

Multiscale Investigation Of A Less-Damaging Friction Reducer To Mitigate Formation Damage In Unconventional Shale Reservoirs

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Abstract

Among the additives in slickwater fracturing, only friction reducers (FRs) are heavy molecular polymers, many of which are polyacrylamide-based. Although they are useful for their intended purpose, FRs rapidly decrease the production rate in shale by damaging the formation. This paper describes the damage mechanism in detail and proposes a less-damaging FR.

Molecular dynamics simulation was used to evaluate how salts potentially encountered during fracturing treatments affect polyacrylamide-based FRs (PAM and HPAM). This work focuses on identifying an ideal less-damaging FR and proposes one based on predictions verified by the experimental results of coreflood simulation tests. Field cases were also conducted, and results show that this less-damaging FR can better mitigate formation damage compared with conventional FRs. Although production decline still occurs in a treated well, it is slower than that of a control well treated with a conventional FR.

The radius of gyration results from molecular dynamics simulations show the salt-tolerant patterns of PAM and HPAM follow a trend in which trivalent ions affect polymers more than bivalent ones, and monovalent ions affect the polymers the least. This result is consistent with results reported in the literature. This research predicts that the polymer chains in a less-damaging FR should be in the medium to short-range, the polymer concentration should be much lower, and nanoparticle fillers are necessary. The turbidities of the less-damaging FR solutions are almost ten times lower than those of HPAM. In addition, this new FR has only a negligible reaction with selected salts. Coreflood test results indicate that the permeability lost via conventional FR is 92.6% to 99.8%. In contrast, the permeability damage via the less-damaging FR is 0.8%. In the field test, two wells on the same platform were treated with two different FRs. After three months of production, a comparative decline of gas production rate in measurable formation damaged by the less-damaging FR (10% reduction of initiated production rate) and a conventional inverse emulsion FR (30% reduction of daily gas production) was observed.

This work simulates the trend of conventional FRs affected by salts for the first time. It further provides a systematic method to mitigate formation damage caused by FRs by combining molecular dynamics simulation, prediction, lab tests, and field tests. This procedure is useful for future work as well. A new less-damaging FR has been identified that will prove beneficial for the industry.

Introduction

Oil and gas have been produced economically from shale plays by combining the horizontal drilling and hydraulic fracturing, ushering in a revolution in the shale oil and gas industry. However, the production of oil and gas from shale has declined rapidly over the past few years. For example, in the present study, the

first three months of operation saw a 30% decline in production, followed by a 70% reduction over three years. The overall estimated ultimate recovery (EUR) is less than 10%.

It is well known that slickwater is the most commonly used fracturing fluid system. However, this popular method may actually be the cause of the low EUR and rapid production decline. Among the chemicals used in slickwater, only the friction reducer (FR) is a heavy, polyacrylamide-based molecular polymer. All other slickwater components are of such small molecular weight that they cannot be considerable factors in formation damage. Slickwater treatments do perform generally well, barring any external effects, such as encountering metal ions during the treatment procedure. However, in shale formations, there are several metal ions (Ca^{2+} , Mg^{2+} , etc.). During fracturing, pad acid reacts with the metal tubulars, and, as a result, Fe^{3+} is produced. This iron precipitation proves very damaging to shale formations, and all of the metal ions mentioned here affect FRs. Some biocides also degrade the performance of slickwater fracturing treatments. Researchers have studied formation damage caused by FRs in different ways; however, no systematic multiscale research has to date been conducted. This paper explains the mechanisms of FRs in shale formation damage caused by slickwater fracturing at the molecular scale, pore scale, core scale (permeability change) and reservoir scale (field case). An effective method is found to improve EUR. The present work focuses on samples obtained from the Otter Park and Evie shales.

Formation Damage Causes Oil and Gas Production Rate Decline. As noted in the previous section, FRs are essential to any slickwater fracturing fluid system in shale. However, the chemical components can damage the formation and reduce production (**Figure 1**). The other elements in Figure 1 includes Zn, Ba, Cu, and Mn elements. Si is excluded from the acid digestion results (Peña-Icart et al. 2011; Tessier et al. 1979). Although the majority of the previous research focused on evaluating the friction-reducing performance of these chemicals, only a few studies have addressed the potential formation damage (Ibrahim et al. 2018). Because of the polymeric nature of these chemicals (typically polyacrylamide (PAM)), a FR can cause damage either by creating a barrier on the surface of the formation or by penetrating deeply to plug the pores. In addition, breaking these polymers at temperatures lower than 200°F remains challenging (Woodroof and Anderson 1977).

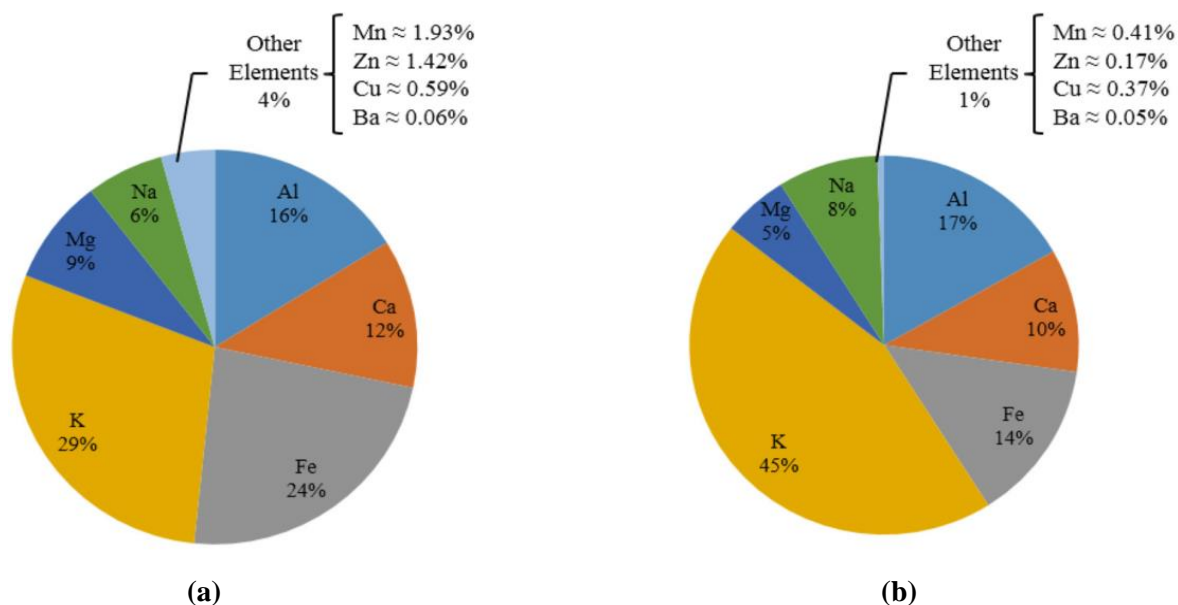


Figure 1—The six major elements of the (a) Otter Park and (b) Evie shale samples obtained by acid digestion.

The Structure of Shale. The pore-size distribution of shales is mainly small, down to several nanometres. Relatively large pores with poor connections can be up to four microns. Pores can also be connected by thin conduits down to 15 nanometres (**Figure 2**) (Sisk et al. 2010; Kuila and Prasad 2011). If big polymers are injected to the formation flocculate, the pore throats most likely would be plugged.

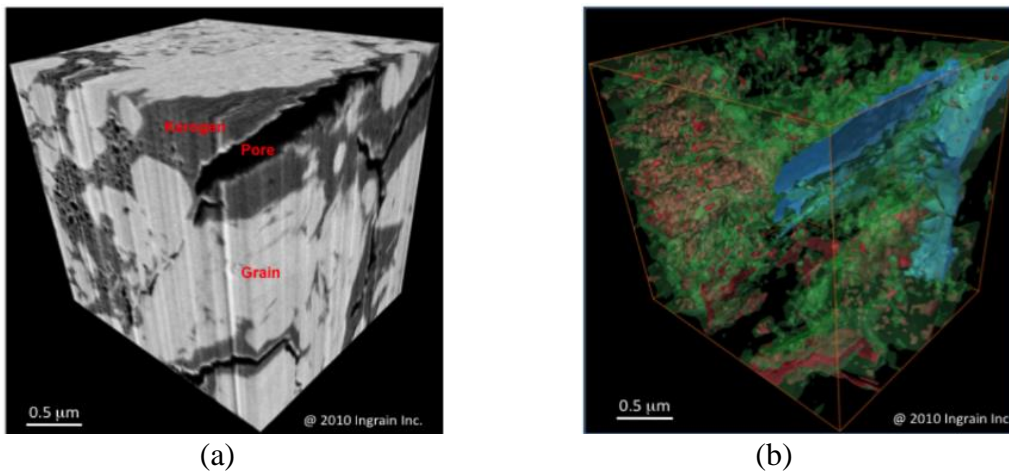


Figure 2—(a) Rendered volume of shale at the highest nano-resolution. (b) Kerogen (green), disconnected pores (red) and connected porosity (blue). The scale is 500 nanometres.

Fracturing Fluids. Slickwater fracturing was developed and used in other unconventional reservoirs, such as tight gas sand and shale (Carman and Cawiezal 2007). The evolution of fracturing fluids has alternated between oil-based, water-based, and liquefied natural gas fracturing fluids (Barati and Liang 2014). Because the FRs primarily used for slickwater fracturing are polyacrylamides, which are synthetic polymers, the perception was that they would be difficult to break.

The Components of Slickwater. In slickwater fracturing fluid, water, and proppant occupy 99% of the fluid-system volume (Jackson et al. 2011). Other additives like acid, FRs, surfactant, potassium chloride, scale inhibitor, pH adjusting agent, iron control agents, corrosion inhibitors, and biocides are also added to fracturing fluid at low concentrations to fulfil different purposes for different fracturing jobs (**Figure 3**).

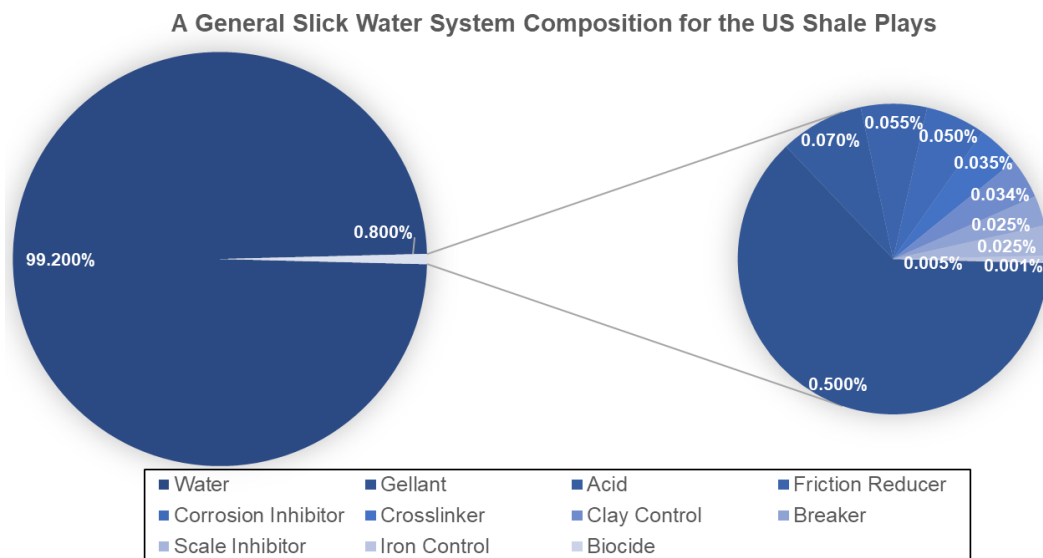


Figure 3—Volumetric composition of a general slickwater system for the US shale plays (edited with source data from www.fracfocus.org).

Metal Ions in Flowback. In flowback, different ions may affect friction reducers (Montgomery 2013) or other long-chain polymers pumped into reservoirs (**Table 1**). PAM and HPAM polymers are unstable when temperature increases. PAM-based FR can precipitate in the presence of divalent and trivalent cations, so formation damage could occur (Seright et al. 2009). The cations in flowback water should be considered carefully to prevent the FR from precipitating.

Table 1—The surface charge density of the focus ions (Essington 2005).

Ion	Charge[C]	Ion Radius [pm]	Surface Area [m ²]	Surface Charge Density[C/m ²]
Na ⁺	1.60E-19	116	1.69E-19	0.9462
K ⁺	1.60E-19	152	2.90E-19	0.5511
Ca ₂ ⁺	3.20E-19	114	1.63E-19	1.9594
Ba ₂ ⁺	3.20E-19	149	2.79E-19	1.147
Cl ⁻	-1.60E-19	167	3.50E-19	-0.4565
SO ₄ ²⁻	-3.20E-19	290	1.06E-19	-0.3028

Hydrochloric Acid (HCl) in Pre-Production Can React with Tubing Steel. In US shale fracturing, an acid stage is always used before the slickwater stage. Hydrochloric acid plays a key role in the hydraulic fracturing process. After a natural gas well's hole is bored, drillers will pump thousands of gallons of water mixed with acid (typically a 15 wt% HCl solution) into the well. The point is to clear out cement debris left over from the drilling stage, and to help open the underground shale fractures. After the acid stage is completed, slickwater and proppant are injected into the well to flush the natural gas out. Although this acid stage serves a useful purpose, the HCl can corrode the tubulars used for pumping. HCL not only corrodes the tubing steel, but also releases ferrous and ferric ions. The PAM-based FRs participate when encountering ferric ions.

Carbon Steel Composition Summary. During the fracturing treatment, the fracturing fluid must pass through many different tubulars made of several kinds of steel (**Table 2**). The materials selected are representative of alloys used as tubular goods or downhole equipment.

Table 2—The representative material of tubulars that fracturing fluids pass through.

Generic Name	C	Mn	S	Ni	Cr	Mo	Others
4130 ^(A)	0.31	0.46	0.018	0.03	0.88	0.20	--
9 CR ^(A)	0.13	0.48	0.010	0.057	8.27	0.96	CU-0.11 CU-0.10
420 ^(A)	0.38	0.36	0.010	0.37	12.70	0.05	N-0.23 Cb+Ta-5.25
2205 ^(A)	0.02	1.83	0.003	5.82	22.33	2.77	Ti-0.95
718 ^(A)	0.04	0.13	0.0002	53.20	18.18	3.12	Al-3.4 V-8.2
BC-Ti ^(B)	0.02	--	--	--	5.90	4.10	Zr-3.1

^(A)Balance Fe
^(B)Balance Ti

FeCl₃ Always Forms After Acid Flush. In fracturing treatments, among other chemicals, hydrochloric acid is largely used to dissolve minerals and initiate cracks in a formation. During the operation, the acid readily dissolves rust in the tubing or casing and corrodes steel equipments where it is mixed and pumped through. The acid also attacks iron-containing minerals in a formation under treatment. Iron could also be presented in dissolved or suspended form in produced water. When the fracturing fluid mixes with subsurface water and reacts with carbonate rocks and shale, the pH increases as the acid/fracturing fluid is consumed, and the dissolved iron starts to precipitate in the form of gelatinous iron hydroxide unless an effective iron control system is applied. The insoluble iron precipitation may accumulate in the reservoir and near the wellbore, thereby plugging or reducing the created and natural permeability of the reservoir. Dill and Smolarchuk (1988) have indicated that the above phenomenon, i.e. precipitation of iron in natural and newly developed fractures, is one of the main causes of formation damage. The iron can also precipitate and form scale within the tubing, which also reduces production.

The dissolved trivalent ferric ions react with polyacrylamide and flocculate in water (Kaşgöz et al. 2003). Water treatments always use this mechanism to remove trivalent ferric ions from water. But this reaction will damage the formation and decrease the friction-reduction rate during slickwater fracturing.

Typical Treatment Procedure of Slickwater Fracking. Several metal ions are generated and dissolved in fracturing fluid and flowback fluid. In the whole procedure, the FR is in a kind of brine environment. Polyacrylamide-based FRs will precipitate when they meet with different salts in water. The sizes of PAM/HPAM polymers are larger than most formation pores but smaller than fracture size. Without metal ions, the formation damage caused by FRs may not be that severe. Reacting with metal ions, however, the PAM/HPAM FRs coil or precipitate, the sizes are much bigger, and the formation damage becomes more serious.

This paper further discusses UV-VIS transmittance tests that indicate how metal ions in water affect HPAM FRs. A new less-damaging FR has much better results in the comparison tests. To summarize, the typical slickwater-fracturing treatment includes the following steps (**Table 3**).

Table 3—Different stages of slickwater fracturing (Holloway and Rudd 2015).

NO.	Pumping Steps of Slickwater Fracturing	Fluid Injected in Each Stage	Function
1	An acid stage	Several thousand gallons of water mixed with a dilute acid such as hydrochloric or muriatic acid	This serves to clear cement debris in the wellbore and provide an open conduit for other frac fluids by dissolving carbonate minerals and opening fractures near the wellbore.
2	A pad stage	Approximately 100,000 gallons of slickwater without proppant material	The slickwater pad stage fills the wellbore with the slickwater solution (described below), opens the formation and helps to facilitate the flow and placement of proppant material.
3	A prop sequence stage	May consist of several substages of water combined with proppant material (consisting of a fine mesh sand or ceramic material, intended to keep open, or “prop” the fractures created and/or enhanced during the fracturing operation after the pressure is reduced)	This stage may collectively use several hundred thousand gallons of water. Proppant material may vary from a finer particle size to a coarser particle size throughout this sequence.
4	A flushing stage	A volume of fresh water sufficient	Flush the excess proppant from the wellbore

Experimental Studies

Molecular Dynamics Simulations for PAM and HPAM FRs in Different Salt Water. Molecular dynamics (MD) simulation helps determine the structures and interactions of molecular components in certain force-filled solutions. MD is also a complement to conventional experimental approaches and enables observation of the different processes microscopically. MD serves as a link between microscopic and macroscopic scales of time and length, predicts the bulk properties by simulating molecular interactions and behaviors, and provides a link between theoretical hypothesis and experimental results in this paper. The mechanism of formation damage caused by polyacrylamide-based FRs is also further explained in a later section.

FR Selection. PAM (Polyacrylamide) and HPAM (Partially Hydrolyzed Polyacrylamide) are commonly used FRs. The concentration of PAM and HPAM in slickwater typically ranges from 0.25 to 2 gal/1000 gal. Considering the less FR concentration, the longer the simulation takes, it is better to use relative higher FR concentration during simulations to accelerate this simulation procedure. And FR-related formation damage always happens in reservoirs or after flowback, when much water molecules already filtrate into

rocks. In that condition, the real FR concentration is high. So, finally, the FR concentration in molecular dynamics simulations was 1.5 wt%, relative higher than normal dose in real treatment on site.

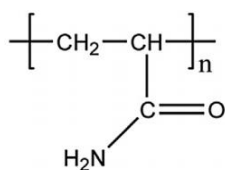
Main Simulation Steps. The main simulation steps included amorphous cells installation, forcite geometry optimization, NPT (NPT means the condition of constant particle number N, constant pressure P, and constant temperature T), NVT (NVT means the condition of constant particle number N, constant volume V, and constant temperature T), forcite analysis, and comparison of results and variables optimization.

Parameters for Characterizing Polymer Solutions. The radius of gyration (R_g) is used to quantify the conformation alteration of polymer chains. For the same polymer chain in salt water, the smaller the R_g , the more the polymer chain coils. Then, the coiled PAM/HPAM chains affected by metal ions lost the friction-reduction function and tend to flocculate. The radius of gyration, R_g , is defined as the root mean square distance of the atoms in the molecule from their common center of mass, that is (Eq. 1),

$$R_g = \sqrt{(\sum_{i=1}^N m_i s_i^2) / (\sum_{i=1}^N m_i)}, \dots \dots \dots (1)$$

where m_i is the mass of atom i , s_i is the position of atom i with respect to the center of mass of the molecule, and N is the total number of atoms.

PAM Polymer in Salt Solutions. Material Studio 2017R2 software was used to simulate molecular dynamics of PAM-based FRs in different salt solutions. For PAM amorphous cells, one 20-repeat units PAM, 5200 H₂O molecules and different number of metal ions (Ca²⁺, Mg²⁺, Fe²⁺ or Fe³⁺) with corresponding number of chlorine ion, Cl⁻ constituted a 53.8 × 53.8 × 53.8 Å (1 angstrom (Å) = 1 × 10⁻¹⁰ meters (m) = 0.1 nanometer (nm)) cube. Smart algorithm, COMPASS force field, 298K temperature, and 20ps simulation time were chosen. As a synthetic FR, PAM is a long-chain polymer composed of repeating units of acrylamide (AM) (Figure 4).



Polyacrylamide (PAM)

Figure 4—Molecular structures of polyacrylamide (PAM).

In this study, 20 repeated units were chosen for molecular dynamics simulations. 3D structure of PAM in this simulation is shown as follows (Figures 5 and 6).

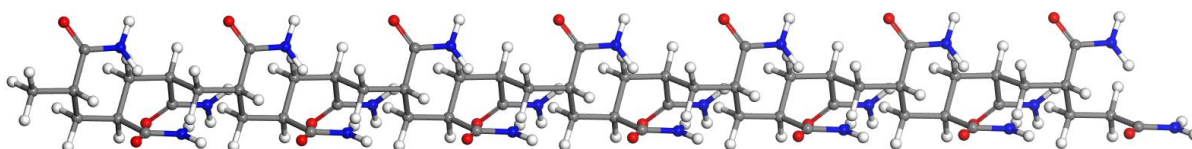


Figure 5—Non-ionic PAM with 20 repeated units.

In Figure 5, the red dots are oxygen atoms, the blue dots are nitrogen atoms, the grey ones are carbon atoms, and the white ones are hydrogen atoms. The whole molecule is composed by 20-repeat units of PAM polymer.

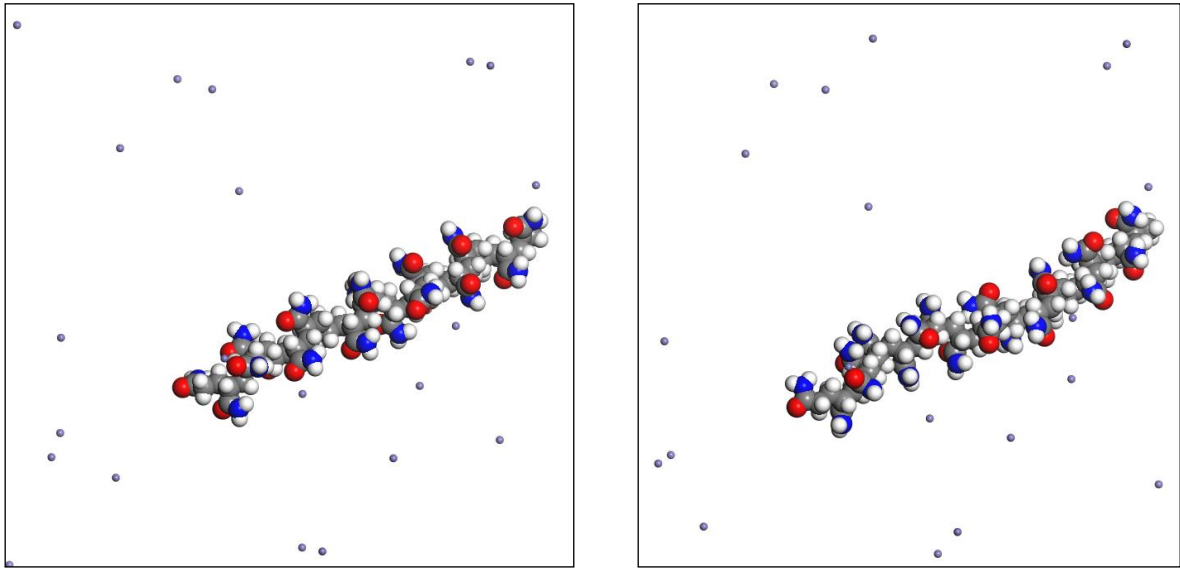


Figure 6—PAM polymer's 3D configuration alteration before NVT beginning (left) and after 20ps simulation (right). Purple dots around the 20-unit PAM molecule are Fe^{2+} .

Take the $FeCl_2$ solution simulation as an example. From the 3D configuration of the PAM molecule changing along with simulation time, it is obviously that the PAM polymer coiled in different metal ions' solutions (**Figure 7**).

The radius of gyration evolution for non-ionic PAM was analysed. The result shows that PAM coils in all studied solutions. And the calcium ions affects PAM-based solutions less than magnesium, but more than ferrous iron.

The PAM polymers coils in all solution candidates. As the concentration of salt goes up, the radius of gyration for PAM becomes smaller. This result means that PAM coils more. This trend matches hydraulic fracturing treatment industrial field experience. PAM FRs, interacting with ferric ions, lose more friction-reduction rate than when interacting with calcium ions. Therefore, ferrous ions affect PAM FRs less than ferric ions and calcium ions.

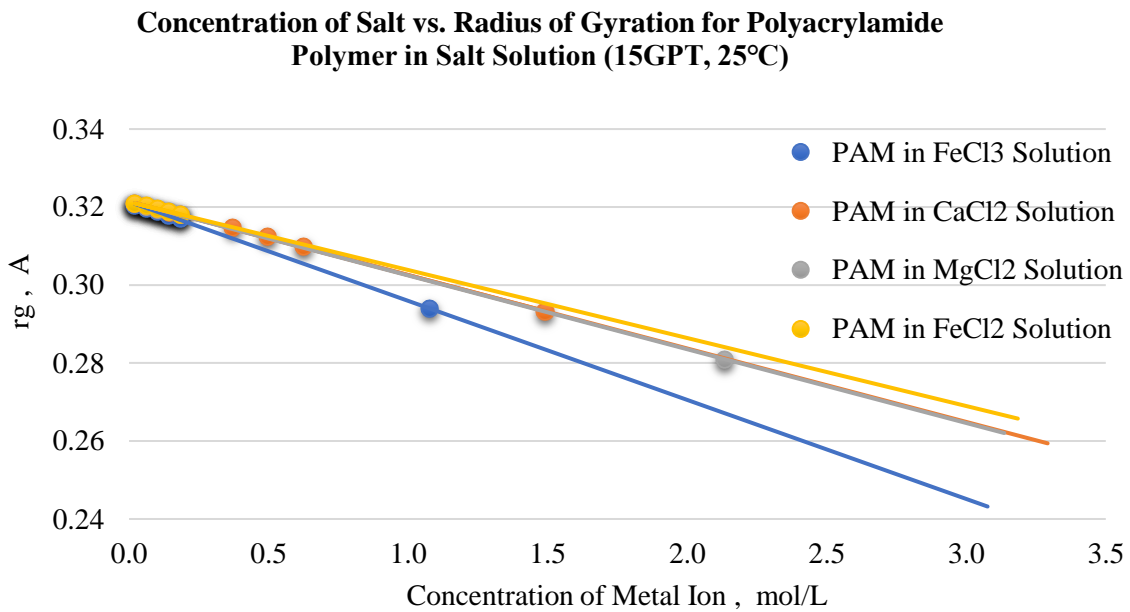


Figure 7—Radius of gyration evolution as PAM interacts with various metal ions in different concentration.

HPAM in Salt Solutions. HPAM (Partially Hydrolyzed Polyacrylamide) is the most common FR available. It is made by reacting sodium acrylate with acrylamide so that approximately 30% of the acrylamide groups are in the hydrolyzed form (**Figure 8**). This hydrolyzed form improves the solubility in water, and makes the polymer more compatible with cationic minerals, and is commonly marketed as a 50% active dispersion in mineral oil. Because it is widely used as a flocculant for water in paper manufacture and the cheapest FR, it is the most widely used in the fracturing treatment(Montgomery 2013).

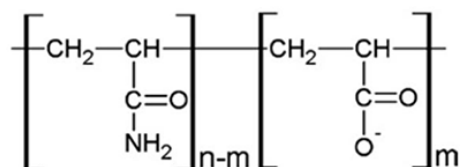


Figure 8—Repeating monomer units of HPAM.

In this study, the structure of HPAM (Yegin et al. 2017) appears below (**Figure 9**). The value of n is 5 and that of m is 2. As shown in **Figure 10**, by converting concentration unit from weigh percentage to mol/L, it clearly shows that all radius of gyrations trend lines with monovalent metal ions are overlapped. The trend lines of bivalent metal ions are together in the plot. The trivalent ions’ line is far beneath the ones of bivalent metal ions. With the same mole of metal ions, the higher the electrovalence, the more severely the metal ion affect the HPAM polymers.

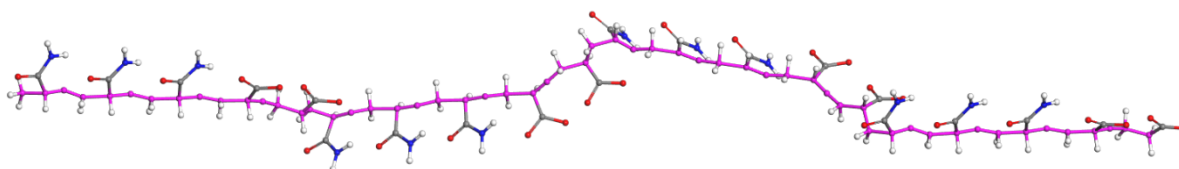


Figure 9—HPAM polymer with 4-repeat units.

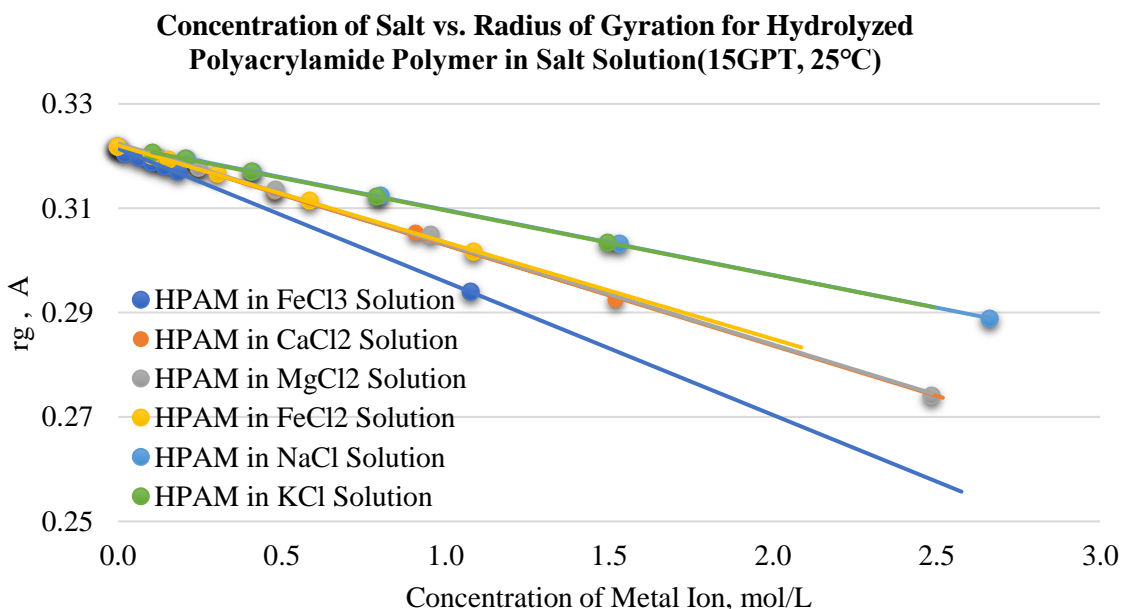


Figure 10—Radius of gyration evolution when HPAM interacts with different metal ions in different concentration.

MD simulations of HPAM also follow a trend that trivalent ions affect polymers more than bivalent ones, and the monovalent affect the polymers the least.

Verifying the Short-time Simulations with Long-time Simulations. To accelerate simulations, one molecule of PAM polymer with 20 repeating units was used instead of hundreds of thousands of repeating units PAM in each cell. After comparing 20ps with 200ps simulation time, the radius of gyration results matched. It means 20ps simulation time is enough for all PAM and HPAM simulations (**Figures 11 through 13**).

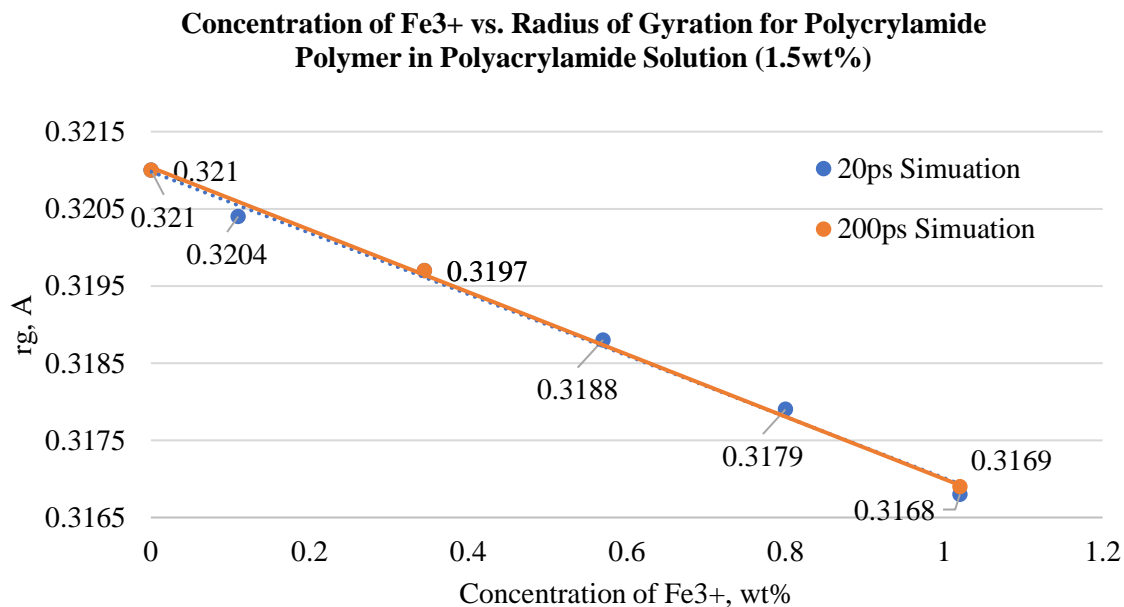


Figure 11—20ps MD simulations vs. 200ps MD simulations in ferric chloride solutions (1ps=10⁻¹² s).

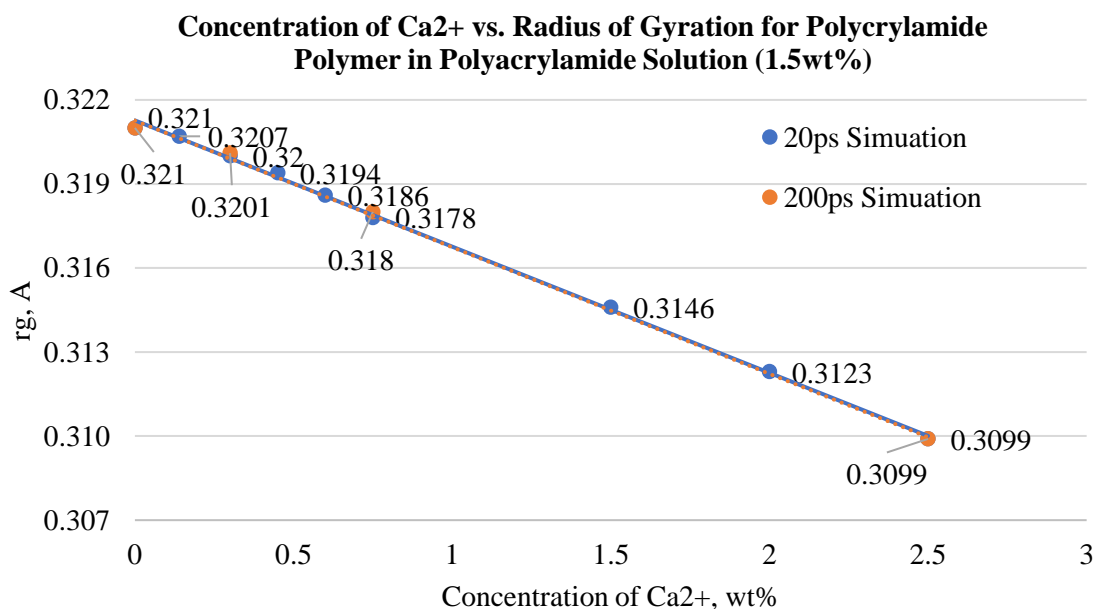


Figure 12—20 ps MD simulations vs. 200ps MD simulations in calcium chloride solutions.

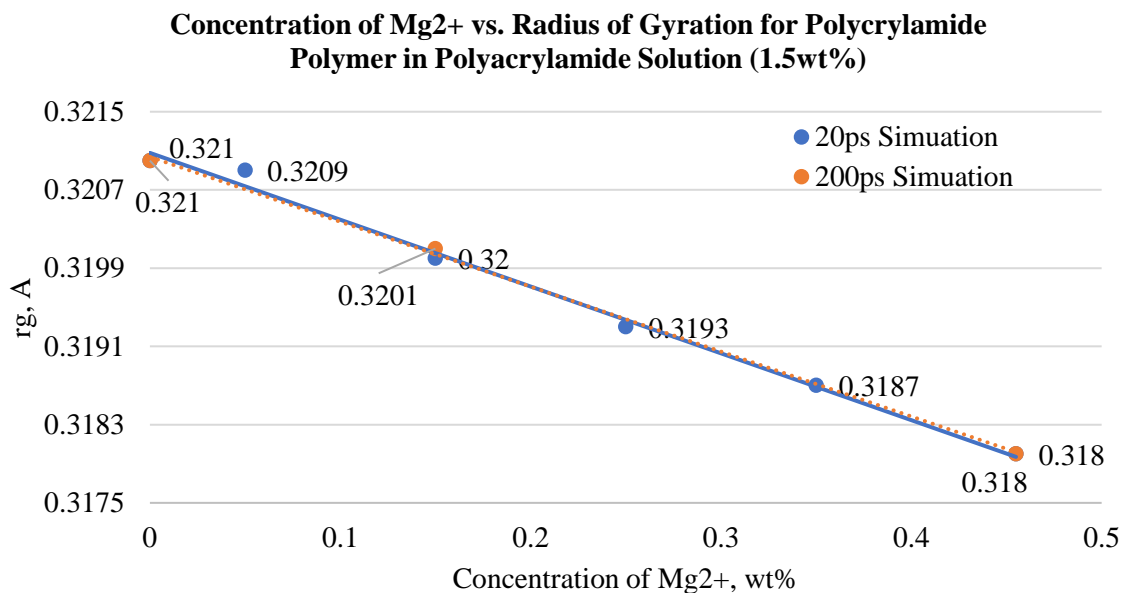


Figure 13—20ps MD simulations vs. 200ps MD simulations in magnesium chloride solutions.

Summary of Simulations Results. The molecular dynamics simulations for typical PAM and HPAM FRs illustrated intra-molecular aggregation so that the R_g decreases. PAM-based FRs coil in salt water. Intramolecular interactions are obvious with formation damage risk. Long chain and being charged are the two main inherent defects.

Prediction of a New FR for Slickwater without Formation Damage. The simulation results show that PAM-based FRs coil in salt water. Formation damage tends to happen after hydraulic fracturing with slickwater. In the molecular dynamics simulations, it shows that long chain and being charged are the two main inherent defects when using PAM-based FRs.

A new FRs can be predicted, at least including the following features.

1. Relatively shorter polymer chain. The shorter, the better, even a chain as short as one micron. Even if the short-chain polymer coils in salt water, its size is small enough to pass the fractures without plugging or blocking the pores.
2. Without the long chain, the friction-reduction rate could be low. Thus, nanoparticles may be introduced to the low velocity flow zone next to tubing walls.

With these two features as guidelines, one new FR mixture is found.

Effects of Metal Ions on HPAM FRs in Water

Few papers have shown transmittance results that FRs affected by metal ions in water. Metal ions force PAM-based FRs coil, so FRs will lose friction-reduction rate. The transmittance tests show how the pure HPAM FRs are affected by each salt solution. Fe^{3+} , Ca^{2+} , Mg^{2+} and Na^+ are the representative metal ions that HPAM FRs can encounter during the whole procedure in a slickwater fracturing job.

Experiments. The formula for calculating transmittance is transmittance equals light exiting the sample divided by light striking the sample. In the experiment, wavelength was 600nm. The HPAM concentration was 0.12v%, based on field treatment experience. The molecular weight of HPAM was around 12 million. Normalized transmittance data was used to eliminate the time effect of friction-solution change. The HPAM solution samples without salt were set to 100 and all the transmittance test results were compared, allowing for a determination of which kind of salt affects the polymers more than others (**Tables 4 and 5**).

Table 4—Transmittance results of HPAM FR solution with different salts.

Salt	ppm	Concentration, w%	Molarity	Transmittance, %	Normalized Transmittance
FeCl ₃	0	0	0.00	7	100.00
	10000	1	0.06	1	14.29
	42300	4.23	0.26	1.9	27.14
CaCl ₂	0	0	0.00	5.2	100.00
	24200	2.42	0.22	6	115.38
	155900	15.59	1.40	11.3	217.31
MgCl ₂	0	0	0.00	6.8	100.00
	51100	5.11	0.54	7.9	116.18
	209000	20.9	2.20	13.2	194.12
NaCl	0	0	0.00	7.3	100.00
	97100	9.71	1.66	11.3	154.79
	198800	19.88	3.40	17.3	236.99

Table 5—Transmittance results of the less-damaging FR solution with different salts.

Salt	ppm	Concentration, w%	Molarity	Transmittance, %	Normalized Transmittance
FeCl ₃	0	0	0.00	101	100.00
	6100	0.61	0.04	104	103.48
	29500	2.95	0.18	98	97.51
CaCl ₂	0	0	0.00	101	100.00
	29800	2.98	0.27	98	97.51
	67600	6.76	0.61	93.6	93.13
MgCl ₂	0	0	0.00	97.2	100.00
	35900	3.59	0.38	99.9	102.78
	57200	5.72	0.60	96.8	99.59
NaCl	0	0	0.00	99	100.00
	41100	4.11	0.70	100	101.01
	81500	8.15	1.39	99	100.00

The transmittance results indicate that with the same concentration, HPAM solutions have a lower transmittance value. Compared with water, the transmittance of HPAM solution with different salts is less than 20%, while the less-damaging FR solutions are almost the same, clear as Distilled (DI) water. Except for FeCl₃, the transmittance value becomes smaller as the metal ion concentration increases. Metal ions force polymers to bend or coil. Without salts, the HPAM polymers mostly relax in water. Most light hits the polymers, and certain wavelength lights are absorbed. So, transmittance is low. As the HPAM polymers are forced to bend or coil as metal ion concentrations increase, more and more space becomes available for light to escape. Therefore, the transmittance becomes smaller and the solutions are clearer (**Figure 14**).

**Concentration of Salt vs. Transmittance for New FR and HPAM in Salt Solution
(0.12v%, 25oC)**

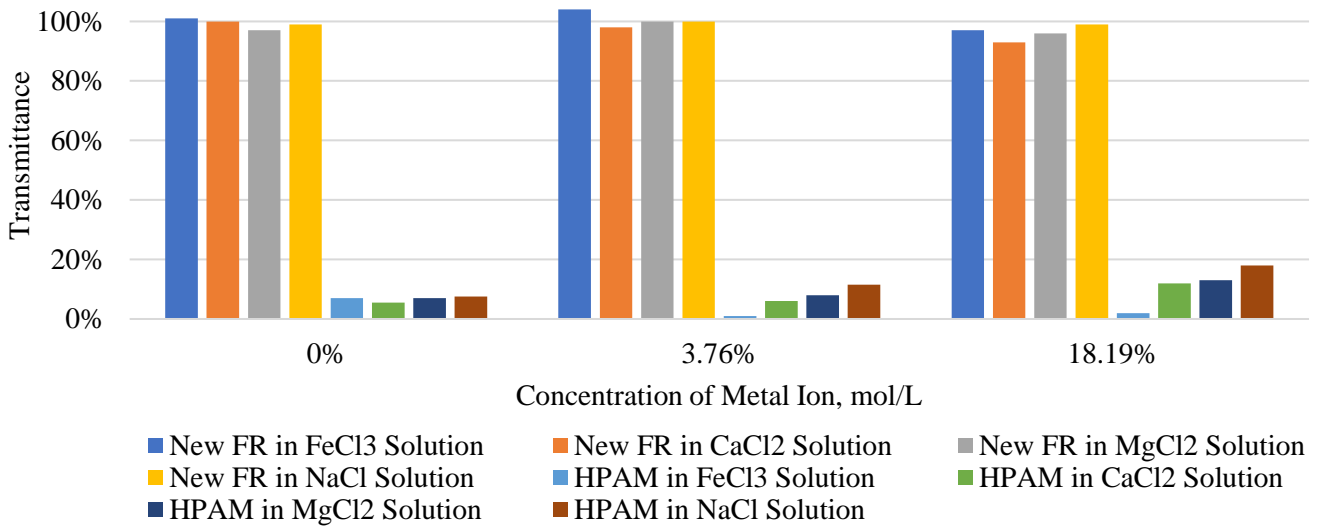


Figure 14—Transmittance results of the less-damaging FR vs. HPAM.

For the less-damaging FR solutions, almost without any large polymers, very few light beams can hit the polymers and be absorbed while penetrating the solutions. In ferric chloride solutions, HPAM reacted with ferric ions and flocculation formed, as shown in **Figure 15**. There is no flocculation for the less-damaging FR.

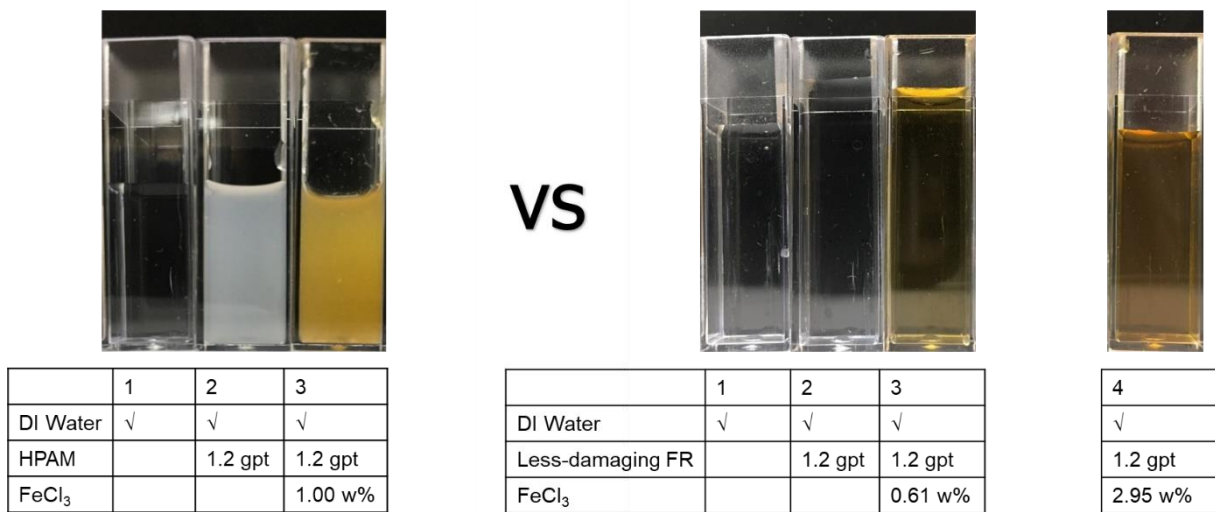


Figure 15—HPAM vs. a less-damaging FR in FeCl₃ Solutions (HPAM: reacted with ferric ions and flocculated; Less-damaging FR: no flocculation).

In HPAM solutions with calcium chloride (**Figure 16**) and the ones with magnesium chloride (**Figure 17**), as the salt concentration increases, some little white dots can be observed. It could be the very early stage of flocculation.

For all the salt solutions in tests, the less-damaging FR does not precipitate or flocculate. Except for FeCl₃ solution, the less-damaging FR's solutions remained as clear as DI water, as shown in Figures 15 through 17. Although, sodium chloride is one of the monovalent salts that affect polymers the least compared with divalent salts and trivalent salts. However, the colors of the solutions with different concentrations are different in Figures 15 through 17. The background is black by design for better clarification of the flocculation process. The higher the concentration of NaCl is, the clearer the solution, i.e., the black background appears unobstructed. It means HPAM polymers stretch like barriers without

NaCl, and the more Na⁺, the more the polymers bend, so more space is available for light to pass through. The dark background (black) intensifies as sodium ion concentrations increase, as shown as **Figure 18** (right), which indicates a clearer solution with fewer flocculates.

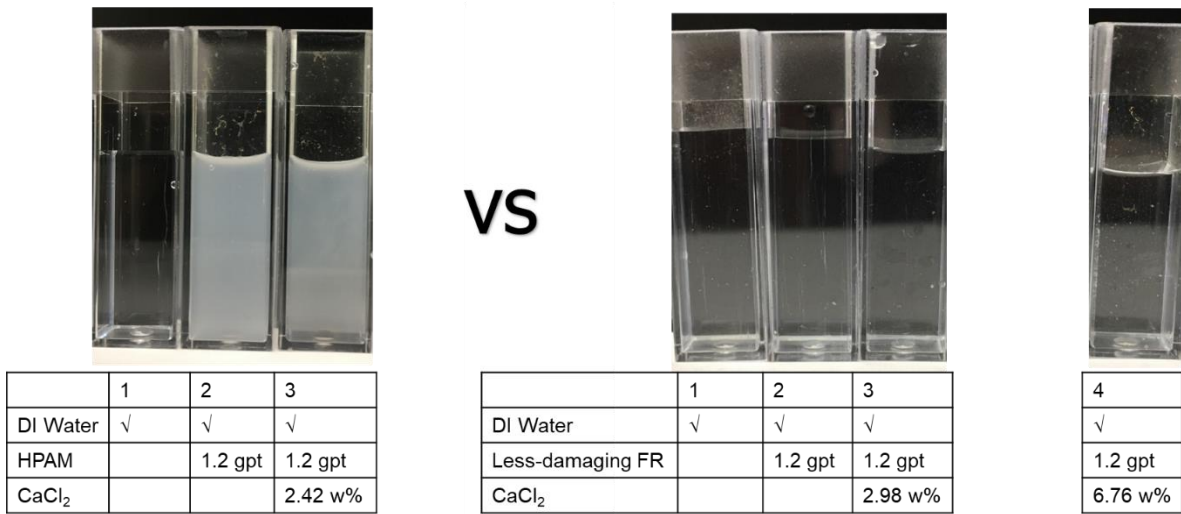


Figure 16—HPAM vs. a less-damaging FR in CaCl₂ solutions.

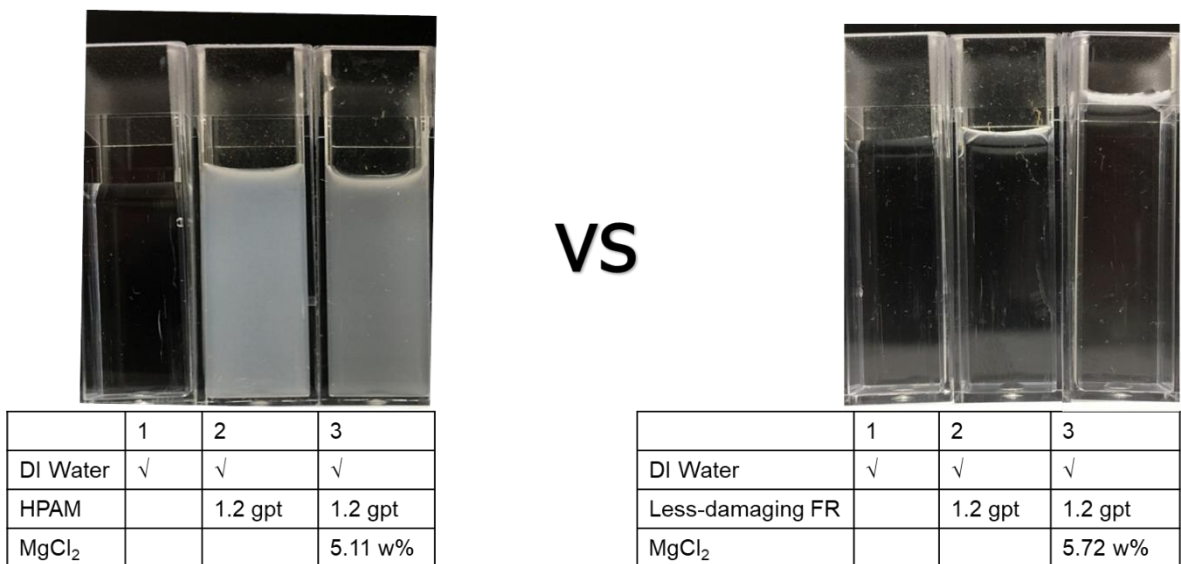


Figure 17—HPAM vs. a less-damaging FR in MgCl₂ solutions.

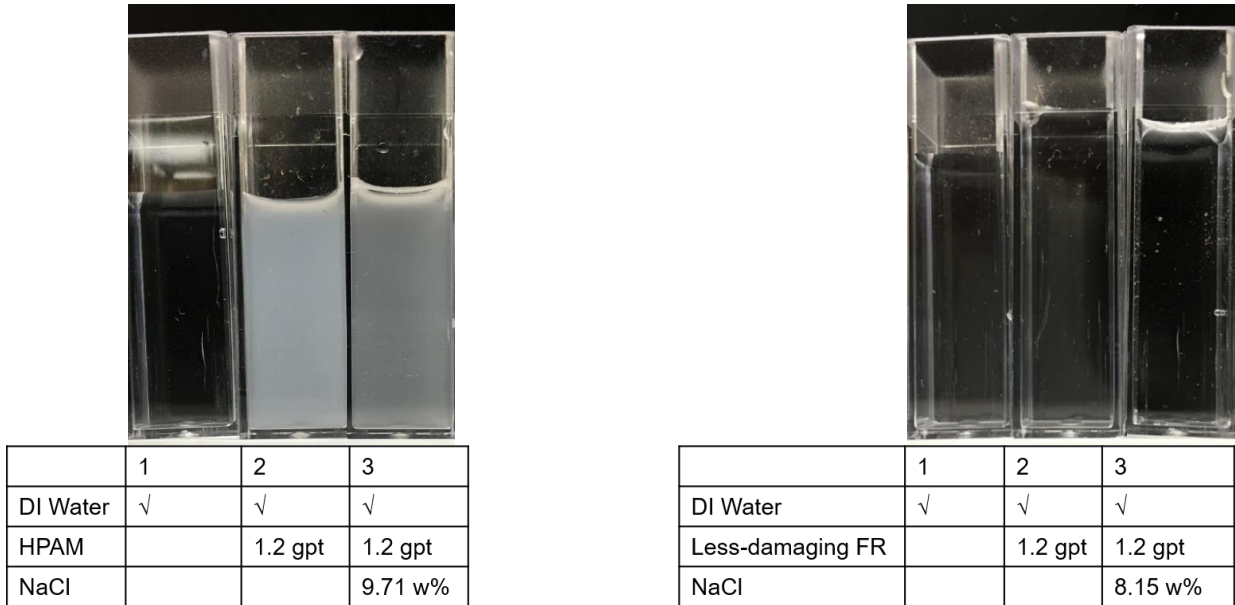


Figure 18—HPAM vs. a less-damaging FR in NaCl solutions.

Viscosity Concerns. For fracturing operations, proppant screenout in treatments is risky for wellbore integrity and equipment safe. Conventionally, viscosity is one of the most important variables for proppant suspension in fracturing fluid (Feng et al. 2017). Stokes’ law was applied to designing most types of fracturing fluids, including guar-based fluids, cellulose-based fluids, and PAM-based fluids, in which the sedimentation velocity is inversely proportional to the medium viscosity. Later, the fluid elasticity was found to be another important variable that dominates proppant suspension (Harris and Harold 2000, Naval and Shah 2001; Hu et al. 2015).

In slickwater fracturing in shale reservoirs, the mechanism of proppant transport is different. Since slickwater has only a small concentration of polymers (up to 2 gpt), it does not have high enough viscosity or elasticity required to keep the proppant in suspension. In this case, the proppant settles faster under static conditions, and proppant transport may be dominated by the movement of the proppant bank itself.

Three proppant transport mechanisms in slickwater have been proposed (Coker and Mack 2013; Sun 2015). At very low velocity, little or no proppant is moved. At higher velocity, proppant grains roll or slide along the surface of the settled proppant bank (reptation creep). At even higher velocity, proppant grains bounce off the surface back into the flow stream (saltation). Dufek and Bergantz (2007) demonstrated that saltation depends on the coefficient of restitution which is defined as the ratio of the velocity with which the object leaves after a collision to the velocity with which it enters the collision. Proppants with a higher coefficient of restitution and a lower friction coefficient than other proppants will be transported deeper into the fracture.

Coreflood Experiment. The goal of fracking is to maximize production, the extent of which is directly linked to how much the formation is damaged after fracking. **Table 6** is a set of coreflood data corroborating the less-damaging nature of less-damaging FR (without using any breaker), which shows greater than 99% regained permeability.

Table 6—Cores data for coreflood.

Items	Value
Material	Synthetic quartz
Dimensions	2.5cm×8cm
Porosity	20%
Permeability	40-200 mD
N ₂ flow time	> 1 hour
Variables to measure	the flow rate and the pressure of N ₂ gas

In contrast, industrial regulars FR-A and FR-B lead to less than 10% regained permeability, under presumably identical conditions. FR-A is a commercial dry powder FR, and FR-B is a regular emulsion FR. K_1 (md) is the initial permeability, and K_2 is the regained permeability (Wu et al. 2017). Arising from this less-damaging nature, the use of the less-damaging FR showed astonishing production enhancement of 5-6 folds or more than conventional means (Table 7).

Table 7—Coreflood results comparison between less-damaging FR to common commercial FRs without breakers.

FRs	K_1 (md)	K_2 (md)	Regained Permeability
FR-A	172.7	12.76	7.4%
FR-B	166.3	0.5	0.3%
Less-damaging FR	147.7	146.5	99.2%

Field Tests

Comparative daily gas production through two wells on the same platform: one well fractured by slickwater with less-damaging FR (Gas Well #1); the other by a conventional inverse emulsion FR (Gas Well #2) (Figure 19).

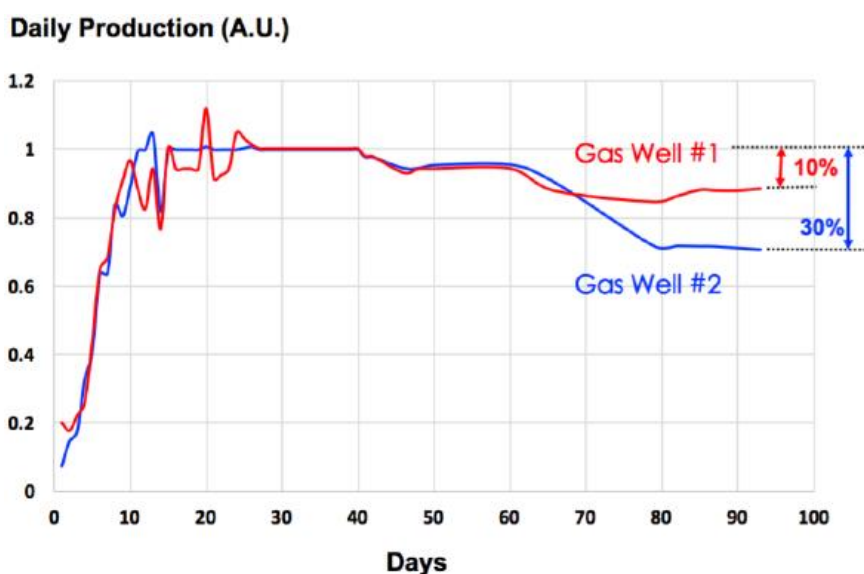


Figure 19—Gas production rate: Less-damaging FR (red) vs. conventional FR (blue).

Results show that the less-damaging FR is three times more effective at increasing daily gas production than conventional inverse emulsion FR.

- Gas well #1: decline rate was 10% after three months of production.
- Gas well #2: decline rate was 30% after three months of production.

Gas well #2 production regime follows the statistical data. The literature reports an average 30% decline after three months of gas production on 838 wells (**Figure 20**). However, the well fractured by slickwater with the less-damaging FR saved 20% of gas production, just by not damaging the formations.

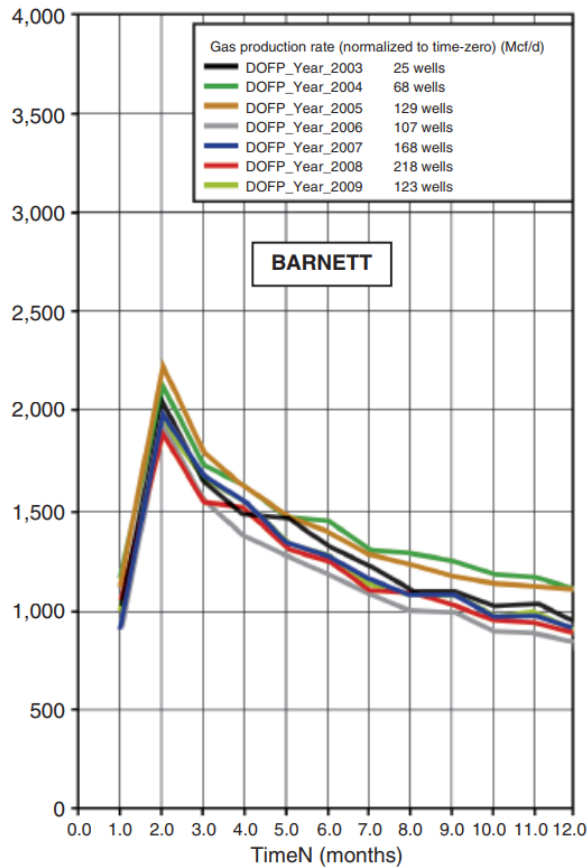


Figure 20—Barnett shale first-year production rates.

Conclusions

Results of the experimental studies and field tests conducted during this research lead to the following conclusions:

1. A systematic method is found to mitigate formation damage caused by FRs.
2. The MD simulations systemically explain how the commonly used FRs interact with different metal ions in water. Potential formation damage caused by FRs in slickwater is confirmed by both MD simulations and lab tests (UV-vis tests and coreflood tests).
3. MD simulation saved time and cost for new formula inventions.
4. The coreflood and field results substantiate the finding/guidance for a less-damaging FR as impressive and directional.
5. The finding that the shrinkage/aggregation of PAM is most sensitive to Fe^{3+} , then Ca^{2+}/Mg^{2+} , then Na^{+}/K^{+} is consistent with the typical FR performance. Most FRs lose performance in the presence of Fe^{3+} . One frequently reduces ferric (by iron reducer) to ferrous to minimize the negative influence of ferric, which is also consistent with our MD simulations.
6. By combining molecular dynamics simulation, prediction, lab tests, and field tests, one more effective FR is found for slickwater with high salt-tolerant, almost non-damage to formations and more gas production.

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Conflicts of Interest

The author(s) declare that they have no conflicting interests.

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