A LABORATORY STUDY ON THE USE OF SEAWATER IN CROSSLINKED-

GELS USED IN HYDRAULIC FRACTURING

A Thesis

by

RAAFAT MAHMOUD YAMAK

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Chair of Committee,	Hisham Nasr-El-Din
Committee Members,	Jerome Schubert
	Stephen Holditch
Head of Department,	A. Daniel Hill

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ABSTRACT

As unconventional reservoirs continue to dominate the current economic climate, there is a great demand for developing innovative and efficient fracture treatment methodologies. Traditionally, the vast majority of hydraulic fracturing systems incorporate a freshwater-based fracturing fluid. However, freshwater is considered an expensive and valuable resource, particularly in the Middle East and for offshore completions. This research discusses the potential of seawater, a more cost-effective and accessible resource, as an acceptable replacement for current water sources.

To develop a successful fracturing fluid system, the chemical composition of seawater, particularly the presence of high concentration cations and anions, must be considered. The primary purpose of this study is to understand how 1) changing temperature, 2) additive concentration, 3) water source, and 4) introducing an oxidizer breaker can affect the gel stability of two types of guar derivative gelling agents: hydroxyl propyl guar (HPG) and carboxymethyl hydroxypropyl guar gum (CMHPG), using High Temperature/High Pressure Chandler Rheometer. Arabian Gulf seawater was used to design and test a seawater-based fracturing fluid in the laboratory.

To simulate fracking environments, a dynamic scale loop was used. The seawater sample and formation water mixture were mixed at a 50/50 ratio. Phosphonate type scale inhibitor was then tested at various concentrations, starting at 3,000 ppm, at a temperature range from 270 to 330ºF. Scale buildup is represented by a dramatic change in pressure.

Results confirmed that seawater fluid stability at greater than 500 cP at a shear rate of 40 s^{-1} for temperatures ranging from 270 to 330°F was feasible. The stability time varied with the given temperature constraint. Additionally, scale loop analysis depicts that scale can be mitigated at temperatures ranging from 270 to 330°F depending on the scale inhibitor concentration used.

This work contributes to understanding how seawater based fracturing fluid can be formulated, and potential applications in hydraulic fracturing treatments. Maximizing the use of seawater could help rule out dependency on the scarce freshwater resources.

DEDICATION

I dedicate this thesis to my parents, siblings, and mentors. Without their guidance and support, my ability to complete this research would not have been possible.

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1. INTRODUCTION AND LITERATURE REVIEW

Hydraulic Fracturing Operations

Hydraulic fracturing remains one of the most useful tools for improving well productivity. It is a process where millions of gallons of fracturing fluid are pumped underground to break apart the rock and release hydrocarbons. The fracturing fluid injection pressure must be higher than the formation pressure to create induced fractures. This is achieved by bypassing wellbore damage by placing a conductive channel near it, extending the depth of the channel to increase productivity and ultimately placing the channel in a way that alters fluid flow in the reservoir. However, there are complexities that arise due to the geologic reality and the inherent multidisciplinary nature of the fracturing process (Smith & Shlyapobersky 2000).

Ultimately, the purpose is to increase the fracture contact area with the unconventional reservoir. As a result, the number of stages have increased per fracturing operation and consequently saw the rise in popularity of horizontal wells. Critical parameters for hydraulic fracturing includes formation permeability, in-situ stress distribution, reservoir temperature, reservoir fluid viscosity, reservoir pressure, among others (Smith & Shlyapobersky 2000). Take for example fracture height, and the importance of its controlled growth to ensure optimal productivity by knowing the relative stresses and its consequent effect on fracturing fluid design. There are three scenarios where fracture height can affect productivity as displayed by Figure 1. If the fracture is initiated near the top of the interval (Figure 1a), then h_f won't be large enough

to contact the entire zone which is not optimal for productivity. The second scenario (Figure 1b) is where the fracture got so big that it contacted mostly non-reservoir rock. This diminishes hydrocarbon production. The third scenario (Figure 1c) is similar to the second case, however, instead, the h_f has grown past the oil-water contact. This can lead to water production and problems can arise such as corrosion because the water can contain salts, scale, bacterial infection, sand production (as water can enhance it), and possibly emulsion. These three scenarios can be portrayed in Figure 1 (Smith & Shlyapobersky 2000):
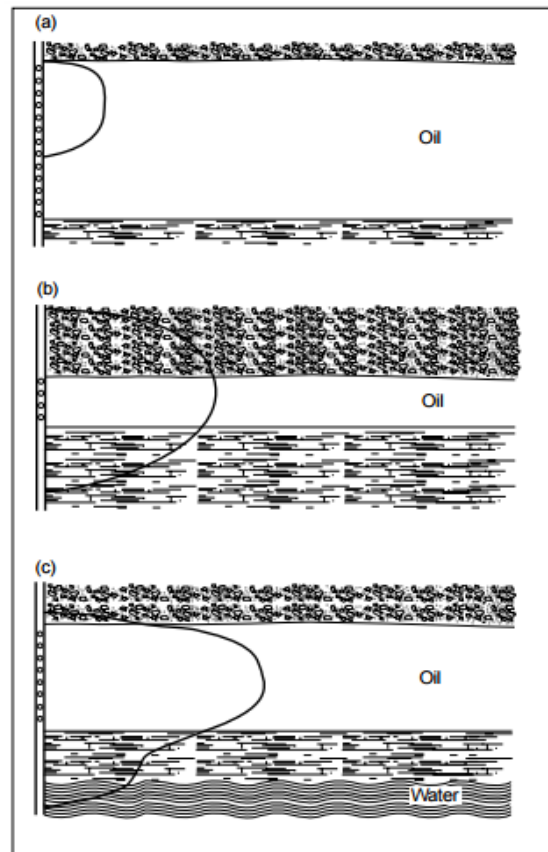
Figure 1 – The Importance of Fracture Height

As a result, fluid selection success is controlled by the ability of the fluid system to control fluid loss without damaging formation, performing at high temperatures for long periods of times while staying within appropriate costs, and maintaining good viscosity to provide good proppant transport.

Proppant admittance is important for hydraulic fracturing in terms of its entrance to the fracture through perforations and its entrance into the fracture directly. As a result, there are two important notes to keep in mind: a minimum perforation diameter is required for proppant to flow through the perforations and that minimum perforation diameter is a function of slurry concentration (Gruesbeck and Collins 1978). At low concentrations (less than 6 ppg) of proppant, perforation hole diameter only has to be slightly greater than the size of the proppant particles. After 6 ppg, perforation hole diameter must be at least six times greater than size of proppant (Smith & Shlyapobersky). The same trend is applied for slurry flow. Once again, critical width plays an important role in proppant admittance. If the width is not sufficient, the proppant will bridge and no longer flow into the fracture creating a loss in permeability and eventually, total screenout. At the conclusion of the treatment, the wellbore is flushed out with a volume of liquid as shown in Figure 2.
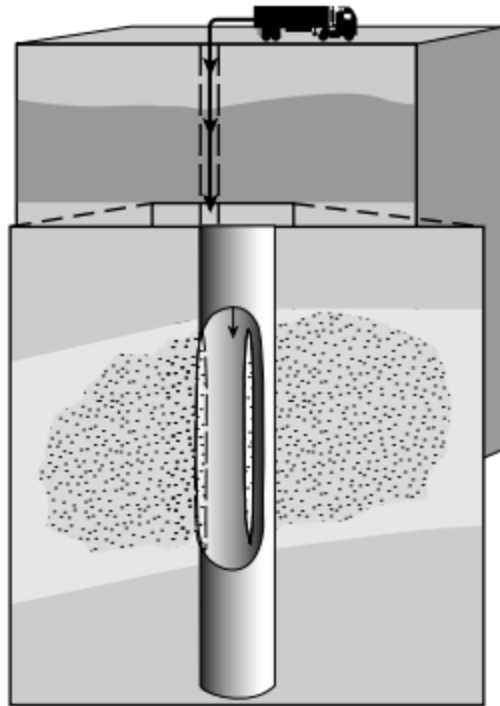
Figure 2- Flushing Wellbore to Leave Propped Fracture

As previously discussed, the main purpose of hydraulic fracturing is open up fractures and consequently transporting proppants to keep the fracture open. A successful hydraulic frack requires fluids with specific properties. Viscosity, the ability of the gel to break, fluid loss control, and ensuring that the fluid treatment is economical are all key things scientists and engineers must juggle. Different types of fluids are available due to the heterogeneity of formations that vary in permeability, porosity, rock composition, cementing material, pore pressure, stresses, temperature, pressure, and more. The first fracturing fluids were oil based but due to environmental concerns and technological advancements, in the late 1950's, water-based fluid with guar thickener became much more popular. In 1969, the first crosslinked guar treatment was performed.

In the industry today, more than 65% of all fracturing treatments use water-based gels viscosified with guar or its derivatives (Gulbis & Hodge 2000). The role of additives is crucial to either increase viscosity, break the gel, or maintain its stability.

Hydraulic Fracturing Fluids

Water-based fluids are the most commonly used type of fracturing fluid because of their relatively low cost, high performance, and ease of handling. Their usefulness is furthered in that even at room temperature, they are viscous enough to be able to suspend proppants. Certain factors, however, like temperature, can significantly alter the viscosity of these fluids. One method of countering this phenomenon is by increasing the gel loading, but simply relying on polymers to increase viscosity is costly. Instead, cross-linking agents are used to exponentially increase the viscous nature of the fluid. In Figure 3, non-crosslinked HPG gel at 40 lb/1000 gal gel loading is compared to a non-crosslinked gel at 60 lb/1000 gal gel loading (Gulbis & Hodge 2000). Although there is an increase in viscosity as the gel loading increases, the exponential increase only occurs once borate crosslinker is introduced.
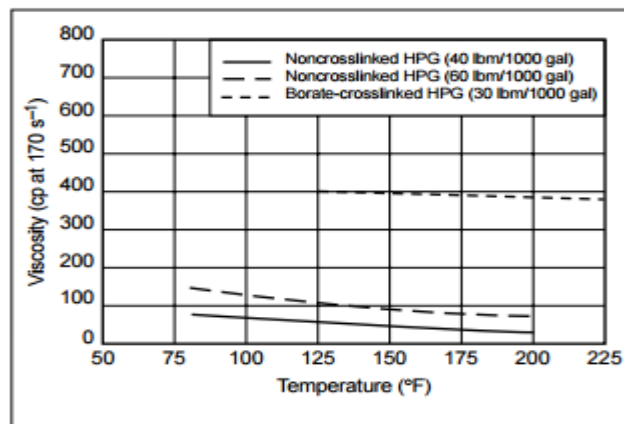
Figure 3 – Effect of Temperature and Crosslinker on HPG Viscosity

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One of the first polymers to be used to viscosify water was guar. Guar, a complex sugar, is a long-chain, high-molecular-weight, polymer composed of mannose and galactose sugars (Gulbis & Hodge 2000). It is part of a class known as biopolymers. For the sake of this paper, the focus will be more directed towards this kind of polymer; however, there are also synthetic polymers which will be briefly touched upon. Biopolymers are complex sugars that consist of guar (generally used for hydraulic fracturing), cellulose (used as viscosifier), starch (used in drilling fluid), and xanthan gum (viscosifier in drilling fluid). All come from plants, except xanthan gum, which comes from bacteria. Biopolymers are attracted to bacteria due to its sugar makeup, thus, it requires biocide to maintain integrity. Additionally, biopolymers generally have excellent mechanical properties with "alpha-helical structures" consisting of two strings. As a result, when subjected to shear, they are very hard to break.

Synthetic polymers are plentiful and can be designed in the lab. One main type of polymer heavily used in the industry is the polyacrylamide and its partially hydrolyzed derivatives. Here, bacteria is not so critical to its integrity. Synthetic polymers have poor mechanical properties due to the lack of helical properties and reliance on "one string", making it easily subjected to shear. Another difference to be noted is that in synthetic polymers, the presence of salt will dramatically decrease viscosity, especially when dealing with partially hydrolyzed polyacrylamide. With respect to polyacrylamide, however, it will not be affected because it is non-ionic. The effect of salt on biopolymers is not as significant as synthetic polymers because of limited electrical charges and

strong molecular intertwined strands. The size or molecular weight of synthetic polymers can be controlled.

The guar polymer remains the most widely used viscosifier. They are composed of sugar units called polysaccharides. As previously stated, guar is derived from plants, but more specifically, from the endosperm of guar beans from the Indian subcontinent. The guar polymer has a high affinity for water, so when it comes into contact, the guar particles begin to swell and hydrate. As the guar polymers become associated with the water molecules, the strands begin to bloat and overlap, which results in the viscosity increase of the solution.

The structure of the guar molecule consists of galactose substituents and mannose backbone. Standard guar, which usually contains 6-8% impurities, can be derivatized with propylene oxide to produce hydroxypropylguar (HPG). The reaction changes some of the –OH sites to $-O-CH_2-CHOH-CH_3$, effectively removing some of the cross-linking sites. This process also reduces the percentage of impurities down to 2-4%. Some studies have claimed that HPG causes less damage to the formation face than traditional guar (Almond 1984), but recent studies are starting to indicate that they both result in the same degree of damage. Hydroxypropyl substitution makes HPG take on higher temperatures of over 300ºF. The hydroxypropyl substituents are hydrophilic, which makes HPG more soluble in alcohol. A popular way to test the hydroxypropyl nature of the guar, and its efficiency, is to add an equal volume of methanol to the polymer solution. Standard guar precipitates while HPG does not (Gulbis & Hodge

2000). Below is an image of the molecule structure of standard guar (figure 4) followed by the molecular structure of HPG (figure 5):
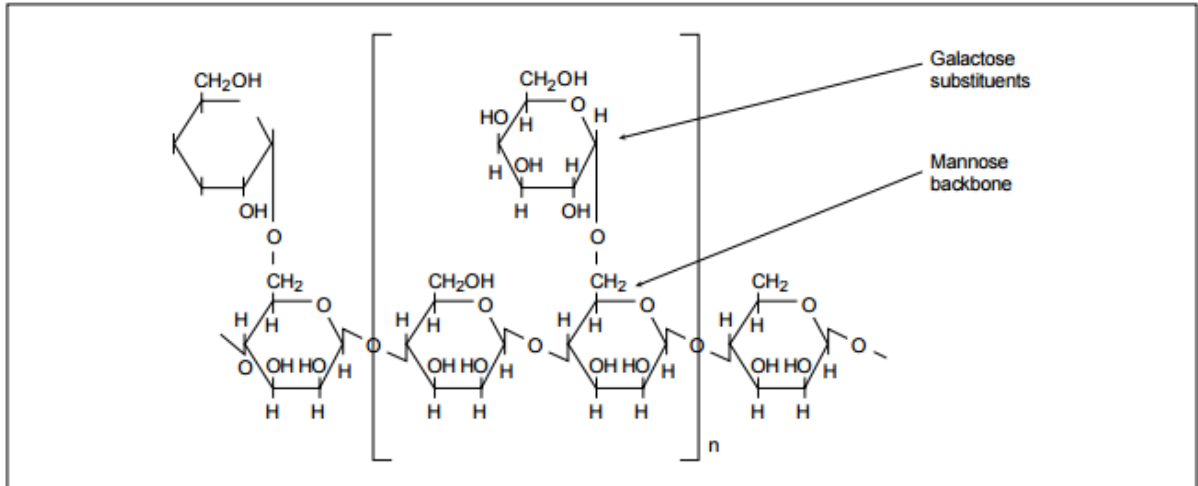
Figure 4 – Structure of Guar
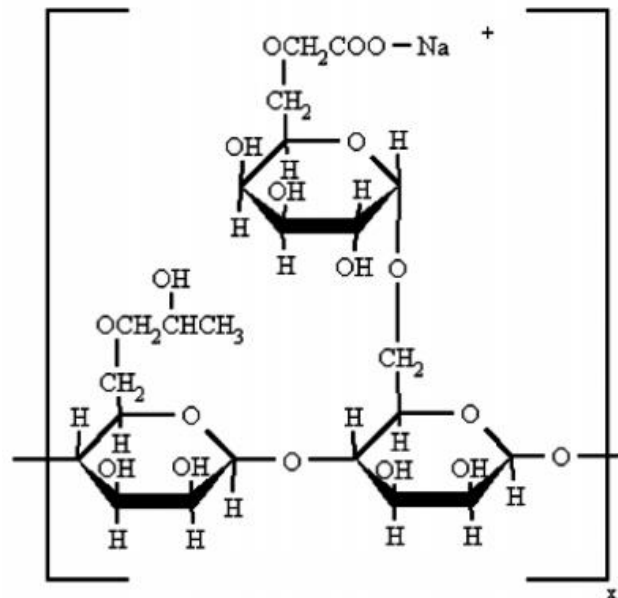
Figure 5 – Structure of HPG

Another guar derivative that has started to be used recently in the oil industry is carboxymethylhydroxypropylguar (CMHPG) whose molecular structure is portrayed below in Figure 6. The difference between CMHPG and HPG is the addition of carboxylic acid substituent. CMHPG was first used for low temperature wells (Almond and Garvin 1984). Through the carboxyl groups, it is usually crosslinked with Al (III). This system is cheaper than the HPG crosslinked with Ti and Zr complexes. More recently, CMHPG has been crosslinked with Zr and Borate crosslinkers to produce high viscosity fluids at higher temperatures than the HPG system. As mentioned before, there are also cellulose, xanthan gum, and other synthetic polymers that can be used.
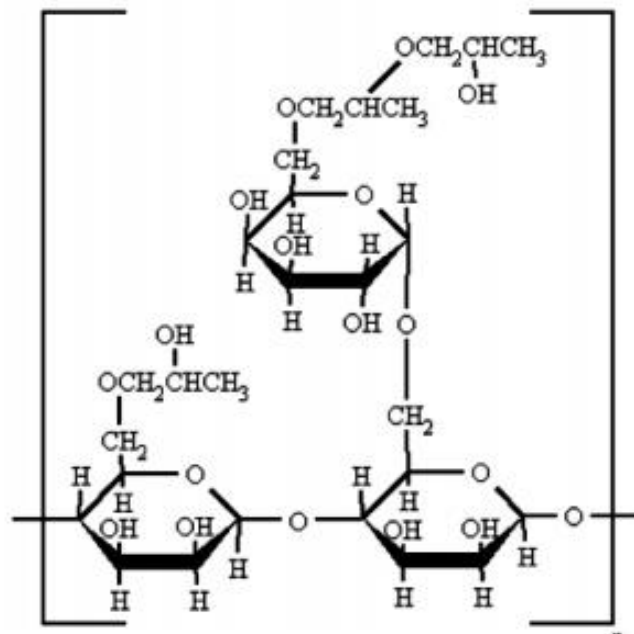
Figure 6 – Structure of CMHPG

Crosslinkers play an important role in significantly increasing viscosity of the fracturing fluid. A number of metal ions can be used to crosslink water-soluble polymers

(Conway 1980). These ions usually have a +3 or +4 charge like Boron, Ti (IV), Zr (IV), and Al (III). Some ions can be toxic. Take for example partially hydrolyzed polyacrylamide (PHP) and the attempted use of Cr (VI). The crosslinking mechanism with the carboxyl group of the PHP has proven to be toxic and later banned from use in the industry.

One of the most common crosslinkers are borate compounds. The borate compounds and transition metal complexes react with guar and HPG through cis-OH pairs on the galactose side chains to form a complex (Gulbis & Hodge 2000) as shown in Figure 7(a). The molecules then overlap with other polymer molecules to form an intertwined polymer network as shown in 7(b). As a result, the polymer can be crosslinked at more than one site due to the multiple cis-hydroxyls which increases the molecular weight creating a more viscous solution.
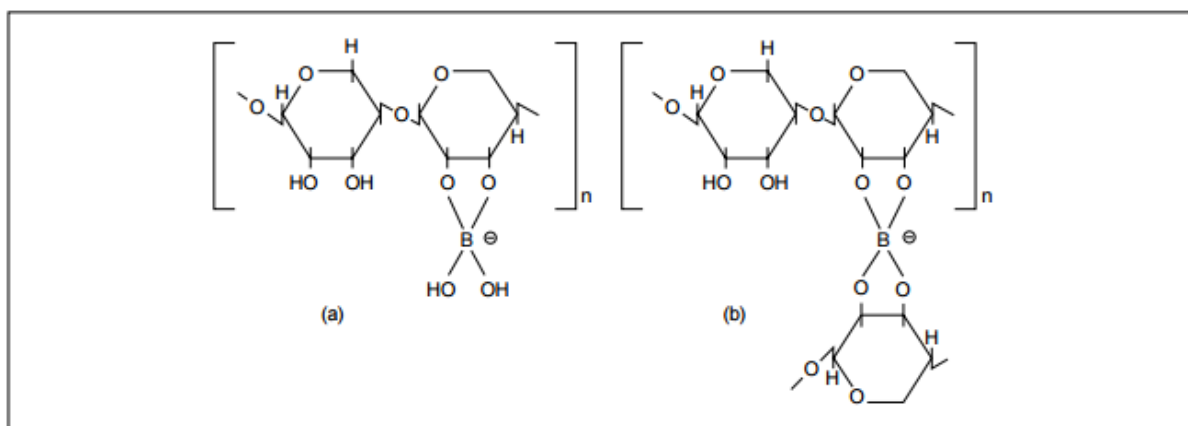
Figure 7 – Proposed Crosslinking Mechanism

One of the most commonly used ions for crosslinking is the borate ion, which can handle temperatures above 300°F at a high pH environment (above pH of 8). It can

form very viscous gels with guar and HPG. However, to increase viscosity, the pH needs to be between 10 and 12, accompanied by raising the concentration of borate. The borate ion is believed to be the crosslinking species $B(OH)_4^-$ (Gulbis & Hodge 2000). It is through this reaction that one can increase the borate concentration at the aforementioned pH levels:

$$H_3BO_3 + OH^- \rightarrow B(OH)_4^-$$

While increasing the pH results in a higher concentration of $B(OH)_4^-$ as shown in the figure 8 below, increasing the temperature reduces the pH, resulting in lower crosslinker concentration and a decrease in viscosity. Increasing H_3BO_3 to compensate the rising temperature effects can cause gel syneresis whose cause is over-crosslinking. The collapse of the gel can lead to many issues like water production.
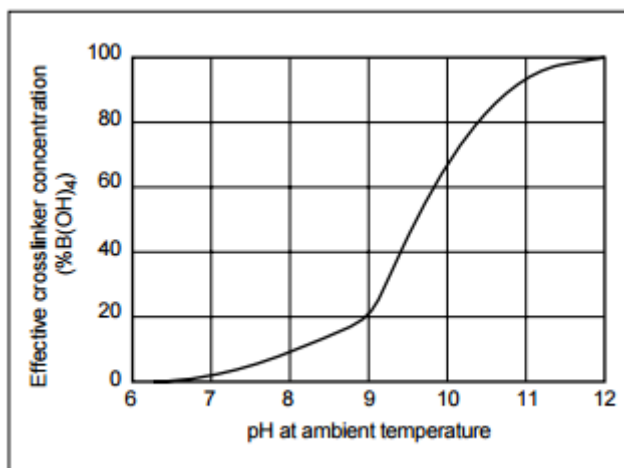
Figure 8 – Borate as a Function of pH

Transition metal crosslinkers have been developed for high temperature and/or low pH conditions. Zirconium and titanium complexes have been used most frequently

because of their ability to react with cis-OH and carboxyl groups and stable +4 oxidation states. The upper temperature limit for these gels is about 350ºF to 400ºF. Although thermally stable, it appears that the limiting factor is the stability of polymer backbone rather than the polymer-metal ion bond (Gulbis & Hodge 2000). Interestingly, there has been more research done on zirconium crosslinking with HPG and results showed that ZrO_2 nanoparticles are what induced the crosslinking effect rather than a ligand exchange reaction that involves the cis-hydroxyl groups. These results suggest that nanoparticles can be presented as a new form of crosslinkers (Hurnaus & Plank 2015).

Due to the fact that fracturing fluids are non-Newtonian, gels thin with shear and heat. However, some gels return to their initial state once shear or heat is removed. The fracturing fluid must go into a positive displacement pump and pumped after a centrifugal pump to ensure the polymer does not shred. Generally, borate crosslinking is reversible as the crosslinks form and then break, and then reform again (Deuel and Neukorn 1949). If the polymer is not thermally degraded, this reversible behavior continues to be accommodated as temperature and shear rate changes. On the other hand, with non-borate crosslinkers, once the bond between polymer and crosslinker is broken, it does not go back to its original state. Therefore, if crosslinking is very high at the high shear rate zone of the tubing, viscosity will suffer and decrease. A fluid that is crosslinked rapidly in the low shear rate zone of tubing will see a very high viscosity value.

To avoid the negative effects of high shear occurring in the tubing, the crosslinking rate is decreased to limit viscosity until it reaches the target zone. This is

why it is necessary to delay crosslinking not only for the aforementioned reason, but to also reduce frictional pressure losses. There are a number of parameters that can be manipulated to delay crosslinking, such as fluid temperature, pH, shear conditions, and crosslinker type. For example, increasing pH accelerates crosslinking, and increasing shear conditions decreases viscosity. Some of these parameters can be controlled so that the crosslinking occurs in the low shear region of the fracture (10 to 200 s^{-1}), rather than the high shear region (generally 500-1,500 s^{-1}) of the tubing. Manipulating these parameters can minimize shear degradation and frictional pressure loss as portrayed in Figure 8 (Gulbis & Hodge 2000).
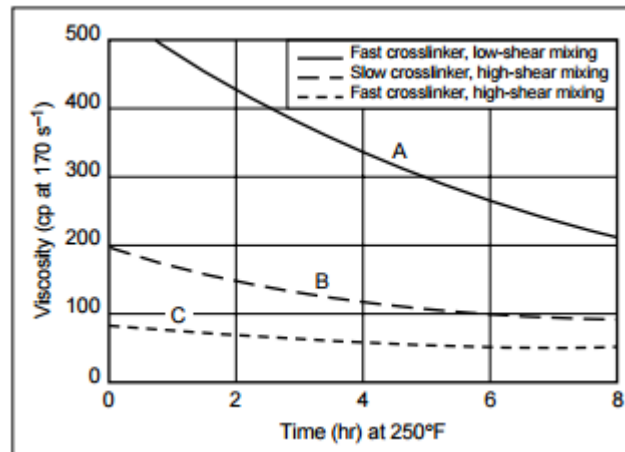
Figure 9 – Effect of Shear and Crosslinking Rate on Viscosity

Crosslinking must take place within an appropriate duration to avoid issues like proppant settling or formation damage. If complete crosslinking occurs too soon, high friction pressure and shear degradation may result. If crosslinking occurs too slowly, inadequate viscosity can cause proppant settling and screenout. As a result, crosslink

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time is crucial to the integrity of the treatment. To avoid problems associated with over-delayed crosslinked fluids, crosslink times of one half to three-fourths of the tubing residence time may be recommended (Cawiezel and Elbel 1990). Another mechanism is to use a dual crosslinker system (Baranet and Ainley 1985). Dual crosslinker systems ensure that the instant crosslinker achieves the adequate viscosity in order to enter the perforation. The delayed crosslinker's role, accelerated by pH conditions and heat in the fracture, is to produce thermally stable, highly viscous fluid. However, delayed crosslinking introduces some risk of near wellbore screenout, especially in low wellbore shear rate zones (Gulbis & Hodge 2000). Finally, to ensure optimum crosslinker performance, one must monitor signs of chemical contamination. A variety of compounds and oilfield products can interfere with the crosslinking reaction and usually extend crosslink time significantly. Examples of these compounds include bicarbonates, silica, and phosphate which are generally found in mixing water. Also, certain chemical additives can react with crosslinkers. One must make sure the mixing tank is pickled, empty, and clean with no iron contamination. Iron is a major problem in the oil industry and at certain concentrations can severely affect the fracturing fluid treatment. Ultimately, it is important to keep all these parameters in mind to ensure the most desired crosslink time and viscosity measurement.

Other Additives

Biocides are added to polymer-containing aqueous fracturing fluids to prevent viscosity loss caused by bacterial degradation of the polymer (Gulbis & Hodge 2000). The biopolymer, which is made up of polysaccharides (sugar), is an excellent food

source for bacteria. This can ruin the gel by degrading the polymer hence reducing its molecular weight, which decreases the viscosity. Additionally, some bacteria can turn the well sour. Once bacteria are introduced into the reservoir, it can reduce sulfate ions to hydrogen sulfide. Materials such as glutaraldehyde, chlorophenates, quaternary amines and isothiazoline are used to inhibit bacterial growth (Ruseska 1982). Usually, the materials kill the bacteria; however, many times they are not able to take out the enzymes produced that break down the polysaccharides. For this reason, biocide is added before the water in the fracture tanks to make sure bacterial enzyme level is low. Biocides are only used in water-based fracturing fluids.

Stabilizers are used to prevent degradation of guar-based gels at temperatures above 200°F. Some of the common stabilizers are methanol and sodium thiosulfate. Sodium thiosulfate is more effective than methanol as it increases the viscosity 2 to 10 fold at elevated temperatures (Thomas and Elbel 1979). They act as oxygen scavengers and prevent rapid gel degradation as a result of the dissolved oxygen (Walker 1995). There are better oxygen scavengers like sodium sulfite; however, their reaction products also cause gel degradation. Additionally, as mentioned before, gel stability with borate and zirconium crosslinkers are best maintained at pH 9-11.

Surfactants are materials that adsorb at the interface between two immiscible substances at low concentration. The surfactant becomes involved at the interface between the two liquids, resulting in the lowering of interfacial tension. Surfactants can change the wettability of the rock. They can also be used as emulsifying agents in the presence of oil-in-water emulsions. However, since the primary focus of this paper is on

water-based fluids, surfactants are used as surface tension reducing agents and formation conditioning agents to promote cleanup of the fracturing fluid from the fracture and for EOR purposes (Penny et al. 1983).

The main purpose of buffers is to adjust the pH of the fluid. This additive is important for polymer hydration, crosslinking mechanism, and eventual gel breaking time. The pH can be adjusted via acidic buffers or basic buffers (i.e. acetic acid and sodium hydroxide respectively).

Another additive is the clay stabilizer. Clays are negatively charged, aluminosilicate particles, with an average size of 2 μm (Moore 1960). There are many kinds of clays, but four main ones are smectite, which swells with the presence of water; kaolinite; illite, which is unstable in the presence of HCl; and chlorite, which contains iron. The negative charge of the clays results when charge balance between positively charged aluminum and negatively charged oxygen are moved through displacement of cations or breaking of particles. Cations from the solution surround the negatively charged clays and form a cationic cloud. As a result of cations being close to each other, the molecules repel, causing displacement, and become prone to migration (Crowe 1979). This became known as fines migration, and this phenomenon can plug pores and decrease permeability. Solutions containing 1 to 3% KCl are used as a base liquid in fracturing fluids to prevent fines migration. Reducing salt concentration diminishes viscosity, thus decreasing the pressure drop, which causes fines migration. Additionally, the organic cation tetramethyl ammonium chloride is an effective stabilizer (Himes and Vinson 1991). These methods are known as temporary clay stabilizers. More permanent

methods involve the use of quaternary amines or inorganic polynuclear cations (Gulbis & Hodge 2000). Quaternary amines possess a positively charged group that attaches to the negatively charged clays. As a result, the hydrocarbon chain portion sticks out, creating a barrier against cations in the solution. One can also use large molecule polymers that surround clays and prevent contact with the water being injected so the clays remain firm. These types of clay stabilizers are generally used for water-based fracturing fluids.

The primary purpose of scale inhibitors is to prevent scale formation inside the formation and wellbore. This can occur by the mixing of two water, namely formation water and the fracturing fluid.

Breakers reduce the viscosity of the polymer backbone into smaller parts. This decreases the molecular weight and thus decreases the viscosity. Breakers can be divided into acids, enzymes, and oxidizers. A breaker should be selected based on its performance in temperature, pH, and desired viscosity profile (stability time) for each specific treatment (Gulbis & Hodge 2000). Oxidizers are used in industry to break gels, however, it is important to keep in mind the free radical sources that can be problematic for flooding and conformance-treatment polymers. The combination of ferric ions and free oxygen is troublesome as it leads to oxygen-free radical degradation of polymers. There are 18 places available on a single guar repeating unit where these radicals can react as displayed by Figure 9 (Brannon 1994):
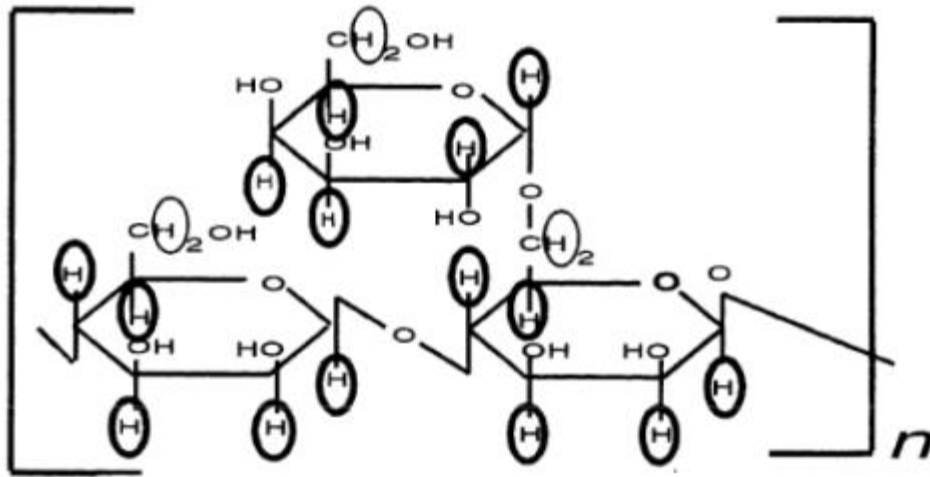
Figure 10 – Breaker Reactivity Sites

The most common types of oxidizers are persulfate $(S_2O_8)^{2-}$ salts which degrade the polymer through free radical reaction by utilizing sulfur.
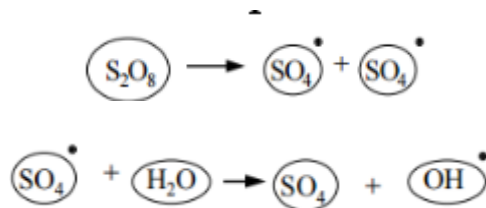
Figure 11 – Persulfate Breaker Mechanism

Another type of breaker are enzymes which break the polymer chain by hydrolysis. Enzymes degrade the polymer through a mechanism called "lock and key" principle. It means that every enzyme has a particular active site with the ability to attach to a particular substrate site on the polymer and degrade it. This makes the range of the enzyme small and polymer-specific. Enzymes do not undergo a change in their structure

during these reactions, so an enzyme can start another reaction after it breaks the polymer at the first site it attached to. Since the enzyme is not consumed during the reaction, it has the possibility to react with an infinite number of guar or any other biopolymer. In theory, enzymes are supposed to be better breakers than oxidizers because of their ability to start an infinite number of reactions and their polymer-specific nature. Enzymes not only attach to a particular biopolymer, but also are specific to the types of linkage they attack, which makes them more effective. Once the biopolymer linkage specific enzyme attaches itself to the biopolymer, it stays put until it degrades the biopolymer. As a result, it will go wherever the polymer goes thus creating a homogenous distribution of breaker throughout the fluid (Brannon and Tjon Joe-Pin 1994). Ultimately, the breaking rate of the fluid will be utilized for design and pumping purposes of the fracturing fluid.

The Use of Seawater in Hydraulic Fracturing

Due to the scarcity of fresh water resources and the rising environmental costs of certain fracture jobs, there has been a renewed interest in finding substitutes to fresh water as a base liquid for fracturing fluids. As a result, the near limitless quantity of seawater has become an increasing possibility to be utilized. Alohaly et al. (2016) showed the applicability of using seawater of a specific ionic concentration with respect to borate and zirconium crosslinked based fracturing fluid. Results showed that the major ions of interest caused delayed hydration and ultimately affected crosslinking operation. By increasing polymer concentration, maintaining appropriate pH, and crosslinker concentration, Alohaly et al. generated a fracturing fluid that maintained its

stability for nearly fifty minutes. High scale formation was associated with the ion's effect on the fluid, especially due to the high content of sulfate in seawater and high barium and calcium concentration in connate water. Scale advisor software results indicated that barium sulfate was the major scale. Additionally, specific ions can severely affect the pH of the fluid inhibiting the operational function of the buffer systems (Cowan and Weintritt 1976).

Almubarak et al. (2016) conducted numerous scale inhibitor tests by using different scale inhibitors. One successful treatment was the use of two types of scale inhibitors simultaneously at 3 and 0.5 gpt concentrations to prevent calcium sulfate scaling. One of the issues Almubarak et al. came across was the precipitation of calcium hydroxide as the pH rose above 9.5. As a result, pH consideration played a major role in ensuring that calcium hydroxide did not precipitate while maintaining the appropriate alkaline environment for an optimal crosslinking mechanism. However, when the buffering agent was removed to eliminate hydroxide scaling and inserted scale inhibitor, it had a negative effect on the fracturing fluid viscosity, even though it was successful in mitigating calcium sulfate (Almubarak et al. 2016).

Scaling is a natural byproduct of seawater based fracturing. As a result, there have been water treatments implemented to decrease scale formation. One way is through nanofiltration technology. It has been proven to be a reliable method for removing sulfate and other divalent ions from the water source (Vo et al. 2017). This membrane filtration method utilizes membranes with 1 to 10 nm pore sizes, which places it in between microfiltration (which are larger than nanofiltration pores) and

reverse osmosis (which are smaller than nanofiltration pores). Results showed that nanofiltration caused sulfate reduction in seawater source to decreases to 300 ppm. This lowers the scaling tendency to a point where it is controllable by conventional chemical treatments (Vo et al. 2017).

Problem Description

According to the American Geophysical Union, oil and natural gas fracking, on average, used more than 28 times the water it used 15 years ago. With the advent of horizontal well fracturing, the amount of water used compared to conventional vertical wells has exponentially increased. This would mean that 9.6 million gallons of water are used per well (Magill 2015). Figure 10 shows the amount of water used during hydraulic fracturing per location.
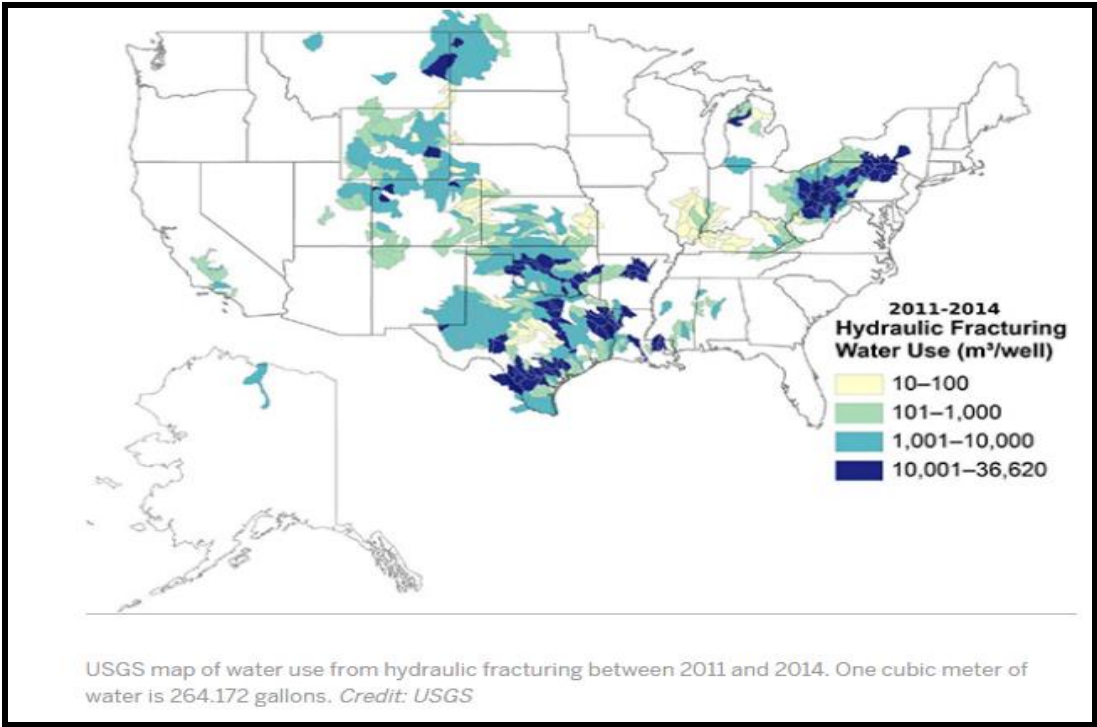
Figure 12 – Hydraulic Fracturing Water Use (Magill 2015)

One example of the typical pricing of dealing with freshwater was a study conducted in the Bakken. It was estimated that water transportation by truck cost from $0.65 to$5.00. Since one truck usually fits 100 barrels, fresh water acquisition alone could reach about $395,000. According to the North Dakota Department of Mineral Resources, a well will require 190 truckloads of water between drilling preparation and drilling. The cost is enormous (Albanese et al. 2016). Below is a summary of water costs in North Dakota as indicated by Table 1.

Cost ($/bbl)	Freshwater	Wastewater
Supply	$.25-$3	$0.0-$0.5
Transport	$0.65-$5.0	$2.0-$9.0
Storage	-	$2.0-$4.0
Disposal	-	$0.5-$1.75

Table 1 – Water costs for North Dakota (Albanese et al. 2016)

In Table 2, water costs were compared in the Eagle Ford which once again shows the massive costs accrued from water-related issues.

Cost Analysis ($/bbl)	Groundwater	Surface water	Wastewater
Procurement	$0.30 – 0.80	$0.30 – 0.80	
Transportation	$1.00 – 4.00	$1.00 – 4.00	$2.00 – 6.00
Storage	$1.00 – 4.00	$1.00 – 4.00	$1.00 – 2.00
Treatment	$0.10 – 0.50	$0.10 – 0.50	$1.00 – 10.00
Transfer	$0.60 – 1.00	$0.60 – 1.00	
TOTAL	**$3.00 – 10.30**	**$3.00 – 10.30**	**$4.00 – 18.00**

Table 2 – Waters Costs for the Eagle Ford (Albanese et al. 2016)

Looking at the Permian Basin, approximately 100% of their water sources come from fresh and brackish underground aquifers. Figure 13 below shows this phenomenon by portraying the two primary Permian subdivisions and their water sources.
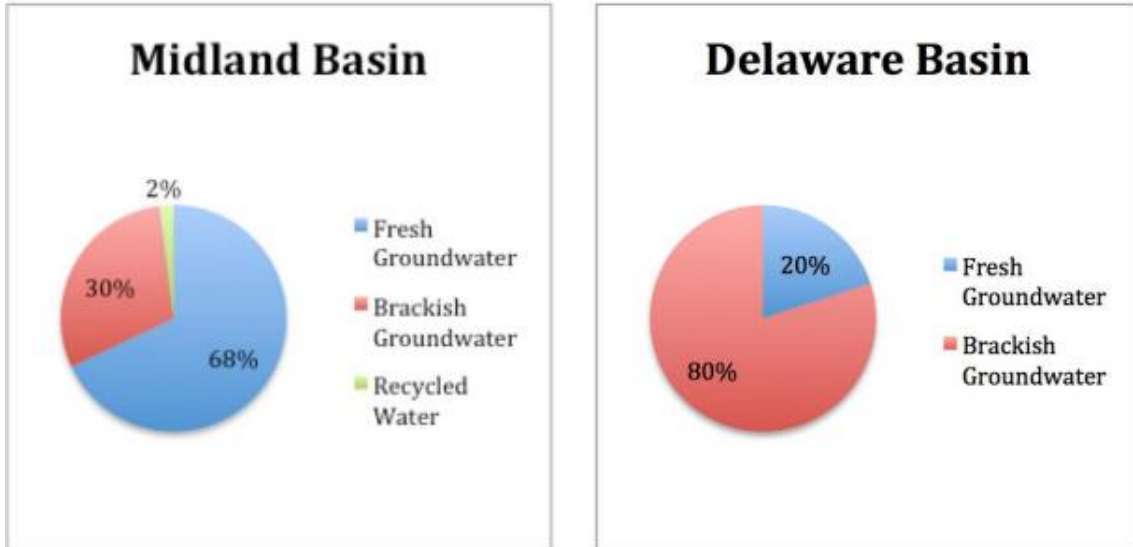
Figure 13 – Water Resources in the Permian Basin (Albanese et al. 2016)

The cost of water use in the Permian is portrayed below in Table 3. Albanese et al. concluded that freshwater is cheaper than the alternatives. However, in areas where water is scarcer, brackish water becomes the viable alternative even though there are treatment costs that aren't taken into account when dealing with freshwater.

Cost ($/bbl)	Fresh Water	Surface Water	Brackish Water	Waste Water
Supply	$0–$1.5	n/a	$0-$0.5	
Transport	$1.5–$4.0	n/a	$1.5–$4.0	
Treatment		n/a	$0.5-$1.0	$1.5-$5.0

Table 3 – Water Costs for Permian Basin (Albanese et al. 2016)

From attempting to use brackish groundwater to wastewater, the treatment costs are the primary cost indicator that differentiates it from freshwater which has little to no treatment costs. As a result, different water technologies have been attempted on various water sources depending on the play. Albanese et al. summarize the various technologies, associated costs, and feasibility to be used per field as portrayed in Table 4.

Typical Water Treatment Technologies						
Name of Technology	Total Suspended Solid (TSS)				Total Dissolved Solid (TDS)	
	Dissolved air flotation	Electro coagulation	Chemical precipitatio n	Filtration	Reverse osmosis	Thermal methods
Cost ($/Bbl)	<$1.0	$0.3-$4.0	$0.5-$4.0	$0.5-$5.0	$0.5-$5.0	$3.0-$8.0
Applicability		Bakken		Bakken		
	Marcellus	Marcellus	Marcellus	Marcellus	Marcellus	Marcellus
	Permian	Permian		Permian	Permian	Permian
	Eagle Ford			Eagle Ford	Eagle Ford	

Table 4 – Water Treatment Technologies Per Field (Albanese et al. 2016)

To address the issue of freshwater scarcity and associated treatment costs of some of the alternatives like wastewater, the use of raw seawater has started to receive attention. The TDS content of the source water used in this report is one of the highest in the world as the Arabian Gulf is known for its hypersaline conditions. Furthermore, the cations present in the water, namely calcium and magnesium are known to cause problems in the formulation process of hydraulic fluid. As a result, it is expected that certain fracturing fluid additives must be increased to meet these challenges and

ultimately create a stable seawater based fracturing fluid system with appropriate gelation timing that meets industry standards.

Objective

The objective of this study is to investigate the feasibility of using raw, hypersaline Arabian Gulf seawater to formulate a successful fracturing fluid system by testing 1) gel stability at temperatures ranging from 270-300ºF 2) comparing effect of increasing additive concentrations 3) testing different polymer systems 4) using scale inhibitor to mitigate scale formation in seawater-formation water mixture at temperature ranges of 270-300ºF and 5) comparing seawater based fracturing fluid gel stability with freshwater based fracturing fluid gel stability.

This study aims at finding a successful alternative to the scarce and costly freshwater. The use of seawater in hydraulic fracturing could solve freshwater acquisition challenges and mitigate environmental impacts.

CHAPTER II

EXPERIMENTAL STUDIES

The objective of this study is to investigate the use of raw seawater sample from the Arabian Gulf to prepare crosslinked-gel-based hydraulic fluid. The following steps were done in this study:

1. Raw seawater sample was analyzed

2. Formation water sample was analyzed

3. Fracturing fluid with typical additives prepared using raw seawater as base fluid

4. Fracturing fluid with typical additives prepared using freshwater as base fluid

5. Fracturing fluid viscosity was analyzed using high pressure, high-temperature viscosity measurements

6. Breaker tests were conducted on the crosslinked gel

7. Scale inhibitor tests were conducted on freshwater/formation water mixture at different temperatures

8. Scale software was run to figure out type of scale found in water mixture

Materials

Experiments were run at the Texas A&M University laboratory. Materials used were polymers, crosslinkers, pH buffers, gel stabilizers, scale inhibitor, and gel breaker. The chemical composition of each additive is shown in Table 5.

Additive	Chemical Composition
Guar Polymer	hydroxyl propyl guar (HPG), carboxymethyl hydroxypropyl guar gum (CMHPG), petroleum distillates
Scale Inhibitor	Phosphonate
Breaker	8-10 wt% Chlorous acid, sodium salt 10-30 wt% Sodium Chloride
Crosslinker	Zirconium, Borate
Buffers	Acetic Acid, Sodium Hydroxide
Gel Stabilizer	Sodium Thiosulfate

Table 5 – Fracturing Fluid Composition

Materials used are guar polymer, borate crosslinker, zirconium crosslinker, pH buffer (acetic acid and sodium hydroxide), gel stabilizer, scale inhibitor and gel breaker. $NaCl$, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $SrCl_2.6H_2O$ and $BaCl_2.2H_2O$ are used as sources for Na^+, K^+, Ca^{+2}, Mg^{+2}, Sr, Ba, and SO_4^{-2} ions. Arabian Gulf seawater and Saudi formation water were utilized with a measured pH of each having 7.42 and 5.08 respectively. The Arabian Gulf seawater and DI water (to simulate freshwater) were utilized to prepare all fracturing fluids.

Equipment

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The ICP, shown in Figure 14, is used to determine the cation concentrations in the seawater and formation water samples. Analyte atoms in solution are excited by a

plasma where they are desolvated, vaporized, and atomized. Ultimately, analyte concentrations will be generated. When energy is applied to the atom, electron gains energy and moves to the upper orbital or to the more excited state. When the electron returns back to its original state, a photon light is emitted with unique set of wavelengths. These wavelengths correspond to certain elements. An illustration of this theory is depicted below in Figure 15:

Figure 14 - ICP
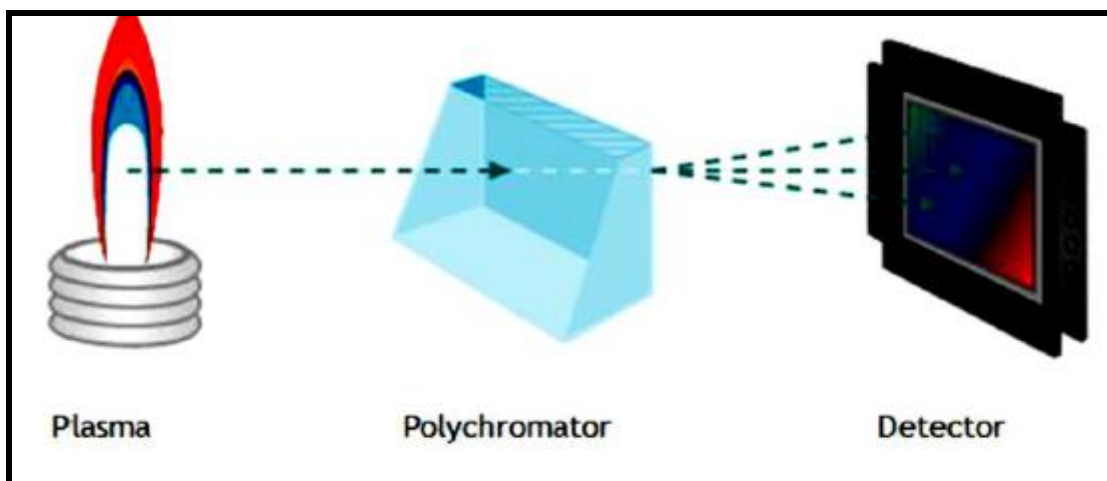
Figure 15 – Theory Behind ICP Use

High Temperature/High Pressure (HT/HP) Rheometer

The apparent viscosity of fracturing fluid was measured using HT/HP 5550 Chandler Rheometer. This instrument is a concentric cylinder viscometer that uses the rotor and bob geometry widely used in the oil industry. This Chandler model goes up to 2000 psi and a maximum temperature of 500°F.

Figure 16 – HT/HP Rheometer

<u>Viscometer Fann 35 Model A</u>

Viscosity measurement of linear gel was done through the Viscometer Fann 35 Model A displayed in Figure 17.

1. Fill the container with the linear fluid

2. Set up viscometer for 300 rev/min rotation with R1 sleeve and B1 bob

3. Turn on viscometer

4. Place sample container on stage, and raise stage to immerse sleeve and bob in fluid until fluid reaches etched line

5. Allow reading to stabilize

6. Record reading on QC form

Figure 17 – Viscometer

<u>Dynamic Scale Loop</u>

The dynamic scale loop, pictured in Figure 18, is a fully automated system that measures the efficiency of scale inhibitors under high temperature and high pressure conditions. The information is then relayed on the accompanying software which portrays scale buildup by changes in pressure. The seawater and formation water samples are pumped through coil tubing and consequently, the differential pressure is measured. This is portrayed in the schematic in Figure 19. Once the differential pressure exceeds the acceptable threshold, the system begins to auto-clean. DI water, acetic acid, and EDTA are utilized to clean scale remnants on the coil tubing to ensure a clean environment for the next experiment.
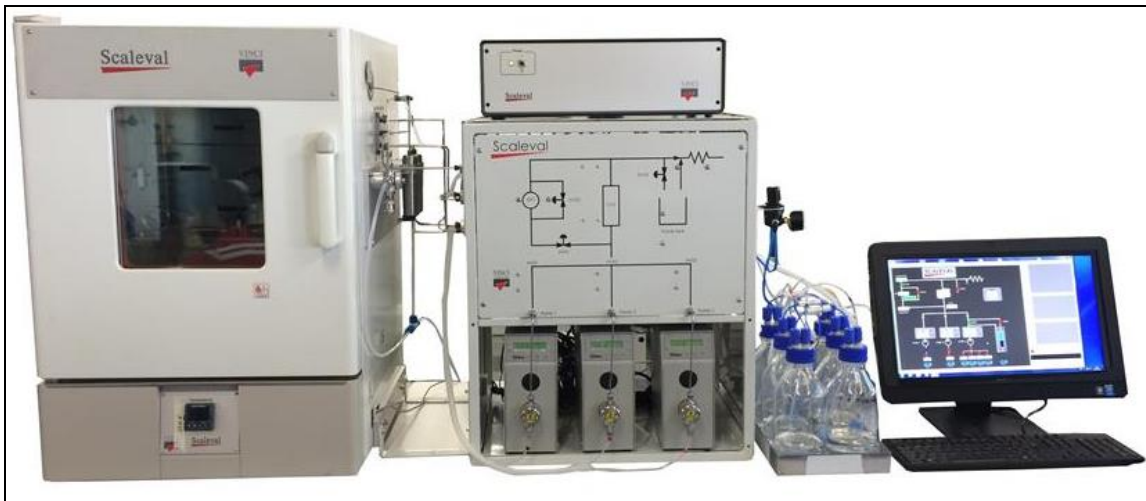
Figure 18 – Dynamic Scale Loop
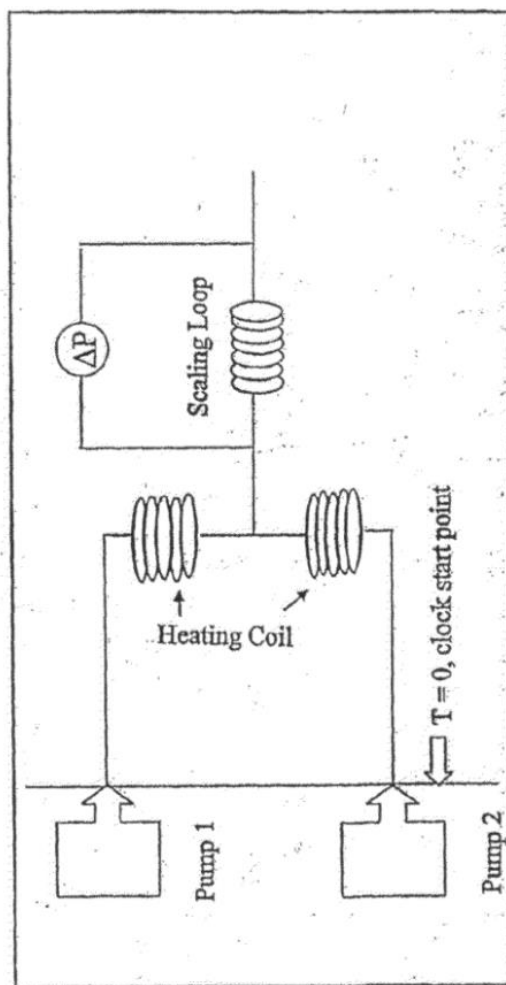
Figure 19 – Schematic of Scale Loop

Experimental Procedures

<u>Water Analysis</u>

The seawater analysis was collected from the Arabian Gulf. The formation water was collected from a field in Eastern Saudi Arabia. The samples were analyzed via the Inductively Coupled Plasma (ICP) to generate the cations' concentration. To measure sulfate and iron, the team used UV-Vis Spectrophotometer machine. Reagents were

added and made sure they dissolved within the seawater sample. The equipment would then read the total mg/liter content.

Synthetic Seawater and Formation Water Mixture Preparation

Salts were added to DI water to generate a 50%-50% formation water – seawater mixture and then separated the anions and cations accordingly. The cation and anion samples would later be used in the scale loop experiments. NaCl, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $SrCl_2.6H_2O$ and $BaCl_2.2H_2O$ are used as sources for Na^+, K^+, Ca^{+2}, Mg^{+2}, Sr, Ba, and SO_4^{-2} ions.

Fracturing Fluid Preparation

Fluids were prepared utilizing typical industry additives as shown in Table 6. The concentration of certain additives varied as temperature increased.

Additive	Concentration
Guar Polymer	50 lb/1000gal
Scale Inhibitor	1500-3000 ppm
High pH Buffer	0.1 mL
Low pH Buffer	0.2 mL
Gel Stabilizer	0.9 mL
Instant Crosslinker	0.02 – 0.03 gpt
Delayed Crosslinker	0.05 – 0.09 gpt
Breaker	0.05 gpt

Table 6 – Fracturing Fluid Recipe

The following procedures were used to prepare all fluid samples:

1. The seawater sample was placed in the blender. The guar polymer was then added.

2. The acid pH buffer was then added and the mixture was allowed to be mixed for thirty minutes to ensure proper hydration.

3. 100 mL of the fluid was taken out and put in a blender. The base buffering agent was then added to increase pH value, followed by the gel stabilizer.

4. The breaker is then added.

5. The delayed crosslinker is added first followed by the instant crosslinker.

6. Wait about ten seconds until the gel becomes visibly more viscous and then remove 23 mL and place the remaining fluid in the rheometer jacket for testing.

Viscosity Measurements

The apparent viscosity of the fluid was measured using a HTHP 5550 Chandler Rheometer. Tests were done at temperatures ranging from 270 – 330 ºF. The test duration was 2 hours or until the fluid viscosity dropped below 500 cp, the stability reference point. The tests were conducted with 77 mL fluid volume.

Scale Loop Experiments

The dynamic scale loop was used to measure the pressure differential in the coil tubing. The pressure differential results were then transferred to a software indicating presence of scale. The seawater and freshwater ratio were kept at 50% - 50% ratio and tested at temperatures ranging from 270 - 330 ºF. A phosphonate based scale inhibitor was used to mitigate scale formation at different concentrations.

CHAPTER III

RESULTS AND DISCUSSION

Seawater Analysis

Analysis of Arabian Gulf seawater sample showed a total TDS content of 54,170 ppm including: Ca, Mg, Na, and K ions of 689 ppm, 1771 ppm, 16,890 ppm, and 785 ppm respectively. Sulfate concentration in the Arabian Gulf seawater sample was 4514 ppm and the Chloride concentration was 32,191 ppm. Table 7 summarizes the chemical analysis of the Arabian Gulf sample:

Test	Seawater (ppm)
pH	7.42
Sodium	16,890
Ammonium	166
Potassium	785
Magnesium	1,771
Calcium	689
Fluoride	14
Chloride	32,191
Nitrite	92
Bromide	57
Nitrate	160
Sulfate	4,514
Phosphate	274
TDS of seawater	54,170

Table 7 – Seawater Composition

Direct Use of Seawater and Freshwater to Prepare Fracturing Fluid

Fracturing fluid was formulated using two kinds of polymers: hydroxyl propyl guar (HPG) and carboxymethyl hydroxypropyl guar gum (CMHPG). The high pH buffer is sodium hydroxide and it was used to increase the pH to around 10 for optimal borate crosslinking with the polymer. Zirconium also has been used to viscosify high pH (10-12) fluids. The increase in pH does create some issues, however, namely the precipitation of hydroxides, primarily magnesium and calcium hydroxides, which affects the overall pH of the system.

Various scientists have tested different polymer loading and crosslinker concentrations to see how this affects gel stability. Moorhouse et al. ran experiments with various zirconium crosslinker concentrations at 245 Fahrenheit at 100 s^{-1} and generated this graph displayed in Figure 20:
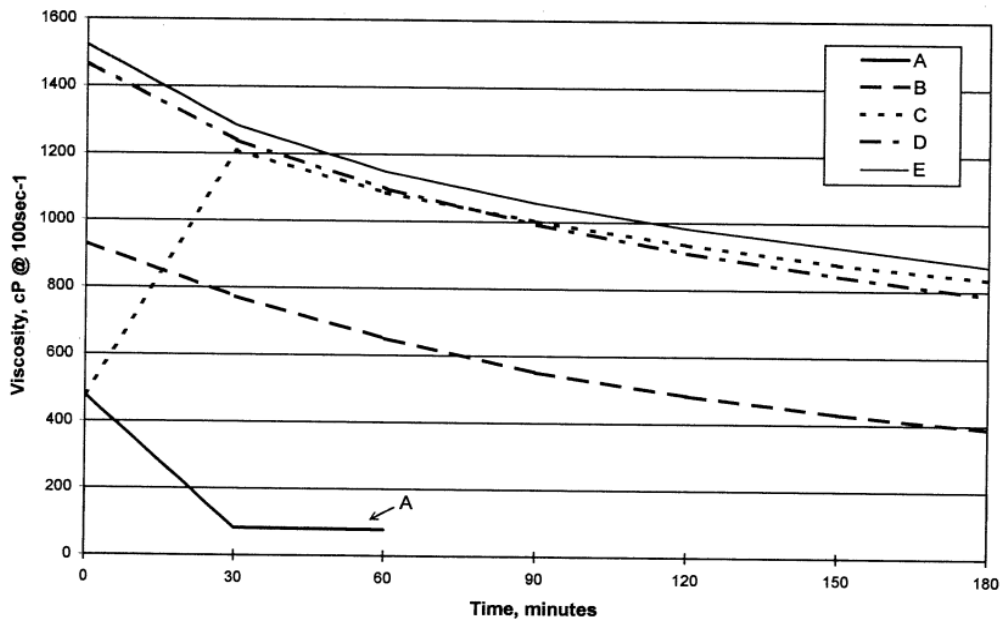
Figure 20 – Crosslinker Concentration Effect on Viscosity

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Curve A demonstrates an overcrosslinked condition that most likely resulted in synergesis. Curve B represents an undercrosslinked condition. Ultimately, the concentration of the crosslinker needs to be somewhere in between these two extremes to have adequate gel stability. Furthermore, traditionally, for high pressure and high temperature environments, fracturing fluid systems will require higher gel loading (Rahim 2013).

Alohaly ran viscosity experiments with 45 lbm/1000 gal gel loading at 300°F utilizing CMHPG and HPG based seawater fracturing fluid. The results, displayed in Figure 21, proved that seawater based fracturing fluid can be generated with 50 minute and 40 minute gel stability for CHMPG and HPG based fracturing fluid, respectively.
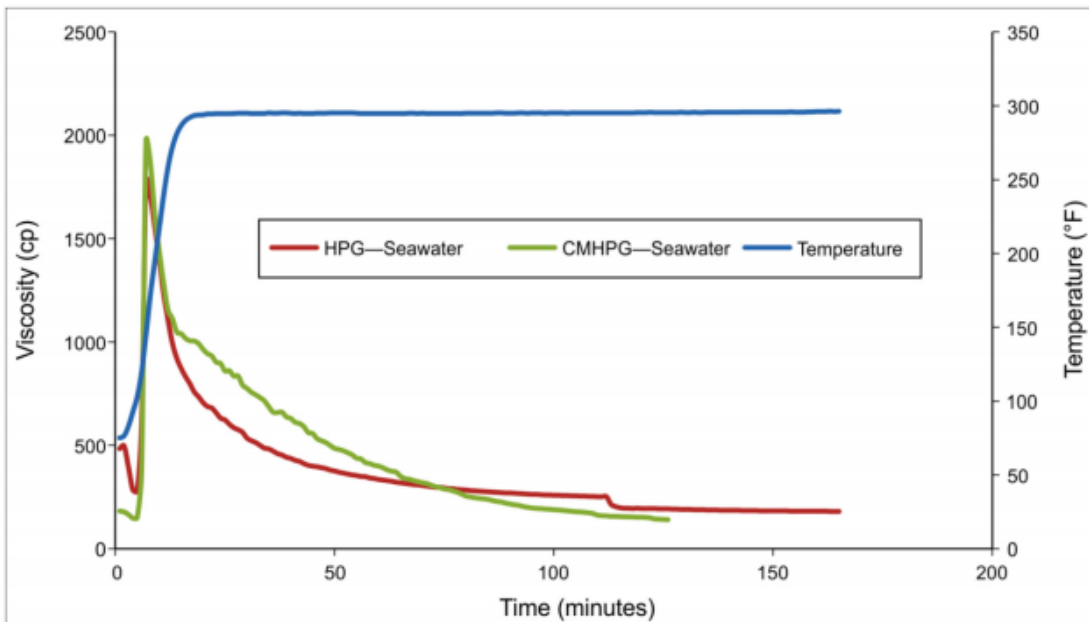
Figure 21 – 45 lbm/1000 gal Gel Loading Results (Alohaly et al. 2016)

As a result, viscosity experiments were run with a 40 lbm/1000 gal gel loading and a reduced crosslinker concentration to see how different or similar my results would be to Alohaly's data. The concentrations of the additives are portrayed in Table 8:

Additives	Concentrations
Gelling Agent, lbm/1000 gal	40
pH adjusting agent, mL	0.2
pH adjusting agent, mL	0.1
Gel stabilizing agent, mL	0.9
Instant Crosslinker, gpt	0.01
Delayed Crosslinker, gpt	0.04

Table 8 – Reduced Additive Recipe

I ran these trial experiments at 270°F and 300°F at 40 s^{-1}. Results are shown in Figures 22 and 23.
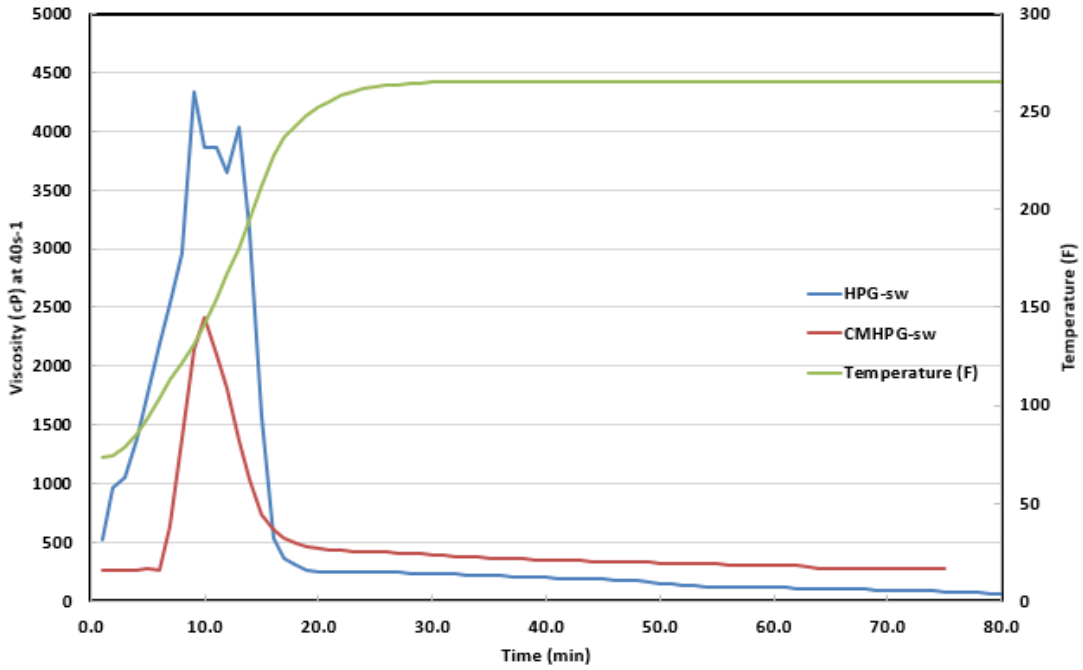
Figure 22- Reduced Additive Rheology at 270ºF
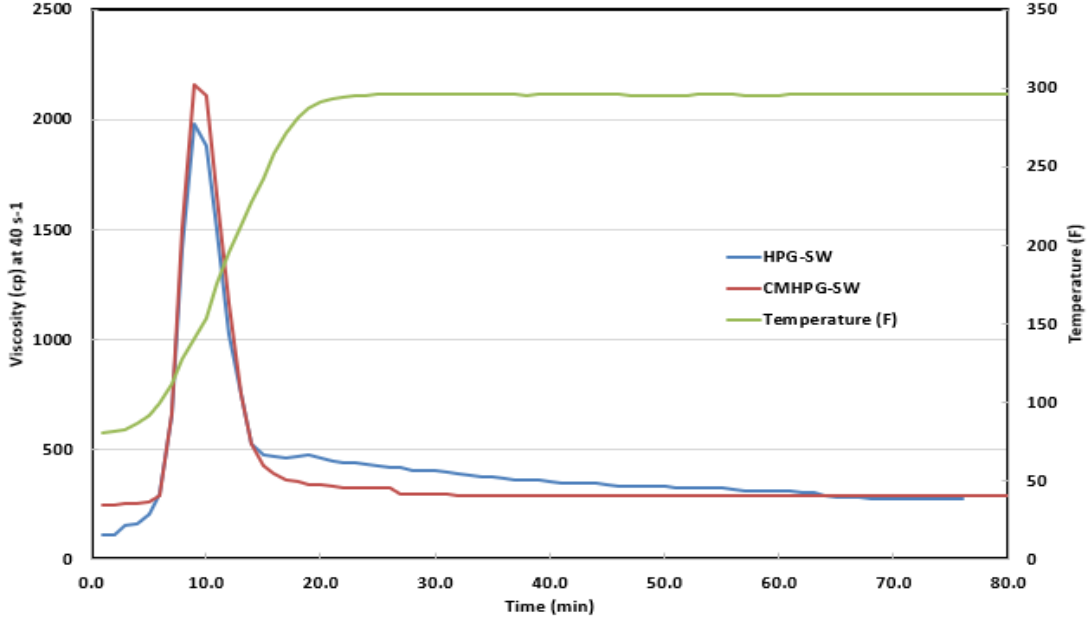
Figure 23- Reduced Additive Rheology at 300ºF

The results are not very encouraging as the fluid breaks very rapidly, nearly less than 20 minutes. Industry standard dictates that crosslink lip time should at least be within the range of 2/3 – ¾ of wellbore volume pump time for the deeper, unconventional wells. These four trial experiments made it clear that attempting to save costs by reducing additive concentration can have a negative effect on gel integrity. As a result, the recipe for the fracturing fluid had to change.

Comparison Between HPG-Based Freshwater and Seawater Fracturing Fluid

Utilizing the new recipe as indicated in table 6, freshwater based fracturing fluid and seawater-based fracturing were compared. This recipe was used for the seawater-based fracturing fluid.

Table 9 – Recipe for HPG-Based Fracturing Fluid for 270°F

HPG, 50lb/1000gal gel loading	
270°F	
1L of Seawater	pH 8.1 - 8.2
6g of HPG	pH 8.3 - 8.5
0.2mL of Acetic Acid Buffer	pH 5.9 - 6.1
Hydrate for 30 mins	49-50 cP, pH 6.1 - 6.2
0.1 mL of NaOH Buffer	pH 9.3 - 9.5
0.9 mL of Gel Stabilizer	-
0.05 gpt Delayed X-linker	-
0.02 gpt Instant X-linker	-
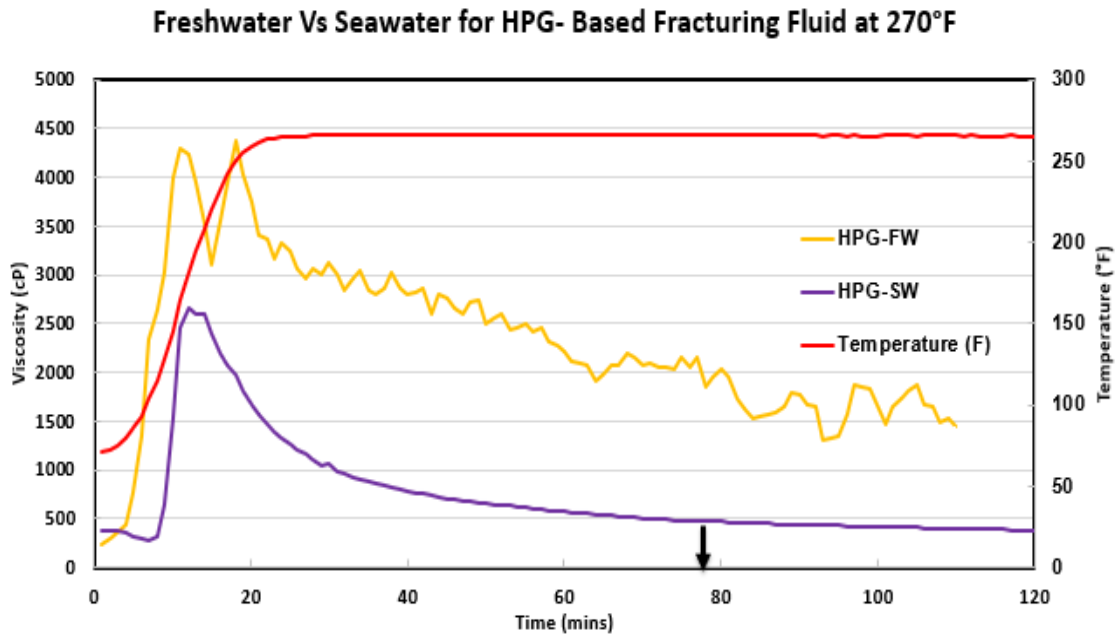
Figure 24 – Freshwater Vs Seawater for HPG Based Fracturing Fluid at 270ºF

In the case for the 270ºF at 40 s^{-1}, as indicated in Figure 24, the freshwater based fracturing fluid does not break. On the other hand, the seawater-based fracturing fluid goes below the 500 cp stability reference point at 78 minutes. It is important to note that this is merely the stability reference point and does not necessarily mean that the gel is broken below 500 cp. The superior result of the freshwater is expected as the cations and anions in the seawater affect the performance of the fracturing fluid. The naturally high ionic strength of seawater lowers the viscosity of the dual crosslinked (zirconate and borate) HPG. Salts can also buffer and strongly influence pH control (Harris et al. 1999).

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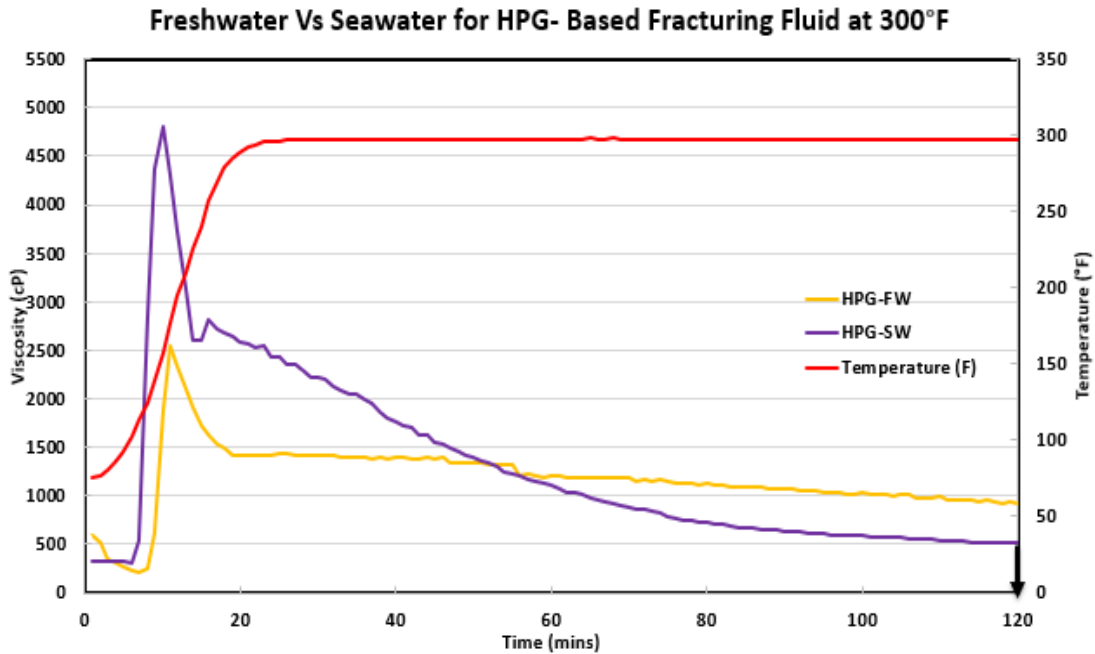
Figure 25 – Seawater Vs Freshwater for HPG Based Fracturing Fluid at 300ºF

At 300ºF, as indicated in Figure 25, the freshwater based fracturing fluid did not break. The seawater-based fracturing fluid lasted for nearly two hours above the stability reference point. As can be seen from Table 10, the delayed crosslinker concentration was increased to offset the effect of thermal degradation of the gel. The delayed zirconate crosslinker was increased rather than the borate crosslinker because while borate crosslinkers are shear tolerant, they are affected by temperature. On the other hand, the zirconate crosslinkers are temperature resistant (Rahim 2013). Ultimately, it is evident that freshwater based fracturing fluid utilizing HPG polymer generates higher gel stability time than seawater based fracturing fluid utilizing HPG polymer.

HPG, 50lb/1000gal gel loading	
300°F	
1L of Seawater	pH 8.1 - 8.2
6g of HPG	pH 8.3 - 8.5
0.2mL of Acetic Acid Buffer	pH 5.9 - 6.1
Hydrate for 30 mins	49-50 cP, pH 6.1 - 6.2
0.1 mL of NaOH Buffer	pH 9.3 - 9.5
0.9 mL of Gel Stabilizer	-
0.08 gpt Delayed X-linker	-
0.02 gpt Instant X-linker	-

Table 10 – Recipe for HPG Based Fracturing Fluid for 300ºF

Comparison between CMHPG – Based Freshwater and Seawater Fracturing Fluid

Utilizing the new recipe, freshwater and seawater-based fracturing fluid were compared utilizing CMHPG. This recipe was used for the seawater-based fracturing fluid:

CMHPG, 50lb/1000gal gel loading	
270°F	
1L of HWYH Seawater	pH 8.1 - 8.2
6g of CMHPG	pH 8.3 - 8.5
0.2 mL of Acetic Acid Buffer	pH 5.9 - 6.1
Hydrate for 30 mins	50-53 cP, pH 6.1 - 6.2
0.1 mL of NaOH Buffer	pH 9.3 - 9.5
0.9 mL of Gel Stabilizer	-
0.05 gpt Delayed X-linker	-
0.02 gpt Instant X-linker	-

Table 11 – Recipe for CMHPG-Based Fracturing Fluid for 270ºF

Figure 26 – Seawater Vs Freshwater for CMHPG Based Fracturing Fluid for 270ºF

At 270ºF, the freshwater based fracturing fluid did not break while the seawater-based fracturing fluid went below the 500 cp stability reference point at 105 minutes as indicated in Figure 26. The freshwater based fracturing fluid shows more stability as the gel does not break. CMHPG is an anionic derivative that is affected by the presence of salts. This results from the reduction of polymer chains through electrostatic repulsion that limits entanglement of polymer chains which hinders viscosity generation (Domelen & Haggstrom 2011).
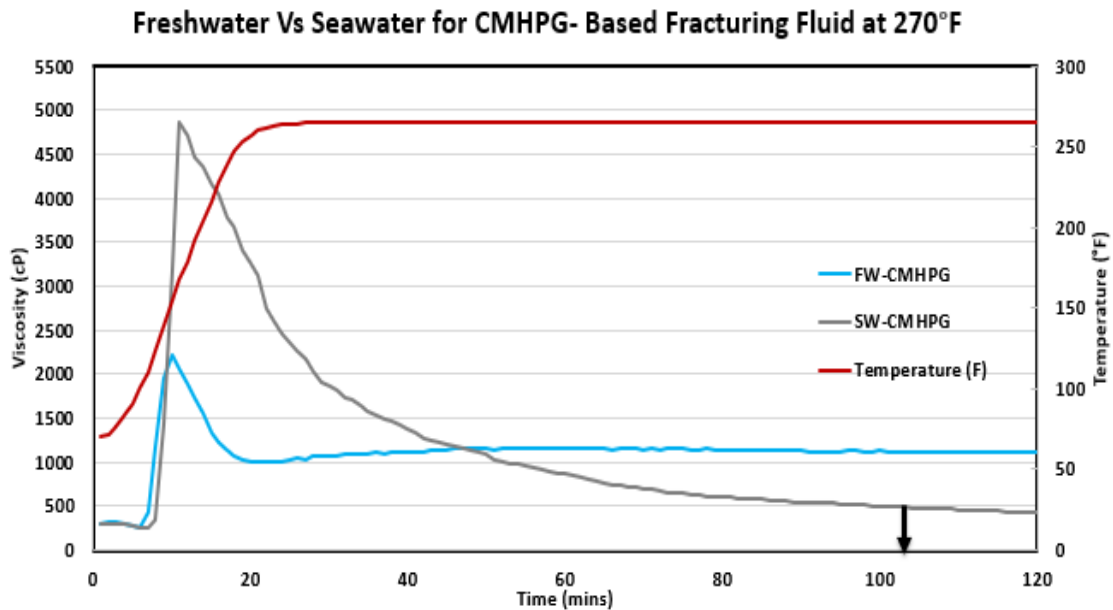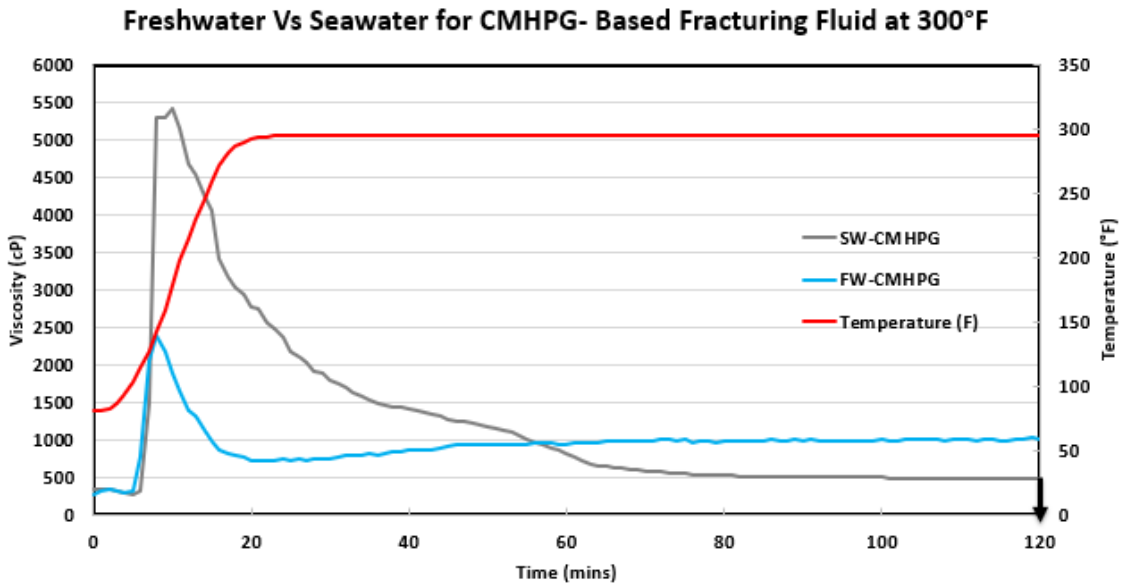
Figure 27 - Seawater Vs Freshwater for CMHPG Based Fracturing Fluid for 300ºF

At 300ºF, the freshwater based fracturing fluid does not break while the seawater-based fracturing fluid lasted for nearly two hours above the 500 cp stability reference point. Similar to the 300ºF range for the HPG based seawater fracturing fluid, the 300ºF range for the CMHPG based seawater fracturing fluid produced the longest duration of gel stability. At this temperature range, the delayed crosslinker concentration was increased to generate the longest stability time as portrayed in Table 12. As the temperature increases, the delayed mechanism of the zirconate crosslinker is triggered. Many scientists have tried to modify the zirconium complex to allow it to crosslink at certain times, instigated by high temperature, unlike the borate gels which are both shear and thermally thinning (Dawson 1991). Almond developed a type of polyhydroxyl zirconium complex as a means of producing a delayed crosslink reaction (Harry et al.

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1999). This why this dual crosslinker system is said to have an "extra advantage" compared borate-based fracturing fluid system. The crosslinker is designed with an early temperature and higher temperature activation mechanism where the higher temperature activated crosslinker crosslinks right before the fluid enters the perforation (Driweesh 2013).

CMHPG, 50lb/1000gal gel loading	
300ºF	
1L of Seawater	pH 8.1 - 8.2
6g of CMHPG	pH 8.3 - 8.5
0.2 mL of Acetic Acid Buffer	pH 5.9 - 6.1
Hydrate for 30 mins	50-53 cP, pH 6.1 - 6.2
0.1 mL of NaOH Buffer	pH 9.3 - 9.5
0.9 mL of Gel Stabilizer	-
0.08 gpt Delayed X-linker	-
0.02 gpt Instant X-linker	-

Table 12 – Recipe for CMHPG Based Fracturing Fluid for 300ºF

Figure 28 – Seawater Vs Freshwater for CMHPG Based Fracturing Fluid for 330ºF

At 330ºF, seawater-based fracturing fluid utilizing CMHPG, a significant reduction in gel stability was observed. At this temperature range, the delayed and instant crosslinker concentrations were increased to generate the highest possible stability time as displayed in Table 13. With respect to the freshwater based fracturing fluid, the gel lasted for 70 minutes above the 500 cp stability reference point while the seawater-based fracturing fluid lasted for 34 minutes. This can be explained by the "thermal thinning" nature of borate-crosslinked gels (Dawson 1991). As a result, many scientists have recommended an increase in crosslinker and polymer concentration to try and offset the temperature effect on the guar-based system.

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CMHPG, 50lb/1000gal gel loading	
330ºF	
1L of Seawater	pH 8.1 - 8.2
6g of CMHPG	pH 8.3 - 8.5
0.2 mL of Acetic Acid Buffer	pH 5.9 - 6.1
Hydrate for 30 mins	50-53 cP, pH 6.1 - 6.2
0.1 mL of NaOH Buffer	pH 9.3 - 9.5
0.9 mL of Gel Stabilizer	-
0.09 gpt Delayed X-linker	-
0.03 gpt Instant X-linker	-

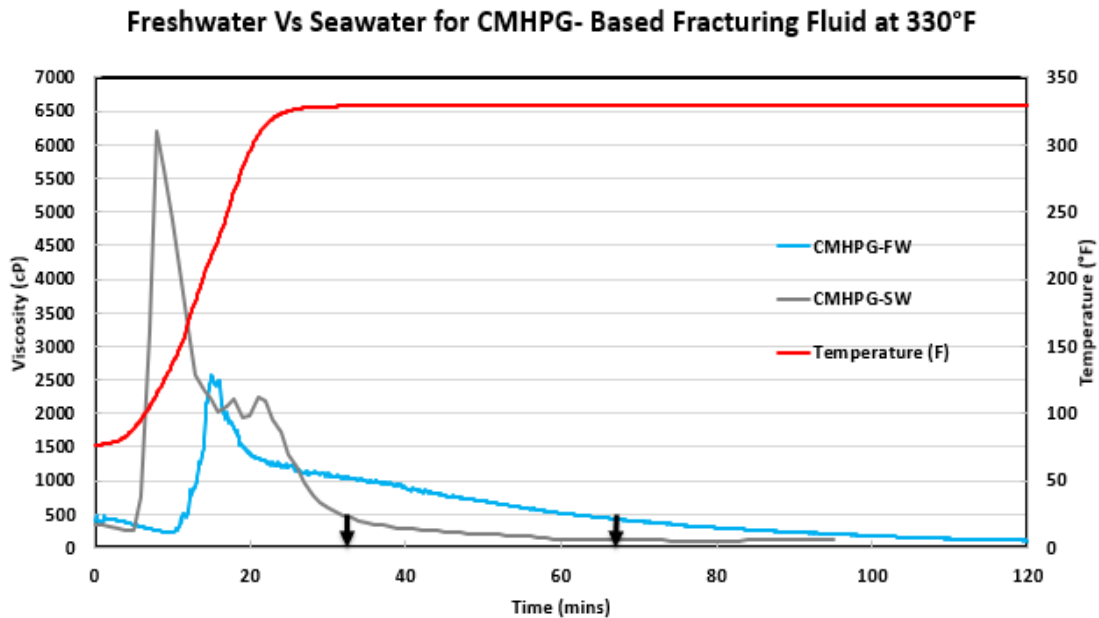**Table 13 – Recipe for CMHPG Based Fracturing Fluid for 330ºF**

Fluid Breaker Tests

The fluid breaker was included in the recipe to test the efficiency of the chlorous acid-based breaker on the CMHPG and HPG based seawater fracturing fluids. The concentration of the breaker was kept constant at all temperatures at 0.05 gpt. Viscosity measurements displayed the evident degradation of the fracturing fluid system with the introduction of breakers. Chlorous acid is well known for its ability to degrade high pH borate gels. Breakers reduce viscosity by cleaving the polymer molecule into smaller

molecular weight fragments. This is accomplished via free radical mechanisms (Nasr-El-Din 2007).

Comparison between CMHPG and HPG Based Fracturing Fluid with and without
Breaker

At 270ºF, CMHPG based seawater fracturing fluid showed gel stability of about 105 minutes while gel stability with the inclusion of the chlorous acid breaker showed 55 minute stability. Including the breaker results in a 48% reduction in stability time. At 300ºF, CMHPG based seawater fracturing fluid showed gel stability of about 120 minutes while the gel stability with the inclusion of the chlorous acid breaker showed 50 minute gel stability as viscosity dips below 500 cP. This shows a 58% reduction in stability time with the inclusion of the breaker. At 330ºF, the use of a breaker was not feasible due to the low stability time of the seawater-based fracturing fluid with no breaker. With increased temperature, the breaker becomes too reactive (Nasr-El-Din 2007). As a result, a comparison was done at this temperature by increasing the crosslinker concentration. With a delayed crosslinker (zirconate) concentration of 80 μL and instant crosslinker concentration (borate) of 20 μL, the stability time was 25 minutes. When the concentration was increased by adding 10 μL to both crosslinkers, the stability time increased to 34 minutes. This led to a 36% increase in the stability time.

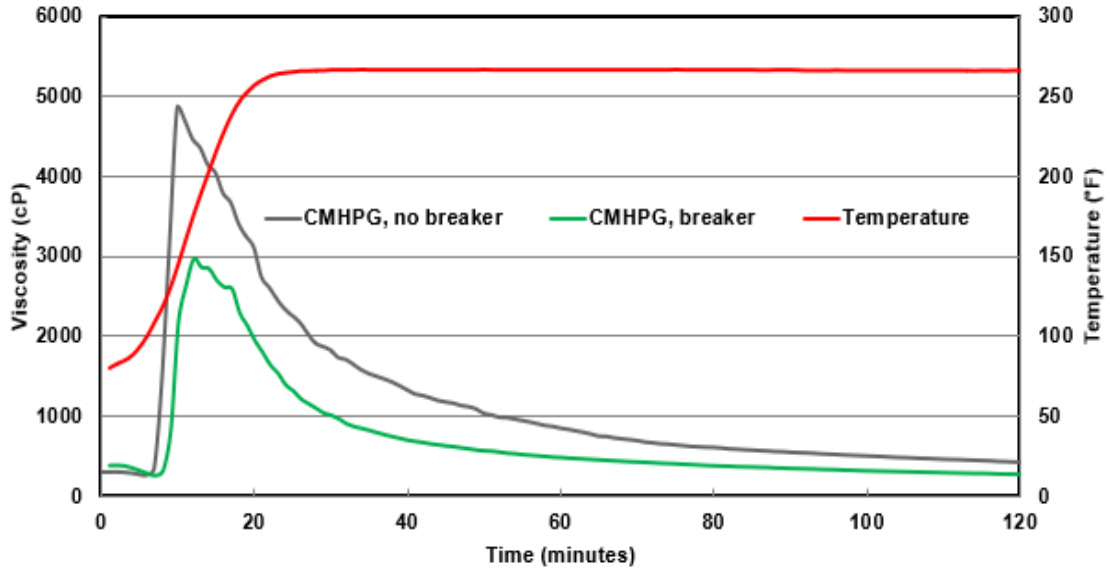**Figure 29 – Breaker Tests for CMHPG Based Fracturing Fluid for 270ºF**
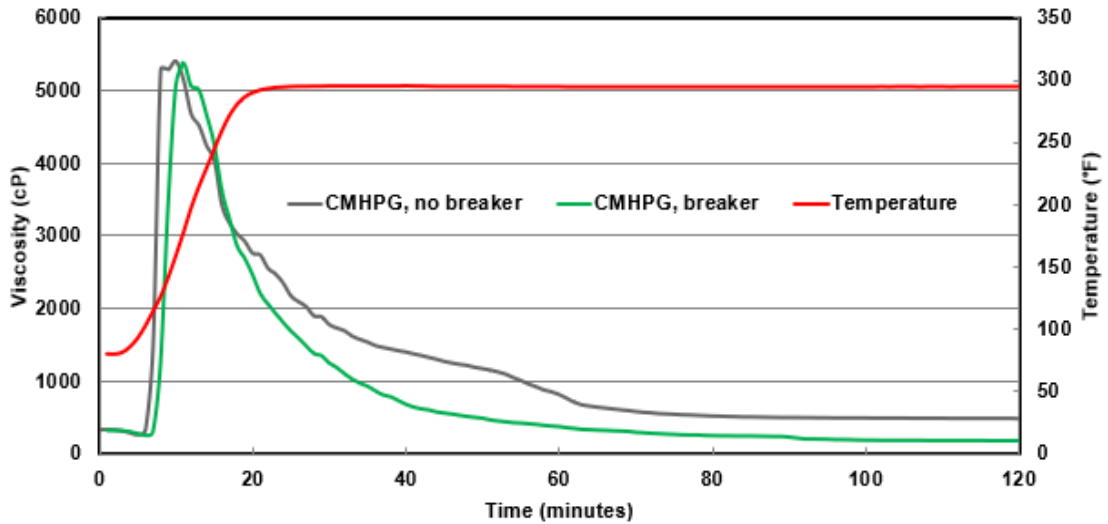
Figure 30 - Breaker Tests for CMHPG Based Fracturing Fluid for 300ºF
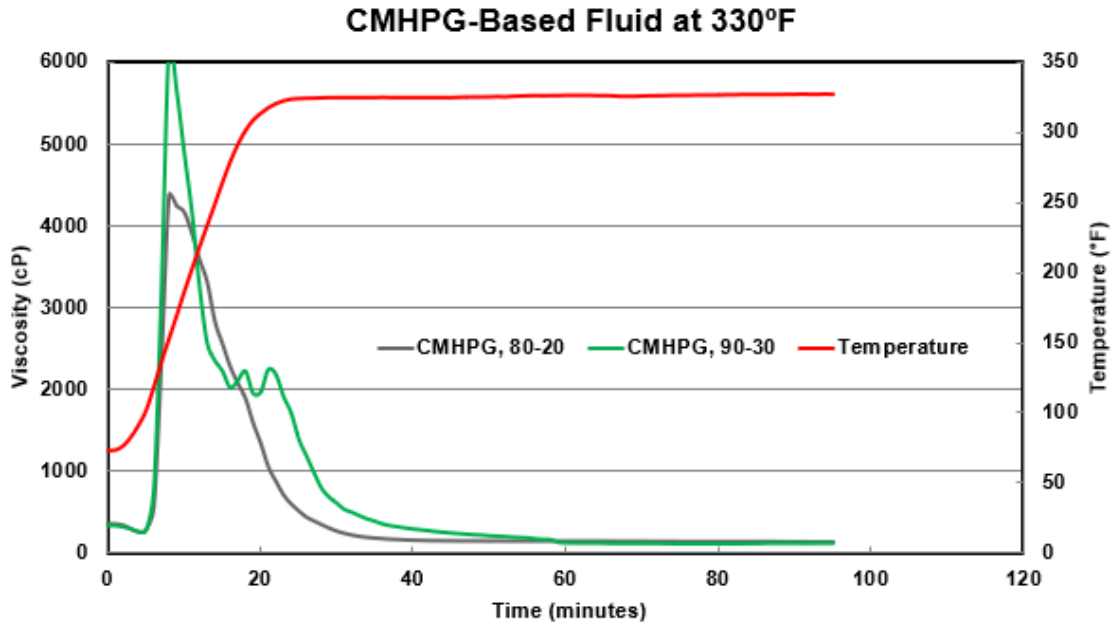
Figure 31 – Crosslinker Concentration Comparison

At 270ºF, HPG based seawater fracturing fluid showed gel stability of 78 minutes while gel stability with the inclusion of the chlorous acid breaker showed 55-minute stability. Including the breaker results in a 31% reduction in the stability time. At 300ºF, HPG based seawater fracturing fluid showed gel stability of about 110 minutes while the gel stability with the inclusion of the chlorous acid breaker showed 65-minute gel stability as viscosity dips below 500 cP. This shows a 41% reduction in stability time with the inclusion of the breaker. At 330ºF, the use of a breaker was not feasible as the stability time of the fracturing fluid with no breaker resulted in a relatively quick collapse. The gel stability time with 90 μL delayed crosslinker and 20 μL instant crosslinker generated nearly 30 minutes of gel stability. The percent increase in stability with the CMHPG based fracturing fluid was higher than the HPG and this could be due

to the lesser impurities found in the former. The rheology data was all summarized
below in Tables 14 and 15.
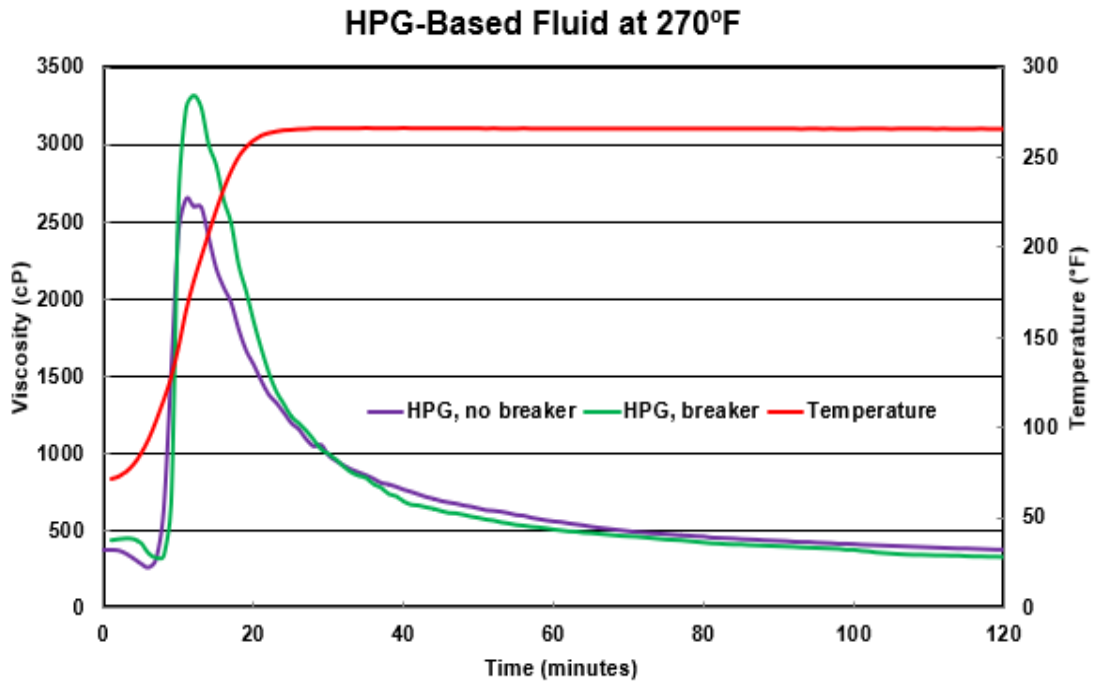
Figure 32 - Breaker Tests for HPG Based Fracturing Fluid for 270ºF
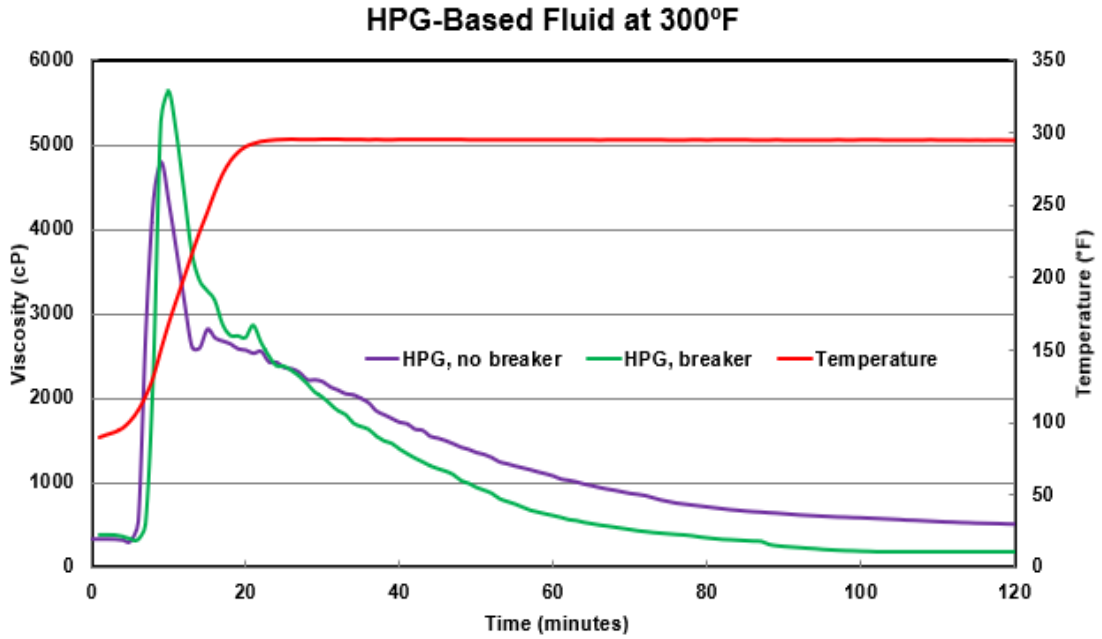
**Figure 33 - Breaker Tests for HPG Based Fracturing Fluid for 300°F**
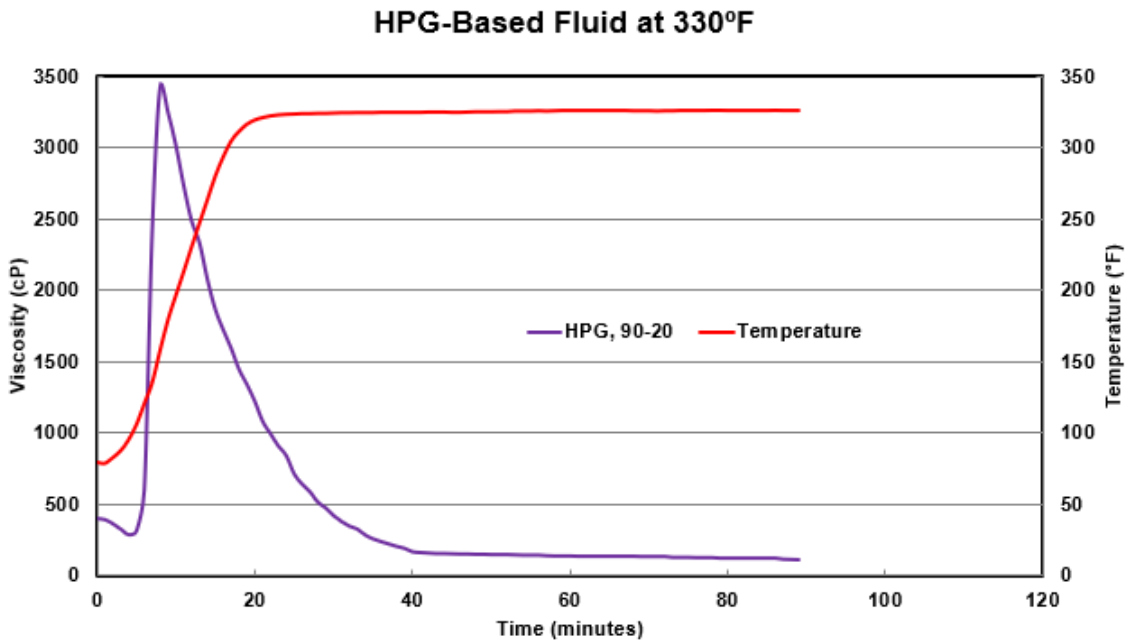
Figure 34 – HPG Based Fracturing Fluid Utilizing Seawater for 330°F

Fluid Stability Without Breaker				
	Freshwater – CMHPG	Seawater – CMHPG	Freshwater - HPG	Seawater – HPG
270F	120 mins	100 mins	110 mins	80 mins
300F	120 mins	120 mins	120 mins	110 mins
330F	70 mins	34 mins	-	30 mins

Table 14 – Fluid Stability Without Breaker

Fluid Stability with Breaker				
	Seawater – CMHPG	Seawater – CMHPG + breaker	Seawater – HPG	Seawater – HPG + breaker
270F	105 mins	55 mins	80 mins	55 mins
300F	120 mins	50 mins	110 mins	65 mins

Table 15 – Fluid Stability with Breaker

Scale Inhibition Tests

The primary purpose of the scale loop is to qualitatively and quantitatively portray the severity of scale formation by looking at pressure differential data. Freshwater and seawater were mixed at a 50%-50% ratio to simulate downhole conditions where scale formation is bound to happen. This ratio, comprised of the Arabian Gulf seawater and Saudi formation water, was chosen because the most expensive to remove and least soluble scale in water (2 mg/L), barium sulfate, was highest in terms of concentration at this ratio. Researchers have tried to find ways to deal with barium sulfate. Attempts to decrease the size of the scale to increase the solubility have been made. Investigators have also found out that freshly precipitated barium sulfate dissolves eight times faster than the scale that is 30 hours old. Barium sulfate is soluble in sulfuric acid, but it forms an acid sulfate so that when it is diluted in water, barium sulfate re-precipitates. Suito and Takiyama ran barium sulfate crystallization tests and concluded that the size of freshly precipitated barium sulfate scale generally increased with the decrease in total concentration of barium sulfate. Ongoing research by Miura and Nagakane have been trying to find sequestering agents that can significantly delay or prevent precipitation of barium sulfate. They showed how citrates can both "retard the precipitation of barium sulfate and alter final size of the particles" (Weintritt 1976).

The 50%-50% ratio generated in this research is similar to what others in the literature have tested. Vo et al. found that barium sulfate was highest at a 60%-40% ratio, close to the ratio for the samples tested in this research (Vo 2016). Looking at the

mineral saturation states at the 50%-50% ratio, barite was the primary scale formed per log Q/K results. This data was generated via a scaling software. The software was run at various seawater and formation water ratios such as 100% formation water, 100% seawater, and in between ratios. Consequently, the barite concentrations were plotted which resulted in a parabolic curve. This shape is expected for this kind of analysis as portrayed in Almubarak's paper with regards to tests on various sulfate scale derivatives (Almubarak 2016).

Test	Formation Water (mg/L)
pH	5.08
Sodium	70,000
Potassium	4,000
Magnesium	2,000
Calcium	25,000
Strontium	2,000
Barium	4,000
Sulfate	200
Chloride	16,000
TDS	123,200

Table 16 – Formation Water Composition

Mineral & Chemical Formula	Log Q/K
Barite ($BaSO_4$)	3.412
Celestite ($SrSO_4$)	1.06
Anhydrite ($CaSO_4$)	0.91
Bassanite ($2CaSO_4 \bullet (H_2O)$)	0.24
Gypsum ($CaSO_4 \bullet 2(H_2O)$)	0.11

Table 17 – Scale Composition of 50%-50% Seawater-Formation Water
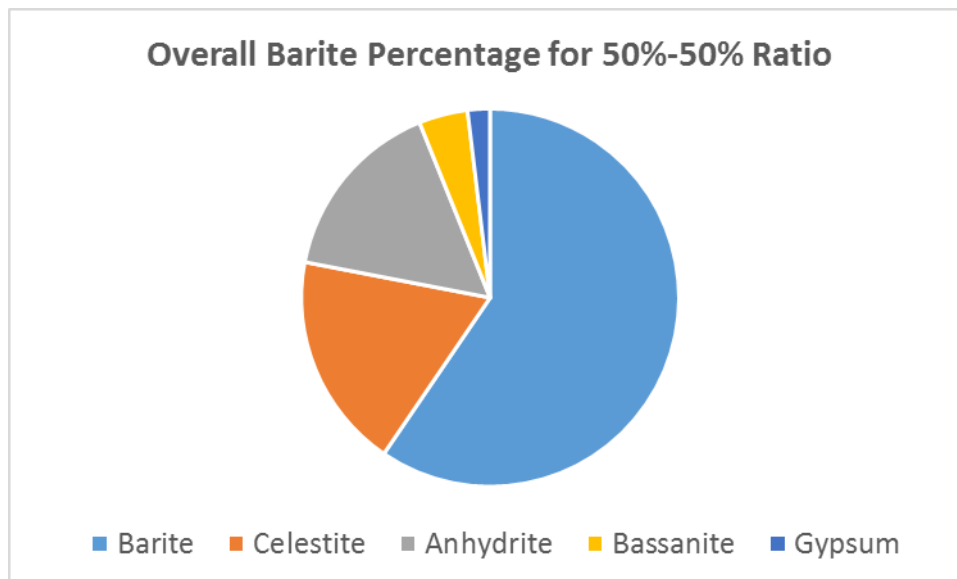
Figure 35 – Overall Barite Percentage for 50%-50% Ratio
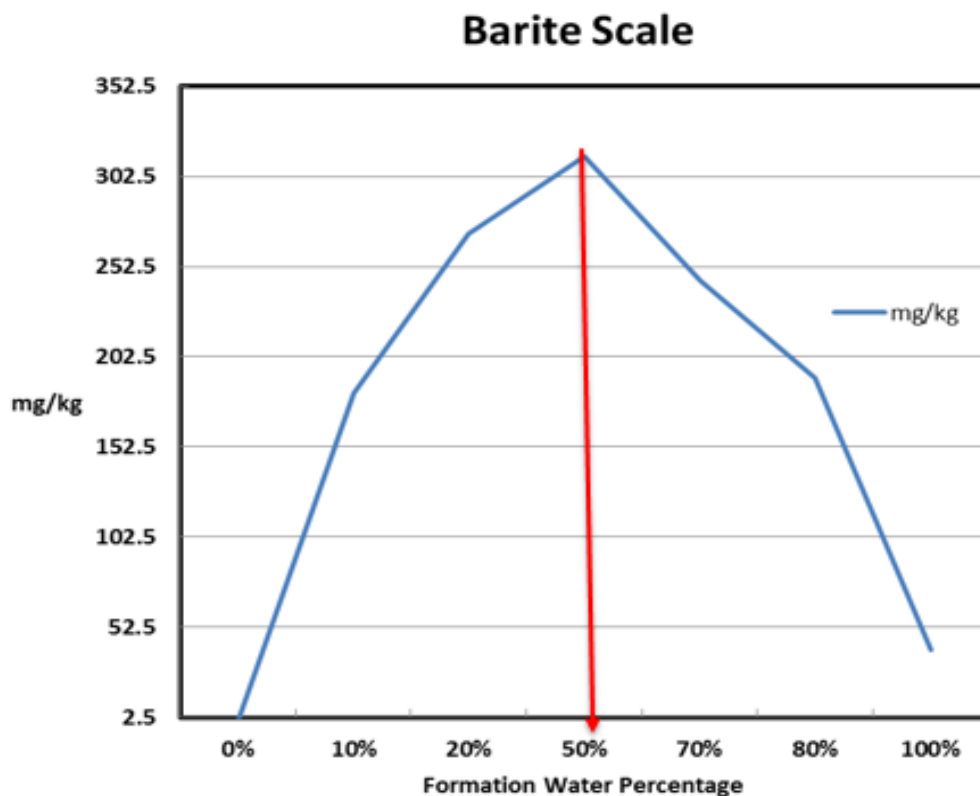
Figure 36 – Scale Tendency of Brine Mix at Various Seawater-Formation Water Ratios

Utilizing the dynamic scale loop, seawater and formation water were mixed at a 50%-50% ratio and tested at 270ºF, 300ºF, and 330ºF. A phosphonate based scale inhibitor was used to find the minimum inhibition concentration (MIC) for the brine mixture at the aforementioned temperature ranges. The phosphonate scale inhibitor products preferentially binds to M^{2+} cations. In the brine mix, the concentration of Mg^{2+} and Ca^{2+} ions are the highest hence making their presence an important feature to study. It is known that Ca^{2+} is useful to the barium sulfate inhibition efficiency of phosphonate scale inhibitors whereas Mg^{2+} is "detrimental and has scale inhibition poisoning effect". This behavior is explained by the size of the two cations where

magnesium cannot be included into the growing barite scale because of its small size (Shaw 2012). Ba^{2+} is even bigger than Calcium making its size a non-issue when it comes to phosphonate binding. The ionic radius of the M^{2+} cations prevalent in the brine mixture is found in Table 18.

Element	Ionic Radius, M^{2+} (picometers)
Magnesium	78
Calcium	106
Strontium	127
Barium	143

Table 18 – Ionic Radii of M^{2+} Cations

Dynamic scale loops were performed to find out the critical inhibitor concentration for the 50%-50% seawater and formation water mixture. Each test began with a blank run where there is no scale inhibitor present. The blank test had a time of 7 minutes before the differential pressure data exponentially increased indicating extreme scale build up. For the tests to pass at the scale inhibitor concentration, it is an industry standard to triple the time for the blank test time, known as the hold time (BinGhanim et al. 2017).

At 270ºF, the scale inhibitor succeeds in mitigating scale at 3000 ppm and 2000 ppm. At 2000 ppm, differential pressure dramatically increases at about 23 minutes which passes the "3X blank test". The blank test serves as a reference point where the

50%-50% brine mixture is tested with the absence of scale inhibitor. This reference point will be included for all scale loop graphs.
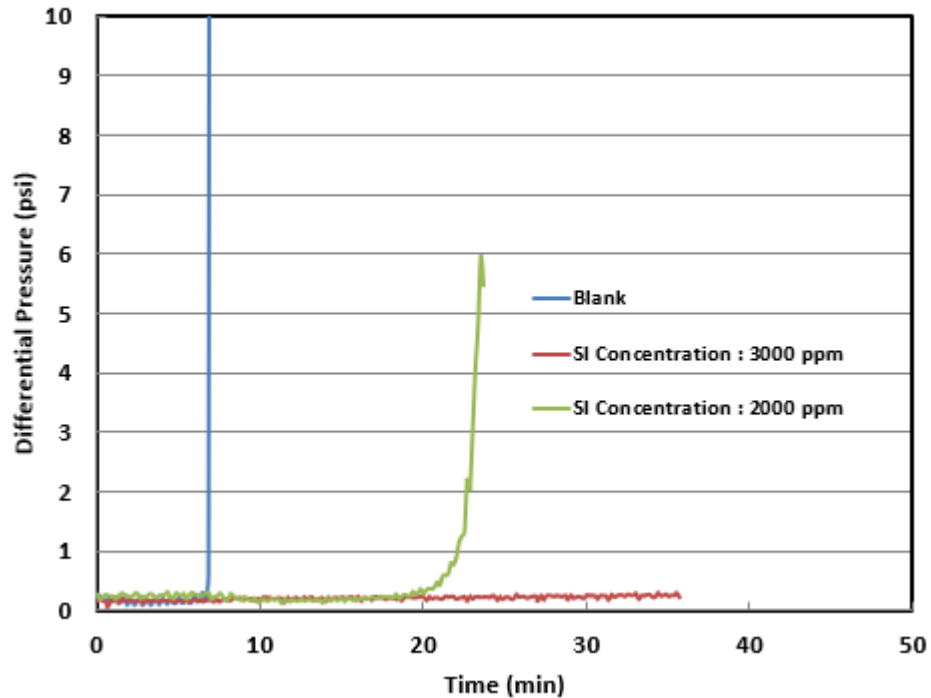
Figure 37 – Scale Inhibition Analysis at 270ºF

At 300ºF, 3000 ppm and 2000 ppm of the scale inhibitor successfully passes the test for over 35 minutes. At 1500 ppm, the differential pressure rises above 1 psi indicating scale formation. However, the scale buildup is not severe and the exponential increase typical of extreme scale buildup is not evident. As a result, chelating agents can be used however this will incur additional costs on the producer. At the same time, the concentration of the scale inhibitor will be less so the trade-off must be examined based on the financial factors involved.
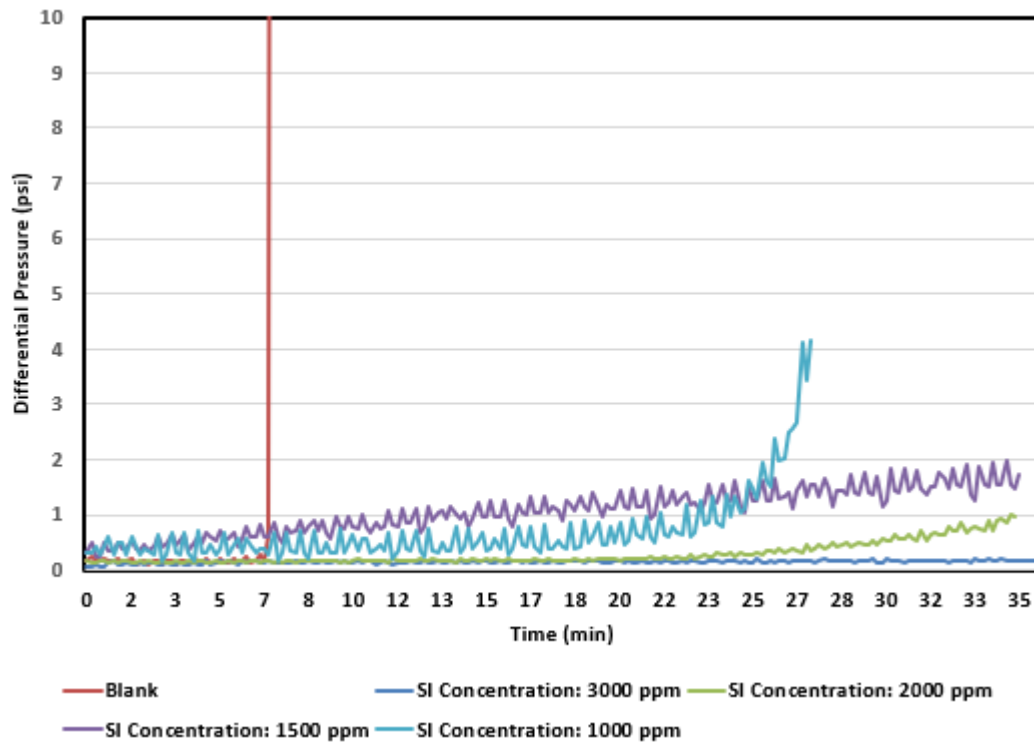
Figure 38 – Scale Inhibition Analysis at 300ºF

At 330ºF, the scale inhibitor concentrations from 250 ppm to 750 ppm were successful in passing the "3X blank" test. At 1500 ppm and 2500 ppm, the scale inhibitor tests did not pass. Interestingly, the higher scale inhibitor concentration showed less successful results. This can be explained by Shaw and Sorbie's research where they focused on precipitation of calcium phosphonates which occurs due to the concentration of calcium, concentration of scale inhibitor, solution pH, and the test temperature (Shaw et al. 2015). Phosphonate based inhibitors are known for thermal instability especially when temperature far exceeds 130ºC. As a result of this high temperature accompanied by the high amount of scale inhibitor, the molar ratio between M^{2+} and phosphonates

will increase and cause precipitation of calcium phosphonate. If high enough concentrations of calcium and inhibitor are brought together, even at room temperature, it is possible to generate calcium-inhibitor complexes (Graham et al. 2000). The fact that the scale inhibitor is also strong ligands that will bind with metal ions contributes to the precipitation phenomena. Inhibitor/calcium precipitate more readily forms at temperature increases (Jordan 1994). Research has been conducted to find the most thermally stable Phosphonate derivative scale inhibitor. According to Graham, the tetra-phosphonate (HMDP) provided thermal stability up to 160 ºC due to $(-CH2-)_6$ linkages that reduce "steric strain within the molecules" (Graham et al. 2000). As a result, less scale inhibitor may yield better results. In Table 19, the scale inhibitor concentrations for all the temperatures tested were summarized.
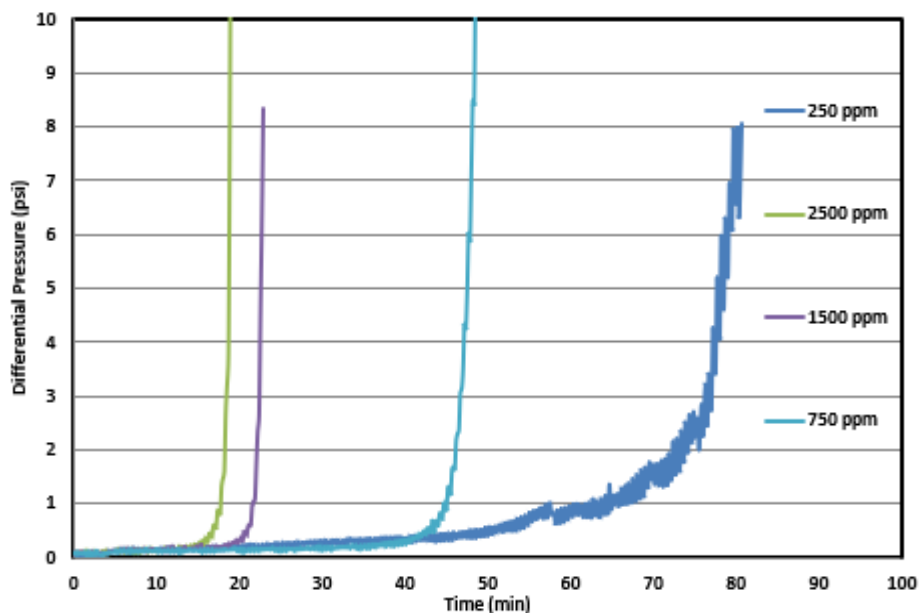

Figure 39 – Scale Inhibition Analysis at 330°F

Temperature (°F)	Minimum Inhibition Concentration
270	2000 ppm
300	1500 ppm
330	250 ppm

Table 19 – Scale Inhibition Summary

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The objective of this study was to experimentally evaluate the use of seawater to generate HPG and CMHPG-based crosslinked fracturing fluid. The results indicated that it is feasible to directly use seawater as base fluid to generate fracturing fluid however issues relating to formation damage ranging from scale buildup to precipitation to polymer hydration, among others, are issues to keep in mind as they will be an issue if not mitigated. Mitigation of scale is possible through the use of scale inhibitor at the appropriate concentration. Breakers were also included to find ways to reduce formation damages that result from polymer residue as the formation is fracked. Based on the results obtained, the following conclusions were drawn:

1. CMHPG and HPG-based seawater fracturing fluid display excellent gel stability at 270 - 330ºF.

2. Seawater-based fluid fracturing fluid provides less stability time than freshwater based fracturing fluid.

3. Increasing gel loading and additive concentration provides higher stability time.

4. Effect of adding a breaker causes more than 50% reduction in stability time for both CMHPG and HPG seawater systems.

5. The breaker had a larger effect on CMHPG based fracturing fluid than HPG based fracturing fluid.

6. Concentration of scale inhibitor must be adjusted to successfully mitigate scale.

7. Scale inhibitor was successful in mitigating $BaSO_4$ scale.

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