the concentrations reported in Table III. The pre-flush fluid was prepared by adding 2 wt % KCl to the field mixing water. The chemical analysis of this water is given elsewhere.¹⁶ Note that the field mixing water was collected from a close field.

The effectiveness of PAM/PEI system was tested in a core-flow setup. Berea sandstone core was first saturated with formation brine given in Table III. Nine pore volumes of brine were injected to determine the initial permeability of the core by using Darcy's law. Then, 2 wt % KCl, prepared in field mixing water, was forwarded through the core to displace the formation brine (two pore volumes were injected). Six pore volumes of the gelant were injected at 1 cm³/min. All the previous steps were done at 116°C, under a back pressure and overburden pressure of 1000 and 2500 psi, respectively. To examine the polymer gel system in Indiana limestone cores, the core-flow setup was slightly modified to simulate the real injectivity in the field. According to a recent study,¹⁶ the residence time for the system inside the tubing before reaching the formation was estimated to be 55 minutes. Coiled tubing was added to the core-

flow system such that the dead volume was about 9 cm³. This volume was heated in the tubes inside the oven before hitting the core face. Therefore, the injection rate was adjusted to 0.15 cm³/min for gelant placement. A total of 15 pore volumes were injected. This includes six pore volumes of formation brine at different flow rates to provide a base for the core permeability to brine. Then, three pore volumes of a pre-flush were injected to cool down the core followed by six pore volumes of the gelant at 0.15 cm³/min to ensure core saturation by the gelant.

Equipment

The dynamic shear tests were performed in a discovery hybrid rheometer (DHR) provided by TA Instrument. This machine is equipped with a high pressure cell in which the gelation experiments were performed. The pressure cell has a cup and bob diameters of 28 and 26 mm, respectively. All experiments were conducted at a temperature of 116°C and a pressure of 500 psi. The pressure cell has a torque range of 100 μN.m to 0.2 N.m and a maximum working temperature of 150°C. It should be mentioned that the viscosity of the gelant was measured by using concentric cylinder geometry at room temperature (25°C).

The core-flow experiments were conducted in a high pressure and high temperature core-flood assembly system. Two Isco Syringe pumps were used with maximum injection pressure of 7500 psi. A Memmert oven was used with an upper temperature limit of 200°C to simulate the temperature in the reservoir. The setup was equipped with a back pressure regulator running at 1000 psi to keep the liquid in solution as well as to prevent gases from escaping from the core. Two Transducers (5–66-Model) were used with a range from zero to 5000 psi. A data acquisition system that is capable of recording data every second was connected to the setup. Figure 1 shows a schematic diagram of the experimental setup.

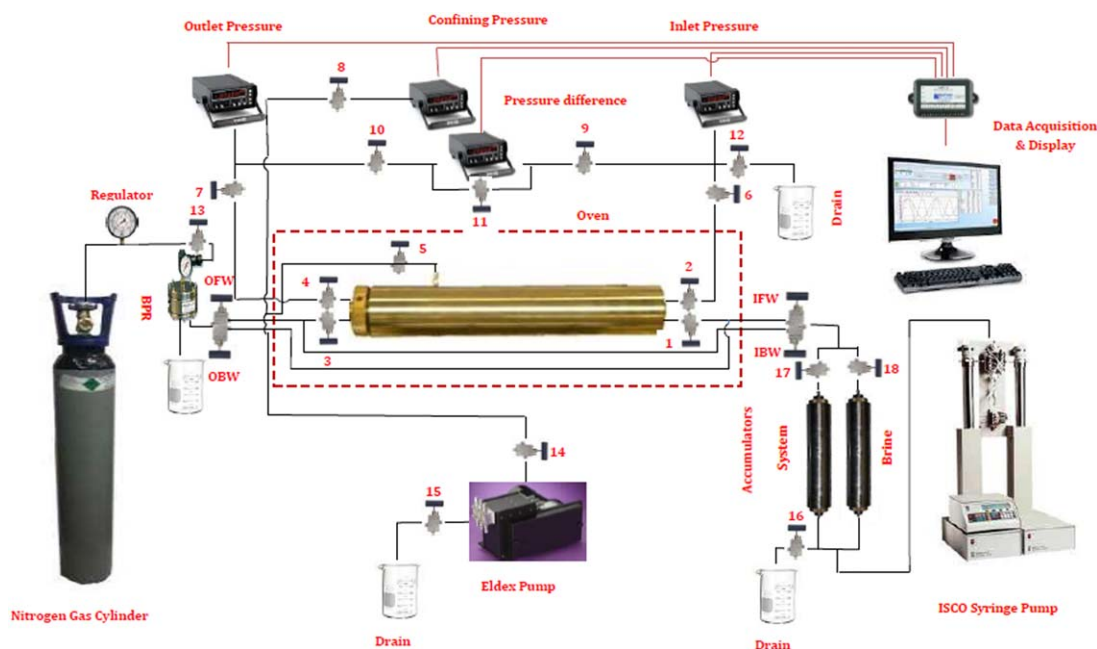
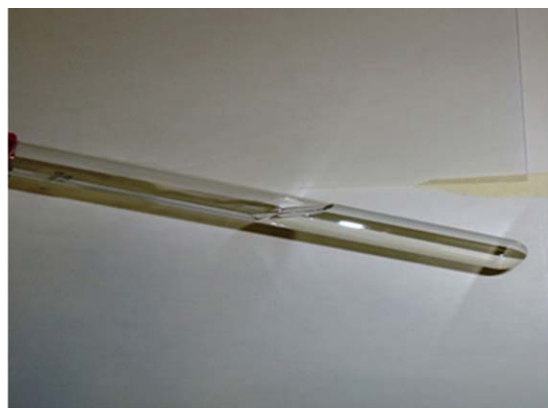
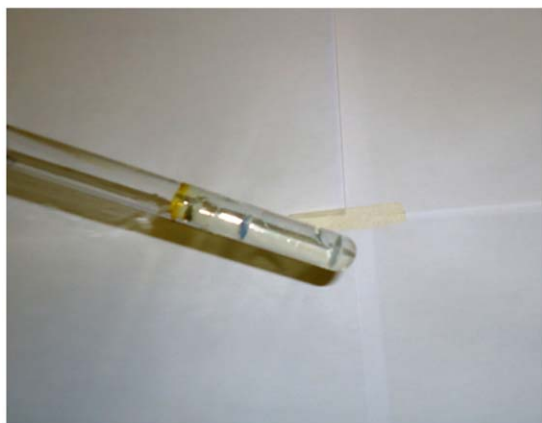


Figure 1. A schematic diagram of the core-flooding apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)



(b)

Figure 2. A sample of PAM/PEI, (9/1) wt % in distilled water after (a) 0 day, (b) 1 day. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The frequency sweep tests of the cured gels were performed in ARES rheometer (with a force rebalance transducer within the range 0.002–100 Nm torque) which is a controlled strain type. Samples were prepared in a Screw-Thread GL 18 Schott-type high thermal resistance glass tubes, and then transferred to the rheometer. A cone with 1° angle and 48 μm truncated gap was used. The sample was placed in the plate and then the cone was brought down to the specified gap. The frequency sweep tests were done at 5% strain which was proved to be within the linear viscoelastic region following a separate strain sweep test.

RESULTS AND DISCUSSION

Thermal Stability of PAM/PEI Gel

The first study of PAM/PEI gel system was reported by Allison and Purkaple in 1988.²⁰ A formation of aqueous gels was noticed at room temperature. PAM/PEI gel system was studied at 130°C (266F).¹⁹ The authors observed a rigid ringing gel system at PAM concentrations of 7 and 9 wt %, and PEI concentrations in the range 0.3–3 wt %. Distilled water was used to examine the stability of the system during a period of 2 months.

Here, the thermal stability of PAM/PEI system is studied in bulk at 150°C (302F) using different salinities. This includes

distilled, field, and sea water. The concentration of PAM ranged from 9 to 3 wt %. PEI concentrations were 1, 0.6, and 0.3 wt %. Figure 2 shows a sample of PAM/PEI before and after one day. The flowable low viscosity gelling solution [Figure 2(a)] turned into a rigid non-flowing gel [Figure 2(b)] by forming a 3-Dimensional (3-D) structure.

For the samples prepared in distilled water, de-gelation occurred after 13 to 35 days for the gelling solution containing 0.3 wt % PEI. For the 0.6 wt % PEI, the de-gelation time ranged from 10 to 44 days. We do believe that increasing PAM concentration will increase the gel strength and consequently enhance the thermal stability, and decreasing PAM concentration will lead eventually to lower strength and lower thermal stability. However, increasing PAM concentration will cause short gelation time which unfavorable from injectivity point of view. Figure 3 shows a sample of PAM/PEI solution of (9/0.3) wt % after ageing to 49 days. At PAM/PEI of (9/1) and (7/1) wt %, a thermally stable rigid ringing gel was observed for 2 months. The physical strength of PAM/PEI at (7/1) wt % decreased after 2 months and a surface deformed gel was observed with water expelled out of the gel structure. This phenomena is called syneresis which was noticed previously with high PEI loading, hence lower thermal stability is expected with high PEI concentrations. The physical strength of the gel systems were described by using Sydansk's³ description method. Table IV shows the observations for polymer gel samples prepared in distilled, field, and sea water.

In sea water, the samples were found to be more stable than in distilled and field water. This may be due to the presence of salts in high concentration. It can be seen from Table IV that the de-gelation occurred only at PEI concentration of 0.3 wt %. The de-gelation period ranged from about 20 to 60 days. At a polymer concentration of 3 wt %, no gel was formed. Syneresis was observed at PEI concentration of 0.6 wt %. On the other hand, samples prepared in field water showed poor stability. Samples containing 9 and 7 wt % PAM and 1 wt % PEI showed surface deformed gel with some flowing gel. De-gelation took place in all other formulations.



Figure 3. Sample of PAM/PEI, (9/0.3) wt % aged for 49 days at 150°C (302F). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Bottle Testing of PAM/PEI Gels After 16 Weeks of Thermal Treatment at 150°C (302F) in Different Types of Mixing Waters

PAM/PEI content (wt %)	Observation			Physical description of the gel		
	Water type			Water type		
	Distilled	Field	Sea	Distilled	Field	Sea
9/1	Brown	Brown	Brown	Moderately deformable non-flowing with syneresis	Highly deformable non-flowing	Ringing rigid
7/1	Brown de-gelation	Brown 30% flow	Brown	NA	Highly deformable non-flowing	Moderately deformable non-flowing
5/1	Brown de-gelation	Brown de-gelation	Light brown	NA	NA	Moderately deformable non-flowing with syneresis
3/1	Brown de-gelation	Brown de-gelation	Transparent gel	NA	NA	No detectable
9/0.6	Brown de-gelation	Brown de-gelation	Light brown	NA	NA	Moderately deformable non-flowing with syneresis
7/0.6	Brown de-gelation	Brown de-gelation	Brown	NA	NA	Ringing rigid gel with syneresis
5/0.6	Brown de-gelation	Brown de-gelation	Light brown	NA	NA	Moderately deformable non-flowing with syneresis
3/0.6	Brown de-gelation	Brown de-gelation	Transparent gel	NA	NA	No detectable
9/0.3	Brown de-gelation	Brown de-gelation	Brown de-gelation	NA	NA	NA
7/0.3	Brown de-gelation	Brown de-gelation	Brown de-gelation	NA	NA	NA
5/0.3	Brown de-gelation	Brown de-gelation	Light brown de-gelation	NA	NA	NA
3/0.3	Brown de-gelation	Brown de-gelation	Transparent gel	NA	NA	No detectable

NA: not assigned to any description.

Generally, the best formulation of PAM/PEI system that is more thermally stable in sea water at 150°C (302F) is the (9/1) wt %. This system was observed to have a good thermal stability in deionized water at 130°C (266F) as reported by Al-Muntasheri *et al.* in 2008¹⁹ by using bottle testing method. At PAM concentration of 9 and 7 wt % and PEI concentration in the range 0.3–3 wt %, the system showed a rigid or rigid ringing gel for 2 months.

Gelation of PAM/PEI System with Retarders

From the thermal stability test which was done through the bulk testing method, it was found that the most thermally stable formulation of the polymer gel at 150°C (302F) is 9/1 wt % (PAM/PEI). So, it is proposed to use this formulation to exam-

ine the stability in porous media through the core-flooding setup. However, the gelation time of 9/1 wt % (PAM/PEI) at 150°C (302F) is less than half an hour. This time is not sufficiently enough for field applications to place the gelling solution safely without prior gelation before reaching the target zone. The time needed for gelling solution placement was reported to be about 55 min.¹⁶ Thus some dynamic rheological experiments were performed prior the core-flooding experiments to come up with acceptable formulation with sufficient gelation time and high strength.

Different retarders were examined at 116°C (240.8F) to identify a formulation with a low viscosity and an acceptable gelation time. This can be accomplished by adding a suitable retarder

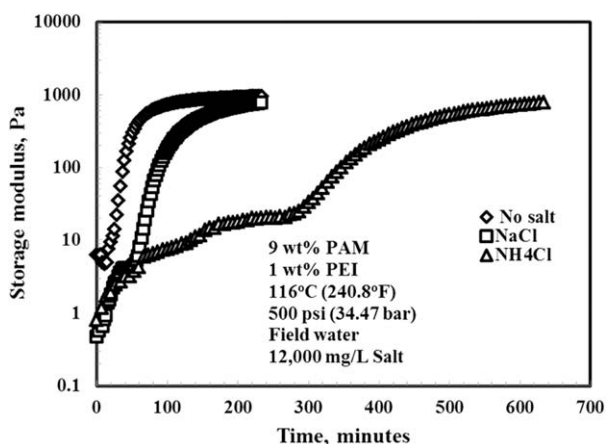


Figure 4. Effect of retarders on the gelation time and storage modulus of PAM/PEI (9/1) wt % gel system.

with the optimum concentration. At the same time, the retarder concentration should not reduce much the final gel strength of the polymer gel. From an earlier study, it was found that sodium chloride (NaCl) and ammonium chloride (NH_4Cl) can increase the gelation time depending on the concentration.²¹ However, gels prepared in the presence of NH_4Cl showed lower strength compared with NaCl at the same time of testing and longer times are required to reach the same equilibrium value. The reduction in the elastic modulus in samples prepared with NH_4Cl can be explained through charge shielding effect. The alkaline hydrolysis of PAM yields negative carboxylate groups and ammonia gas. We do believe that NH_4^+ shields the carboxylate groups more compared with Na^+ (This was noticed with the gelation of PHPA with PEI in a previous study²¹). This eventually reduces the cross-linking sites available to PEI and hence, the reduction of elastic modulus. Thus, it is required to optimize the formulation taking into account the gelation time as well as the gel strength (storage modulus).

Sodium chloride and ammonium chloride were added initially at a concentration of 100 lb/1000 gal (12,000 mg/L). As can be seen from Figure 4, the gelation time was about 70 min only in the case of NaCl which was lower than the target (more than

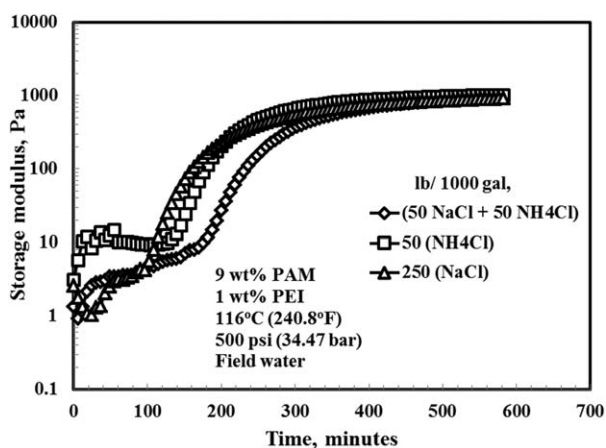


Figure 5. Effect of retarders on the gelation time and storage modulus of PAM/PEI (9/1) wt % gel system at different salt concentration.

120 min). This time was planned to inject more pore volumes into the cores without any pre-gelation which can cause tubings blockage. It was stated earlier that the system needs 55 min to reach the core face; hence 120 min will allow more volumes to be injected safely. When NH_4Cl was added at the same concentration, the gelation time was increased to around 295 min, but the plateau strength was very weak as the storage modulus was about 690 Pa only. The higher retardation achieved by NH_4Cl can be reasoned to the stronger charge shielding effect (compared with NaCl) which was noticed previously in the gelation of PHPA with PEI.²¹ It should be mentioned that after about 200 min, the sample with NaCl began to reach the plateau value (700 Pa), whereas, the sample with NH_4Cl exhibited only about 18 Pa. Thus, it was planned to examine either the combination of the two salts or to increase the concentration.

As a sample was prepared by adding 50 lb/1000 gal (6,000 mg/L) from the two salts, the gelation time and the storage modulus were observed to be about 189 min and 910 Pa, respectively. In another tests, the concentration of NaCl was increased to 250 lb/1000 gal (30,000 mg/L) and the concentration of NH_4Cl was decreased to 50 lb/1000 gal (6,000 mg/L). The results from Figure 5 show that the option of using NH_4Cl at a concentration of 50 lb/1000 gal (6000 mg/L) is the optimum one since the gelation time is about 150 min and the storage modulus is 1017 Pa. Therefore, it was decided to use NH_4Cl with 50 lb/1000 gal (6000 mg/L) in the evaluation of the polymer gel for water shut-off. The viscosity of the gelling solution which contains NH_4Cl was measured by using a concentric cylinder geometry. The viscosity was found to be about 40 cP in the range from 1 to 2500 1/s as shown in Figure 6.

Efficiency of PAM/PEI System in Porous Media

Core-flooding experiments are widely used to evaluate the developed systems for the application in petroleum reservoirs for enhanced oil recovery.^{22–27} For water shut-off, PAM/PEI was evaluated in Berea sandstone core at 90°C (194F), where the system showed a permeability reduction of 100% for a period of 3 weeks.¹⁹ Other publications discussed the mechanism of water shut-off by polymer gels.^{28,29} In the following sections, core-flooding will be used to examine the efficiency of

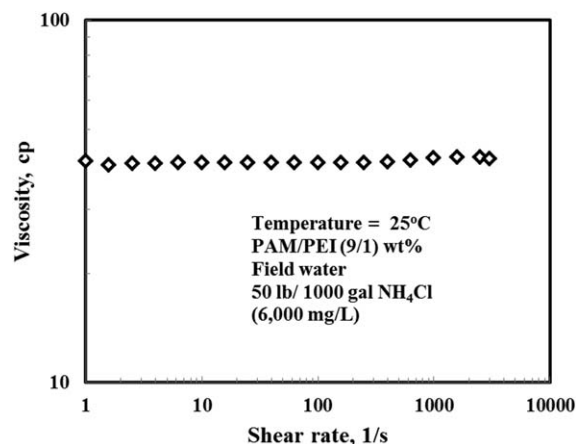


Figure 6. Viscosity vs. shear rate for the 9/1 PAM/PEI gelant at 25°C.

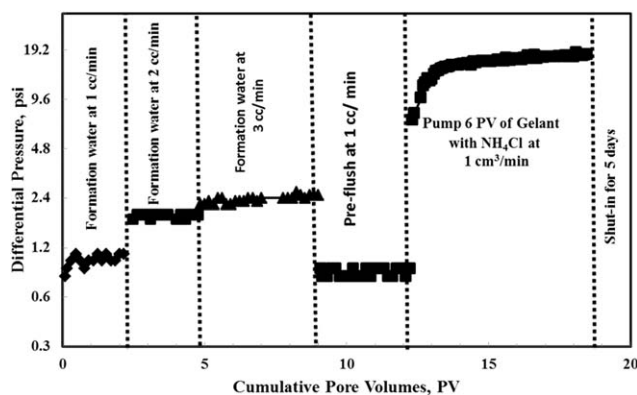


Figure 7. Pressure drop as a function of pore volumes in a core-flow experiment in Berea sandstone core.

PAM / PEI for water shut-off at an extendable temperature of 150°C (302F) in different lithologies (different core types).

Berea Sandstone Core

From the previous rheology results, 6000 mg/L NH_4Cl was chosen to elongate the gelation time of PAM/PEI. At this salt concentration, the expected gelation time and storage modulus are ~ 2.5 h and ~ 1017 Pa, respectively. Berea sandstone core was used to examine the injectivity of the gelant. After saturating the core with brine, the initial permeability to brine was found to be 45.45 mD. Then, 2 wt % KCl prepared in field mixing water was used to displace the brine. After that, a gelant containing 9 wt % PAM, 1 wt % PEI, 6000 mg/L NH_4Cl , 2 wt % KCl was injected through the core. All the previous steps were done at 116°C. A sample was collected from the core effluent in a high thermal resistant tube. This tube was put inside the oven to make sure that the gel did form inside the core. The pressure drop across the core during the injectivity of brine and gelant is shown in Figure 7. As can be seen, the pressure drop increased during gelant placement in comparison with brine injection. This is due to the fact that the gelant viscosity is higher than



Figure 8. Sample from Berea sandstone core effluents [(PAM/PEI) 9/1 wt % with 6,000 mg/L NH_4Cl] aged beside the core-holder for 5 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Percent Permeability Reduction (R_k) in Berea Sandstone Core at 150°C (302F) for 5 Months

Time (days)	Permeability reduction R_k (%)
0.04	100
0.21	100
1	99
2	98
5	98
6	97
8	97
9	96
11	96
12	95
13	95
14	94
15	94

brine viscosity. The placement time is about 1.36 h after which the temperature was increased to 150°C. Then, the core was shut-in for 5 days to mature the gel in the core. The sample in the tube showed a rigid gel (Figure 8). After the shut-in time (5 days), 2 wt % KCl was injected in the backward direction to simulate the production in the field. A constant pressure of 2050 psi was maintained in the pump. Within 2 minutes, the inlet pressure was increased from 1050 to 2000 psi. Hence, the pressure drop across the core was maintained at 1000 psi (86.95 Bars). No flow was initiated through the core. The PAM/PEI (9/1) wt % showed a high efficiency in shutting-off water in Berea sandstone cores. As shown in Table V, the system reduced the permeability to brine by $\sim 94\%$ for a period of 2 weeks.

Indiana Limestone Core

To test the effectiveness of the developed gel system in carbonate formations Indiana limestone cores were used. One core was saturated with formation brine first, and then the initial permeability was measured to be 2.98 mD by injecting different flow rates. A gelant containing 9 wt % PAM, 1 wt % PEI, 50 lb / 1000 gal NH_4Cl was prepared in 2 wt % field mixing water, and then forwarded to the core at 0.15 cm^3/min . The injectivity was conducted at a temperature of 116°C, 2500 psi confining pressure, 1000 psi back pressure. Figure 9 shows that during the gelant injection the differential pressure across the core was higher than that of brine. The high gelant viscosity is the reason behind this observation (see Figure 6). However, the differential pressure continued to increase more than 1000 psi and some valves leaked since it reached its maximum allowable pressure and the injection was terminated. This is an indication of the gel formation inside the core. Approximately two pore volumes were injected in about 120 min as shown in Figure 9. This finding confirms that more retardation is needed to place and saturate the core with more pore volumes. The more needed delay in gelation time in tight carbonate cores could be reasoned to the low permeability where the gelant solution cannot be

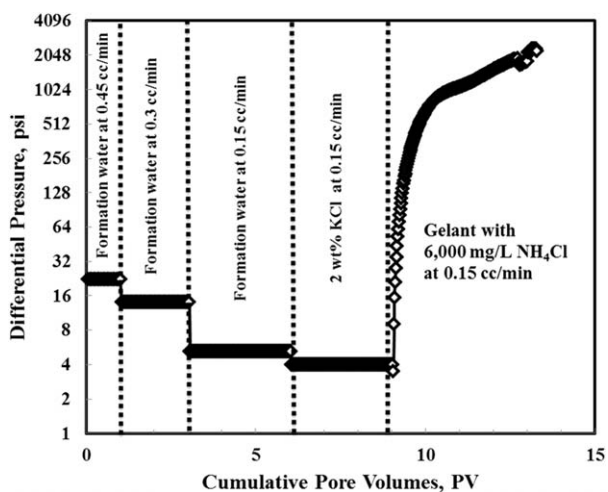


Figure 9. Pressure data as a function of pore volumes injected in Indiana limestone core with initial permeability to brine of 2.98 mD.

transmitted in a short time which leads to the gelation in the small pores before saturate the whole core. Consequently, it was decided to increase the retarder (NH_4Cl) concentration in the second trial.

Another Indiana limestone core was selected which has initial permeability to brine of about 6.5 mD. The same previous injectivity plan was implemented by increasing the concentration of NH_4Cl to 300 lb/ 1000 gal (36,000 mg/L). This concentration resulted in sufficient retardation when a copolymer was used with PEI in a previous study.¹⁶ The differential pressure during the gelant injectivity at 116°C was increased to a plateau value of about 50 (a factor of 11.1) as shown in Figure 10. The stable differential pressure during the injectivity of the gelant is a proof for the retardation feature of the new concentration of NH_4Cl . It should be mentioned that the gelant injectivity took about 8 hours where about 6 pore volumes were placed. After that, the core was shut-in for 5 days for the gel to mature. When the shut-in period was completed, 2 wt % KCl was injected in a back flow direction. The differential pressure

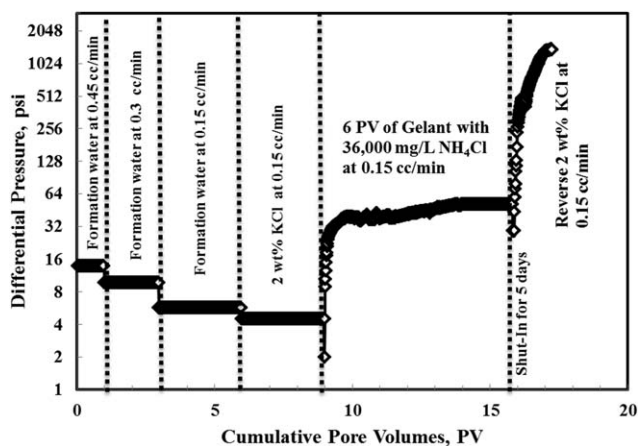


Figure 10. Pressure data as a function of pore volumes injected in Indiana limestone core with initial permeability to brine of 2.98 mD.

Table VI. Percent Permeability Reduction (R_k) in Indiana Limestone Core at 150°C (302F) for 5 Months

Time (days)	Permeability reduction R_k (%)
0.04	100
0.21	100
1	99.8
7	99.8
14	99.8
21	99.8
22	99.8
145	99.7

increased to more than 1000 psi without any flow through the core (Figure 10). This is an indication of the efficiency of the gel to reduce water production. Few drops were observed after one day of treatment. From Table VI, the post-treatment showed a permeability reduction by about 99% for more than 5 months.

Effect of Aging on Gel Strength

To investigate the effect of time on the gel strength, the same formulations used in core-flooding experiments were aged for different times. The first sample (9/1) (PAM/PEI) wt % contains 6000 mg/L NH_4Cl was injected into Berea sandstone core. The other sample contains 36,000 mg/L NH_4Cl was injected into Indiana limestone core. Figure 11 shows the storage modulus as a function of frequency in the range 0.1–100 rad/s for samples containing 9 wt % PAM, 1 wt % PEI, and 6000 mg/L NH_4Cl aged at 150°C (302F) for four days. The gel lost about 46% of the gel strength after 4 days. This is in agreement with what was found with other organically cross-linked gels.³⁰ The equilibrium value of the storage modulus after 4 days was about 2131 Pa. The gel has almost stabilized at this value after one day of aging.

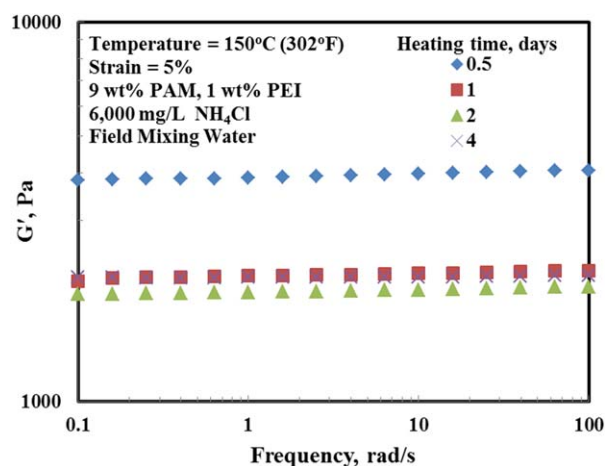


Figure 11. Frequency sweeps for (PAM/PEI) 9/1 wt % with 6,000 mg/L NH_4Cl with different gel ages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

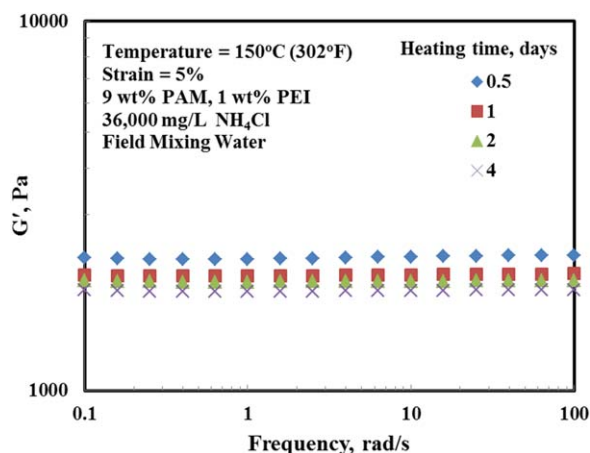


Figure 12. Frequency sweeps for (PAM/PEI) 9/1 wt % with 36,000 mg/L NH_4Cl with different gel ages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the high NH_4Cl concentration (36,000 mg/L), the samples were aged at the same conditions and results are presented in Figure 12. The value of the storage modulus is lower than the low NH_4Cl concentration. The equilibrium value of the storage modulus after 4 days was about 1860 Pa. So, increasing NH_4Cl by about 83% resulted in a decrease in the storage modulus by about 13%. The equilibrium value decreased from 2290 Pa (after 12 h) to 1860 Pa (after 4 days). The value of the storage modulus has stabilized during the 4 days. From Figures 11 and 12, it can be concluded that one day shut-in is more than enough for the gel to be cured inside the core.

CONCLUSIONS

Laboratory tests were conducted for PAM/PEI gel system as an alternative for PatBA/PEI. Dynamic rheology and core-flooding measurements were performed. A thermally stable formulation of PAM/PEI (9/1) wt % at 150°C (302F) was used. Compatible retarders (NaCl and NH_4Cl) with PAM/PEI at a salinity of the target reservoir were chosen for gelation time delay to perform successful placement of the system. PAM/PEI was evaluated in a core-flooding system at 150°C (302F) using Berea sandstone and Indiana limestone core with initial permeability of 45 and 6.5 mD, respectively. The following conclusions can be drawn from this study:

1. At the same salt concentration, NH_4Cl is more efficient in delaying gelation compared with NaCl.
2. During the cross-linking of PAM with PEI the gel with NH_4Cl showed lower strength compared with NaCl for a given time and the addition of NH_4Cl requires longer shut-in times to reach higher values of storage modulus.
3. The combination of NaCl and NH_4Cl resulted in decreasing the gel strength. This means that any addition of NH_4Cl will delay gelation and decrease the gel strength at any given time but the ultimate gel strength will remain almost the same.
4. NH_4Cl was chosen for retardation at a concentration of 50 lb/1000 gal (6,000 mg/L) where it exhibited strength of ~ 1017 Pa with acceptable gelation time (>2 h).

5. PAM/PEI was injected successfully in Berea sandstone core with initial permeability to brine of ~ 45 mD.
6. The post-treatment in Berea sandstone core at 150°C (302F) showed a reduction in permeability to brine of $\sim 94\%$ during a two weeks period.
7. Gelant placement in tight carbonate cores requires long retardation time. Hence, higher concentrations of retarders should be used.
8. The post-treatment in Indiana limestone cores showed a reduction in permeability of $\sim 99.8\%$ for more than 5 months.
9. Although the placed gel system was cured for more than 4 days inside the cores, however, rheological tests on cured gels indicate that one day is enough for the gel strength to be stabilized in the cores.

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