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**EVALUATION OF HIGHLY VISCOUS POLYMERIC FLUIDS AND
RECROSSLINKED DEGRADED GEL**

by

DANLU ZHANG

A THESIS

**Presented to the Faculty of the Graduate School of the
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY**

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

in

PETROLEUM ENGINEERING

2016

Approved by

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PUBLICATION THESIS OPTION

This thesis consists of the following two articles that will be submitted for publication in as follows: Paper I, Pages 3-42 is prepared for publication in Journal of Society of Petroleum Engineers. Paper II, pages 43-82 is prepared for publication in Journal of Society of Petroleum Engineers.

ABSTRACT

This work presents the evaluations of two products. One can be used for hydraulic fracturing to achieve viscosity stable under high shear rate, and the other is potential to be applied to enhance oil recovery from mature oilfield.

The first experiment is to synthesize and evaluate a new polymeric fracturing fluid that can resist high shear rate of 511 s^{-1} with favorable viscosity. Zirconium crosslinked fracturing fluids are lack of self-healing ability after shearing, and the difficulties still exist in maintaining viscous with lower polymer content exposed to high shearing conditions, therefore, the research is trying to develop a new product to fix the problem. As a result, optimal formulation of polymer and crosslinker is obtained, and the impacting factors to viscosity improvement are discovered specifically. Experiment shows that sample with a polymer concentration at 5 gpt can stay viscous greater than 10 mPa S after 3 mins shearing. The result is encouraging and the product is potential to be used in oilfield application by further optimization.

The second evaluation is to characterize the interactions and impacting factors of degraded gel in recrosslinking process. Reusing the degraded gel from producing water is in sake of reducing the cost. The research is expected to get strong gels with a cost-effective manner. Experiments were conducted towards clay optimization, degraded gel selection, thermos-stability and other parameters that influence gel performance. Polymer concentration at a range of 0.5 wt% to 0.7 wt% can bring the recrosslinked gel with both better elastic and rigid properties, with proper additives of clay and crosslinker.

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SECTION

1. INTRODUCTION

Since approximately only one third of original oil in place can be produced from a reservoir, the way to improve oil recovery has been a heated topic in last a few decades. The technology of hydraulic fracturing has been widely use to increase the production of oil and gas from a reservoir. The reservoir containing oil and gas is known as porous media, allowing the fluids flow to production wells. However, a large amount of oil and gas are trapped in the reservoir due to the heterogeneity and the poor conductivity of the formation matrix, and so on,. Therefore, it has not been easily or even possible to drive the tremendous quantities of oil and gas from a reservoir in cost-effective manner. Therefore, hydraulic fracturing, a process to develop fractures inside the formation to stimulate the oil and gas wells, especially low-permeability wells, has been implemented to enhance well performance. When fracturing, the fracture will be initiated as critical pressure is achieved by continuously pumping the fluids to the geologic formation. The fracturing process involves the injection of fracturing fluids that contains water, proppants and gelling agents or polymers. The first study is to synthesize and evaluate a viscous polymeric fluid that can be used in hydraulic fracturing.

Additionally, excess water production can lead to extra operating cost or well abandonment in conventional oil and gas reservoirs. It is a worldwide problem that has a significant negative influence on the profitable of hydrocarbon production. Inadequate profile injection and low sweep efficiency are key challenges for improving the oil recovery. Fractures, high-permeability channels, or other heterogeneity zones are easily providing paths of least distance for fluids, resulting breakthrough earlier than they

supposed to be. The common and effective way to mitigate the problem is to maximize the amounts of swept oil from the reservoir by placing blocking agents into the flow paths. Gel treatment emerges as one of the most effective methods to reduce the excess water production, and enhance oil recovery. In-situ gel is one of the methods used in gel treatment. The second study aims to develop a new in-situ gel system that can be used in field operations for conformance control.

PAPER

I. EVALUATION OF HIGHLY VISCOUS POLYMERIC HYDRAULIC FRACTURING FLUIDS AT HIGH SHEAR RATE

Abstract

The research is to synthesize and evaluate a new polymeric fracturing fluid that can resist high shear rate of 511^{-1} with favorable viscosity. Zirconium crosslinked fracturing fluids are lack of self-healing ability after shearing, and the difficulties still exist in maintaining viscous with lower polymer content exposed to high shearing conditions, therefore, the research is trying to develop a new product to fix the problem. As a result, optimal formulation of polymer and crosslinker is obtained, and the impacting factors to viscosity improvement are discovered specifically. Experiment shows that sample with a polymer concentration at 5 gpt can stay viscous greater than 10 mPa S after 3 mins shearing. The result is encouraging and the product is potential to be used in oilfield application by further optimization.

Introduction

The technology of hydraulic fracturing has been widely use to increase the production of oil and gas from a reservoir. The reservoir containing oil and gas is known as porous media, allowing the fluids flow to production wells. However, a large amount of oil and gas are trapped in the reservoir due to the heterogeneity and the poor conductivity of the formation matrix, and so on,. Therefore, it has not been easily or even possible to drive the tremendous quantities of oil and gas from a reservoir in cost-effective manner. Therefore, hydraulic fracturing, a process to develop fractures inside the formation to stimulate the oil and gas wells, especially low-permeability wells, has been implemented to enhance well

performance. When fracturing, the fracture will be initiated as critical pressure is achieved by continuously pumping the fluids to the geologic formation. The fracturing process involves the injection of fracturing fluids that contains water, proppants and gelling agents or polymers.

The application of hydraulic fracturing makes remarkable progress of oil and gas production, for example, the Bakken formation underlying parts of North Dakota and Montana has experienced spectacular improvement that approximately 9 % more of US production was brought to the surface by the end of 2013 (US EIA 2013a). Additionally, hydraulic fracturing has altered the estimates of oil and gas reserves. The potential US oil and gas has incremented to 35% and 38% respectively by this technology (US EIA 2013b). Recent investigation shows that over 52,000 oil and gas wells across the United States have been implemented by hydraulic fracturing in unconventional oil and gas exploitation (Shao, 2015).

Hydraulic fracturing makes great contributions to improve oil recovery in the energy industry since it was first introduced to the petroleum industry by the Standard Oil in 1948 (Hubbert and Willis, 1957). The fracturing fluid plays a critical role in successful hydraulic fracturing treatments. Research shows that the high effective transmissivity of the fracture can result in increased well productivity (Howard and Fast, 1970). One way to achieve high transmissivity is to pump granular solids called “proppant”, to keep the fracture open. The main function of fracturing fluid is to carry the proppants transporting along the fractures in depth. By the mid-1960’s, a normal trend of using low-cost water as fracturing fluid to stimulate low permeable wells was a requirement to achieve economic gas flow rates and recovery. However, low viscosity fluid like water cannot carry the

proppants efficiently, therefore it is necessary to increase the viscosity by adding chemicals to the fracturing fluids. In early 1970's, the idea of using viscous fluid was gradually accepted to improve the conductivity of the fracture by carrying more proppants. The low viscous fluid contains water, clay stabilizers, surfactants, and friction reducers. Until 1990's, crosslinked polymers were considerably applied to fracturing fluids to carry higher amount of proppants for reservoir application (Malpani, 2007).

The physical and chemical characteristics of the fracturing fluid affect the treatment notably. To be specific, the fracturing fluid should be compatible with formation materials and fluids, and is easy to clean out the residue to diminish the formation damage; it should remain viscous during the treatment but break down afterwards that should not carry the proppants back during the flow back; most importantly, it should be simple to perform in the field with cost-effective composition. Many different fracturing fluids are developed to accommodate particular reservoir conditions regarding to temperature, permeability, pore pressure and rock composition (Economides and Nolte, 2000). Most popular ones include water-based fluids, oil-based fluids, polymer-based fluids, alcohol-based fluids, emulsion fluids, foam-based fluids, noncomplex gelled water fracture, nitrogen-foam fracture, complexed gelled water fracture, premixed gel concentrates etc. By 2003, water-based fluid is still the predominant type in real applications (Fink, 2003).

Water-based hydraulic fracturing fluids are commercially available, easily viscosified and controlled. Fresh water is a good base for chemicals to form stable network structure, thus the fluid is readily to be thicken to achieve higher viscosity, which entails fracturing fluids favorable carrying capability. The operations require large amount of water that causes the challenge of fresh water acquisition. Cases show that it could reach

six million gallons per treatment on hydraulic fracturing. The cost of fresh water keeps increasing while in some areas, it is even hard to obtain. To solve this problem and reduce the costs, produced water has gained increased attention in a few years. However, produced water often contains high Total Dissolved Solids (TDS) content, which could affect fracturing fluid rheology significantly. Therefore, more research should be conducted on the performance of crosslinked fluids formulated by produced water as well as the effect of salts and other characteristics on rheology (Elsarawy, 2016).

The major rheology, viscosity, can reflect the capability of proppants transport during the treatment, and influences hydraulic fracture design, proppant settling, fluid frictional pressure loss, and fluid loss among others. Viscosity can be affected by shear rates, polymer properties, crosslinking reaction, salinity, temperatures and other factors. In this research, the main task is to evaluate the factors on the viscosity of post-crosslinked fracturing fluids to meet the needs of onsite applications.

Literature Review

General Properties of Fracturing Fluids

A large number of various fracturing fluids are designed to accommodate different hydraulic fracturing operations. Fluids are used in the fracture initiation and proppant propagation in ultralow to moderate permeability reservoirs. The most typical composition of fracturing fluid consists of water and other gelling agents. The natural polymer derived from guar beans is very common for the fracturing operations.

The functions of fracturing fluids are to initiate the fracture, transport the proppant throughout the fracture. The fluids should be easy to return to the surface as well.

Successful operations need effective fracturing fluids that meet all requirements as below (Fridley et al, 1989):

- Compatible with formation materials and formation fluids.

This is the most important characteristic of the fracturing fluids since any reaction that causes the clays swelling in the formation which will plug the pore channels. The emulsion forms lead to the migration of fines. If the fluids dissolve the cementing materials, the grains of the sandstone will be held together, which will result in undesirable failure of the treatment.

- Ability to suspend proppants and carry them for a long distance inside a fracture.

Increasing the viscosity is the way to improve the carrying ability of the fracturing fluids. Despite of the sufficient fracture width, the proppants should be transported deeply throughout the fracture.

- Low fluid additives loss.

The fracturing fluids should be evaluated in laboratory before onsite application. A lot of fluid leak-off occurs when ineffective fluids are used. The materials loss to formation will not enable the fluids achieving the original goal of fracturing, so it is crucial to ensure that the additives loss is acceptable. The fluids loss determines the fracture area, and the fluid efficiency of 40% to 60% will be optimal option to the treatment. Too much material loss (80% to 90%) will lead to insufficient fracture creation, while too low efficiency (10%-20%) will cause the fracture closing down slowly after the treatment (Howard and Fast, 1957).

- Easy to remove from the target formation after a treatment.

After carrying the proppants to the target areas, the fluids should be easily broken down as low viscous fluids. The viscosity reduction is very important since the residual in fractures is not favorable for production. The presence of highly viscous fluids plug some channels, and in return the hydrocarbons will have trouble to be produced. After treatment, the fluids should be easy to clean up from those fractures. Degradation is the key to viscosity reduction. Adding breaking agents such as enzymes, oxidizers, or weak acids can help control the degradation process. Normally, the high temperature will also cause the viscosity loss due to the thermal degradation. To prevent the fluids trapped around the flowing areas, removing the fluids afterwards plays a significant role during the fracturing operations.

- Low friction pressure in the wellbore.

A fracturing fluid will not be considered if it cannot be easily pumped down through the tubing. Fluids with high friction pressure leads to more pressure loss which needs more pressure to pump into the pipes. The friction reducer that can reduce friction pressure is promising to reduce the operational cost and benefit to hydraulic fracturing.

- Stable enough to maintain good viscosity during a fracturing process.

The fracturing fluid should have the ability to maintain high viscosity at the bottomhole temperature. High shear rate and thermal degradation decrease the viscosity. The additives should make the fluids stable enough under reservoir conditions, which is the most critical requirement in fracturing fluid design.

- Easy to prepare and simple to perform in the field.

Large amount of fracturing fluids are needed during operations. Therefore the fracturing fluids should be easy to prepare, transport, and perform in the field. Although

tedious experimental process is not unachievable in laboratory, yet complicated synthesis procedure will bring difficulties at a field scale.

- Cost-effective.

The raw materials should be low cost and easy to prepare. Analysis should be done prior to the applications in order to achieve economical investment.

General Types of Fracturing Fluids

Various types of fracturing fluids are developed to meet the needs for different reservoir conditions. Using suitable fracturing fluids can minimize formation damage and improve the efficiency of operations. The most common kinds contain water-based, oil-based, alcohol-based, emulsion, foam-based and others. The **Table 1** summaries the fracturing fluids technique used in hydraulic fracturing operations (Fink, 2003).

Table 1 -- Fracturing fluids types and remarks

Type	Remarks
Water-based fluids	Predominant
Oil-based fluids	Water sensitive; increase the hazard
Alcohol-based fluids	Rare
Emulsion fluids	High pressure, low temperature
Foam-based fluids	Low pressure, low temperature

Water-based Fracturing Fluids Water-based fracturing fluids are the most common type using in an oilfield. Compared to other techniques, the water-based fluids are much cheaper, and easier to control. Water is relative readily to get and the good performance in increasing

viscosity as a base solution makes it outstand out of other fluids, such as oil, methanol, or acid.

Oil-based Fracturing Fluids Oil based fracturing fluids make less damage to reservoir formations. The initial viscosity is very promising and the fluids can be used for water-sensitive oil producing formations. However, using oil based fluids has the possibility to induce fire hazard which is very dangerous to operations. Other disadvantages are the high pumping friction and pressure of oil-based fracturing fluids compared to the water-based fluids. The most important is that the costs of oil based fracturing fluids preparation and application are very expensive. The characteristic of the oil is difficult to control and it requires much more care than water.

Alcohol-based Fracturing Fluids Alcohol-based fracturing fluids are compatible with water-sensitive formations. They are often used for removal of the water blocks since the alcohol can reduce the surface tension of water. It has great influence on temperature stability for its hydrogen scavenging property. The problem is that the breakers must be used for fully degradation of the fluids when using high concentration.

Foam-based Fracturing Fluids Foam based fracturing fluids are created by injecting gas into water or oil phase to form foams. Approximately about 60 to 90 % gas of total volume can make the foam stable at given temperature and pressure. The common types of foam in industrial application are nitrogen foam and carbon dioxide foam. Large amount of gas minimizes the amount of fluid placed in the formation, and the energy in gas also can assist in improving recovery as well as cleanup process. The gas bubbles bring the fluids with high viscosity and excellent proppant-carrying capability. Nevertheless, the loss in stability

of foam will result in poor performance unless the mixing rate and other factors are proper. The pumping pressure is higher in foam fracturing process than using water-based fluids.

Emulsion Fracturing Fluids The emulsions consist of two basic types: oil in water and water in oil. Water-external emulsion has water as continuous phase while oil-external is using oil as continuous phase. The good viscosity enables emulsion fracturing fluids has great ability of proppant transport property. Relatively higher in pumping pressures and costs make it limited in use compared to conventional fracturing fluids.

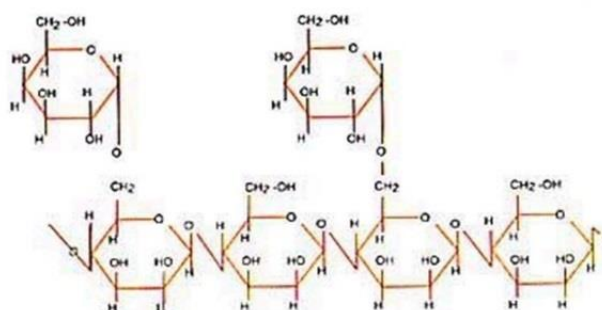
Other types of fracturing fluids include energized fracturing fluids, unconventional fluids, etc. Each of the fracturing fluids has its unique properties and compatibility. In conclusions, the conditions of their uses are different. Matching each type with specific reservoir enables the fracturing fluid to maximum its functionality. However, water-based fluids are still predominant in hydraulic fracturing applications. **Table 2** summarizes the fracturing fluids with its condition of use.

Recent Development of Fracturing Fluids System

Linear Polymer Linear fracturing fluids are the first emerging fluids used to increase viscosity of pure water. Starch is the main component in the early stage, and has been replaced by guar gum due to its shear sensitivity, poor thermal stability and bacterial degradation. Guar gum is considered as water viscosifier via its structure of linear polymer. The polymer naturally comes from guar beans, and it is commercially sold in powder (**Fig. 1**). Water is the trigger for guar polymer, and the polymer chains will uncoil with attaching the water molecules to form viscous fluids. However, when mixing the dry powdered guar with water, a mixer with high energy should be used and the pH of base water should keep above 7 to avoid fisheyes.

Table 2 -- Fracturing fluids and conditions for their use (EPA-2004)

Based fluid	Fluid type	Main composition	Application
Water-based	Linear fluids	Gelled water, GUAR< HPG, HEC, CMHPG	Short fractures, low temperatures
Water-based	Crosslinked fluids	Crosslinker + Guar, HPG, CMHPG, CMHEC	Long fractures, high temperatures
Foam-based	Water-based foam	Water and foamer + N ₂ or CO ₂	Low pressure
Foam-based	Acid-based foam	Acid and foamer + N ₂	Low pressure, water sensitive formations
Foam-based	Alcohol-based foam	Methanol and foamer + N ₂	Low pressure, water blocking problems
Oil-based	Linear fluids	Oil, gelled oil	Water sensitive, short fractures
Oil-based	Crosslinked fluids	Phosphate ester gels	Water sensitive, long fractures
Oil-based	Water external emulsions	Water+ Oil + Emulsifier	Good for fluid loss control

**Chemical Structure of Guar Gum****Figure 1 -- Commercial guar gum and its chemical properties (Ajit Patel, 2015).**

Guar-based fracturing fluid is one of the common types of water-based fracturing fluids for wells under 300 °F. To improve its thermo-stability, other guar based polymers such as HPG have been derived and optimized to reach this goal (Montgomery, 2013). Guar's derivatives have also been used as liner polymers such as HydroxyPropyl Guar (HPG), CarboxyMethyl Guar (CMG) and CarboxyMethyl HPG (CMHPG). Since a lot of residue still occurs by using guar, which has a negative effect on viscosity, HPG and CMG are developed to reduce the residue and enhance the thermo-stability. HPG is obtained by the reaction between propyl oxides with the guar molecule so that the stability is improved in the presence of propylene-oxide-groups. Furthermore, CMHPG is more advanced by the reaction between HPG and chloroacetic acid, which offers even lower residue than that of HPG. However, this product is used only in crosslinked gel applications (**Fig. 2**).

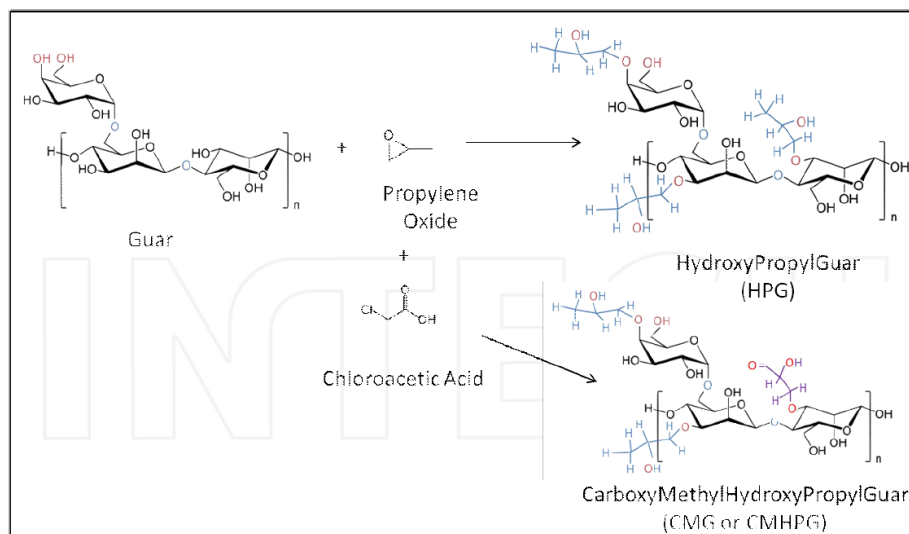


Figure 2 -- HPG, CMG, CMHPG formulations from Montgomery (2013).

In spite of guar, Hydroxy Ethyl Cellulose (HEC) is another material in linear polymer system. Including its derivatives Carboxy Methyl Cellulose (CMC) and Carboxy

Methyl Hydroxy Ethyl Cellulose (CMHEC), these cellulose polymers are usually taken as synthetics compared to naturally born guar. HEC and CMHEC are non-toxic and has been widely used as viscosifier and emulsion stabilizer. These products can reach high viscosity without residue upon degradation. However, because of the trans-position of hydroxyl group in HEC, it can only be used as linear polymer while CMHEC can be crosslinked due to its carboxy methyl group (**Fig.3**).

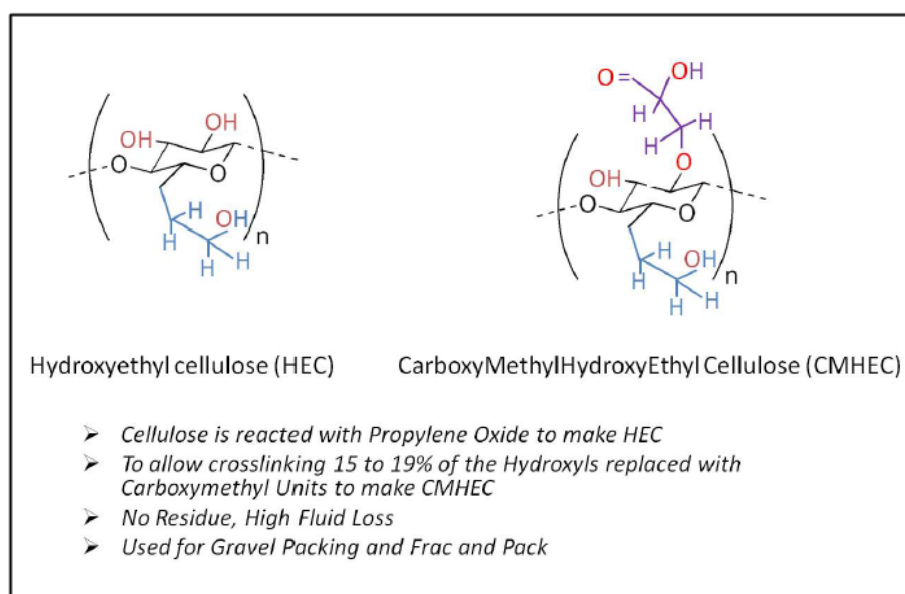


Figure 3 -- The structure of HEC and CMHEC (Sidley Chemical, 2013)

Another type of linear polymer is xanthan gum, of which the major use in stimulation is taken as thickener for hydrochloric acid. Linear fracturing fluids are very simple to synthesize and have good performance in viscosity enhancement. However, the undesirable proppants suspension capability and poor temperature stability get this type abandoned in most of fracturing cases.

High concentration of the polymer can result in higher pumping pressure and large damage to the formation. Moreover, industrial products of guar consist of insoluble residues, which lead to inefficient degradation of crosslinked gel (Sun and Qu, 2011).

Due to the poor thermal stability of guar polymers at temperatures greater than 400 °F, new alternatives have been developed in oil and gas industry. Compared with the increasing price of guar, polyacrylamide (PAM) is one of the synthetic polymers with fair prices.

Crosslinked System The better choice to linear fracturing fluids that only contain polymer is crosslinked fracturing fluids. Crosslinkers are used in combination with polymers to increase the molecular weight as well as contribute to higher viscosity. In 2010, Holtsclaw and Funkhouser stated that PAM-based polymer can effectively carry proppants in fracturing applications, and the copolymer system consisting of 60% AMPS, 39.5% Amide, and 0.5% acrylate can effectively crosslink with zirconium, which the gelant produced can reach a viscosity of 700 cp for more than 1.5 hr at a temperature of 402 °F under shear rate of 40 sec⁻¹ in laboratory (Al-Muntasheri, 2014). Their experiments showed that if using CMHPG as based polymer, the viscosity cannot even reach 50 cp under the same circumstance. This system has been put into field applications in two wells in south Texas at 399 °F, and the viscosity can stay viscous from 200 to 450 cp at a shear rate of 100 sec⁻¹ for two hours (Funkhouser et al. 2010). In 2011, Gupta and Carman reported that the system they designed based on partially hydrolyzed polyacrylamide (HPAM) crosslinking with zirconium can maintain the viscosity of 1000 cp at 425 °F for 2 hours under shearing at 100 sec⁻¹. No field data has been reported in his paper, but the author mentioned maintaining low pH of 5 can keep the gel stable and function well. Another author, Gaillard

(2013) indicated that three PAM-based polymers had been tested for the application of hydraulic fracturing. It showed good viscosity at shearing from 0.1 to 100 sec-1.

For biopolymer fracturing fluids, the only way to improve viscosity is by increasing polymer concentration, however, proppants and dispersing fluid-loss additives are difficult to be added into high concentrated solutions. To eliminate the problems, crosslinkers has been introduced to generate favorable viscosity with less polymer concentration. . For guar and CMHEC based gels, metal crosslinkers are very popular. The attraction between metals and the hydroxyl or carboxyl groups will put polymers chains into 3D structure. This interaction will bring the linear fluids to pseudo plastic fluid. Each crosslinker has its own unique requirement and behavior.

Borate and metallic crosslinkers including zirconium and titanium are two major types of crosslinkers companion with polymer-based fracturing fluids. Experiments from Sun and Qu (2011) showed that borate-based crosslinkers can increase the viscosity up to several orders of magnitudes. Crosslinker size determines the viscosity value, however, it is not practical to apply to oilfield operations due to its cost. Moreover, high shear rate is still the problem that causes the viscosity loss of crosslinked fluids. Zirconium crosslinked gels are shear sensitive and cannot recover their viscosity upon shear reduction (Al-Muntasheri, 2014). Therefore, delayed crosslinked system is brought into the applications.

Putzig and St.Clair (2007) reported a system that using chelating agent to delay crosslinking for zirconium crosslinked gels. The chelating agent contains alcohol, carboxylic acid, and amine functional groups. A delayed crosslinked system is to control the crosslinking time which indicates delaying the initiation time of the reaction between crosslinker and base polymer fluids. The first advantage of the system is, it can help a

crosslinker better dispersed in the solution and enable the fluids achieve higher viscosity. Additionally, in many cases, it is desirable to delay the reaction in order to reduce the frictional losses brought by the surface pumping equipment, well tubing, and perforations (Al-Muntasheri, 2014). Since the zirconium crosslinked gels are not self-healing under high shear rates, delaying the crosslinking time will have less chance in proppant screenout. Delaying agents are designed to minimize viscosity buildup until the fluids pass the high shearing zones of wellbores and perforations.

In 2012, Kalgaonkar and Patil developed a shear stabilizing chemical for zirconium crosslinked gels at high temperatures from 149 to 191°C. At low shear rate of 127 s⁻¹ and 24 °C, 75 mins are needed to make the gel crosslink, with a viscosity below 100 cp. Then increasing the temperature to 176 °C, the viscosity of gel goes up to over 400 cp for more than 60 mins. This system needs two buffers – potassium carbonate and sodium carbonate to ensure the solution with the pH of 10.2. However, without the buffers, the gel crosslinked fast (< 5 mins) and the viscosity can reach over 500 cp.

The benefits of this system are obvious: i) higher viscosity, ii) effective fluid loss control, iii) better proppants carrying capability, iv) thermos-stability, and v) lower cost of polymer. However, to authors' best knowledge, few results related to the resistance of high shear rates and salts have been investigated of crosslinked fracturing fluids.

Research Purpose In this research, the viscosity of the crosslinked fracturing fluids will be tested to show its compatibility with brine under high shear rates. The main purpose is to analyze the feasibility to keep the viscosity at a favorable range at low polymer concentration under high shearing condition. The crosslinked fracturing fluid should be able to resist high shear rate to carry proppants efficiently when pumping downhole. The

research will further include the effect of pH, salinity, temperature and other factors that may have impacts on fracturing fluids. The main goal is to develop of a highly viscous polymeric fracturing fluids at high shear rates with salt a resistance property.

Experimental

Materials

Three types of high molecular weight PAM based copolymers were used in this study: cationic, anionic, and zwitterion, with an active polymer content of 25%. The copolymers were all provided by Solvay.Inc. Zirconium acetate was purchased by Aldrich. Zirconyl chloride octahydrate and lactic acid were received from Sigma. Potassium chloride was purchased by Fisher Chemical. Water used in the following experiments was deionized (DI) water provided by Missouri University of Science and Technology. HAAKE MARS Rheometer was used for viscosity measurement. All the chemicals used in the experiments were as received.

Experimental Procedure

2% KCl had been prepared before which copolymers were added at concentration of 2 – 5 gpt. The mixtures were put into sealed bottle for fully dispersed and swelled. Selected crosslinkers at a range of 48 – 8000 ppm will be added into the solution for fast crosslink. Then, the HAAKE MARS Rheometer was used to measure viscosity of the mixtures right after 30 seconds stirring. Varied temperature, shear rate and reaction time were assigned by specific experiment design. The steps described as figure below (**Fig 4**).



Figure 4 -- Experimental procedure

Results

Polymer Candidates Evaluation

Three types of PAM based copolymers were evaluated to deploy the best polymer candidate for viscosity at shear rate of 511 s^{-1} . They were ionically modified copolymers for improved hydration and final gel properties. Each was labeled as Product 01, 02, 03 for cationic, anionic, and zwitterionic specifically (**Fig. 5**).

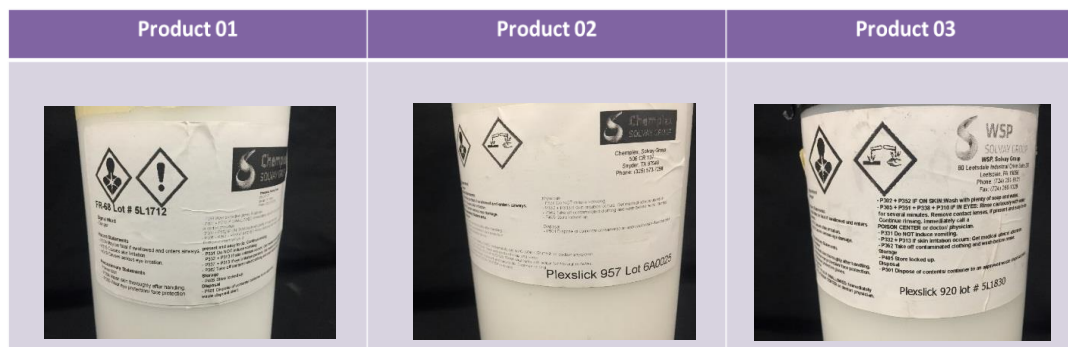


Figure 5 -- Commercial copolymers

The copolymers were put into 2 % KCl solutions overnight for fully swelled at the concentration of 2 gpt. Then the emulsions were tested by using rheometer at different

shear rates. The results showed that the product 03, which is zwitterionic copolymer, got the highest viscosity at high shear rate as 511 s⁻¹ (**Fig. 6**). Thus, the Product 03 was selected as the optimal option in the fluids optimization. Anionically or cationically modified polymers, like product 01 or 02, may be expand or uncoil in 2% KCl due to the repulsion of like charged moieties on the polymer backbone, reducing the crosslinking ultimate effect (US 7786050 B2, 2008).

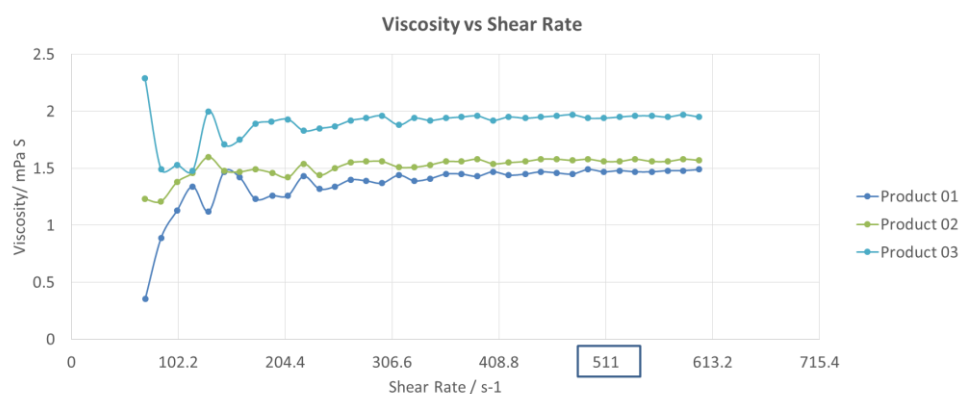


Figure 6 -- Polymer selection based on the viscosity

Crosslinker Optimization

Popular crosslinkers contain a metal ion such as aluminum, zirconium and titanium as well as those capable of providing borate ions (WO 2013116422 A1, 2013).

In this study, three types of crosslinkers were used and mixed together to define the most effective crosslinker to increase fluids viscosity. The crosslinker were added to the swelled polymer solutions with concentration of 1600 ppm, and the polymer concentration was 5 gpt. Crosslinkers were labeled as X01, X02, X03, X04, and X05, which stands for 100% zirconium acetate, 100% zirconyl chloride octahydrate, 50% zirconium acetate and

50% zirconyl chloride, 50% zirconium acetate and 50% lactic acid, and 50% zirconyl chloride and 50% lactic acid, specifically. The results are shown as below (**Fig. 7**).

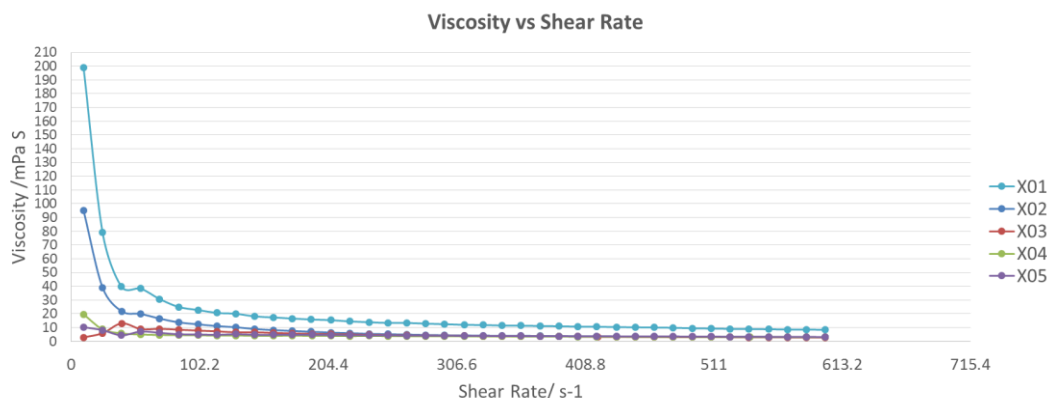


Figure 7 -- Crosslinker selection based on the viscosity

Based on the result, we can see that the X01, which is 100% Zirconium Acetate, should be selected as the optimal crosslinker in this system. Zirconium acetate will be used in the following test afterwards.

Crosslinker Effect on Fluids Viscosity

Viscosity is highly influenced by crosslinking degree. Understanding crosslinker effect will be helpful determining the function of fracturing fluids. The experiments aimed to find how crosslinker works under different conditions. The polymer concentration was ranging from 2 to 5 gpt, and the polymer: crosslinker ratio (p/c) was from 133:1 to 2:1. **Fig. 8** indicates the impact of crosslinker on linear polymer. Some outliers may not be used due to the equipment errors or the points at the very beginning of turbulent stage.



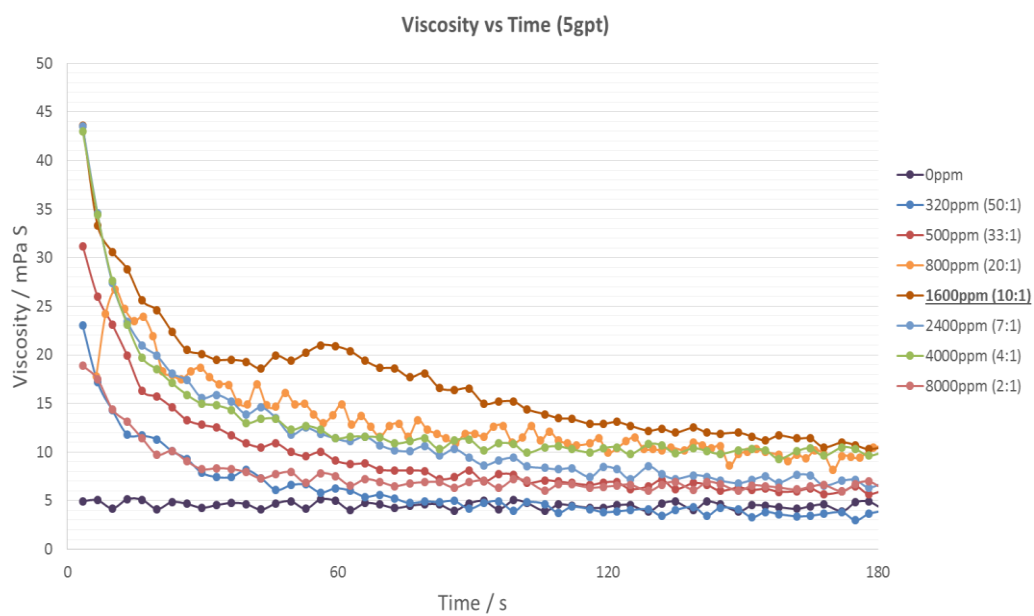
Figure 8 -- Impact of crosslinker on linear polymer

The viscosity of the non-newtonian fluids are dependent on shear rate. Either shear-thickening or shear thinning occurs with the presence of increasing shear rates due to the structural reorganization of the fluid molecules regarding to the flow.

At different polymer concentration, the viscosity as a function of time were shown from **Figs. 9 to 12**. The crosslinker concentration curves were distinguished by color. Shear thinning effect was observed in these experiments and the viscosity decreased by increasing time. Read from the curves, the best crosslinker concentration varied by polymer concentration, For example, at 5gpt, the best concentration should be 3400 ppm where p/c equals 10:1, while others were not the same. From **Figs. 13 to 16** the peak value clearly defines the best crosslinker concentration. Overcrosslinking may lead to stiffness, where the polymer chains will clasped that cannot resist for high shear rates. When crosslinker concentration was too low, the crosslinking points will not be enough to form 3D Network, which causes poor in viscosity. The results of best p/c were summarized as **Table 3**.

Table 3 -- Best polymer: crosslinker ratio selection

5gpt	4gpt	3gpt	2gpt
			133:1
		100:1	100:1 (64 ppm)
	80:1	80:1	80:1
	60:1	60:1 (160 ppm)	60:1
50:1	50:1	50:1	50:1
33:1	40:1 (320 ppm)	40:1	40:1
20:1	20:1	20:1	20:1
13:1	13:1	13:1	
10:1 (1600 ppm)	10:1		
7:1	7:1		
4:1	4:1		
2:1			

**Figure 9 -- Viscosity as a function of time at 5 gpt**

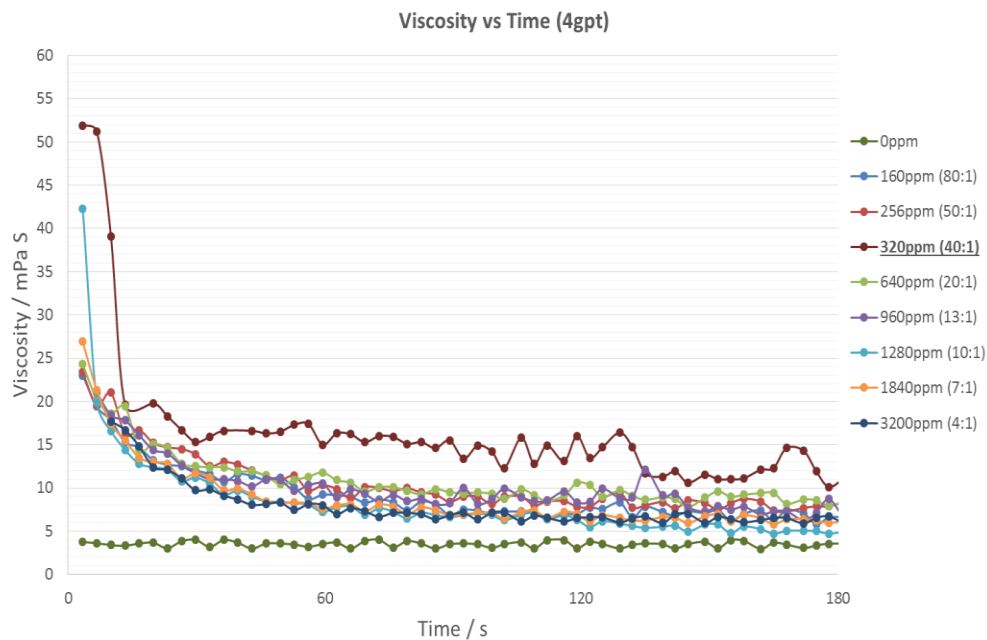


Figure 10 -- Viscosity as a function of time at 4 gpt

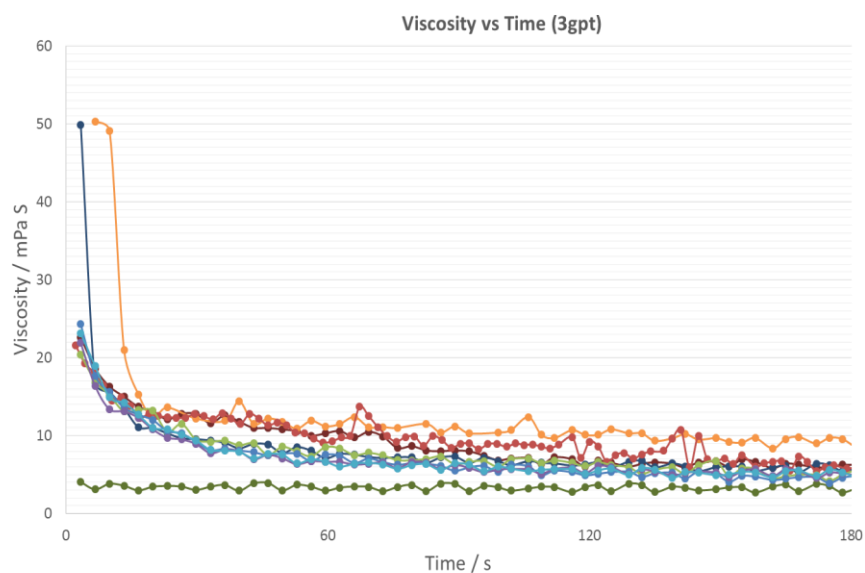


Figure 11 -- Viscosity as a function of time at 3 gpt

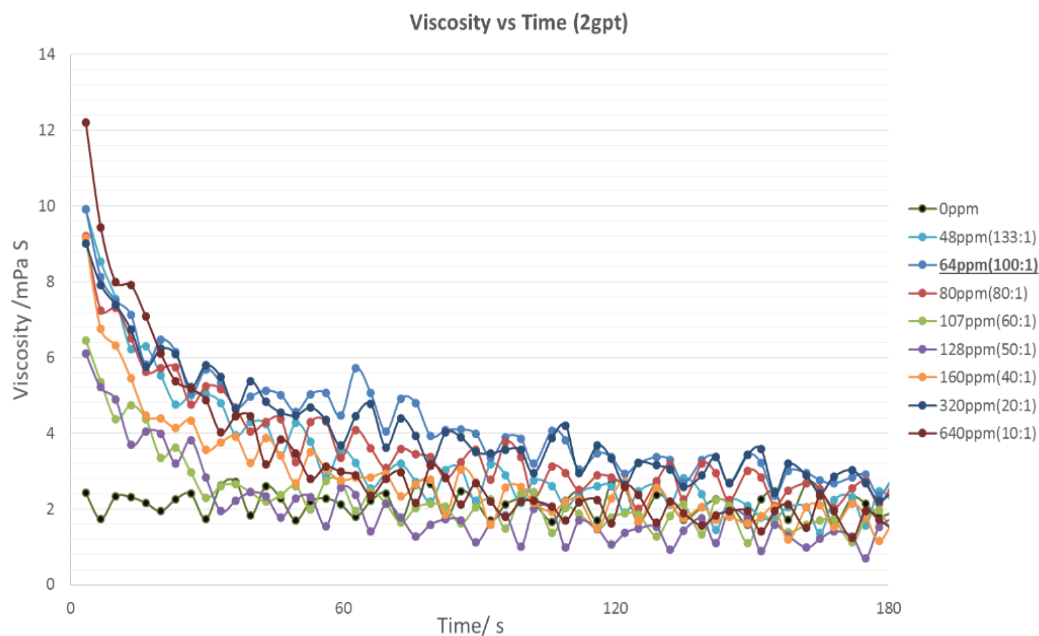


Figure 12 -- Viscosity as a function of time at 2 gpt

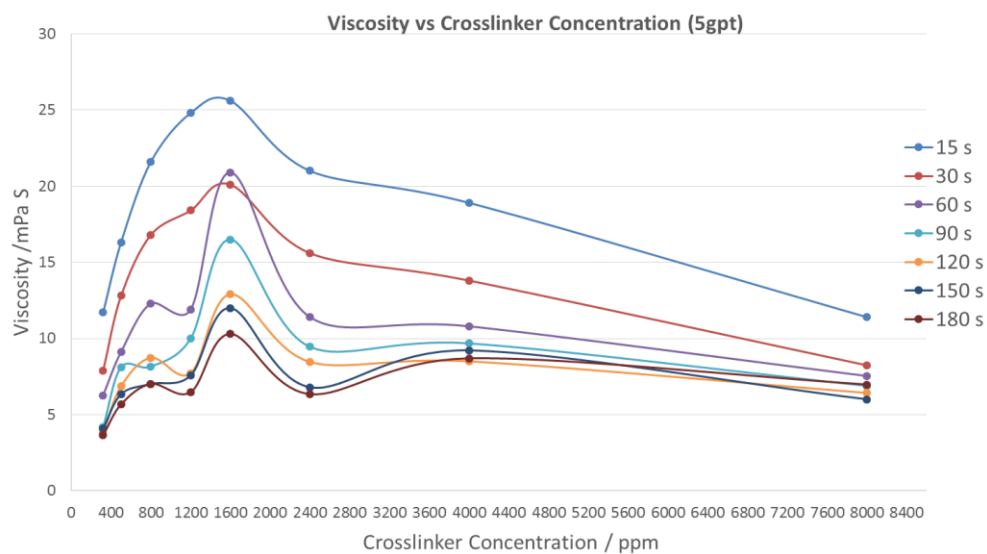


Figure 13 -- Viscosity as a function of crosslinker concentration at 5gpt

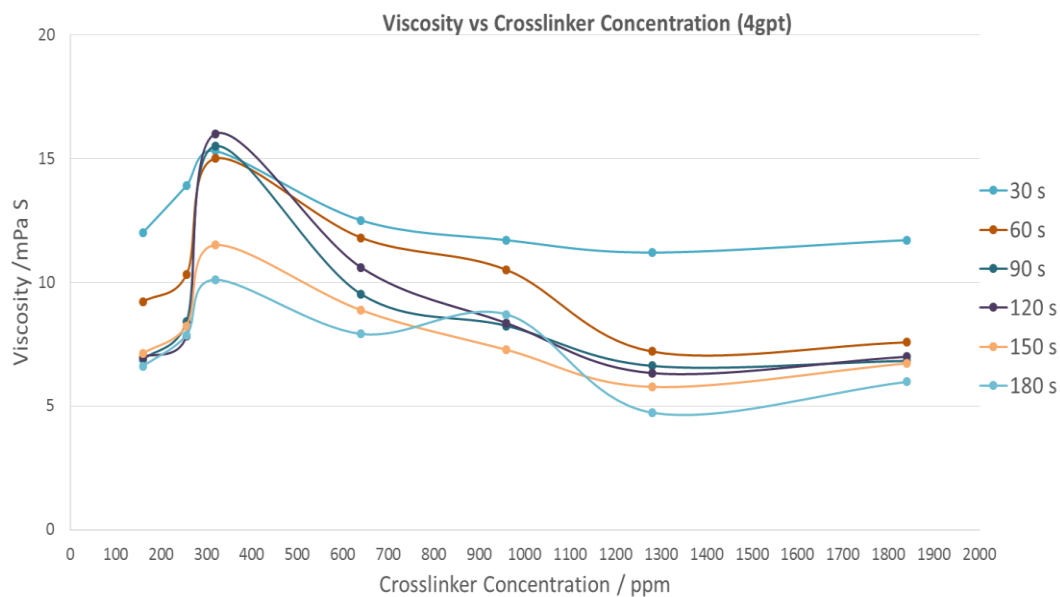


Figure 14 -- Viscosity as a function of crosslinker concentration at 4gpt

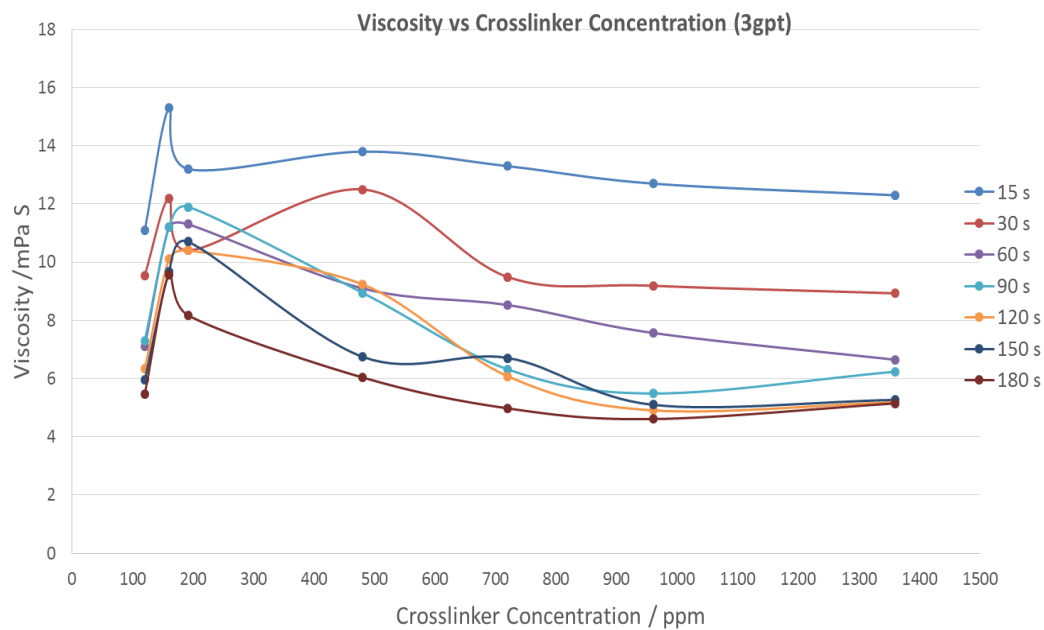


Figure 15 -- Viscosity as a function of crosslinker concentration at 3gpt

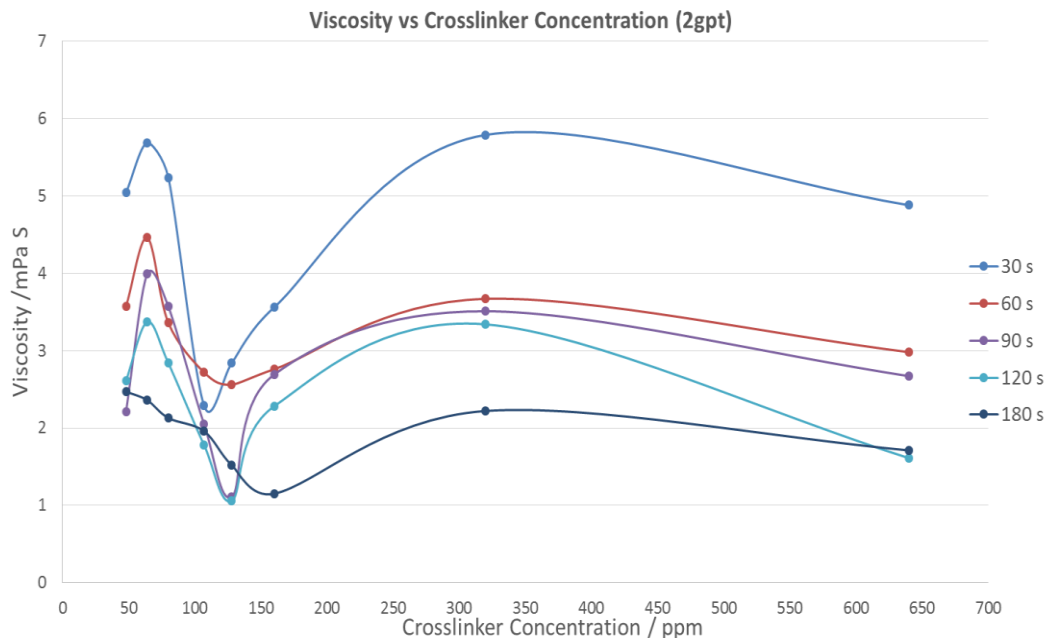


Figure 16 -- Viscosity as a function of crosslinker concentration at 2gpt

In a conclusion, zirconium acetate is the best crosslinker due to its good performance on viscosity improvement. Based on the abundant experiments result, there should be an optimal crosslinker concentration to generate highly viscous fracturing fluids. The best ratio of p/c for high viscosity depends upon polymer concentration. At higher crosslinker concentration, the crosslinked polymer is prone to be more brittle through our observation. However, it can be easily broken down under high shear rate (511 s^{-1}) condition.

Viscosity Comparison of Linear and Crosslinked Polymeric Fluids

Not only influence by crosslinker, polymer concentration also affect viscosity in a trend. The factors impacting the viscosity include molecules' shape, molecular weight, hydrophilic nature, and interaction of polymer molecules with the solvents (Van Krevelen,

1990). Higher concentration of dissolved polymer also contributes to higher in viscosity (Fig. 17).

Without crosslinker, the viscosities were measured at each concentration level at shear rate of 511 s^{-1} . The result is demonstrated in consecutive time and it is said that polymer fluids at higher concentration (5 gpt) has better viscosity. The linear polymers do not have wall effect from the measurement.

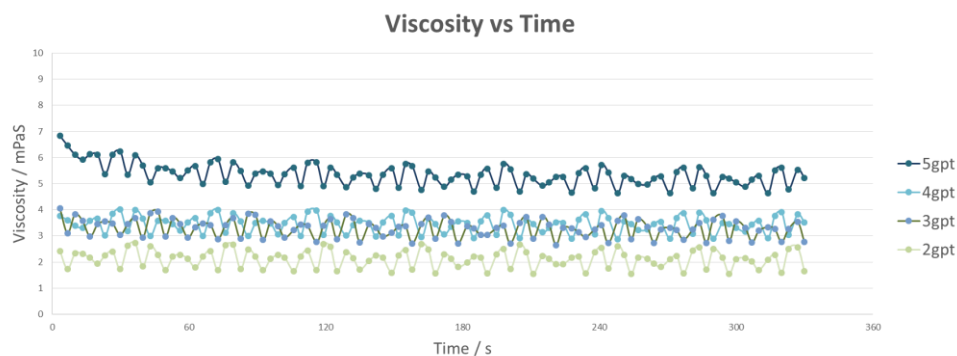


Figure 17 -- Polymer concentration on viscosity

On the contrary, as for crosslinked polymeric fluids, the shear-thinning behavior occurs in the presence of crosslinker (Fig. 18). The viscosity increases by 2 to 9 times after addition of crosslinker.

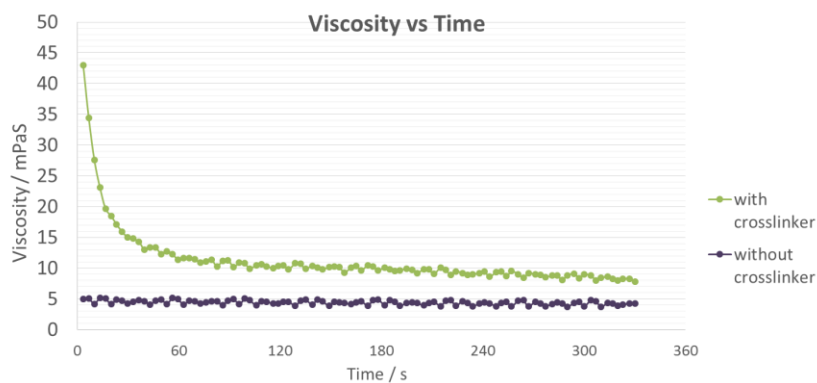


Figure 18 -- Crosslinker effect on polymeric fluids

Applied with the best crosslinker concentration, the experiments were conducted by changing polymer concentration at shear rate of 511 s⁻¹. The result is shown in the following graph (**Fig. 19**), and it indicates denser in polymer concentration will result in higher viscosity.

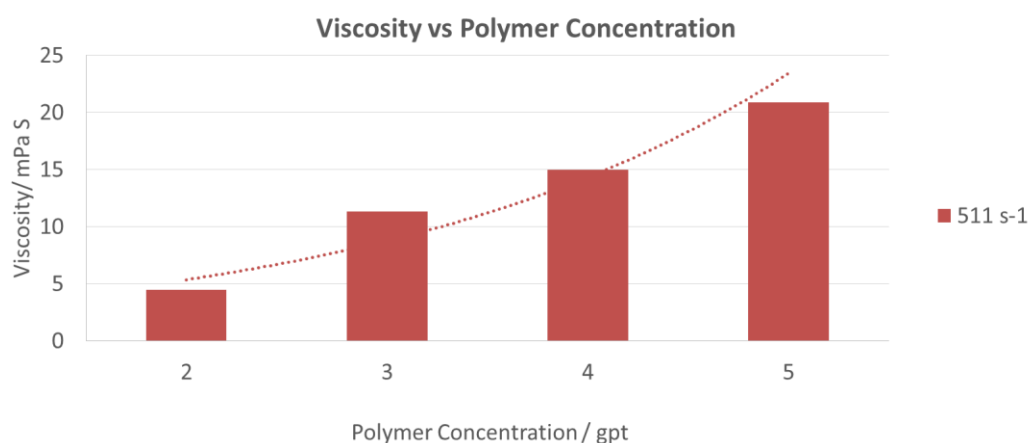


Figure 19 -- Viscosity as a function of polymer concentration.

Moreover, the increasing rate was shifting by reaction time. Viscosity at different polymer concentration with different reaction time can be concluded in **Fig. 20**. From the chart, increasing polymer concentration will result in viscosity improving. However, during the first 60 seconds, the impact was notably while afterwards, increasing in polymer concentration will not have a great contribution in viscosity. In other words, the crosslinked polymer will not as stable as within the first minute under current system.

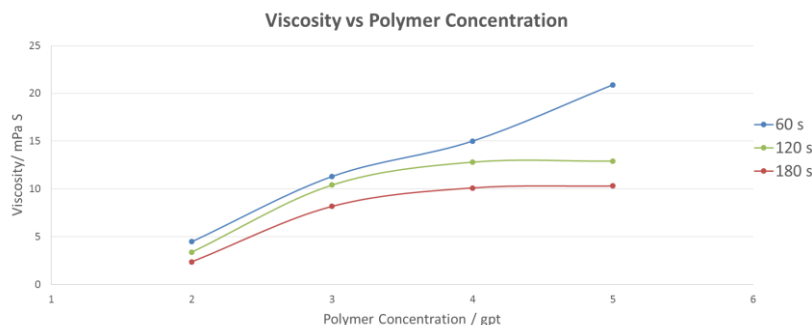


Figure 20 -- Viscosity as a function of polymer concentration during first three minutes.

In summary, in absence of crosslinker, the viscosity at the concentration of 2 and 5 gpt ranged from 2 to 6 mPa.S. The viscosity had a flat line and acted more like a “Newtonian fluid”. In the presence of Xlinker, the viscosity increases with polymer concentration. Increase in time leads to shear thinning behavior of the crosslinked polymer.

Aging Effect on Effect on Viscosity

Since crosslinking of linear polymer causes a network structure, the network will be broken when crosslinker degrades. Longer in reaction time may lead to further degradation of the crosslinker. In this study, two aging effects on polymer degradation and crosslinked polymer degradation will be demonstrated by a few experiments.

Aging Effect on Polymer Degradation

Reduction in viscosity may be induced by polymer or crosslinker degradation. The first step is to see if polymer degradation is a major reason to viscosity. The first experiment was to measure viscosity of the freshly prepared polymer after crosslinked. The second experiment was to prepare the polymer in advance, wait 48 hours, then add crosslinker and measure the viscosity. The result will show if aging time will cause the polymer degrades.

The polymer concentration used fixed at 5 gpt, and the crosslinker used was zirconium acetate at 1600 ppm (**Fig. 21**).

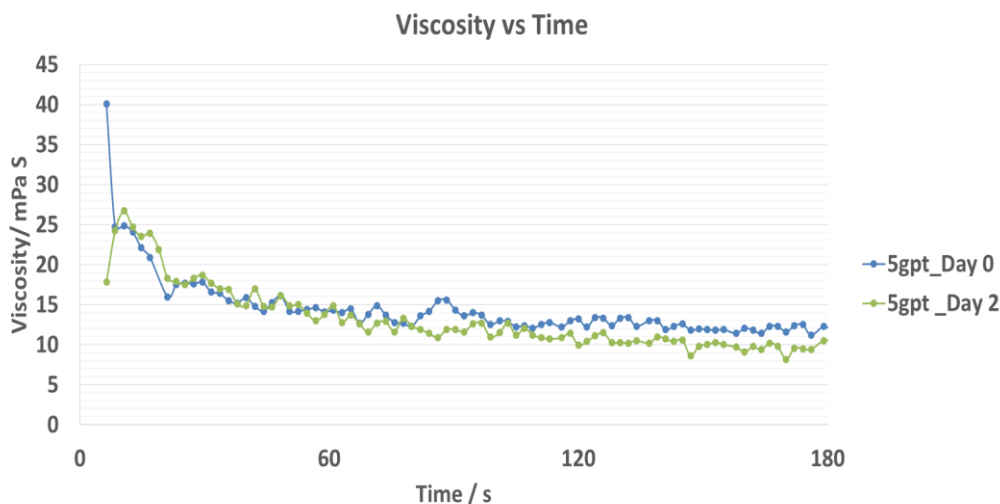


Figure 21 -- Viscosity as a function of time

From the chart, we can see that the degradation of the polymer has negative effect on viscosity. The viscosity is higher when using the fresh-made polymer to crosslink.

Aging Effect on Crosslinked Polymer Degradation

Forming 3D Network is beneficial to the stability of crosslinked polymer. Whether aging time will have an effect on crosslinked polymer can be illustrated in the following results.

The first one was to measure the viscosity immediately after crosslinking combining with the one measuring the viscosity 10 mins later, and the second one is the viscosity measured under 65 °C for 12 hours after crosslinking compared to its original. From the result, it showed that after crosslinked, the viscosity does not change in 10 min (**Fig. 22**). However, it will decrease significantly if the sample is put into oven at 65 °C for 12 h (**Fig. 23**).

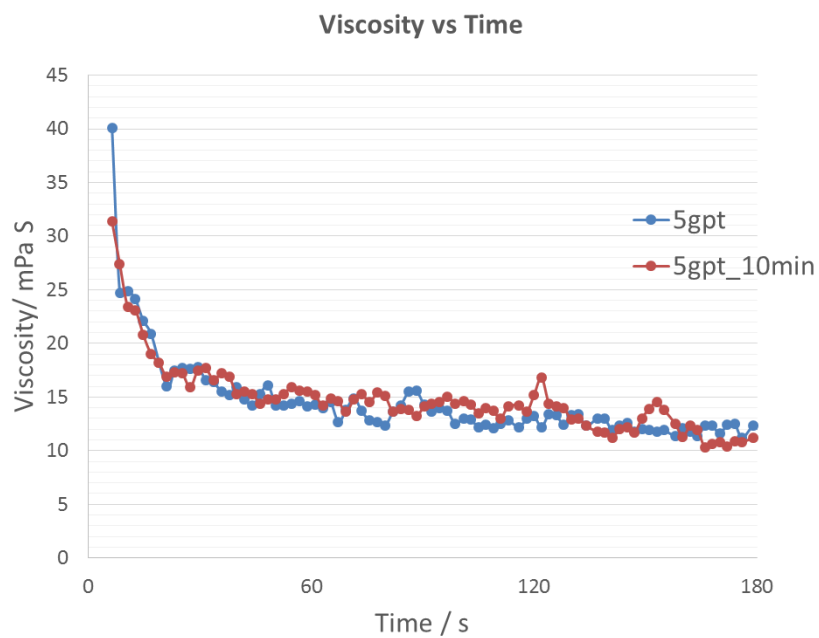


Figure 22 -- Viscosity as a function of time for 10 mins shearing

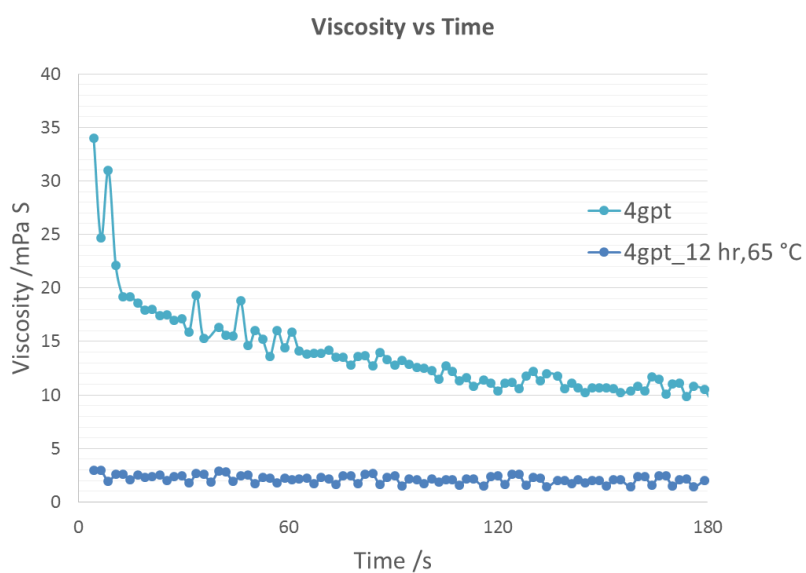


Figure 23 -- Viscosity as a function of time after 12 hrs

Temperature Effect on Viscosity

Three levels of temperature, 25 °C, 65 °C, and 90 °C, had been considered to explore the influence on viscosity. The experiments were designed using polymer concentration from 2 to 5 gpt, with each best crosslinker concentration specifically. At 25 °C, polymer concentration higher than 3 gpt can reach beyond 10 mPaS over three minutes (**Fig. 24**). Increasing temperature to 65 °C, only the one of 5 gpt can stay above 10 mPaS (**Fig. 25**) while at 90 °C, all of them were under 10 mPaS (**Fig. 26**). Viscosity decreases dramatically at any of the polymer concentration when temperature increased (**Figs. 27 to 30**).

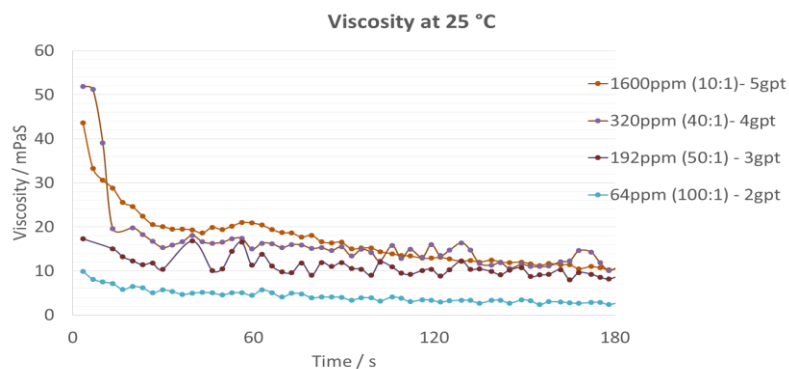


Figure 24 -- Viscosity of polymeric fluids at 25 °C

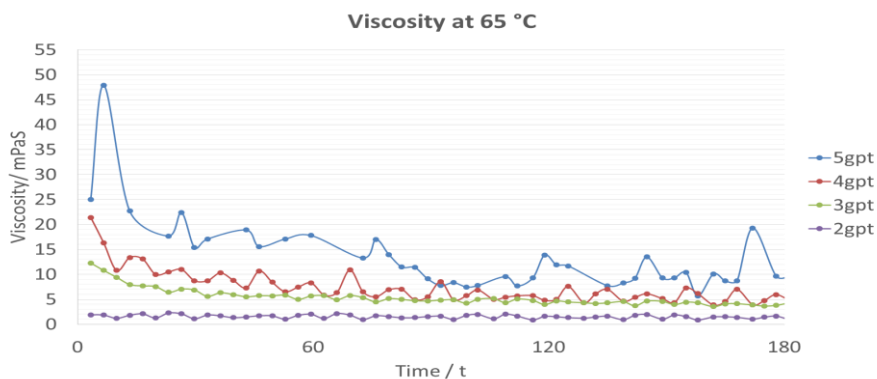


Figure 25 -- Viscosity of polymeric fluids at 65 °C

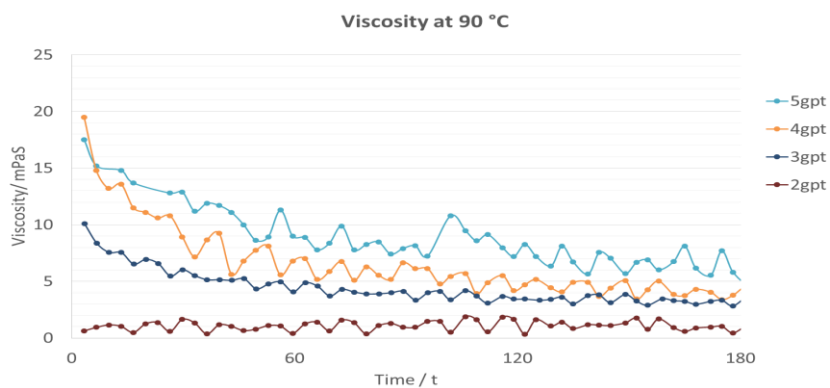


Figure 26 -- Viscosity of polymeric fluids at 90 °C

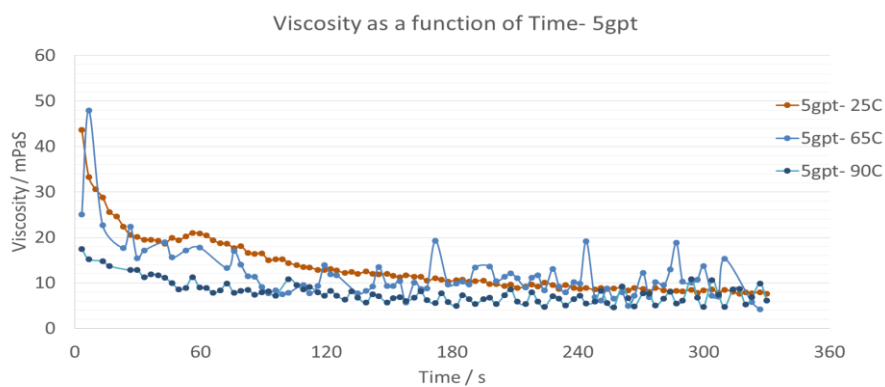


Figure 27 -- Viscosity of polymer at 5 gpt under different temperature

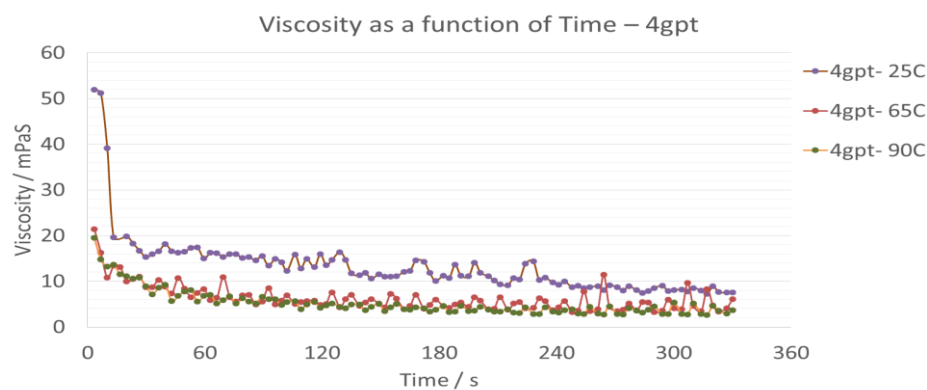


Figure 28 -- Viscosity of polymer at 4 gpt under different temperature

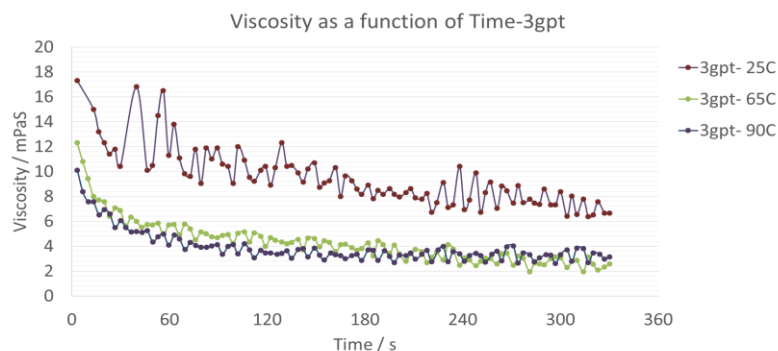


Figure 29 -- Viscosity of polymer at 3 gpt under different temperature

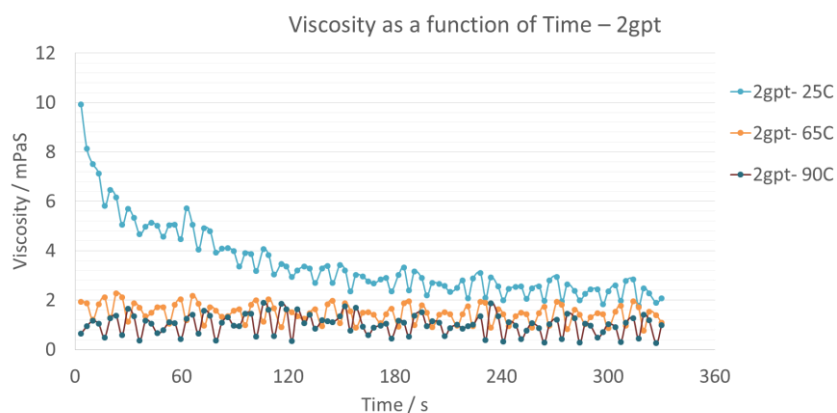


Figure 30 -- Viscosity of polymer at 2 gpt under different temperature

Increase in temperature leads to viscosity reduction of the crosslinked polymer. Crosslinked polymers can stay viscous above 10 mPaS in 3 mins (**Table 4**):

Table 4 -- Viscosity greater than 10 mPaS at different temperature

Temperature (°C)	Sample viscosity above 10 mPa S		
	5gpt	4gpt	3gpt
25°C	5gpt		
65°C	5gpt		
90°C	None		

pH Effect on Fluids Viscosity

pH condition is very important to crosslinking efficiency. In this study, pH were accommodated during brine preparation process. 2% KCl solutions were divided into three bottles, and two of them were added HCl or NaOH to adjust pH to 3.2, or 11.7. The one without any additives were measured pH equaling 6.3. The results shown from the graphs (Figs. 31 to 33) at a polymer concentration range between 2 to 5 gpt.

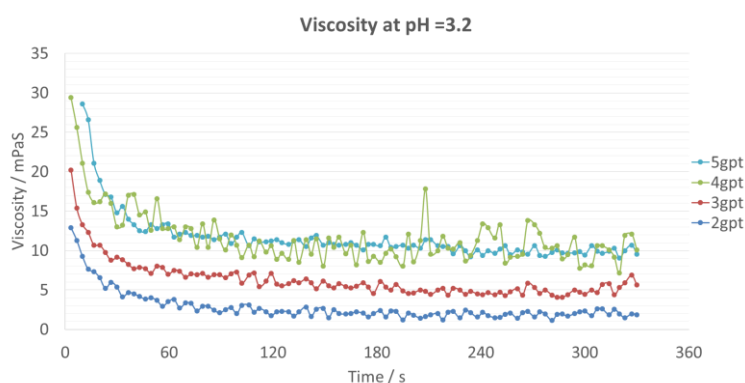


Figure 31 -- Viscosity as a function of time at pH = 3.2

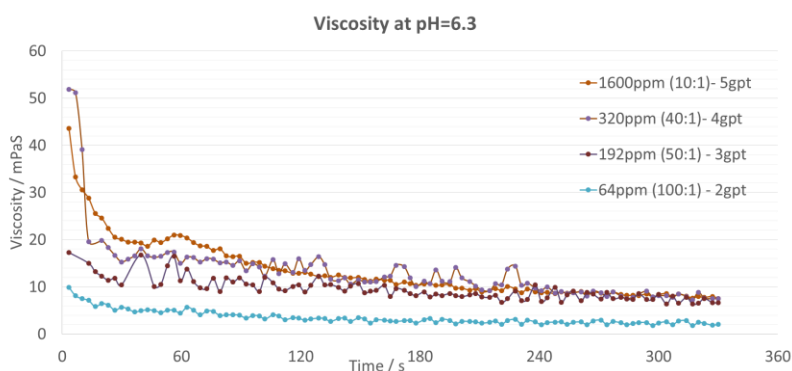


Figure 32 -- Viscosity as a function of time at pH = 6.3

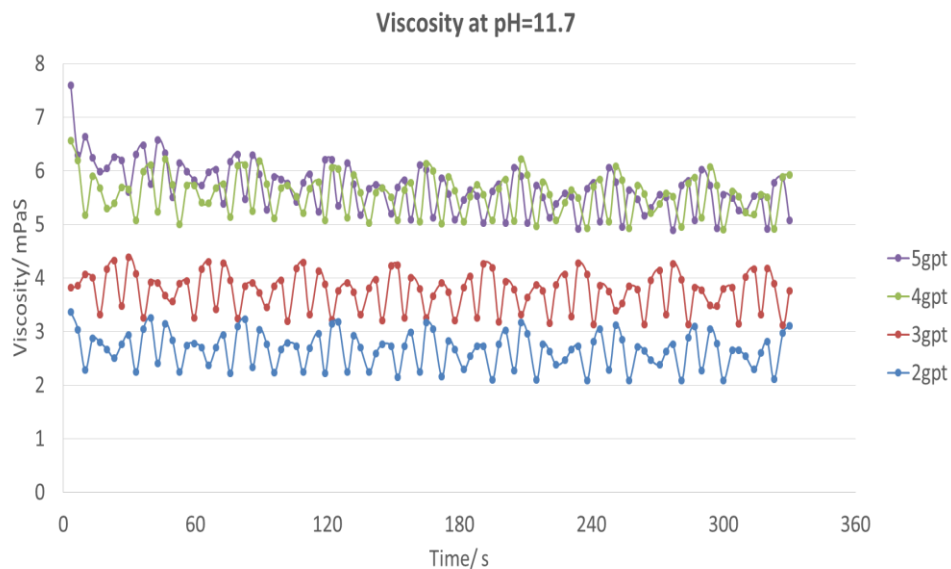


Figure 33 -- Viscosity as a function of time at pH = 11.7

Based on the results, the crosslinking is more effective under pH equals to 6.3. The reason can be found from crosslinker. $ZrAc_4$ is favorable for neutral condition since too much H^+ will inhibit Zr^{4+} concentration, however, for base condition, too much OH^- will precipitate or react with Zr^{4+} , which all lead to decreasing in crosslinking efficiency.

Viscosity of Highly Viscous Polymeric Fracturing Fluids at Low Shear Rate

These polymeric fluids have shear-thinning behavior shown in previous experiments. Reducing shear rate should be helpful in viscosity. In China, Bohai Bay hydraulic fracturing operation is using 170 s^{-1} of shearing for rheology testing (Wang, 2014). In this section, low shear rate substituted of high shear rate, demonstrating a better performance in viscosity (**Fig. 34**). Compared with **Fig. 35**, the viscosity increases up to 3 times at low shear rate (170 s^{-1}). Thus, decrease in shear rate will contribute to higher viscosity.

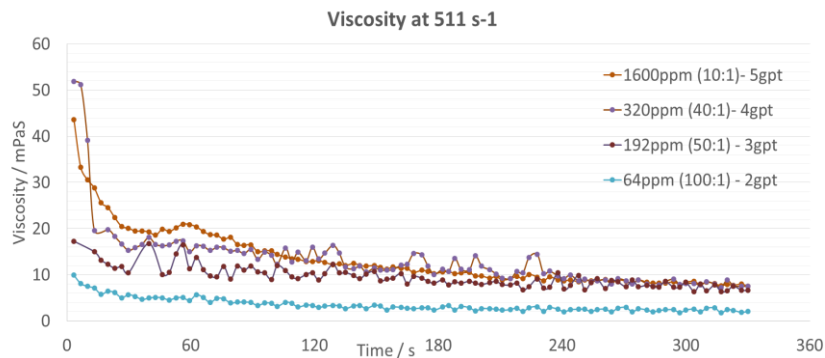


Figure 34 -- Viscosity as a function of time at shear rate of 511 s⁻¹

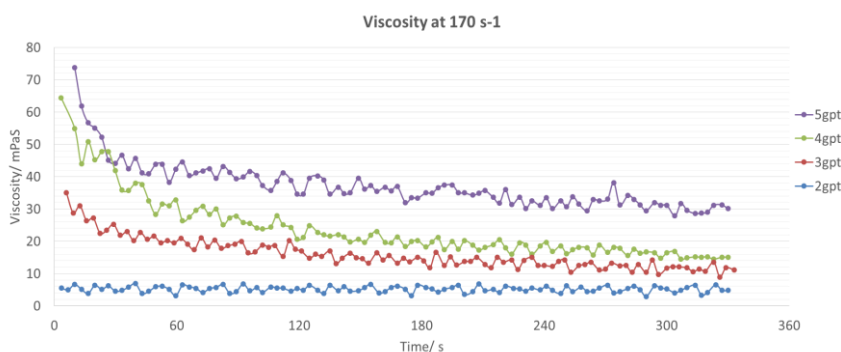


Figure 35 -- Viscosity as a function of time at shear rate of 170 s⁻¹

Conclusions

In this study, the PAM based zwitterion copolymer was selected as the best functional polymer used in fracturing fluid design. Zirconium acetate was chosen as the crosslinker due to its best performance in evaluation. The samples were prepared by using 2 % (KCl) solutions and tested at low polymer concentration from 2 to 5 gpt with crosslinker concentration ranging from 48 to 8000 ppm. HAAKE MARS Rheometer was used for viscosity measurement.

The best ratio of polymer: crosslinker depends upon polymer concentration, and the viscosity increases up to 9 times after addition of crosslinker. There is an optimal crosslinker concentration to generate highly viscous fracturing fluids. Polymer concentration at 2 gpt is good to crosslink, however, it does not tolerate high shear resistance unless increasing the concentration above 3 gpt. At higher crosslinker concentration, the crosslinked polymer is prone to be more brittle through observation, which demonstrates it can be easily broken down under high shear rate (511 s^{-1}) condition. However, decrease in shear rate will contribute to higher viscosity, where the experiments shows 3 times of enhancement on viscosity at low shear rate (170 s^{-1}) condition. In the presence of crosslinker, the viscosity increases with polymer concentration, and increase in time leads to shear thinning behavior of the crosslinked polymer. The degradation of the polymer has negative effect on viscosity. The viscosity is higher when using the fresh-made polymer to crosslink. After crosslinking, the viscosity does not change in 10 min. However, it will decrease significantly if the sample is put into oven at 65°C for 12 h. Increase in temperature will enhance the viscosity reduction of the crosslinked polymer, where under 90°C , none of any crosslinked polymers can stay viscous above 10 mPaS after 3 minutes. This system favors neutral condition, too acid or base environment will either inhibit Zr^{4+} concentration or precipitate out the solution.

In the future, further research work should be considered to obtain higher viscosity. More functionalized polymers and crosslinkers could be applied to enhance the gel performance. Moreover, the method to keep the viscosity stable as at 1 min (above 15 mPaS) should be taken into consideration.

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II. RECROSSLINKED CHARACTERIZATION OF INTERACTIONS BETWEEN DEGRADED GEL AND CLAY FOR CONFORMANCE CONTROL

Abstract

The second evaluation is to characterize the interactions and impacting factors of degraded gel in recrosslinking process. Reusing the degraded gel from producing water is in sake of reducing the cost. The research is expected to get strong gels with a cost-effective manner. Experiments were conducted towards clay optimization, degraded gel selection, thermos-stability and other parameters that influence gel performance. Polymer concentration at a range of 0.5 wt% to 0.7 wt% can bring the recrosslinked gel with both better elastic and rigid properties, with proper additives of clay and crosslinker.

Introduction

Excess water production can lead to extra operating cost or well abandonment in conventional oil and gas reservoirs. It is a worldwide problem that has a significant negative influence on the profitable of hydrocarbon production. Inadequate profile injection and low sweep efficiency are key challenges for improving the oil recovery. Fractures, high-permeability channels, or other heterogeneity zones are easily providing paths of least distance for fluids, resulting breakthrough earlier than they supposed to be. The common and effective way to mitigate the problem is to maximize the amounts of swept oil from the reservoir by placing blocking agents into the flow paths. Gel treatment emerges as one of the most effective methods to reduce the excess water production, and enhance oil recovery. For the gel treatments, it can be concluded into four categories: in-situ crosslinked polymer gels, PPG, CDGs, and silicate systems.

In-situ gel is one of the methods used in gel treatment. The base polymer and crosslinker are mixing together on the surface, and then the viscous gelant will be pumped downhole. The gelation occurs that creates a strong gel barrier, which fills the porosity of channels in the target zone, proving the desired seal and flow diversion for following sweeping-fluid injection under the reservoir. However, problems like material loss, formulation change, and uncontrollable gelation time are still exist in this system. Many factors that may influence on gel properties such as polymer adsorption, crosslinker retention, shear effect, molecular diffusion and mechanical entrapment of polymer molecules. The negative effects caused by those factors may lead to the ineffectiveness of gelants displacement, failing in gelation, poor gel strength and cost increasing.

In past few years, improvements were made to in-situ gel applications. These relate to some novel discoveries on gel system, and new developments on crosslinking system. In this research, author aims to develop a novel system by reusing the degraded preformed particle gel to form a cost effective in-situ gel. The gels were tested to be elastic, thermo-stable and well functional under laboratory experiments.

Literature Review

In this research, degraded gels were used instead of HPAM. However, degraded gels still function as polymers like HPAM in the gel treatment. Polymer adsorption is one of the factors that determines the efficiency of final gelation. Polymer adsorption makes the polymer loss in material as well as the possibility to failure in gelation. Possible reasons for adsorption may consist of wall effects, adsorption rates influenced by polymer concentration, and retention rates due to the polymer molecular weights etc. Those factors are necessary in selection of polymers (degraded gel) or some special pre-treatments to

experimental materials. For example, controlling chain lengths of the polymer (degraded gel) may help to get lower retention rates in the reservoir.

Especially, clay were used in the following experiments to increase the gel strength, thus how clay usually interacts with polymers should be understood before experiments. Cr, a common metallic crosslinker will be used in the recrosslinking process in the combination with degraded gel and clay. However, the Cr^{3+} still has the retention problems due to various factors which will lead the recrosslinking unsuccessful.

In situ gels are expected to start forming gel until they reach the target zones at a specific reservoir condition. Gelant that includes polymer, clay, and crosslinker is in flowing phase that will influenced by polymer adsorption, charge attraction of clay, crosslinker retention. Moreover, shear rates will change the viscosity of the gelant that may lead to material screenout or non-functional formulation. Higher in viscosity gains the cost in pumping and operations as well.

Because of the negative effects brought by the uncontrollable aspects of in-situ gel system, this review will provide some summarized information of polymer adsorption, clay interaction with polymer, crosslinker retention, and shear effects on in-situ gel properties.

Polymer Adsorption

Mechanism Adsorption of polymer to the rock surface may have a great effect on the effectiveness of gel treatment. Many researchers and industries focus on PAM/HPAM, which is one of the popular polymers applied in a reservoir. The adsorption of an uncharged, linear polymer on to the rock surface will disorder the water molecules from the surface. From the data shown from Parfitt and Greenland (1970a), the uncharged high molecular weight polymer gains the entropy by this movement, and the driving force will cause the

polymer attached on the surface, which can be considered as an “entropy driven” process (**Fig. 1**). The adsorption is not occurring only on the edges of the polymer chains, but an average of 40% of the segments of the chain will be attracted. The polymer then tends to be in a more “flat” orientation attached on the surface, and make the total energy very large since there are so many segments being interacted.

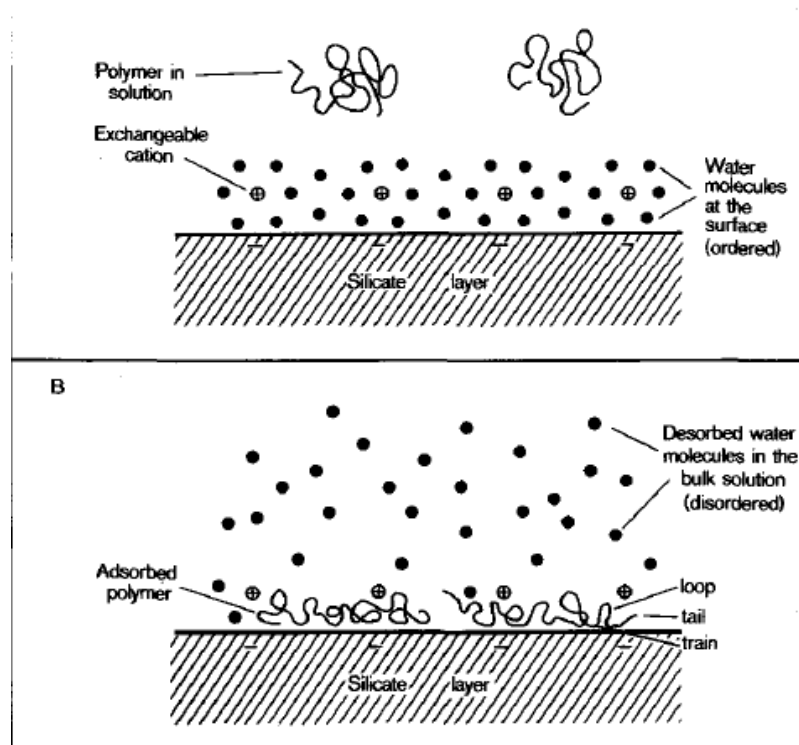


Figure 1 -- Uncharged linear polymer adsorption (Theng, 1982)

Wall Effects High molecular weight polymers are known to adsorb irreversibly on minerals. As the mechanism part mentioned, due to the large amount of the attachment points between the polymers and rock surface, the polymers can be very “sticky” that hard

to remove. For example, examined by some researchers, the case of a polyacrylamide polymer with a molecular weight of 107 diatoms was shown that monomer molecular weight was 71.

Therefore, the number of lateral groups carried by the polymer chain is around 150,000. If only one group on 1,000 is linked to the surface, then the macromolecule is attached by 150 bonds. This implies that (1) even if each bond is weak, the sum of bonds can lead to a strong bonding force, and (2) the probability that all the bonds break down simultaneously is very low (Zaitoun et al, 1998). When the polymer adsorption occurs on the pore walls, three effects will be induced: steric, lubrication, and wettability modification (**Fig. 2**).

(1) Steric Effect

The steric effect (**Fig. 2**) is due to the adsorption of polymers that the thickness of the polymer layer will occupy a significant fraction of the pore volume. Compared to the pore size, the “wall” thickness cannot be neglected and is expected to reduce the average pore diameter by 0.8 μm (diameter of a 100 mD sandstone = 3 μm).

(2) Lubrication Effect

After the wall forms, the oil will be easy to flow as the polymer layers provides a water film which decreases the roughness of the rock surface.

(3) Wettability Changes

Like HPAM, the adsorption of hydrophilic polymer will attach to the oil-wet parts of the rock and then turns the wettability to water-wet. This phenomenon also contributes to the DPR.

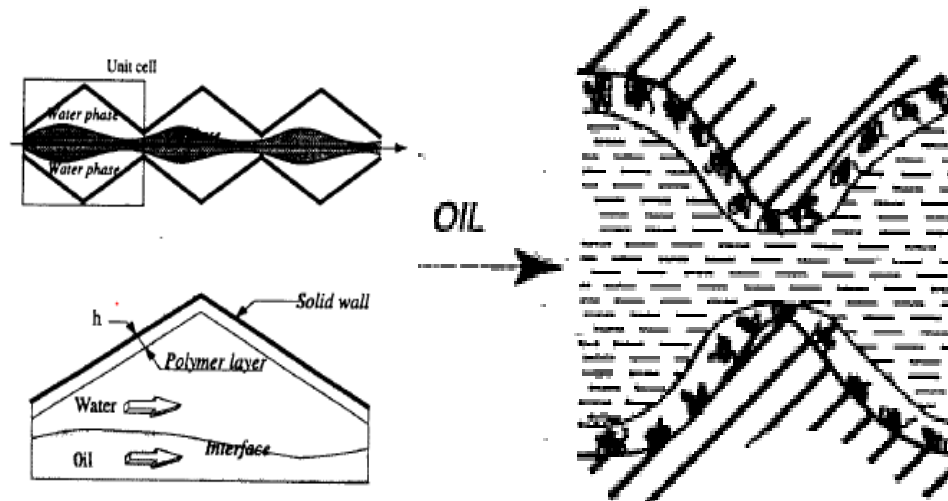


Figure 2 -- Wall effects

Concentration Effect

Changing the concentration of the polymer solution may cause the adsorption rate different. Based on the three concentration regimes proposed (De Gennes 1979; Ying and Chu 1987), the polymer interaction at different concentrations can be summarized as three phases: dilute ($c < c^*$), semidilute ($c^* < c < c^{**}$), and concentrated solution ($c^{**} < c$). C^* and C^{**} are the critical concentration value of the change occurs from dilute to semidilute solution, and semidilute to concentrated solution respectively. They indicates the overlap concentration crossover the different phase (**Fig. 3**).

In the dilute solution, the polymer molecules existed in solution as free coils where little interaction occurs. In the semi-diluted solution, macromolecules start to contact each other, intermolecular interactions occur. In the concentrated regime, intermolecular entanglements dominate the interaction, resulting in the formation of network structure.

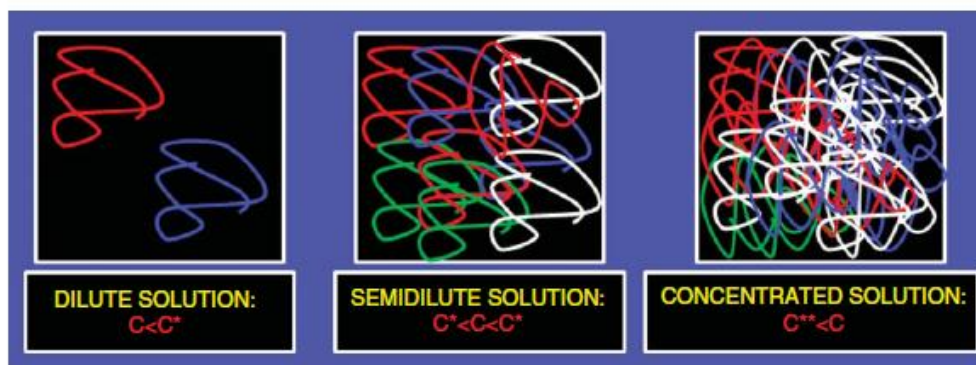


Figure 3 -- Polymer-molecule interactions (Zhang and Seright, 2013).

The concentration effects under these three regimes are quite different (**Fig. 4**). In the dilute regime A, when the polymer chains adsorb on rock surface, they tend to take a flat orientation that most of molecular segments are in contact with the surface. The “flat” orientation type of the polymer adsorption is considered as 2D adsorption. In this dilute region, 2D dominates the retention until the maximum coverage reached. Thus, it is independent with the polymer concentration.

In the regime B, the intermolecular interaction in solution will result in a mixed adsorption that some molecules will be adsorbed with all segments whereas others will be adsorbed with only partial segments (edges). The latter “edge” orientation type is considered as 3D adsorption. When the 2D adsorption reaches the maximum coverage, the adsorption rate will increase along with the 3D adsorption. At this time, the polymer adsorption is dependent with the polymer concentration since increasing concentration will increase the level of 3D adsorption.

In the regime C, the molecular entanglement caused the 3D adsorption to dominate. Therefore, when both 2D and 3D adsorption reach the maximum coverage, almost no

additional adsorption will be added since all sites are taken. Under this regime, the polymer adsorption again, is independent with the polymer concentration.

Due to this property, a porous medium is first contacted with dilute HPAM solution to satisfy the retention, no significant additional retention occurs when exposed to higher concentrations. Therefore, maybe the polymer retention reduced by first injecting a low-concentration polymer bank (Zhang and Seright, 2013).

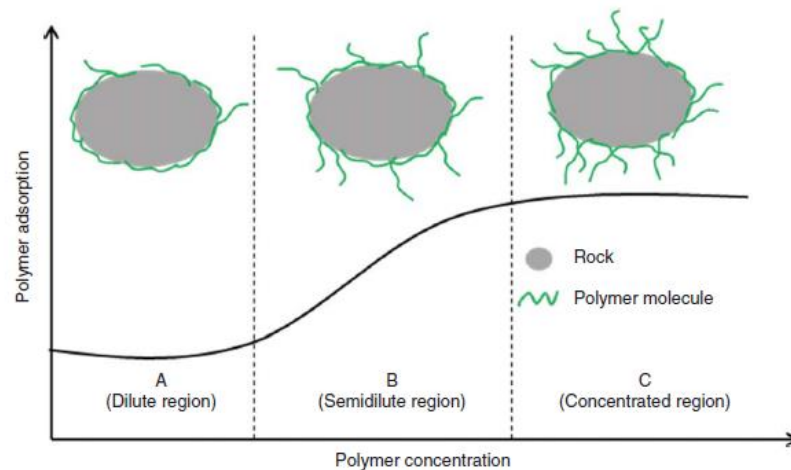


Figure 4 -- Polymer adsorption vs polymer concentration (Zhang and Seright, 2013)

Molecular Weight Effect

Experiments conducted to measure the distributions of PAM/HPAM polymers in core effluents by size-exclusion chromatography (SEC) (He, 1990) can be used to reflect the molecular weight effect on polymer adsorption. Average polymer size affects polymer transport in porous media, so the retention rates will be different to the various sizes of the polymer.

Under certain conditions, the retention rate should be significantly influenced by diffusion rate. For smaller molecules, they would diffuse to the surface faster and therefore have a greater opportunity to be retained (He, 1990). The retention of the smaller molecules not only reduces the retention of larger molecules, but also causes a drop in the population of low-MW polymer in the following stream. Therefore, from the **Fig. 5**, we can see that the average polymer size is tending to increase dramatically after passing through the cores, which causes the effluent most filled with high molecular weight polymer. Possible reasons for this phenomenon include both steric-exclusion effects and size-dependent retention rate, and the curve distributions of the continuous injection of polymers may reflect the result that continued retention of low-MW molecules.

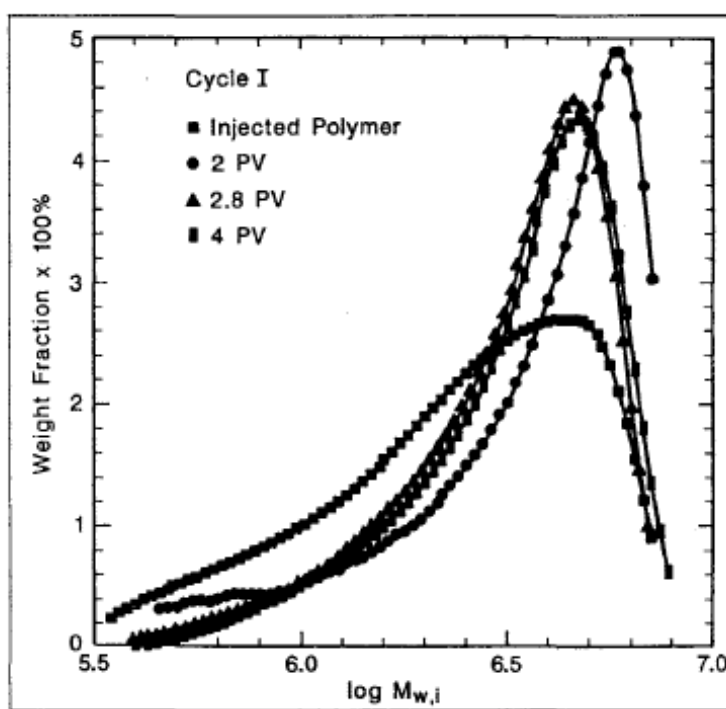


Figure 5 -- Effluent molecular weight distributions (He, 1990).

Other Effects on Polymer Adsorption

Except for molecular weight and concentration effects, there are many other factors that may also affect the adsorption (Zitha and Zaitoun, 1995; Zitha, 1998; Zaitoun, 1998).

Those factors include:

- 1) Flow rate. Above a critical shear rate (around $50\text{-}100\text{ s}^{-1}$), the plugging rate increases with flow rate.
- 2) Pore size. The plugging rate is larger when decreasing the core permeability. Bridging adsorption is absent above a critical permeability, estimated as $k \approx 2 D$ for high molecular-weight PAM.
- 3) Adsorption energy. Bridging adsorption is absent under non-adsorbing conditions. Experiments performed with hydrolyzed polyacrylamide (HPAM) showed a much weaker plugging tendency than with PAM (in accordance with their lower adsorption level on SiC). The skin resulting from polymer bridging adsorption could be removed by adding a desorption agent to the brine.
- 4) Core heterogeneity. Its presence increases the critical shear rate for bridging adsorption and decreases the plugging rate. Bridging adsorption becomes more difficult in heterogeneous media, since the distance between pore throats increases and more time for coil relaxation is available.
- 5) Residual oil saturation. The presence of residual oil favors bridging adsorption i.e. it decreases the critical shear rate and increases the plugging rate. In water-wet porous media residual oil consists of oil droplets trapped by capillary forces in front of pore throats. This reduces the pore cross-section and increases strongly the elongation forces.

Clay Interaction with Polymer (HPAM)

The interaction between charged polymer and clay is more complex. It involves the electronic force caused by the opposite charge, and the attraction will in response to the changes in pH and ionic strength of the solvent. For example, like HPAM, the carboxyl groups (negative charge) are likely to be paired by the cationic ion on the rock surface, and the repulsion between those carboxyl groups will keep the chain stretching and more segments will provided to attach on the surface. When pH becomes larger, more carboxyl groups will be ionized, the attraction then will be enhanced.

However, when pH becomes smaller, the amino group will form amino acids (NH_3^+), which can be attracted by the negative charge on the clay layers and keep the adsorption still exists (**Fig. 6**). If stronger ionic strength being applied, the adsorption will be enhanced. Nevertheless, whether the polymer chain will be more collapsed or stretched responding to those changes is still under researched, which is also of great importance to the influence of adsorption.

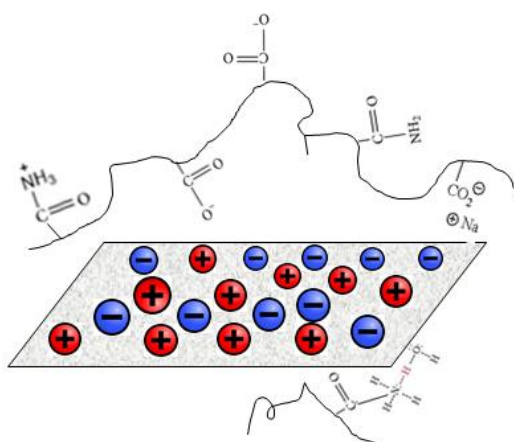


Figure 6 -- Clay interaction with HPAM due to the opposite charges.

Crosslinker Retention

Rock-fluid interactions can lead to loss of crosslinker, inhibit gelation, and limit the depth of penetration of a gel treatment. For the different crosslinker, like organic crosslinker and inorganic species may have different rates of the retention. For this report, the crosslinker type will mainly focus on the CrAc_3 in carbonate rocks, as its popularity application in the gel treatment.

From lots of research conducted, the precipitation of chromium is the principal retention mechanism. The chemical function maybe simplified as $\text{Cr}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq}) \rightleftharpoons \text{Cr}(\text{OH})_3(\text{s})$ chromium hydroxide, and $\text{Cr}(\text{OH})_3(\text{s}) + \text{OH}^{-}(\text{aq}) \rightleftharpoons \text{Cr}(\text{OH})_4^{-}(\text{aq})$ (green). However, the reaction should be more complex under the real situation. The retention rates of CrAc_3 in carbonate rocks perhaps caused by the following factors: reaction time, pH, salinity, flow rate, temperature, and acetate concentration (Zou, et al., 2000; Jin, et al., 2002).

Reaction Time Effect

Longer reaction time can enhance the Cr^{3+} retention. From the experiment result shown below, the Cr concentration in effluent keeps constant at 200 ppm during the first 180 mins. This time period can be taken as induction time --- the time required for chromium to produce precipitation (the ion needs time to be ionized). After 180 mins, the concentration decreases as the reaction time increases.

This reflected the Cr retention in the cores occurs with the residence time increasing (**Fig. 7**).

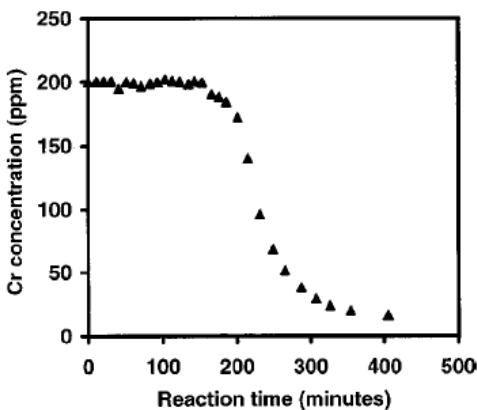


Figure 7 -- Cr concentration in effluents vs reaction time (Zou, 2000).

pH Effect

Higher pH will increase the precipitation rate and enhance Cr^{3+} retention. The effect of pH on chromium precipitation at 25°C is shown. The pH was controlled at values between 7 and 10. The length of induction period decreased from 1,200 minutes to less than 200 minutes as pH increased from 7 to 10. The precipitation rate was faster at higher pH values (Fig. 8).

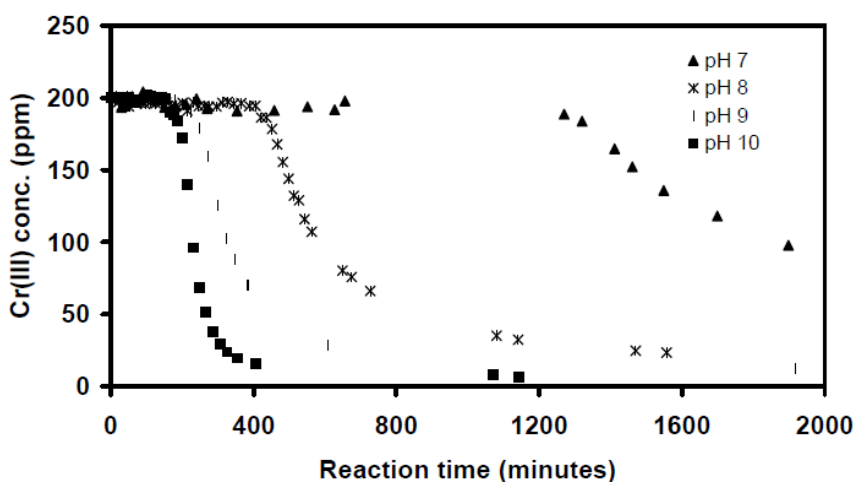


Figure 8 -- Cr concentration in effluents vs reaction time at different pH (Jin, 2002).

Salinity Effect

Higher salt concentration can enhance the Cr^{3+} retention. The effect of salinity was studied by adjusting the potassium chloride concentration from 0 to 5% in the chromium solutions. Experiments were performed at 25°C and the pH was controlled at 9. The length of the induction period decreased and the precipitation rate increased with increased potassium chloride concentration. Precipitation in the solution containing 5% potassium chloride occurred immediately, while little precipitation was observed for three days in the solution containing no potassium chloride (Fig. 9).

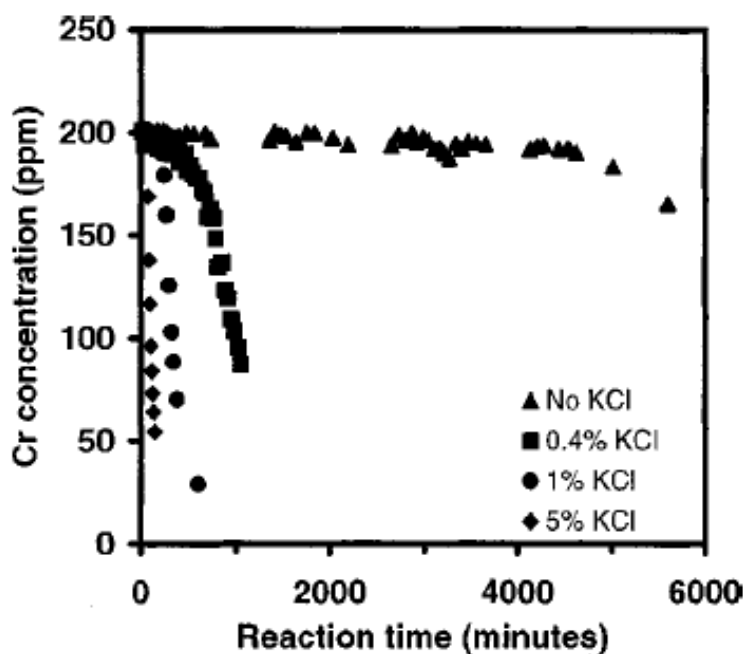


Figure 9 -- Cr concentration in effluents at different concentrations of KCl (Zou, 2000).

Flow Rate Effect

Higher flow rate can reduce the Cr^{3+} retention. Short residence time will cause the propagation higher in flow rate. When the residence time reduced, the retention rate should

be smaller. From the curve shown below, the Run 1 used higher flow rates at 1ml/ min while the Run 2 switched to 0.02 ml/min. At 1.5 pore volumes injected, we can see that about 80% of the CrAc_3 in Run 1 succeed in transport, but at lower flow, which in Run 2, only 20% has been detected (**Fig. 10**).

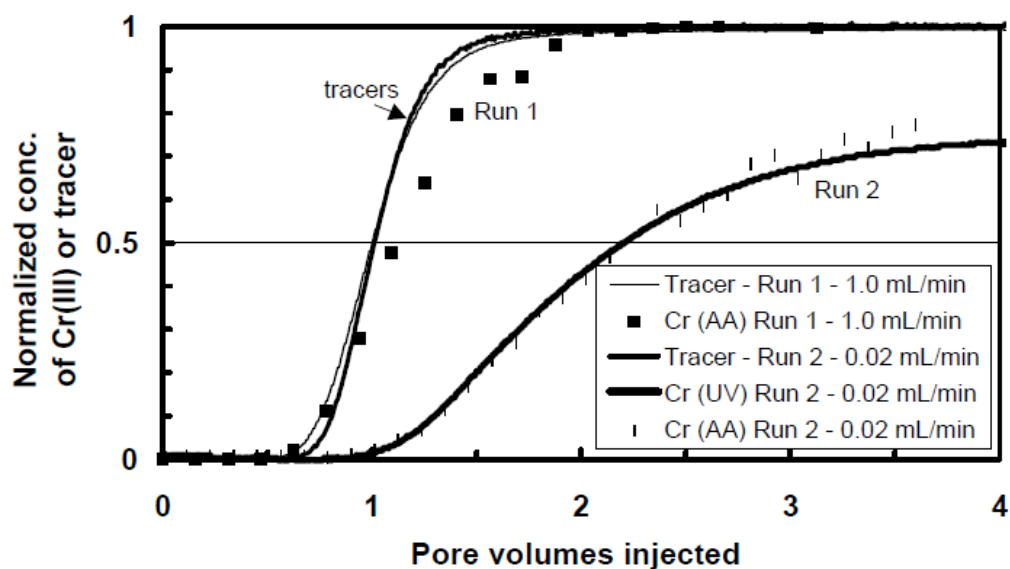


Figure 10 -- Cr concentration in effluents vs PV injected at different flow rates (Jin, 2002).

Temperature Effect

Increasing temperatures can enhance the Cr^{3+} retention. The effect of temperature is shown below. The runs were conducted at 25, 35, and 45°C and the pH was controlled at 9. The length of the induction period decreased sharply with increasing temperature. The precipitation rate increased with temperature (**Fig.11**).

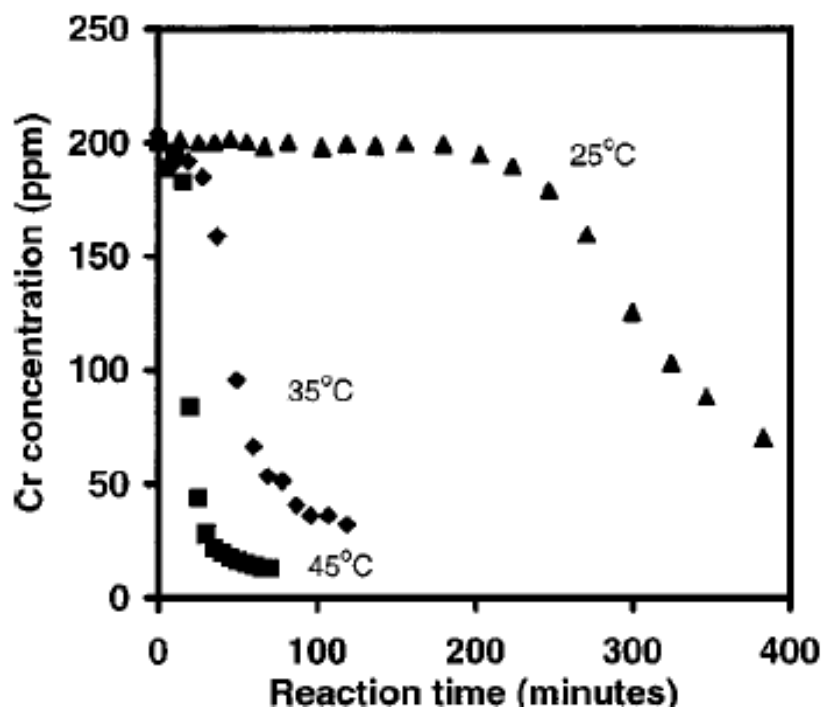


Figure 11 -- Cr concentration in effluents at different temperatures (Zou, 2000).

Acetate Concentration Effect

Increasing acetate concentration can reduce the Cr^{3+} retention. The effect of acetate ligand concentration was studied by varying the acetate-to chromium ratio from 3 to 9. A ratio of 3 represents a solution prepared with the chromium acetate salt without added acetate. The average ionic strength varied from 0.155 to 0.173, which should not significantly affect the chromium precipitation. The results of this series of runs are shown below. No significant change in the length of the induction period and a slight delay in the precipitation rate were observed for acetate-to-chromium ratios between 3 and 9 (**Fig. 12**).

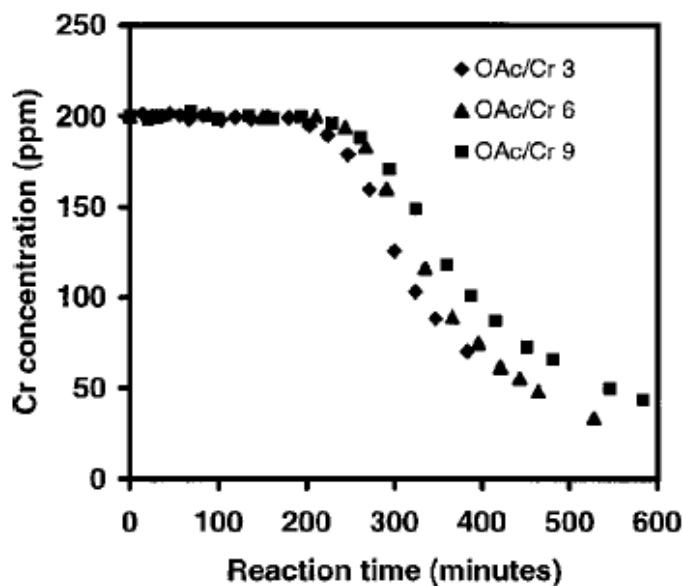


Figure 12 -- Cr concentration in effluents at different acetate concentration (Zou, 2000).

Shear Effects

The gel properties are of great importance to the final gel strength. However, injecting the gelant may lead to change in formulation due to the shear effects. Before crosslinking, shear induced by pumping time will influence the gelation time, and after crosslinking, shear may impact on the final gel strength which related to the maximum differential pressure that the gel can resist in the matrix or fracture.

Shear Effect before Crosslinking The investigation from Broseta in 2000, both high and low molecular weight polymers have been used to discover the shear effects on different polymer size formulation. As for high-molecular-weight HPAM/Cr (III) gelant ($M_w = 5 \times 10^6$), the authors take it as non-Newtonian fluid while Newtonian for low-molecular-weight HPAM/Cr (III) formulation ($M_w = 2 \times 10^5$). Both of the gelants are succeed in application in the real reservoir gel treatments. The high-molecular-weight is designed for plugging fractures, and the low-molecular-weight is applied for porous matrix.

The authors define the gelation time as in relation to its viscosity rises. Before the gelation occurs, shear rate will influence on non-Newtonian formulation (A) which shows a shear thinning effect. But for Newtonian formulation (B), it is independent as the shear rates change (**Fig. 13**).

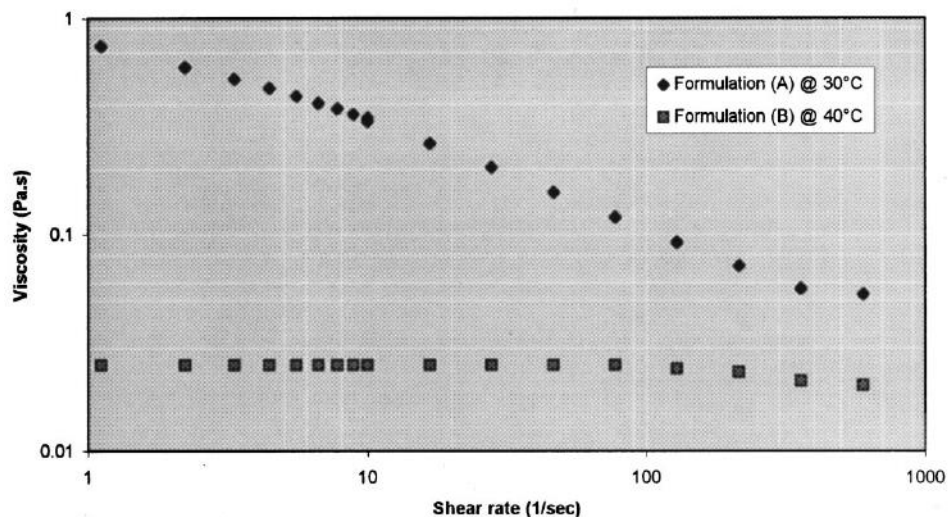


Figure 13 -- Shear effect on gelant before crosslinking (Broseta, 2000).

As the reaction time keeps increasing, the crosslinking gradually started. Viscosities at the applied shear rates of high-molecular-weight formulation are shown in **Fig. 14**. The viscosity of the initially shear-thinning formulation (A) increases with time, in a manner that strongly depends on the applied shear rate. The viscosity increase is rather limited for the first one or two hours. This could be considered as the induction time for crosslinking.

From the figure we have seen, first two lower shear rates, increasing fast. However, at other higher shear rates, **Fig. 14** shows that at long times the viscosity levels off to some

constant value that is lower for higher shear rates. They clearly indicate that shear delays and limits the increase in the viscosity of gelling solutions.

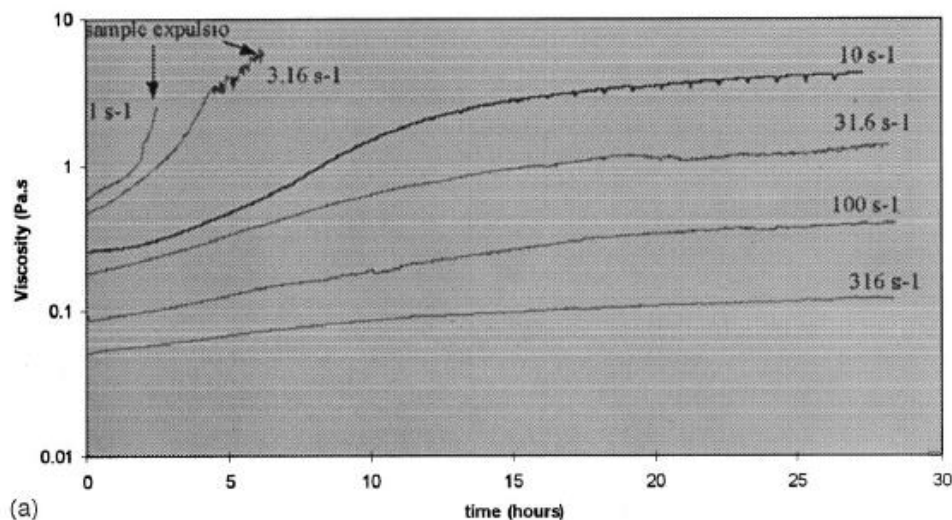


Figure 14 -- Shear effect on HMW formulation at different shear rates (Broseta, 2000).

Viscosities at the applied shear rates of low-molecular-weight formulation are shown in **Fig. 15**. The viscosity of the initially Newtonian formulation (B) increases very slightly during an induction period of around 2 hours 30 minutes in a manner that does not depend on the applied shear rate. The solution remains Newtonian during this time period.

The viscosities then start increasing. For the other shear rates, the figure also shows that at long times the viscosities level off to some constant value that is lower for higher shear rates. Therefore, for the initially Newtonian formulation (B), shear also limits the viscosity increase but does not affect the time at which the viscosity starts increasing.

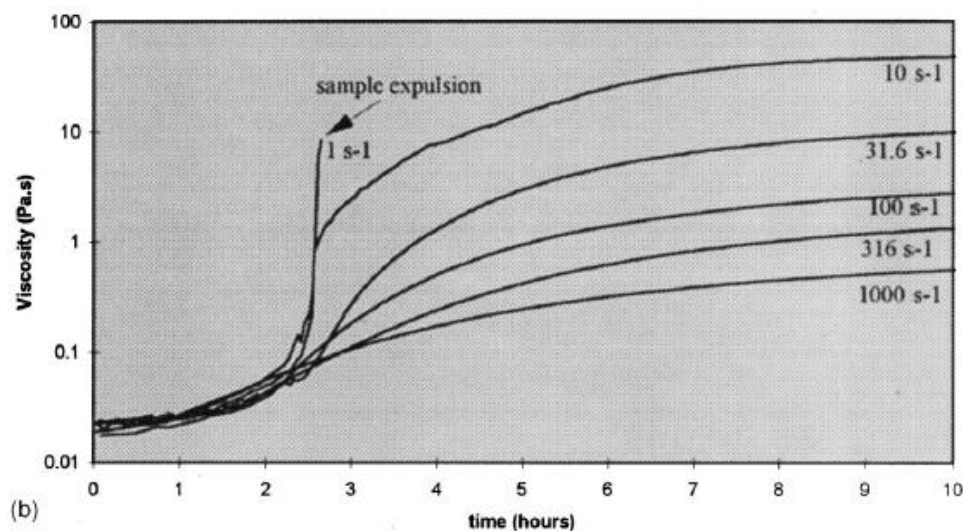


Figure 15 -- Shear effect on LMW formulation at different shear rates (Broseta, 2000).

Shear Effect after Crosslinking From the last part, we get known that shear will limit the viscosity increase of HPAM gels. However, if the shear will also limit the final gel strength is also of great importance in gel application. Thus, the latter experiments of formulation (A) and (B) are designed to test the G' and the final yield stress for gel strength.

Read from the **Fig.16**, in both solutions for high molecular weight (left) and low molecular weight (right) indicate: lower G' for higher shear rates. The increase is quite significant, however, even for the highest shear rates. For a viscous system, the expectation is that the low frequency storage modulus is negligible. A possible explanation for the observations is that 1 Hz is not a low enough frequency compared to the inverse relaxation time of the large aggregates of micro gels formed under shear (Broseta, 2000).

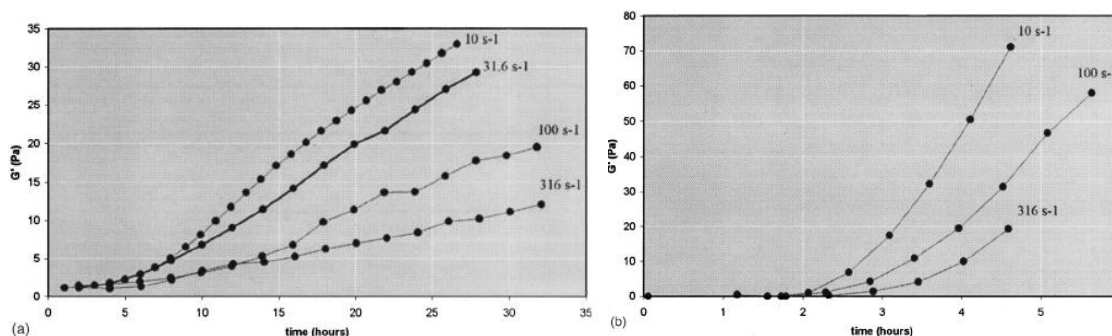


Figure 16 -- G' at different shear rates as a function of time (Broseta, 2000).

The final yield strength are recorded after dropping the shear rate to zero and allowed the samples to rest for several hours (18 hours for formulation (A) and 10 hours for formulation (B)). The results are listed below (**Table 1**).

Table 1 -- Final yield stresses of formulations A and B (Broseta, 2000).

TABLE 2--FINAL YIELD STRESSES OF FORMULATIONS (A) AND (B) SUBMITTED TO AN INITIAL PERIOD OF STEADY SHEARING AND THEN TO AN EXTENDED PERIOD OF REST		
Shear rate 1/second	Yield Stresses (Pa)	
	Formulation (A) (Resting Period: 18 Hours)	Formulation (B) (Resting Period: 10 Hours)
0	260	3,200
0	270	3,500
10	170	3,800
31.6	250	3,400
100	215	Not determined
316	150	

Following this period of rest, all the gels recovered approximately the same yield stress. The measured yield stresses were in the same range. In other words, there is no

“memory” of the initial shearing on the final gel strength, provided the HPAM/Cr (III) gel has been allowed to rest or “re-heal” during a sufficient amount of time.

Different base polymer may influence the “re-heal” property of gel. From the experiments shown from (Tseu, 1992), the typical curve of Xanthan/Cr (III) gel applying with shear is demonstrated in **Fig. 17**. This curve implies that gel will breakdown at some point and start to re-heal itself. Gel performance observed as three phases: initial gelation phase, shearing phase, and re-gelation phase.

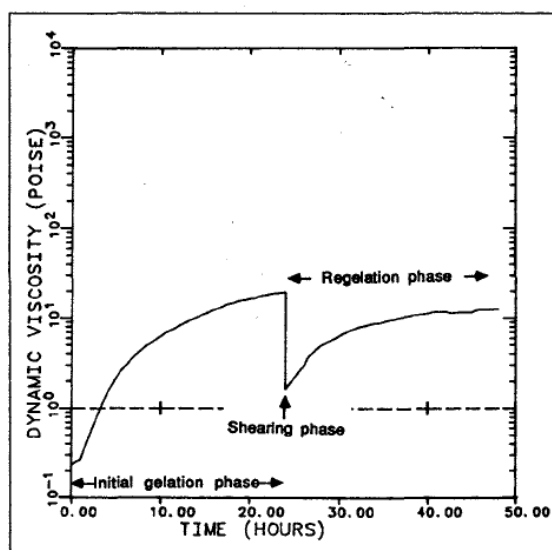


Figure 17 -- Typical curve for Xanthan/ Cr (III) gels.

To test its re-formability (**Fig.18**), both of weak (left) and strong (right) gels haven been tested for their re-formability. Shear at three different rates (100, 1000, 2000/sec) are applied continuously, then the Xanthan/Cr (III) gels become re-formable to some extent after shear degradation.

Nevertheless, the level of re-formability depends on gel strength. We could see that the weak gel shows the capability to re-form its gel strength to what it was before shear degradation. Strong gels, however, recovered less gel strength after being sheared. Unlike PAM/Cr (III) gel, shear will have an effect on the final gel strength for Xanthan/ Cr (III) gels.

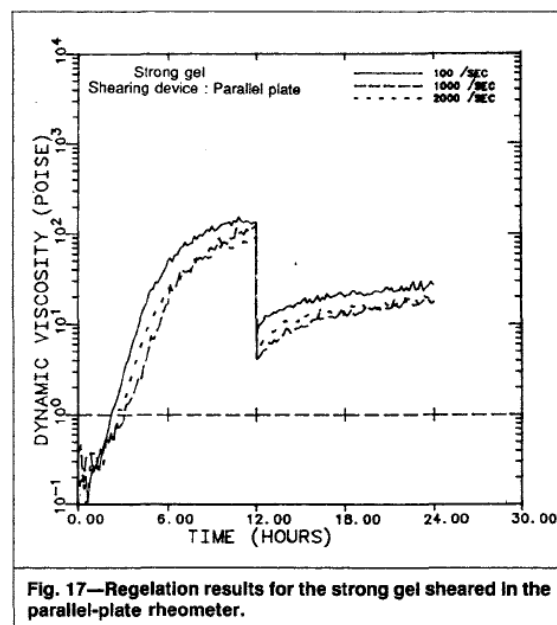
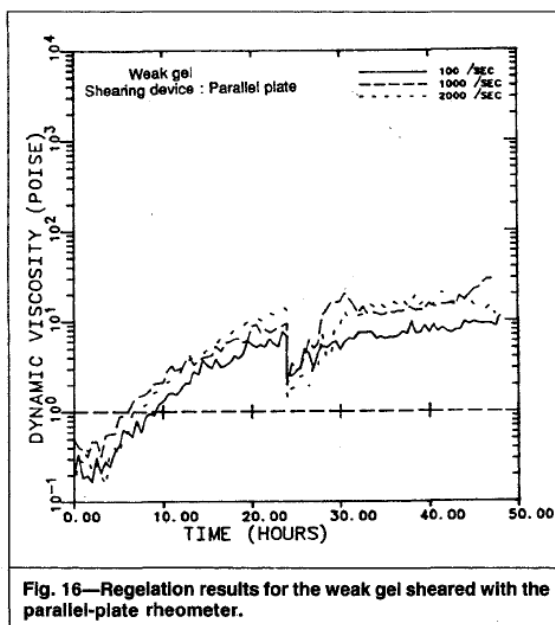


Figure 18 -- Comparison of the re-formability between weak and strong gels (Tseu, 1992).

In summary, gel properties will be affected by the adsorption of polymer, retention of crosslinker and the shear rates applied on the gelants.

1. Linear polymer adsorption occurs by electrical attraction and entropy driven process.
2. Polymer adsorption will cause the wall effects that consist of steric effect, lubrication effect, and wettability changes.

3. Polymer adsorption rates can be influenced by concentration, molecular weight and other factors.
4. Precipitation is the principal retention mechanism of chromium acetate as crosslinker.
5. Precipitation rates are influenced by reaction time, pH, salinity, flow rates, temperature, and acetate concentration.
6. Before crosslinking, shear delays and limits the increase in the viscosity of gelants, but will not affect the time at which the viscosity starts to increase for Newtonian formulation (low molecular weight gelant).
7. After crosslinking, shear ranging from 1 to 1000 s⁻¹ will not influence the final strength of PAM/Cr (III) gel, but will affect the re-formability of the Xanthan/ Cr (III) gel under 100 to 2000 s⁻¹ shear rates applied.

Experimental

Materials

Acrylamide, Acrylic Acid, PEGDA200, urea, ammonium hydroxide, NaHCO₃, NaCO₃, and TEMED were used to synthesize PPG. Chromium acetate was purchased by Aldrich. Sodium chloride was purchased by Fisher Chemical. Laponite XLG was purchased by. Water used in the following experiments was deionized (DI) water provided by Missouri University of Science and Technology. HAAKE MARS Rheometer was used for G' measurement. All the chemicals used in the experiments were as received.

Experimental Procedure

The clay were pretreated by blending and ultrasonic to decrease the electrostatic attraction before used. 0.6% NaCl was used as the base solution in the experiments. PPG-VV was synthesized by using AM, AA, PEGDA200, urea, ammonium hydroxide, TEMED at 4 - 9

°C. The gelant was purged for 30 mins before the redox. Then, the bulk gel was formed in 12 hours and then was put into base solution at 0.1% to 1% under 65 °C for fully degradation. The degraded gel, also mentioned as polymer in the following paragraphs, was used to recrosslink with a new crosslinker (CrAc_3) and pretreated clay in order to form a new strong gel. The mixture including polymer, CrAc_3 , and clay was finally put into oven at 80 °C. The experiments were designed to find the interaction among the gelants.

Results

Shear Rate Effect on Gelants

In situ gel treatment is a method to pump the gelants down into the wellbore. Shear rate is one of the factors that influencing the gelation efficiency before the gel forms. Low shear rate were applied to HPAM and degraded gel in order to compare the viscosity difference between commercial polymer and degraded gel (**Fig. 19**). From **Fig. 20**, either distilled water or brine based polymer has shown better viscosity with degraded gel.

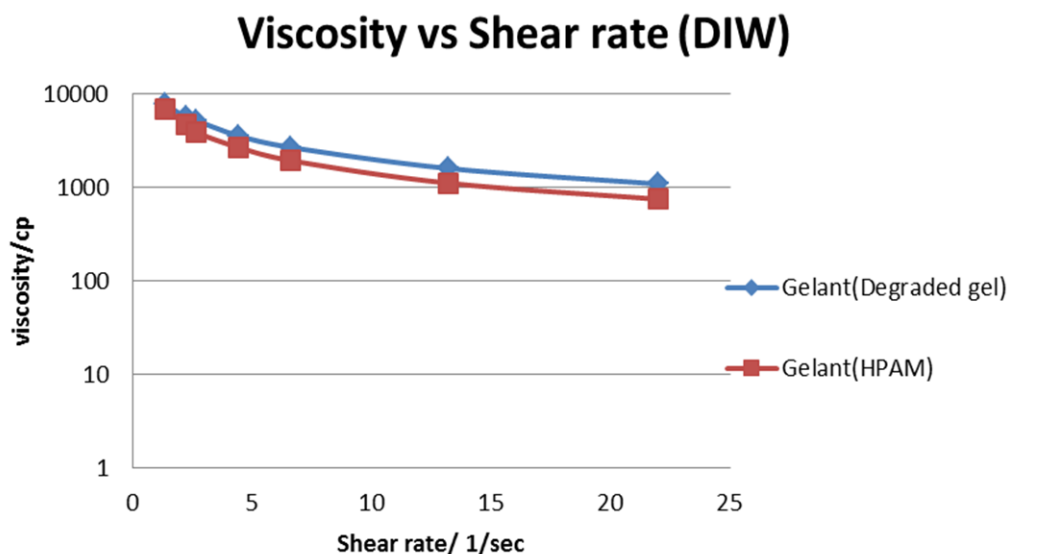


Figure 19 -- Viscosity comparison of degraded gel and HPAM of distilled water.

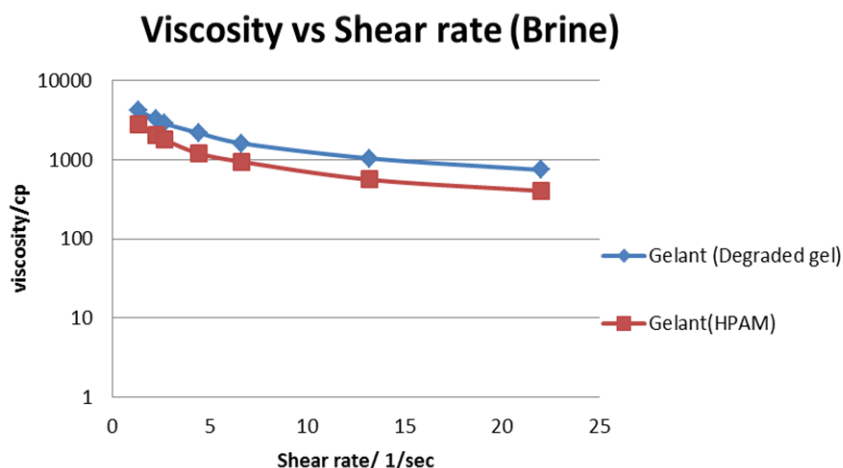


Figure 20 -- Viscosity comparison of degraded gel and HPAM of brine.

Clay Effect on Gel Strength

Clay is expected to increase viscosity for gels. Nine of different clay types was chosen to select the optimal one for the following experiments. DQ stands for clay from Daqing, and VV is for sample name (**Table 2**). Samples were synthesized by first diluting degraded gel at a concentration of 0.5%, and then mixed with clay powder at an amount of 1.2 times as the polymer (**Fig. 21**). Rheometer was used to test the G' as **Fig. 22**.

Table 2 -- Clay type.

#	Clay Type	#	Clay Type
VV260	DQ 1	VV265	Hydrogel XLG
VV261	DQ 2	VV266	Laponite RDS
VV262	DQ 3	VV267	SCP Cloisite Ca++
VV263	DQ 4	VV268	SCP Cloisite 10A
VV264	DQ 5		

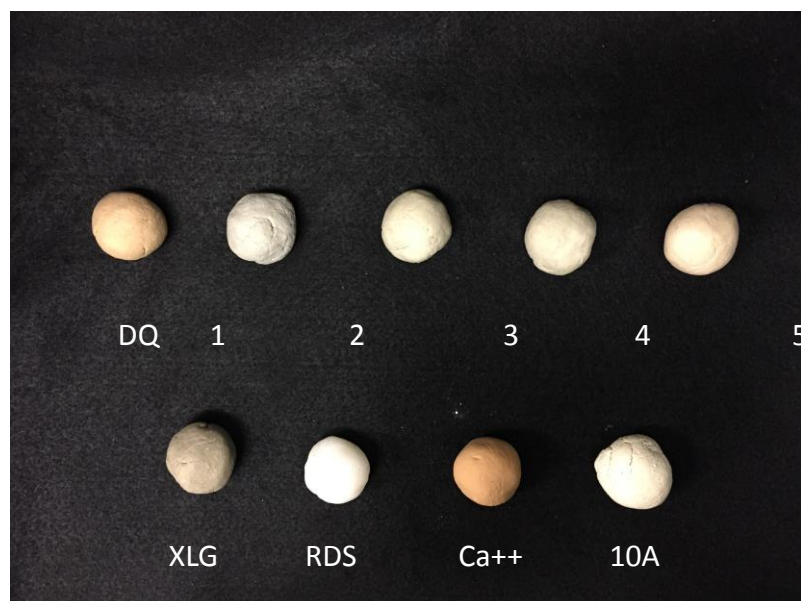


Figure 21 -- Clay mixing with degraded gel.

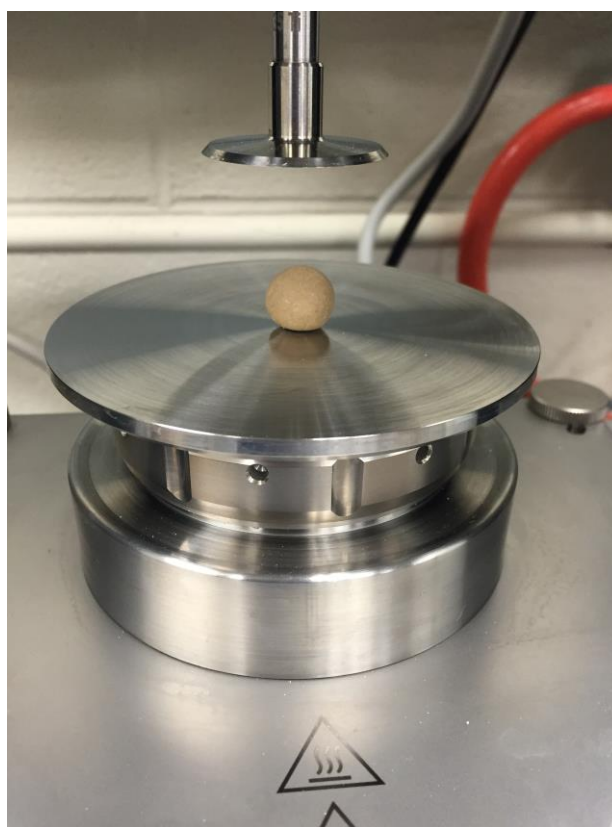


Figure 22 -- Rheometer that used for test G'.

Result shown in **Fig. 23** indicated that the gel used of DQ 3 got the best performance compared with others. However, DQ series got very limited amount left in the laboratory and it was hard to obtain, the author used hydrogel XLG as a substitute.

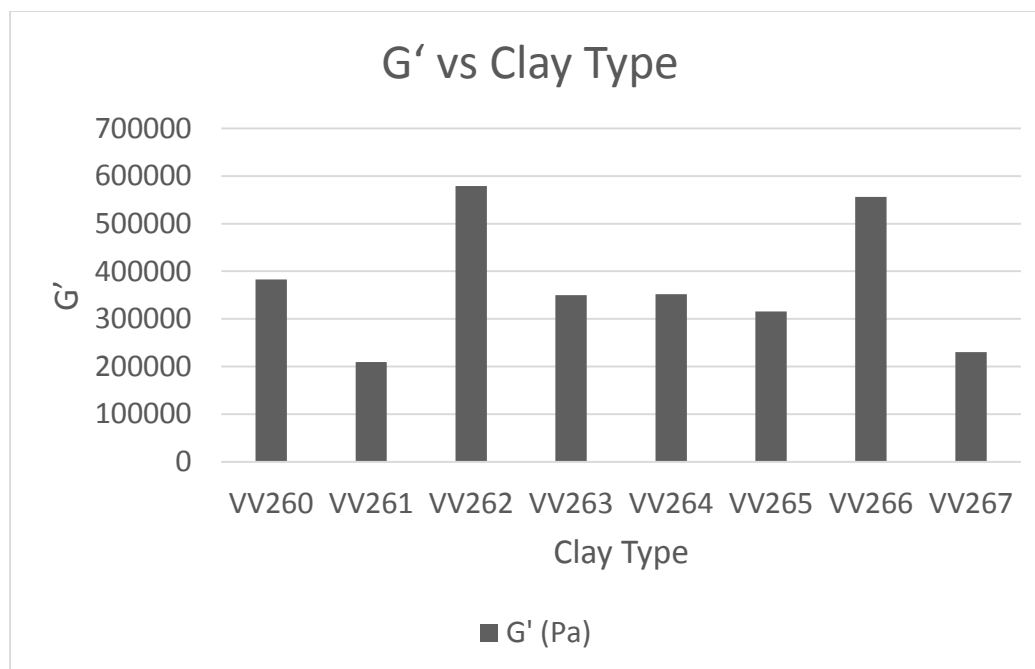


Figure 23 -- G' of the gel prepared by different clays.

The degraded gel (polymer) was prepared at concentration of 0.65 %, and clay used hydrogel XLG at 3.5% without other crosslinker (Cr^{3+}). The obvious viscosity improvement of gelant was shown after clay had been added to degraded gel in brine condition (**Fig. 24**). The viscosity increased about 1.5 times after clay applied. Therefore, hydrogel XLG is beneficial to viscosity enhancement in this system.

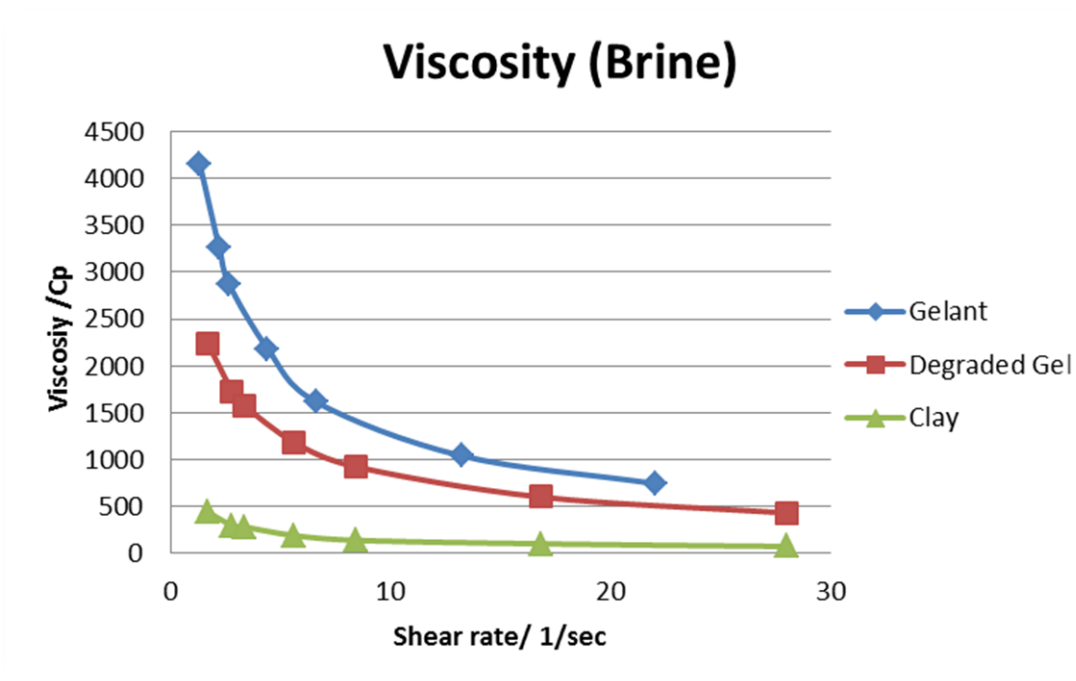


Figure 24 -- Viscosity of the gelant, degraded gel and clay.

Another experiment was conducted to test the relationship between G' and clay. In this experiment, a small amount of crosslinker was added to the mixture of degraded and clay solution. From the result, as increasing the concentration of clay, G' was proved to be increased (**Fig. 25**).

However, the strength in hardness was improved while the elasticity was poor (**Fig. 26**). Higher in clay concentration will contribute to the brittleness property of gel. Therefore, clay is favorable to gel rigidity and G' may not be the best choice to reflect the gel strength, which includes both elasticity and rigidity. To achieve a good result of strong gel, clay concentration is better to be in the range from 3.5% to 6.5%.

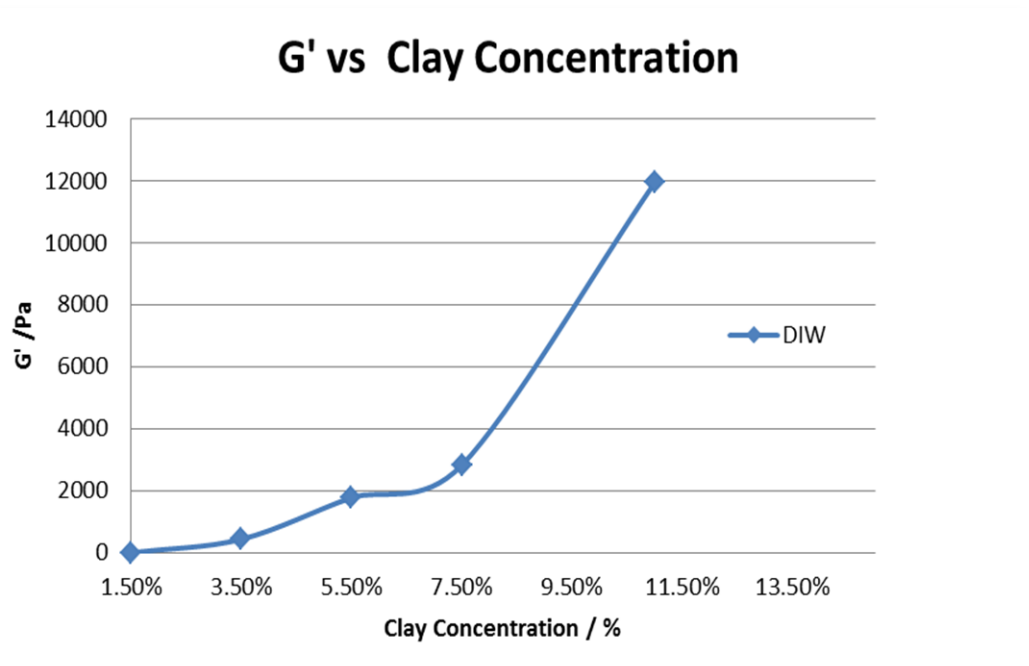


Figure 25 -- G' as a function of clay concentration.



Figure 26 -- Viscoelasticity measured by observation -1.

Polymer Effect on Gel Strength

The experiments were implemented by fixing the clay concentration was fixed at 5.5% while increasing the polymer concentration from 0.1% to 0.7%. Under both conditions of brine and distilled water, G' showed a corresponding relationship. At polymer concentration of 0.35%, the G' curve got its peak (**Fig. 27**), however, from observation we knew that the best performance of elasticity was at the concentration of 0.7% (**Fig. 28**).

Combined with both results, to get an elastic and strong gel with relative low cost, the range of polymer concentration should be 0.5% to 0.7%.

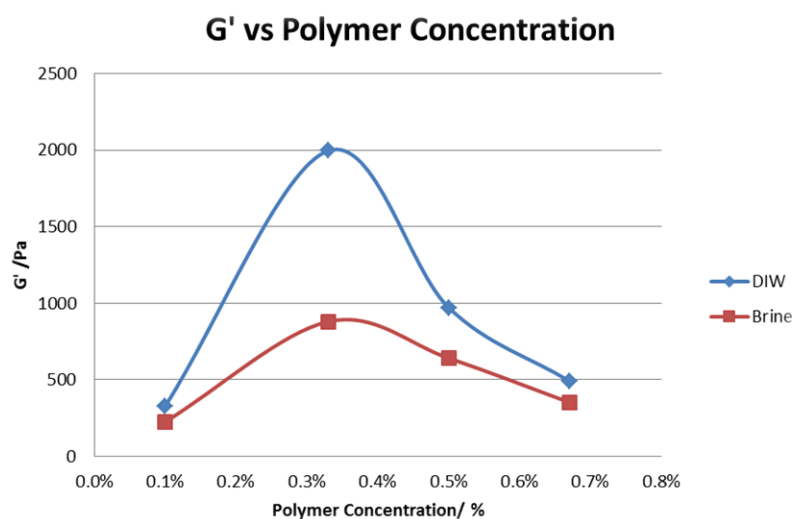


Figure 27 -- G' as a function of polymer concentration.

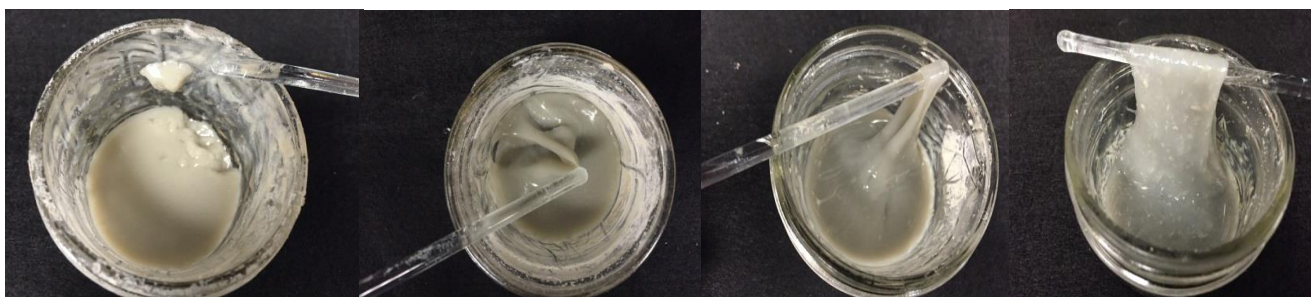


Figure 28 -- Viscoelasticity measured by observation -2.

Impacting Factors on Recrosslinking Reaction

Recrosslinking Time The experiments were designed to find the gelation time of the recrosslinking reaction under different temperature. The degraded gel was prepared at a concentration of 0.65%, and the clay was at 3.5%. The based fluids used brine and distilled water, and the temperatures of gelation were at 40 °C, 60 °C, and 80 °C. Sydansk code was referenced here to define the gel state. Four states of the gel were chosen to describe the gel forming at each stage (**Fig. 29**). The gelation time was recorded based on observation of the gel phase and the result were shown as follows (**Fig. 30**).

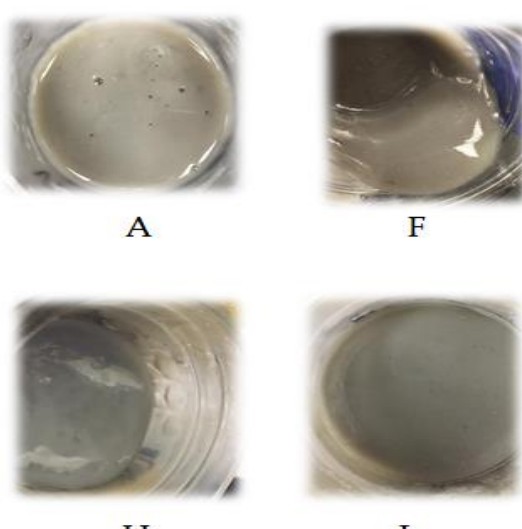
Gel State	Description	Recrosslinking Stage	
A	No detectable gel formed. Gel appears to have some viscosity (fluidity) as original polymer solution and no gel is visually detectable.	 <div style="display: flex; justify-content: space-around; margin-top: 10px;"> A F </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> H I </div>	
F	Highly deformable non-flowing gel. Gel does not flow to bottle cap upon inversion (gel flows to just short of reaching bottle cap)		
H	Slightly deformable non-flowing gel. Only gel surface deforms slightly during inversion		
I	Rigid gel. There is no gel-surface deformation upon inversion		

Figure 29 -- Gelation stage.

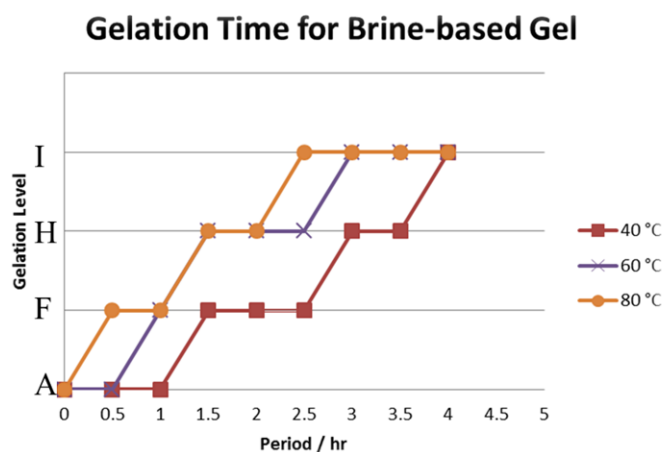
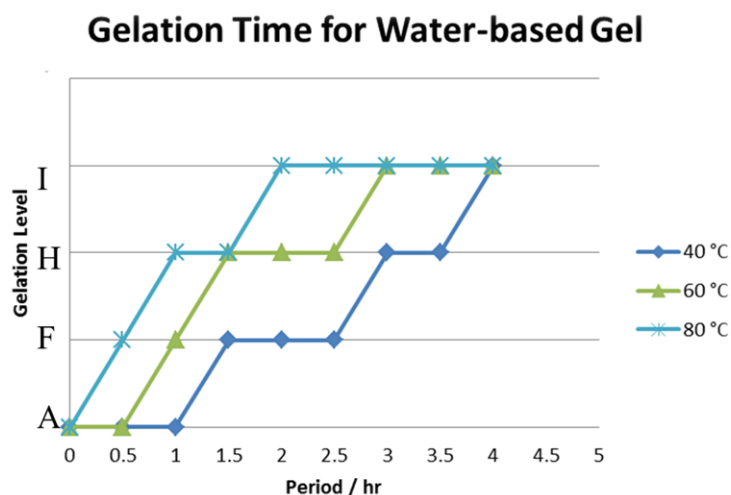


Figure 30 -- Gelation time by observation.

Temperature Effect Not only influences on reaction time, temperature also has an impact on gel strength. Synthesized of polymer at 0.65% with 3.5% of clay, the samples were put into three ovens at 40 °C, 60 °C, and 80 °C specifically. Increase in temperature will lead to poor performance of gel prepared with distilled water while vice versa for samples synthesized with brine. The result shown in **Fig. 31**.

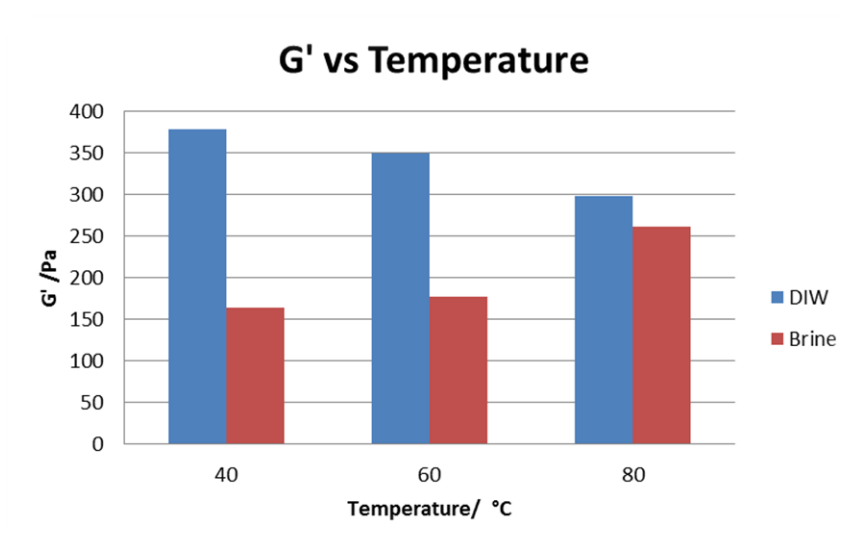


Figure 31 -- Temperature effect on G'.

Brine Influence on Gel Viscoelasticity Since G' is affected by gel made of brine, viscoelasticity should be influenced as well. From the picture **Figs. 32** and **33** shown, the gel performed better using distilled water although the brine-made gel demonstrated elastic property as well by observations.



Figure 32 -- Gel prepared with distilled water.



Figure 33 -- Gel prepared with brine.

Thermostability of Recrosslinked Gel After gelation completed, the gel prepared with brine had been cut out as a small cube with 2 cm length. Then, the piece was put into a testing tube with 1% NaCl at 60 °C. From the **Fig. 34** Shown, the gel swelled about 2.5 times in first 3 days and stayed stable afterwards up to 279 days.

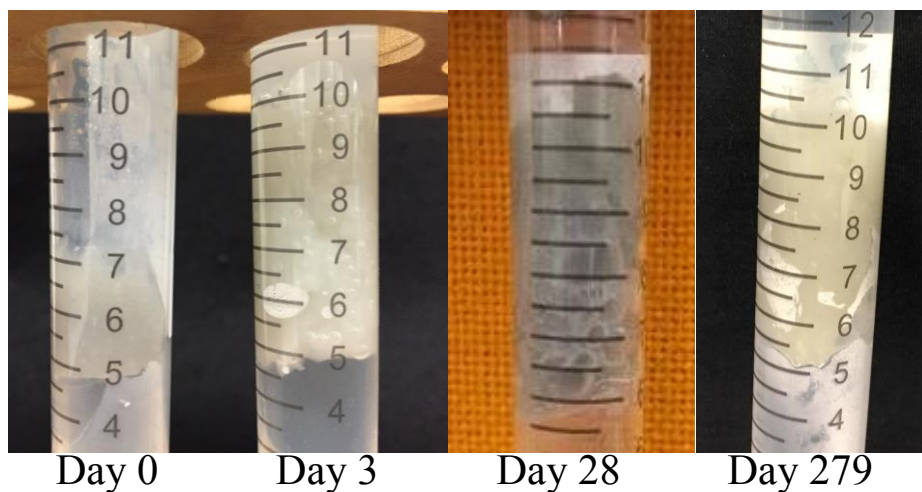


Figure 34 -- Thermostability under the temperature of 60 °C.

Conclusions

In this study, degraded gel had been used instead of industrial polymer in order to lowering the cost. The gel before degradation was synthesized at low temperature for longer chain length of the polymer. After then, the degraded gel was diluted in the brine and distilled water at a concentration from 0.1% to 1%. The clay (bentonite) in brine was pretreated by physical blending and ultrasonic to achieve homogenous state of the solution. CrAc_3 was chosen as the crosslinker in the reaction, while clay acted as a viscosifier of the gelant as well as reinforcing agent of gel strength. The viscosity of the gelant was proved to be closed to HPAM's. Clay can increase the viscosity of gelant and viscoelasticity of the gel.

At low polymer concentration, good viscoelasticity was shown both for DIW and Brine systems; at same polymer concentration, G' increased as clay concentration increased. The gelation time of recrosslinked gel with brine and distilled water is between 2 to 4 hours. Higher in temperature will lead to faster in gelation. The recrosslinked gel was tested stable for 279 days by observations. The cost of the material were competitive.

In the future, a new method to evaluate viscoelasticity should be developed since G' cannot reflect the gel strength and characteristic completely. More optimized experiments can be conducted to achieve stronger gel, even without crosslinker.

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SECTION

2. CONCLUSIONS

In this study, two different oilfield chemicals have been evaluated in a purpose of improving oil recovery. In the first research, a new polymeric fracturing fluid has been tested successfully remaining viscous under high shear rate of 511 s^{-1} . More results shown in the experiments indicate:

- a) The viscosity increases to 9 times after addition of crosslinker
- b) Increase in time leads to shear thinning behavior of the crosslinked polymer
- c) The best ratio of <polymer : crosslinker> varies with polymer concentration
- d) After crosslinking, the viscosity does not change in 10 min
- e) Polymer concentration at 2 gpt is good to crosslink, however, it does not tolerate high shear unless the concentration is greater than 3 gpt.
- f) The increase in temperature leads to viscosity reduction of the crosslinked polymer.
- g) ZrAc₄ is favorable for neutral condition.
- h) The decrease in shear rate leads to a higher viscosity. The viscosity increases up to 3 times at low shear rate (170 s^{-1}).

In the second research, a novel gel system has been developed by reusing the degraded preformed particle gel to recrosslinked with Cr and clay. The gels were tested to be elastic, thermo-stable and well functional under laboratory experiments. Evaluation shows:

- a) Clay will increase the viscosity of gelant and the strength of gel
- b) At low polymer concentration, good viscoelasticity is shown by observation; at same polymer concentration, G' increases as clay concentration increases

- c) The gelation time is between 2.5 to 4 hrs
- d) The recrosslinked gel swelled about 2.5 times in first 3 days, and stayed stable afterwards up to 279 days.

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She had interdisciplinary research interests in the areas of oilfield chemicals for conformance control and hydraulic fracturing fluids. More specifically, her research included the in-situ gel and highly viscous polymeric fracturing fluids.