MINIMIZING WATER PRODUCTION FROM UNCONVENTIONAL GAS WELLS USING A NOVEL ENVIRONMENTALLY BENIGN POLYMER GEL SYSTEM

A Thesis

by

KUSH GAKHAR

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Petroleum Engineering

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Approved by:

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	Jerome Schubert
Committee Member,	Yuefeng Sun
Head of Department,	Stephen Holditch

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ABSTRACT

Minimizing Water Production from Unconventional Gas Wells Using a Novel
Environmentally Benign Polymer Gel System. (December 2011)

Kush Gakhar, B.Tech., University School of Chemical Technology, GGSIPU

Co-Chairs of Advisory Committee: Dr. Robert Lane
Dr. Jerome Schubert

Excess water production is a major economic and environmental problem for the oil and gas industry. The cost of processing excess water runs into billions of dollars. Polymer gel technology has been successfully used in controlling water influx without damaging hydrocarbon production in conventional naturally fractured or hydraulically fractured reservoirs. However, there has been no systematic investigation on effectiveness and placement conditions of polymer gels for shutting off water flow from fractures with narrow apertures in shale and tight gas reservoirs. The existing polymer gels, like those based on Chromium(III) Acetate, as a crosslinker will exert very high extrusion pressure to effectively penetrate the narrow aperture fractures present in shale and tight gas reservoirs. This gives rise to a need for a new polymer gel system that can be used for selectively shutting off water flow from narrow aperture fractures in shale and tight gas reservoirs. The new gel system will have a longer gelation time than the existing polymer gels; this ensures minimum crosslinking of the gel by the time it reaches bottom hole. The gelant solution will be pumped at low pressure so that, it penetrates only pre-existing fractures in the formation with ease.

This study for the first time focuses on developing an environmentally benign polymer gel system based on high molecular weight HPAM, as a base polymer and a commercial grade PEI as an organic crosslinker. Gel samples of different concentration ratios of the polymer and crosslinker were prepared and classified under Sydansk code of gel strength to find optimum concentration ratios that gave good gels. The gel system was characterized using Brookfield DV-III Ultra Rheometer and Fann-35 Viscometer.

DEDICATION

This thesis is dedicated to my father, Mr. Udesh Gakhar, for always being there for me. It is also dedicated to my mother, Mrs. Pratibha Gakhar, my brothers Shvetabh and Karan, and my girlfriend, Geetika, for their selfless and incomparable love, support and sacrifice.

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I would like to thank my committee co-chairs, Dr. Robert Lane and Dr. Jerome Schubert, for giving me their expert guidance and insightful advice on the subject matter. Dr. Robert Lane's knowledge and experience played an invaluable role in success of this work. I am grateful to him for entrusting me with a great research project and motivating me during testing times. I would like to thank him for giving me the very essential freedom of thought and execution. I am also very thankful to him for providing my research assistantship and also for allowing me visit my family in India periodically over last two years. I believe that I worked with the best teacher and the best boss I could ever have.

I would also like to thank my committee member, Dr. Yuefeng Sun. Thanks also goes to, Dr. David Schechter for letting us use his CT-Scan apparatus, and also to the department facility coordinator, John Maldonado, for his help in fracturing Mancos shale core samples. I would also like to thank my colleague, Ehsaan Ahmed Nasir, for his help in conducting CT-Scan experiments, and Kemira Industries for providing us commercial grade PEI.

I also extend my gratitude to everyone at the Harold Vance Department of Petroleum Engineering, Texas A&M University for providing me a top tier education and an overall enriching experience.

Finally, thanks to all my friends at Texas A&M University for being there for me.

NOMENCLATURE

C	Celsius
Conc.	Concentration
Cr	Chromium
CT	Computed Tomography
cp	Centipoise
Da	Daltons
F	Fahrenheit
g	Grams
HPAM	Partially Hydrolyzed Polyacrylamide
ID	Internal Diameter
kj	Kilo Joules
l	Liters
L – R	Left to Right
m	Meters
N	Normal
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
Pa	Pascal
PAM	Polyacrylamide
PEI	Polyethyleneimine
ppm	Parts Per Million

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Water Shutoff Using Polymer Gel Technology

Excess water production is a major economic and an environmental problem faced by oil and gas industry. It can lead to reduction in well productivity, increasing in operating costs and premature abandonment of the well. Further, there is an additional cost associated with separation, treatment and reinjection of the excess water (Al-Muntasheri et al., 2006). It can also lead to problems such as scaling, corrosion and requirement of an artificial lift. The cost of processing excess water runs into billions of dollars. Well testing and various logging technologies can be used for identifying water producing zones in the formation.

Production of unwanted excess water from oil and gas fields can be minimized by many mechanical and chemical water control techniques. One of the most widely used processes for water shutoff is based on the use of polymer gel technology (Simjoo et al., 2009). This technology has proved to be very successful in controlling water influx without damaging hydrocarbon production in conventional fractured or faulted reservoirs (Lane and Seright, 2000).

This thesis follows the style of *SPE Journal.*

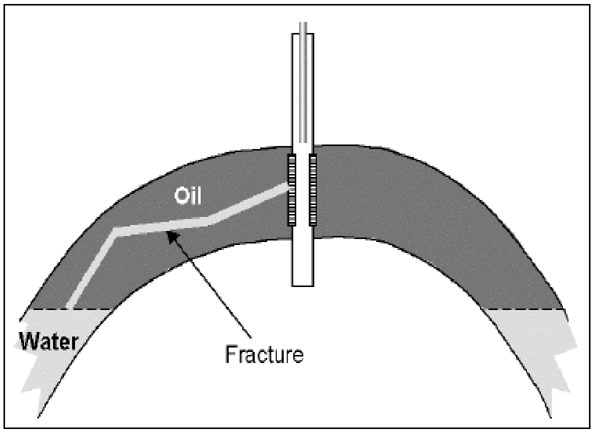


Fig. 1 - Fracture Connecting Aquifer to a Production Well (Mennella et al., 1999)

Fig. 1 illustrates a water producing fracture connecting an aquifer to a hydrocarbon producing well. The mechanism for selective placement of water shutoff polymer gels is similar to selective extrusion of a hydraulic fracturing gel into a created fracture. In both cases, extrusion pressure for the gel to enter matrix is greater than the formation breakdown pressure. Both the gels loose fluid to matrix forming a dehydrated gel cake at the fracture and formation interface. However, the hydraulic fracture gel is designed to be fully cosslinked by the time it reaches bottom hole, unlike the fracture penetrating water shutoff gel which is only partially crosslinked. The two gel systems also differ in the injection pressures, while the hydraulic fracturing gels are placed at high pressures enabling them to create new fractures in the formation, the water shutoff polymer gels are injected at low pressures so as to penetrate only into the existing fractures and form minimal dehydrated gel cake. The water shutoff gels are also designed to be stable for months to years at reservoir conditions on the other hand the hydraulic fracturing gels are designed to be easily removable with the help of breakers.

Polymer gels can be placed into water producing zones by ‘Bullheading’ (Fig. 2) or ‘Zonal Isolation’ (Fig. 3) techniques (Jaripatke and Dalrymple, 2010).

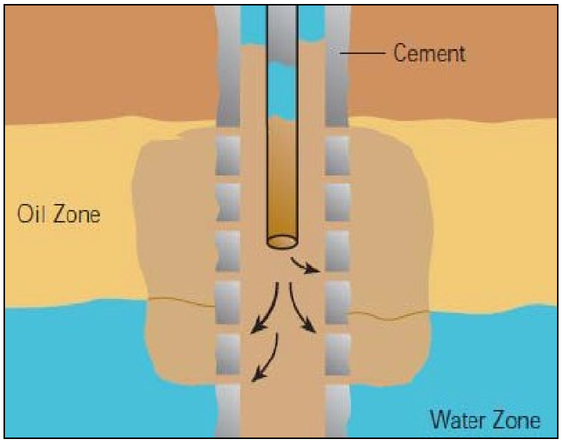


Fig. 2 - Bullhead Placement (Jaripatke and Dalrymple, 2010)

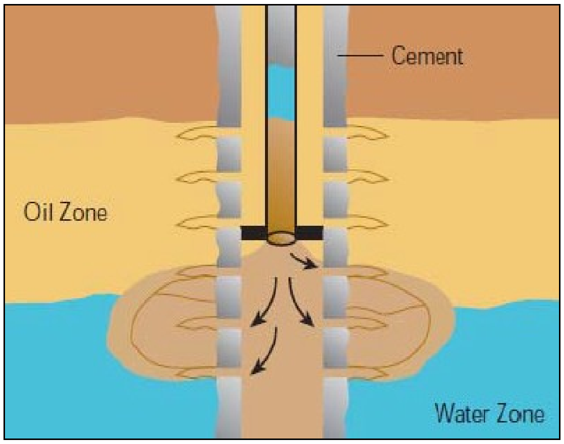


Fig. 3 - Zonal Isolation Placement (Jaripatke and Dalrymple, 2010)

In ‘Bullhead Placement’ which is also known as full-bore placement (Lane and Sanders, 1995), water shutoff gel is pumped down hole without isolating the water producing zones. It is the most economical means of gel placement, but can sometimes lead to sealing of both water and hydrocarbon producing zones. On the contrary in 'Zonal Isolation' technique, mechanical packers or bridge plugs are used to isolate the target zones. Water shutoff gel is then pumped into water producing zone through certain section of perforations or openhole sections. This placement technique minimizes water production without effecting hydrocarbon production significantly.

Ideal placement location for a water shutoff gel is far from the wellbore (Fig. 4), this allows the fracture to still produce hydrocarbons from the region near the wellbore (Seright, 1995). If the excess water is being produced through vertical fractures connected to an underlying water source, then gravity forces can be exploited to ideally place the gel. Gravity forces the gel into fractures connecting the underlying aquifer to well, thereby plugging the water producing zone.

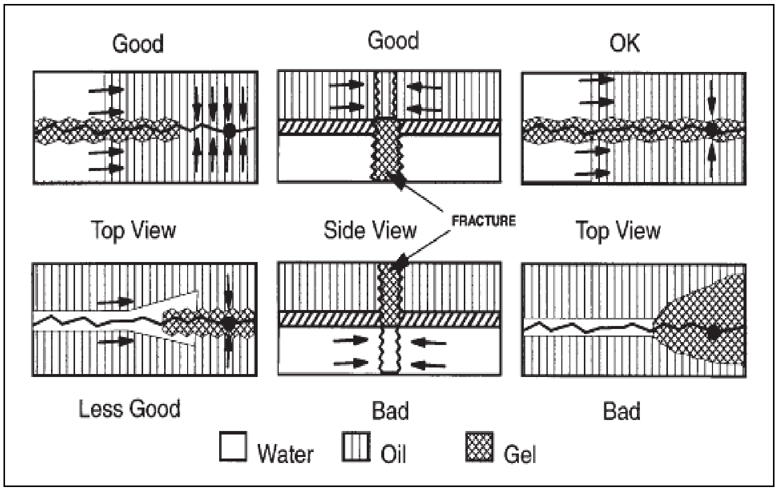


Fig. 4 - Ideal Placement Locations for Gels in Fractures (Seright, 1997)

It has been found from previous studies that hydrocarbons, unlike water can make their way through the polymer gel placed in water producing fractures (Mennella et al., 1999). This has been explained as a consequence of shrinkage of polymer gels which dehydrate on coming in contact with hydrocarbons, making a way for them to pass through. Water on other hand, rehydrates the polymer gel causing it to swell back leading to blocking its pathway (Fig. 5). This phenomenon of reducing water production without significantly effecting hydrocarbon production is also known as 'Disproportionate Permeability Reduction' (DPR). It has also been found that it is much more difficult to shutoff gas flow than either liquid hydrocarbon or water flow (Sanders et al., 1994).

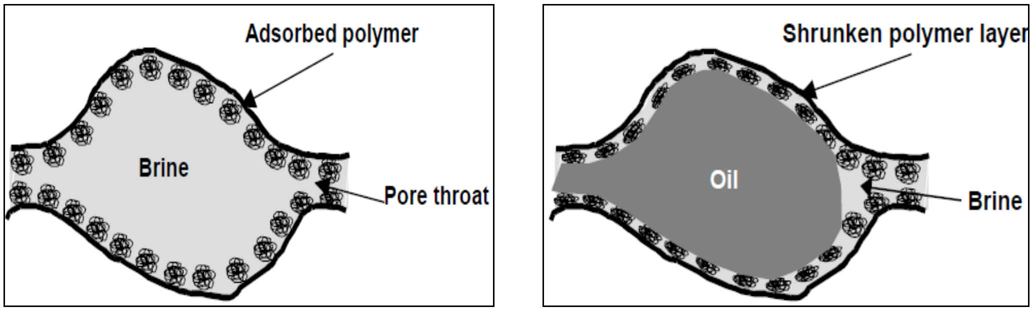


Fig. 5 - Disproportionate Permeability Reduction (Mennella et. al 1999)

1.2 Inorganically Crosslinked Polymer Gels

A water shutoff polymer gel is generally composed of a water soluble acrylamide based polymer and a crosslinker. The crosslinker used can be organic or inorganic. Chromium(III) crossslinked PAM is the most commonly used inorganic water shutoff polymer gel. Lower cost and easy availability of acrylamide polymer and chromium(III) crosslinker makes this gel system a cost effective solution for water shutoff applications. The reaction between the polymer and Chromium(III) crosslinker

(Fig. 6) occurs by complexation of Cr(III) oligomers with carboxylate group on PAM (Reddy et al., 2003). According to previous studies (Al-Muntasheri et.al. 2006) inorganically crosslinked gels like those based on Chromium(III) crosslinker, result from ionic bond formation between positively charged cations like Cr^{+3} and negatively charged carboxylate group on the base polymer.

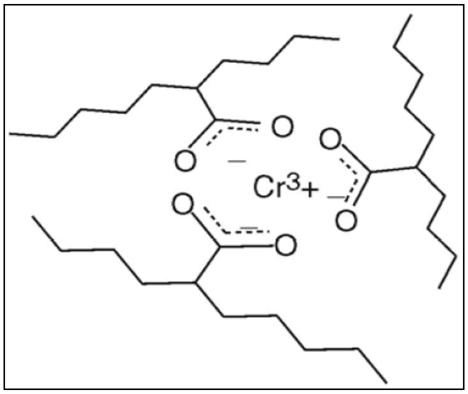


Fig. 6 - Complexation of Carboxylate Group by Chromium Species (Reddy et. al 2002)

Such inorganically crosslinked polymer gels, because of weak ionic bonding are known to be unstable at high temperatures (Al-Muntasheri et.al 2007). However, these gels have been successfully investigated at temperatures up to 260 °F and high salinity conditions for near wellbore water shutoff treatments (Sydansk, 1988). It has also been found (Reddy et al., 2003) that at higher pH crosslinking reaction between Chromium(III) and carboxylate group on the base polymer leads to formation of an insoluble chromium precipitate. The Chromium(III) crosslinked polymer gels are also known to form weak gels at low polymer concentrations and exhibit 'Syneresis', which is expulsion of water due to excessive crosslinking at higher crosslinker concentration (Sydansk, SPE Advanced Technology Series, Vol. 1, No.1). There are also concerns associated with injection of Chromium(III) based polymer gels because of its short gelation time. However, this problem is believed to have been solved by the use of low molecular weight polyacrylamide as a base polymer (Sydansk, 1988). Other than operational limitations, inorganically crosslinked polymer gels like those based on Chromium crosslinker, because of their carcinogenic nature are also a health and an environmental concern.

1.3 Organically Crosslinked Polymer Gels

Polymer gels based on low to medium molecular weight PAM (Fig. 7), HPAM (Fig. 8) or copolymers of PAM and PAtBA as base polymers and research grade PEI, as an organic crosslinker have been investigated in previous studies for water shutoff application (Tapia et al., 2010).

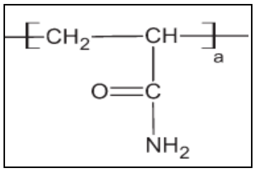


Fig. 7 - PAM (Al-Muntasheri et al., 2007)

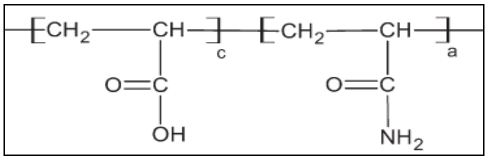


Fig. 8 - HPAM (Al-Muntasheri et al., 2007)

PEI has been found to be a less toxic crosslinker and has been approved by USFDA for food contact (Reddy et.al. 2002). According to previous literature the crosslinking reaction between PAM and PEI can be explained as a transamidation reaction (Fig. 9). It is a nucleophilic substitution reaction in which nucleophilic imine nitrogen on PEI replaces the amide group on PAM.

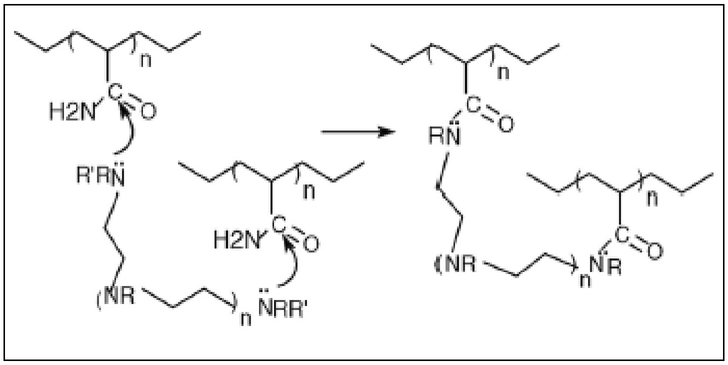


Fig. 9 - Transamidation Reaction between PAM and PEI (Reddy et al., 2003)

Reaction between PAM and PEI leads to formation of a covalent bond between the two this provides gel system the stability to withstand high temperature conditions (Al-Muntasheri et al., 2007). In the previous studies organic polymer gels based on PAtBA and PEI have been found to be stable at temperatures around 160 °C (Al-Muntasheri et al., 2006). Gel based on PAM and PEI has also been investigated at temperatures as high as 140 °C (Al-Muntasheri et al., 2006). The PAM and PEI based water shutoff gels investigated in previous studies are generally based on low molecular weight PAM, with a molecular weight of around 250,000 – 500,000 Da and research grade PEI with a molecular weight of around 70,000 Da (Al-Muntasheri et al., 2007).

1.4 Laboratory Evaluation of Water Shutoff Polymer Gels

Water shutoff polymer gels are prepared by adding calculated amount of polymer like PAM to water while stirring the solution continuously. Stirring process is continued till the polymer is completely hydrated and a clear polymer solution is obtained. Appropriate amount of crosslinker is then added in a drop wise manner, while the polymer solution is being stirred (Al-Muntasheri et al., 2008). Stirring is carried out for a few minutes before the gelant solution is ready to be poured into a storage container.

Rheological study of organic and inorganic polymer gels has been successfully carried out in the past. These studies mainly concentrated on measuring gelation kinetics, gel strength and effectiveness of the polymer gels in plugging the artificially induced fractures in sandstone and carbonate core samples. Organically crosslinked polymer gels have been tested for the effects of polymer and crosslinker concentration, salinity and pH on gelation time using steady shear viscometers (Al-Muntasheri et.al. 2006). Gelation point is identified as the point of inflection or sudden rise in viscosity on viscosity versus time curve (Fig. 10).

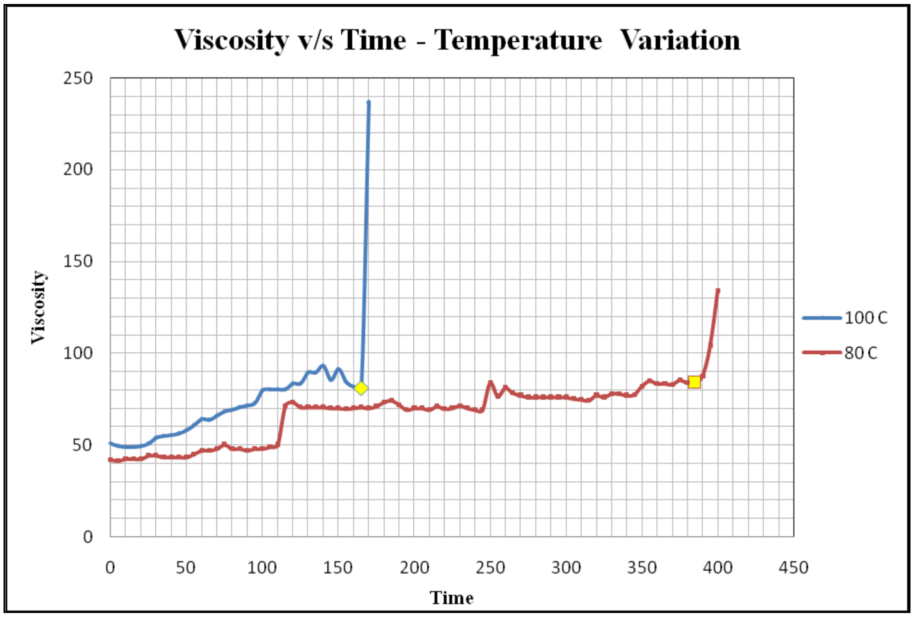


Fig. 10 - Gelation Point Highlighted on Viscosity v/s Time Curve

Such experiments are usually carried out using steady shear viscometers at constant shear rate and temperature. Accurate estimation of gelation time is important to assess available pumping time for water shutoff treatment. Underestimation of the gelation time can lead to pumping of completely crosslinked polymer gels which might damage the formation. Overestimation of gelation time can lead to pumping of insufficiently crosslinked gels, which might lead to failure of the treatment (Al-Muntasheri et al., 2008).

It has been found from the previous studies (Nasr-El-Din et al., 2006) on PAM and PEI based gels that, the gelation time decreases with increasing temperature. This has been explained on the basis of Arrhenius type equation:

$$GT = M \exp(\frac{Ea}{RT})$$

In the above equation GT stands for gelation time, M for frequency factor, Ea for activation energy, R is universal gas constant, and T is absolute temperature. A similar decrease in gelation time is observed with increasing concentration of the polymer like PAM and/ or crosslinker like PEI. This can be explained using reaction rate equation:

$$Rate = k\ (A)^{\alpha}\ (B)^{\beta}$$

k is the rate constant, A is the concentration of polymer, B is the concentration of crosslinker, and α and β are constants.

Polymer gels based on PAM and PEI have also been found to be sensitive to pH (Nasr-El-Din et al., 2008). Gelation time was found to decrease with increasing pH. Increase in pH leads to increased hydrolysis of PAM (Fig. 11), which forms negatively charged carboxylate ions (COO^-). These negatively charged ions repel each other leading to extension of polymer chain network. The extended polymer chain provides more accessible crosslinking sites on the polymer, leading to faster gelation.

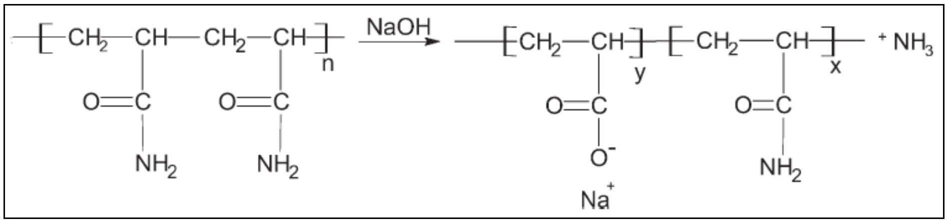


Fig. 11 - Hydrolysis of PAM (Zitha et al., 2008)

Presence of salts like sodium chloride (NaCl) in the gelant solution is known to delay the gelation process (Nasr-El-Din et al., 2008). This phenomenon might be caused by shielding of negatively charged carboxylate ions formed on hydrolysis of PAM, by positively charged sodium ions (Na^+). This might lead to shrinkage of the polymer chain network leading to increased gelation time.

Gel strength of water shutoff polymer gels has also been studied in the past using a semi quantitative measurement technique also known as ‘Bottle Testing’ developed by R. D. Sydansk (Sydansk, 1988) listed in Table 1 below. It involves, putting the gel sample in a bottle such that it occupies half of the volume. The bottle is then inverted and on the basis of flow characteristics of the gel sample under gravitational force, it is assigned a gel code depicted by a letter. There are gel strength codes for samples that are highly flowing to the samples that form rigid ringing gels. This technique is used to classify gels in a fast and inexpensive manner. It relies purely on visual observation and gives a semi quantitative measurement of gel strength and gelation rate. It is also a convenient way to determine gel stability over long periods of time.

Table 1 – Sydansk Gel Code (Sydansk, 1993)

Sydansk Code	Description
A	No Detectable Gel Formed
B	Highly Flowing Gel
C	Flowing Gel
D	Moderately Flowing Gel
E	Barely Flowing Gel
F	Highly Deformable Non Flowing Gel
G	Moderately Deformable Non Flowing Gel
H	Slightly Deformable Non Flowing Gel
I	Rigid Gel
J	Ringing Rigid Gel

2. DEVELOPING A NEW HPAM/ PEI POLYMER GEL SYSTEM

2.1 Need for a New HPAM/ PEI Gel System

Polymer gel technology has been successfully used for controlling water influx in conventional fractured reservoirs. It has been found from previous studies that about fifteen percent of gas wells in Barnett Shale produce greater volume water than that has been injected during drilling, completion, stimulation or any other treatment (Awoleke and Lane, 2010). Excess water production has also been found from horizontal wells drilled in locations where there is a barrier between the production interval and the underlying Ellenberger aquifer. Hydraulic fractures in shale and tight gas reservoirs that are often connected to open natural fractures are of narrower apertures than hydraulic or natural fractures in conventional reservoirs. There has been no systematic investigation on effectiveness of the polymer gels in shutting off water flow from narrow aperture fractures present in shale and tight gas reservoirs. This study for the first time focuses on developing an environmentally benign polymer gel system that is capable of extruding into the narrow aperture fractures present in shale and tight gas reservoir.

The new gel system is based on high molecular weight Partially Hydrolyzed Polyacrylamide (HPAM) as a base polymer and a low cost, commercial grade Polyetheyleneimine (PEI) as an organic crosslinker. Polymer gels based on HPAM and a low molecular weight research grade PEI have also been tested in this study. The new gel system has been designed to exert low extrusion pressure while penetrating fractures with narrow aperture in unconventional formations. It also has a longer gelation time and provides a more rigid final product than the benchmark water shutoff gels based on low to medium molecular weight HPAM and chromium(III) acetate of comparable concentrations. The new system with longer working time offers greater ease of placement in narrow aperture fractures.

2.2 Chemicals and Equipments

2.2.1 Base Polymers – HPAM and PAM

Polymers gels that have been investigated in this study are based on high molecular weight HPAM. It had a molecular weight of around 2 to 5 million Da. HPAM is an organic polymer and is thus biodegradable. It is also actively used as potable water clarifier.

High molecular weight non-ionic PAM, Flopam - FA 920 by SNF Floerger has also been evaluated as a base polymer. The PAM used has a bulk density of 0.75 and an approximate Brookfield viscosity of 20 cp at a concentration of 2.5 g/ l. Highly pure, research grade PAM from Sigma Aldrich sold under the product code 92560 was also tested with commercial grade PEI. The research grade PAM was in a powder form with a density of 0.750 g/ cm^3. It had a viscosity of 2 MPas in 0.1 % wt. water solution and had a high cost of $ 63/ 10 g.

2.2.2 Crosslinkers – PEI and Chromium Acetate

Research grade and commercial grade PEI have been investigated as organic crosslinkers in the new water shutoff polymer gel system. Low molecular weight, research grade PEI sold under a product code of 408700 by Sigma Aldrich, was used as an organic crosslinker. It finds application in detergents, adhesives, water treatment, dyes, cosmetics, printing inks, paper industry, lamination primers, fixative agents, flocculants, cationic dispersants, stability enhancers, surface activators, chelating agents and scavengers for aldehydes and oxides. Properties of the research grade PEI have been listed in the Table 2 below.

Table 2 – Properties of Research Grade PEI

Properties of Research Grade PEI	
Physical Form	Liquid (Branched Polymer)
Molecular Weight	Average Mw ~ 2000 by LS
Active Weight Content	50 wt.%
Density	1.08 g/ ml at 25°C
pH	12
Cost	$ 51/ 100 ml

The commercial grade PEI sold under the name of Retaminol-2S was provided by Kemira. It is a low cost, technical grade commercial product. The product is widely used in paper and pulp industry and has been approved by USFDA for food contact. The product has an active weight content of 25 wt. %. It has certain content of proprietary material, concentration and composition of which has been kept as a trade secret. Properties of the commercial grade PEI are listed in the Table 3 below.

Table 3 – Properties of Commercial Grade PEI

Properties of Commercial Grade PEI	
Physical Form	Liquid
Molecular Weight	500,000 to 120,000 Da
Color	Yellow to Brown
Odor	Slight
pH	7 - 8 at 50g/ l
Freezing Point	-5 °C
Boiling Point	100 °C (212 °F) at 1,013 hPa
Specific Gravity	1.06
Viscosity, Dynamic	150 - 350 mPa.s at 23°C (73.4 °F)
Cost	$ 2/ lb

Performance of gelant samples based on organic crosslinker like PEI was compared to gelant samples based on Chromium(III) Acetate as an inorganic crosslinker. Properties of Chromium(III) Acetate used are listed in the Table 4 below.

Table 4 – Properties of Chromium(III) Acetate Crosslinker

Properties of Chromium(III) Acetate	
Physical Form	Powder
Molecular Weight (Da)	603.32
Density	0.5 mg/ m^3
Active Weight Content (%)	100
Cost	~ $ 40/ 100 g

Magnetic stirrers were used to stir the polymer and crosslinker solutions. An Orion Star LogR pH (Fig. 12) meter was used to measure the pH of gelant solutions. The meter is capable of measurement in range of -2 to 19.99 with an accuracy of ± 0.002. It can operate at temperatures ranging from 0 °C to 100 °C.

Fig. 12 - Orion Star LogR pH Meter (thermoscientific.com)

2.3 Experimental Procedure – Preparing the New HPAM/ PEI Gel

The new environmentally benign polymer gel is prepared using the steps listed below.

Step 1. Calculated amount of base polymer HPAM or PAM (Fig. 13) was added to fresh water or saline water (0.1 wt. % NaCl solution). In this study the gel samples based on research grade PEI, prepared in both fresh water and saline water have been characterized. Gel samples based on commercial grade PEI were prepared only in saline water.

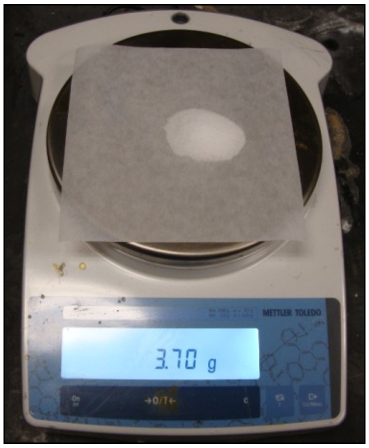


Fig. 13 - Mettler Toledo PB-3002L Weigh Balance

Polymer was added very carefully to the solution while it was being stirred (Fig. 14), such that there was no ‘fisheye’ (Lane, 1998) formation. To avoid this, polymer was added slowly into the vortex, which was formed while stirring the solution. Stirring process was continued till a clear polymer solution was obtained (Fig. 15). The stirring time varied with the concentration of polymer and was usually around 30 to 60 minutes for a 100 ml sample.

Fig. 14 - Careful Addition of HPAM to Water

Fig. 15 - Clear Polymer Solution

Step 2. Once a clear polymer solution had been prepared, a calculated amount of crosslinker, PEI (research or commercial grade) or Chromium(III) Acetate was added in a drop wise manner, while the polymer solution was being stirred (Fig. 16). The stirring process was continued for a few minutes after adding the crosslinker to obtain the gelant solution.

Fig. 16 - Addition of PEI

Step 3. pH of the gelant solution was then measured using Orion Star LogR pH meter (Fig. 17).

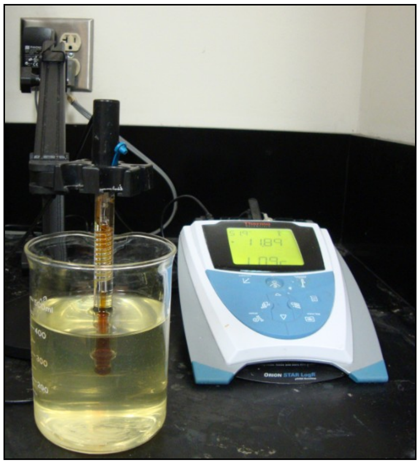


Fig. 17 - pH Measurement

Gelant solutions prepared using the research grade PEI were found to have a pH of around 10. Perfectly clear gelant solutions (Fig. 18) of different concentrations were prepared and were found to be stable at both room temperature and at high temperatures of around 200 °F. On the other hand gelant solutions prepared using commercial grade PEI, were found to have a pH of around 7. These gelant solutions were cloudy in appearance (Fig. 19) and were also found to be unstable on being stored at room temperature and at 200 °F.

Fig. 18 - HPAM/ PEI (Research Grade) Gelant Solution. Clear in Appearance

Fig. 19 - HPAM/ PEI (Commercial Grade) Gelant Solution. Cloudy in Appearance

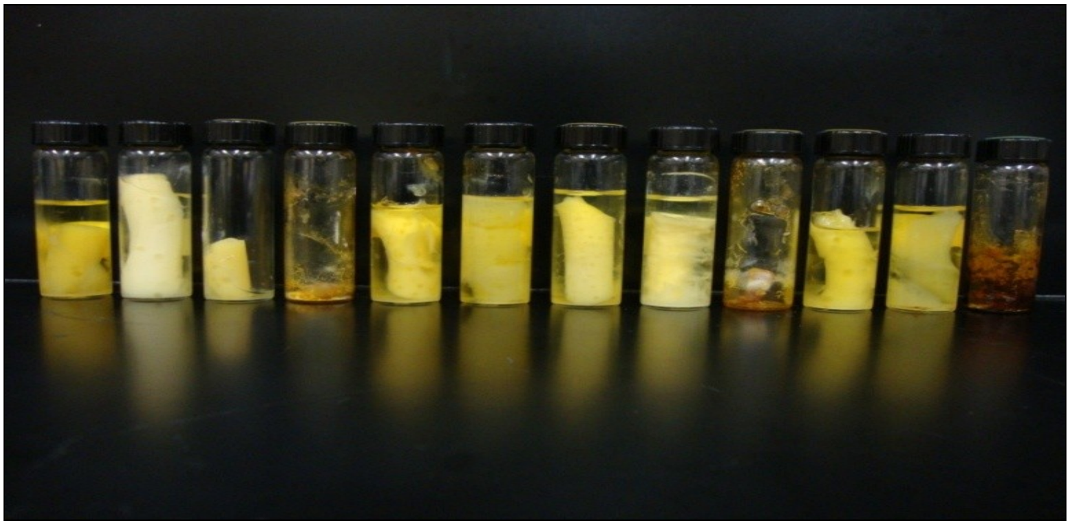


Fig. 20 - HPAM/ PEI (Commercial Grade) Gel Samples – Poor Results at Low pH

After a series of failed experiments (Fig. 20), it was found that the gelant solution became perfectly clear when the pH of the HPAM/ PEI (Commercial Grade) gelant solution was raised to around 10 using 1 N NaOH solution (Fig. 21).

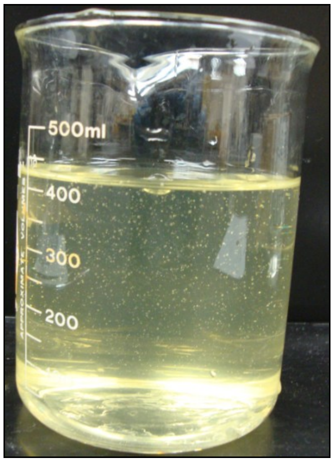


Fig. 21 - HPAM/ PEI Gelant Solution, Clear in Appearance at High pH

Step 4. The gelant solutions were then transferred to vials, which were kept in an oven maintained at 200 °F, for testing its stability at high temperature (Fig. 22).

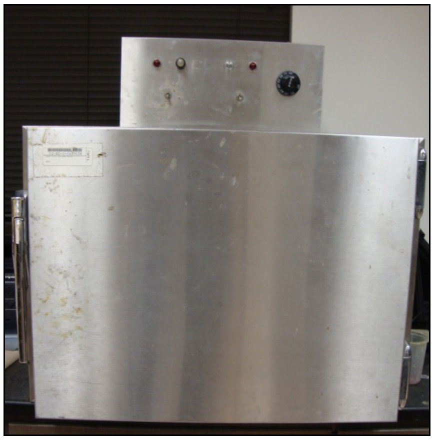


Fig. 22 - Oven Used to Test Gel Samples at 200 °F

The HPAM/ PEI (Commercial Grade) gel samples with a pH of 10 or above were found to be more stable at room temperature and at 200 °F (Fig. 23), than the samples with the original pH of around 7 to 8 when tested over a longer period of time.

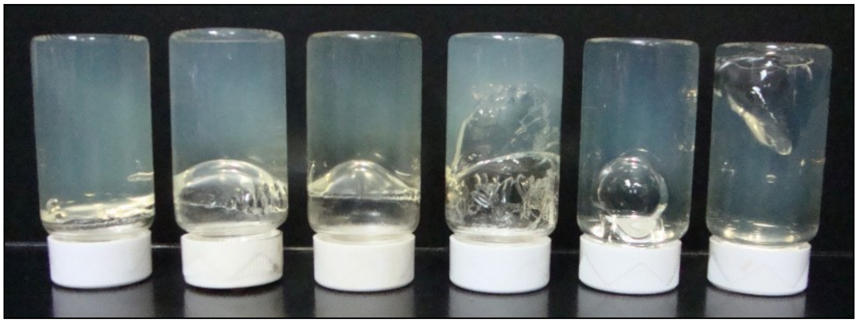


Fig. 23 - HPAM/ PEI (Commercial Grade) Gel Samples, Good Results at High pH

3. OPTIMUM CONCENTRATION DETERMINATION

3.1 Optimum Concentration Ratio of HPAM and PEI

A series of experiments were performed using the ‘Bottle Testing’ technique developed by R.D. Sydansk, to determine optimum concentration ratios of HPAM and PEI that formed good gels. It is an inexpensive and easy to use method for determining gelation time and gel strength over a period of time while varying parameters like polymer and crosslinker concentration, temperature, pH and salinity. This method has been found to be convenient for testing long term stability of the gel samples, as it does not require the samples to be removed from the storage container thereby, preventing undue exposure to oxygen which might damage the sample.

Around thirty five gelant samples were prepared using research grade PEI as the crosslinker and HPAM as the base polymer. The concentration of these samples was varied from as low as 3000 ppm of HPAM with 2000 ppm of research grade PEI to as high as 9000 ppm of HPAM with 10,000 ppm of research grade PEI. Gel samples of similar concentrations were also prepared using the commercial grade PEI. These samples were then stored in glass vials with their lids tightly closed to limit exposure of gelant to oxygen. The gelant samples were then placed in an oven at 200 °F for a period of three weeks allowing them to gel. ‘Bottle Testing’ technique was then used to classify these gels on the basis of their strength. Glass vials containing gel samples were inverted and on the basis of the flow characteristic of gel sample observed, it was assigned a letter code as prescribed by Sydansk gel code. Gel samples with wide ranging flow behaviors were prepared, samples that were highly flowing were categorized under the code ‘B’ and those that formed rigid ringing gels were classified under code ‘J’. Each sample was classified under Sydansk gel code for each of the twenty one days to examine their stability at high temperature over a long period of time. Polymer and crosslinker concentration ratio that gave a gel with Sydansk gel code of at least ‘G’ was termed as an optimum concentration ratio. Code ‘G’ according to Sydansk gel code stood for a ‘moderately deformable non flowing gel’.

Gel strengths of the samples prepared using the benchmark Chromium(III) Acetate crosslinker, the concentration of which was as prescribed by ‘Margel’ software from Marathon Oil Co. and with similar concentration of HPAM, as in the HPAM/ PEI gels was determined. It was found from this study, that the new HPAM/ PEI gel system prepared using the commercial grade PEI gave a more stable and stronger gel than those based on research grade PEI or Chromium Acetate crosslinker. It was found from the study that a rigid ringing gel which is classified under the code ‘J’ could be obtained for a minimum concentration of 7000/ 6000 ppm of HPAM/ PEI (Commercial Grade). Gel of same strength with research grade PEI required a minimum concentration of 9000/ 5000 ppm, HPAM/ PEI (Research Grade); and with Chromium(III) Acetate as a crosslinker it was not possible to obtain a rigid ringing gel with similar concentration of HPAM. Performance of different gel samples has been summarized in the tables and figures below.

3.2 Optimum Concentration – HPAM/ PEI (Research Grade)

Gel samples with different concentration (ppm) ratios of HPAM and PEI (research grade) after being kept in an oven at 200 °F for three weeks appeared to be as shown below (Fig. 24 – Fig. 29):

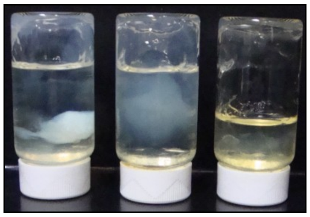


Fig. 24 - Gel Samples with 3000 ppm HPAM and Research Grade PEI. (L - R) - 3000/ 5000, 3000/ 3000, 3000/ 2000

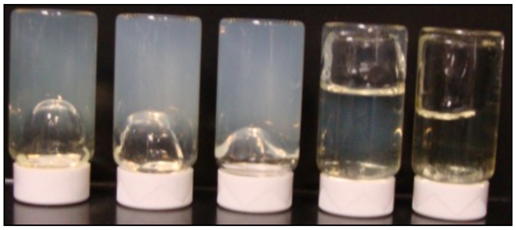


Fig. 25 - Gel Samples with 4000 ppm HPAM and Research Grade PEI. (L - R) - 4000/ 6000, 4000/ 4000, 4000/ 3000, 4000/ 2000, 4000/ 1000

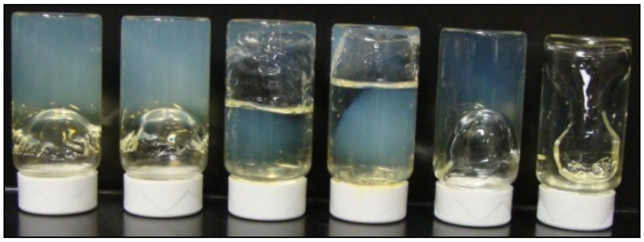


Fig. 26 – Gel Samples with 5000 ppm HPAM and Research Grade PEI. (L - R) - 5000/ 7000, 5000/ 6000, 5000/ 5000, 5000/ 4000, 5000/ 3000, 5000/ 2000

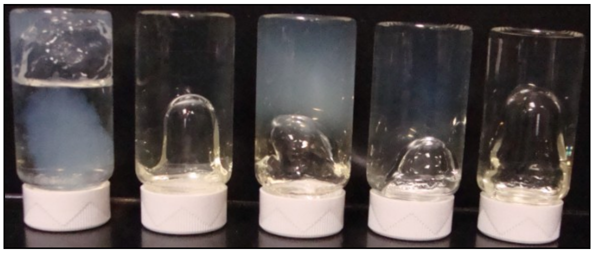


Fig. 27 Gel Samples with 6000 ppm HPAM and Research Grade PEI. (L - R) - 6000/ 8000, 6000/ 6000, 6000/ 5000, 6000/ 4000, 6000/ 3000, 6000/ 2000

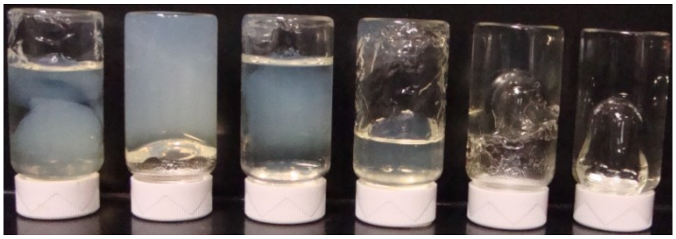


Fig. 28 Gel Samples with 7000 ppm HPAM and Research Grade PEI. (L - R) - 7000/ 9000, 7000/ 7000, 7000/ 6000, 7000/ 5000, 7000/ 4000, 7000/ 3000, 7000/ 2000

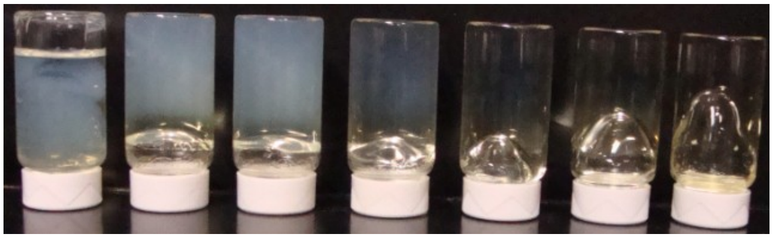


Fig. 29 Gel Samples with 9000 ppm HPAM and Research Grade PEI. (L - R) - 9000/ 9000, 9000/ 7000, 9000/ 6000, 9000/ 5000, 9000/ 4000, 9000/ 3000, 9000/ 2000

Minimum concentration ratio of HPAM and PEI (Research Grade) required to obtain a gel with Sydansk gel code of at least ‘G’, has been highlighted in the Table 5 below.

Table 5 – Results from Bottle Testing HPAM/ PEI (Research Grade) Gels

HPAM/ PEI (Research Grade)									
HPAM/PEI (ppm)	pH	Number of Days – Sydansk Gel Code							
		1	3	6	9	12	15	18	21
3000/ 2000	10.52	B	D	D	D	D	-		
3000/ 3000	10.64	B	D	D	D	D	-		
3000/ 5000	10.75	B	D	D	G	G	G	G	G
4000/ 1000	10.34	B	D	D	D	D	D	D	D
4000/ 2000	10.45	C	G	G	G	G	G	G	-
4000/ 3000	10.59	C	G	G	G	G	G	G	G
4000/ 4000	10.65	D	G	G	G	G	G	G	G
4000/ 6000	10.84	D	G	G	G	G	G	G	G
5000/ 2000	10.48	C	G	G	G	G	G	G	G
5000/ 3000	10.58	C	G	G	G	G	G	G	G
5000/ 4000	10.7	D	G	H	H	H	H	H	-
5000/ 5000	10.61	D	H	H	H	H	H	H	-
5000/ 6000	10.73	D	H	H	H	H	H	H	H
5000/ 7000	10.82	D	H	H	H	H	H	H	H
6000/ 2000	10.39	C	G	G	G	G	G	G	G
6000/ 3000	10.39	C	H	H	H	H	H	H	H
6000/ 4000	10.64	D	H	H	H	H	H	H	H
6000/ 5000	10.62	D	H	H	H	H	H	H	H
6000/ 6000	10.69	D	H	H	I	I	I	I	I
6000/ 8000	10.85	D	H	H	I	I	I	I	-
7000/ 2000	10.45	H	H	H	H	H	H	H	H
7000/ 3000	10.5	H	H	H	H	H	H	H	H
7000/ 4000	10.6	I	I	I	I	I	I	I	I
7000/ 5000	10.65	I	I	I	I	I	I	I	-
7000/ 6000	10.72	I	I	I	I	I	I	I	I
7000/ 7000	10.79	I	I	J	J	J	J	J	J
7000/ 9000	10.83	I	I	J	J	J	J	J	J
9000/ 2000	10.41	H	H	H	H	H	H	H	H
9000/ 3000	10.45	I	I	I	I	I	I	I	I
9000/ 4000	10.56	I	I	I	I	I	I	I	I
9000/ 5000	10.68	I	J	J	J	J	J	J	J
9000/ 6000	10.84	J	J	J	J	J	J	J	J
9000/ 7000	10.76	J	J	J	J	J	J	J	J
9000/ 9000	10.8	J	J	J	J	J	J	J	J
9000/ 10000	10.86	J	J	J	J	J	J	J	J

3.3 Optimum Concentration - HPAM/ PEI (Commercial Grade)

Gel samples with different concentration (ppm) ratios of HPAM and PEI (commercial grade) after being kept in an oven at 200 °F for three weeks appeared to be as shown below (Fig. 30 – Fig. 35):

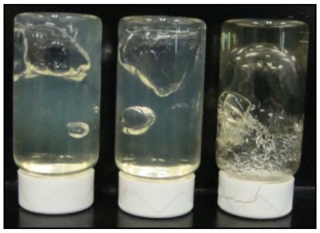


Fig. 30 Gel Samples with 3000 ppm HPAM and Commercial Grade PEI. (L – R) - 3000/ 5000, 3000/ 3000, 3000/ 2000

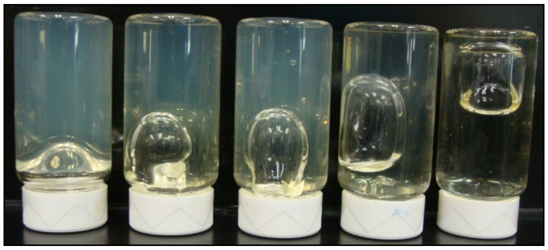


Fig. 31 Gel Samples with 4000 ppm HPAM and Commercial Grade PEI. (L - R) - 4000/ 6000, 4000/ 4000, 4000/ 3000, 4000/ 2000, 4000/ 1000

Fig. 32 Gel Samples with 5000 ppm HPAM and Commercial Grade PEI. (L - R) - 5000/ 7000, 5000/ 6000, 5000/ 5000, 5000/ 4000, 5000/ 3000, 5000/ 2000

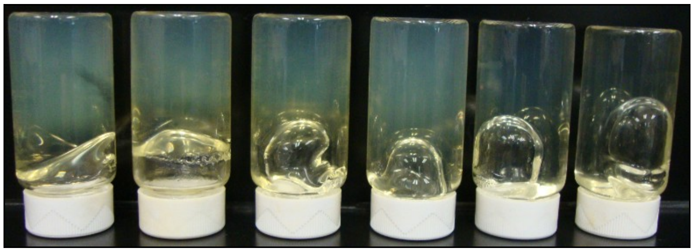


Fig. 33 Gel Samples with 6000 ppm HPAM and Commercial Grade PEI. (L - R) 6000/ 8000, 6000/ 6000, 6000/ 5000, 6000/ 4000, 6000/ 3000, 6000/ 2000

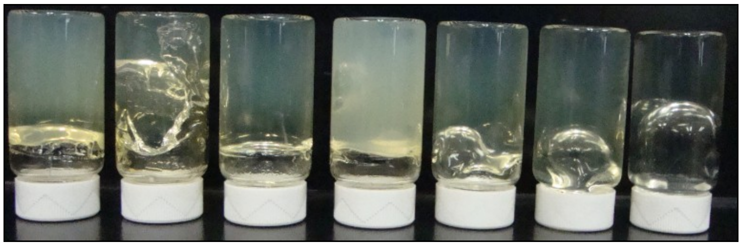


Fig. 34 Gel Samples with 7000 ppm HPAM and Commercial Grade PEI. (L - R) 7000/ 9000, 7000/ 7000, 7000/ 6000, 7000/ 5000, 7000/ 4000, 7000/ 3000, 7000/ 2000

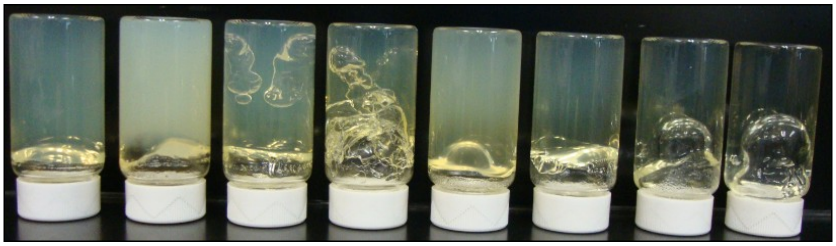


Fig. 35 Gel Samples with 9000 ppm HPAM and Commercial Grade PEI. (L - R) 9000/ 10000, 9000/ 9000, 9000/ 7000, 9000/ 6000, 9000/ 5000, 9000/ 4000, 9000/ 3000, 9000/ 2000

Minimum concentration ratio of HPAM and PEI (Commercial Grade) required to obtain a gel of code ‘G’, has been highlighted in the Table 6 below.

Table 6 – Results from Bottle Testing HPAM/ PEI (Commercial Grade) Gels

HPAM/ PEI (Commercial Grade)									
HPAM/PEI (ppm)	pH	Number of Days – Sydansk Gel Code							
		1	3	6	9	12	15	18	21
3000/ 2000	12.4	E	E	E	E	E	E	G	G
3000/ 3000	12.1	G	G	G	G	G	G	G	G
3000/ 5000	12.2	H	H	H	H	H	H	H	H
4000/ 1000	12.5	C	D	D	D	D	D	D	D
4000/ 2000	12.4	F	G	G	G	G	G	G	G
4000/ 3000	12.0	G	G	G	G	G	G	G	G
4000/ 4000	12.2	H	H	H	H	H	H	H	H
4000/ 6000	12.3	H	I	I	I	I	I	I	I
5000/ 2000	12.4	G	G	G	G	G	G	G	G
5000/ 3000	12.1	H	H	H	H	H	H	H	H
5000/ 4000	11.7	H	H	H	H	H	H	H	H
5000/ 5000	11.5	I	I	I	I	I	I	I	I
5000/ 6000	12.1	I	I	I	I	I	I	I	I
5000/ 7000	11.3	I	I	I	I	I	I	I	I
6000/ 2000	12.4	G	G	G	G	G	G	G	G
6000/ 3000	12.4	H	H	H	H	H	H	H	H
6000/ 4000	12.1	H	H	H	H	H	H	H	H
6000/ 5000	12.3	H	H	H	H	H	H	H	H
6000/ 6000	12.3	I	I	I	I	I	I	I	I
6000/ 8000	12.3	I	I	I	I	I	I	I	I
7000/ 2000	12.6	H	H	H	H	H	H	H	H
7000/ 3000	12.3	H	H	H	H	H	H	H	H
7000/ 4000	12.2	I	I	I	I	I	I	I	I
7000/ 5000	11.5	I	I	I	I	I	I	I	I
7000/ 6000	12.4	I	I	I	I	I	I	I	I
7000/ 7000	12.4	J	J	J	J	J	J	J	J
7000/ 9000	12.2	J	J	J	J	J	J	J	J
9000/ 2000	12.6	H	H	H	H	H	H	H	H
9000/ 3000	12.4	I	I	I	I	I	I	I	I
9000/ 4000	12.2	I	I	I	I	I	I	I	I
9000/ 5000	11.8	I	I	I	I	I	I	I	I
9000/ 6000	12.4	J	J	J	J	J	J	J	J
9000/ 7000	12.2	J	J	J	J	J	J	J	J
9000/ 9000	11.2	J	J	J	J	J	J	J	J
9000/ 10000	12.1	J	J	J	J	J	J	J	J

3.4 Comparison with Chromium(III) Acetate Based Gels

Fig. 36 HPAM/ Chromium(III) Acetate (g) Gel Samples. (L – R) - 0.9/ 0.2, 0.7/ 0.05, 0.6/ 0.2, 0.5/ 0.036, 0.4/ 0.036, 0.3/ 0.2

Table 7 - Results from Bottle Testing HPAM/ Chromium(III) Acetate Gels

HPAM/ Chromium Acetate								
HPAM/ Chromium Acetate (g)	Number of Days – Sydansk Gel Code							
	1	3	6	9	12	15	18	21
0.3/ .02	B	B	B	B	B	B	B	B
0.4/ 0.036	C	C	C	C	C	C	B	B
0.5/ 0.036	G	G	G	G	G	D	D	D
0.6/ 0.2	G	G	G	G	G	D	D	D
0.7/ 0.05	H	H	H	H	H	H	E	E
0.9/ 0.2	H	H	H	H	H	E	E	E

Results from bottle testing of HPAM/ Chromium(III) Acetate gels have been summarized in Table 7 above. Fig. 36 illustrates HPAM/ Chromium(III) Acetate gel samples of different concentrations after being tested at 200 °F for three weeks. It was found from the study that polymer gels with chromium(III) acetate as a crosslinker required a minimum 5000 ppm of HPAM to form a gel of code ‘G’.In contrast gels with PEI (research or commercial grade) required a minimum polymer concentration of 3000 ppm to form a gel of same strength. It was also observed that HPAM/ PEI (Research Grade) required a minimum concentration of 9000/ 6000 ppm to form a rigid ringing gel of code ‘J’, while HPAM/ PEI (Commercial Grade) gels of same strength could be obtained at a concentration of 7000/ 6000 ppm.

3.5 PAM/ PEI Gel System

Gels samples of 4000/ 4000 ppm, PAM/ PEI (Commercial Grade) were prepared while using two different types of PAM – commercial grade, high molecular weight PAM (Flopam - FA 920) from SNF Floerger and highly purified research grade PAM (product code – 92560) from Sigma Aldrich. It was observed that the gel sample prepared using the commercial grade PAM was cloudy in appearance and formed a gel of code ‘F’. On the other hand gel sample prepared using research grade PAM was perfectly clear and had a gel strength code of ‘H’ (Fig. 37).

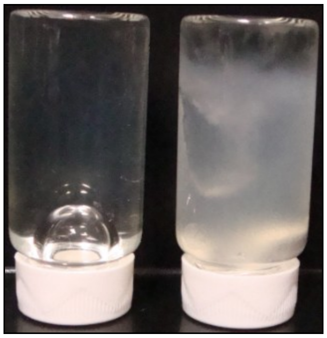


Fig. 37 (L-R) - PAM (Research Grade)/ PEI and PAM (Commercial Grade)/ PEI

4. CHARACTERIZING THE HPAM/ PEI GEL SYSTEM

Rheological characterization of the new HPAM / PEI gel was conducted using a Brookfield DV-III Ultra Rheometer and a Fann-35 Viscometer. The characterization process involved estimation of gelation time at constant shear rate and temperature using the Brookfield DV-III Rheometer. Fann-35 Viscometer was used to study effect of shear rate variation on viscosity of the HPAM/ PEI gelant solutions.

4.1 Brookfield DV-III Ultra Rheometer

Brookfield DV-III is a rotational viscometer that measures torque required to rotate a spindle immeresed in a fluid being tested. The spindle is rotated with the help of a motor which is connected to a caliberated spring. The test fluid exerts a viscous drag on the rotating spindle which leads to winding of the spring. For a particular spindle geometry and rotational speed, the increase in viscosity of test fluid leads to increase in deflection of the spring.

A stepper driver motor or a synchronus motor is located inside a housing at the top of the instrument (Fig. 38). Inside main case of the viscometer is a caliberated beryllium copper spring. One end of the spring is connected to a pivot shaft and its other end is connected to the dial. The dial is driven by a motor drive shaft, which drives the pivot shaft through the caliberated spring. The relative angular position of the pivot shaft is detected by a rotational variable displacement transducer and is shown as viscosity reading on a digital display.

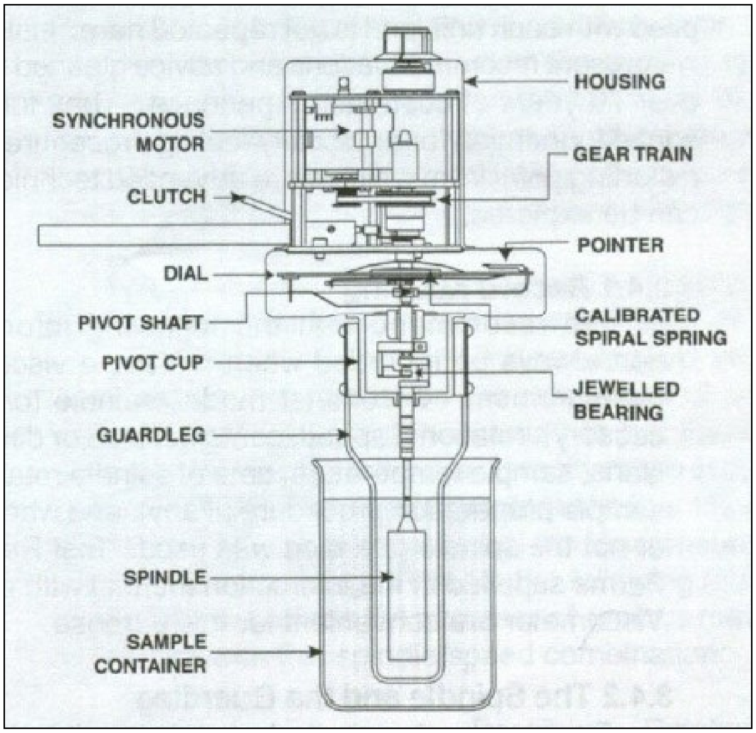


Fig. 38 – Mechanical Subassemblies of Brookfield DV–III Ultra Rheometer (Brookfield)

The Brookfield DV-III Rheometer (Fig. 39) is capable of operating at speeds ranging from 0.01 to 250 rpm, temperatutres from -100 °C to +300 °C and fluid viscosity ranging from 15 to 6,000,000 cp. It has an accuracy of ± 1% or 1 cp . It comes equiped with spindles of different geometries like disk, cylidrical, coaxial, cone/ plate and t-bar. These spindles are made of 300 series stainless steel with corrosion resistant coating and low maintainance requirements. The best method for selecting a spindle and speed is by trial and error. The combination of spindle type and a speed level that gives a torque reading between 10 % and 100 % for a particular fluid, is considered suitable for the experiment. If the torque reading is above 100 % a lower speed and/ or smaller spindle is selected and if it is lower than 10% higher speed and/ or larger spindle is selected.

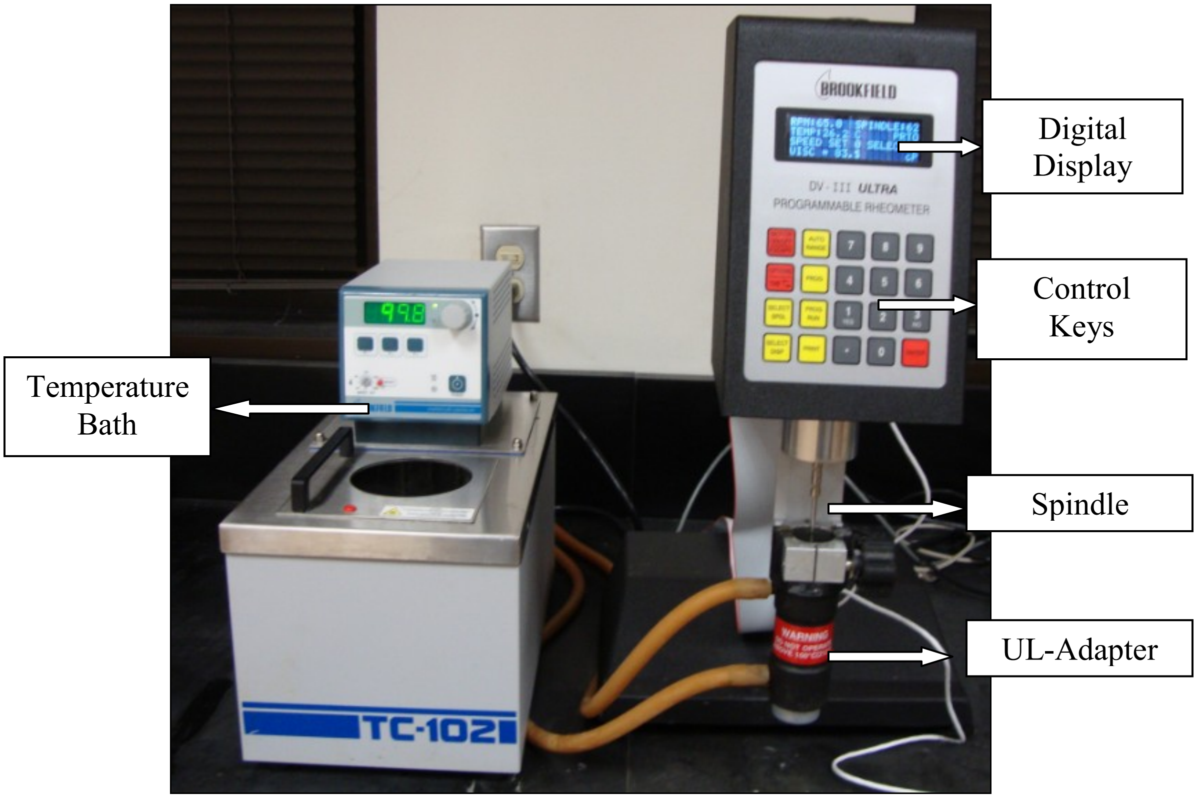


Fig. 39 - Brookfield DV–III Ultra Rheometer with TC–102 Temperature Bath

For conducting experiments at higher temperatures, a Brookfield TC-102 Temperature Bath is used along with the rheometer. In such experiments the test fluid is stored in a UL-Adapter and a spindle is immersed into it, such that the fluid level is at least upto middle of shaft indentation on the spindle. The UL-Adapter is of co-axial cylinder geometry with a detachable polyethylene cap fitted at bottom of its outer cylinder. It is capable of withstanding temperatures upto 100 °C. The sample placed inside the adapter is heated by a heating fluid, which is circulated from the temperature bath by a pump through the flow lines connecting the bath with the adapter. Specially designed heating fluids can allow the temperature bath to raise temperatures upto 270 °C. Since, the UL-adapter is capable of operating at a maximum temperatur of 100 °C, a mixture of ethylene glycol (50%) and water (50%) was used as the heating fluid in this study. This heating fluid could be used to maintain temperature of the UL-Adapter in the range of -30 °C to 100 °C.

4.2 Procedure for Estimating the Gelation Time

Gelation time was identified as a point of inflection on viscosity versus time curves. Experiments for estimating gelation time were conducetd at a constant shear rate and temperature, while varying parameters like polymer and crossslinker concentration, temperature, pH and salinity using the Brookfield DV-III Ultra Rheometer. The experimental process involved follwing steps:

- **Step 1.** Around 100 ml of gelant solution was prepared.
- **Step 2.** Brookfield DV–III Rheometer was then switched on and stand alone mode was selected by pressing key ‘2’. The version of operating firmware and model number was displayed on the screen. After a brief pause a message stating *“ REMOVE SPINDLE, LEVEL RHEOMETER AND PRESS THE MOTOR ON/ OFF KEY TO AUTOZERO”* was displayed.
- **Step 3.** The spindle was then removed and the rheometer was leveled. Correct level was identified by using the position of bubble located on top of the head of equipment. Motor was then turned on to begin ‘autozero’ process. Once the

‘autozero’ process was completed, a message stating *“AUTOZERO IS COMPLETE REPLACE SPINDLE AND PRESS ANY KEY”* was displayed.

- **Step 4.** It was found from trial and error that, disk shaped spindle of spindle number ‘62’, gave torque reading between 10 % and 100% for different gelant samples investigated in this study (Fig. 40). The spindle was then connected to the rheometer and spindle number which was 62, was entered using the ‘SELECT SPDL’ key.

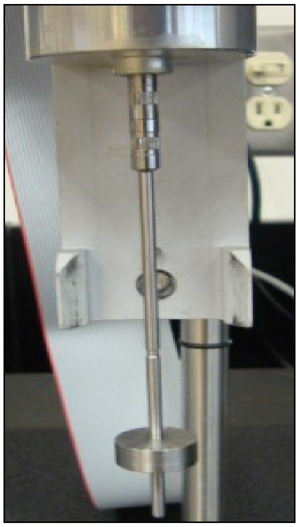


Fig. 40 - Disk Shaped Spindle (Spindle Number 62)

- **Step 5.** The Brookfield TC-102 temperature bath unit was then switched on. Desired temperature of 100 °C was then set using the select/ set knob on the device. On switching on the temperature bath heating fluid which was a mixture of ethylene glycol and water was immidiately circulated through the UL-Adapter. The circulation of heating fluid was continued till the end of experiment.

- **Step 6.** Gelant sample was then placed inside the UL-Adapter which was maintained at 100 °C.
- **Step 7.** UL-Adapter was then attached to the rheometer through a coupling nut; and spindle was introduced inside the gelant sample (Fig. 41).

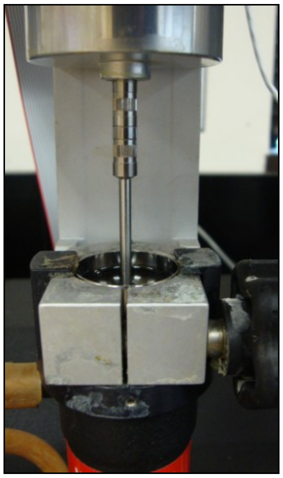
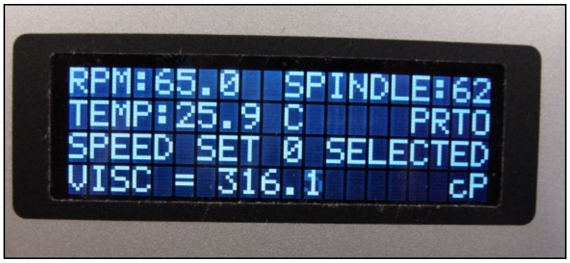


Fig. 41 – Spindle Immersed into the Gelant Sample Inside UL–Adapter

- **Step 8.** Rotation speed of the spindle was then entered using the control keys and 'ENTER' key was pressed. It was found from trial and error that, with spindle number 62, a rotational speed of around 65 rpm gave a torque reading between 10 % and 100 % for gelant samples investigated in this study.
- **Step 9.** Viscosity measurements for the sample at set temperature and shear rate were then displayed on the screen (Fig. 42). These readings were recorded from the display screen after every 5 minutes.



```
RPM:65.0  SPINDLE:62
TEMP:25.9 C     PRTO
SPEED SET 0 SELECTED
VISC = 316.1      cP
```

Fig. 42 - Viscosity Reading Displayed on Brookfield DV–III Ultra Rheometer

4.3 Results and Discussions – HPAM/ PEI (Research Grade) Gel System

4.3.1 Polymer Concentration Variation

HPAM / PEI (Research Grade) gelant samples were prepared in both fresh water and saline water (0.1 wt. % NaCl sloution). Concentration of the base polymer, HPAM was varied from 4000 ppm to 6000 ppm, while the concentration of research grade PEI was kept constant at 5000 ppm. Gelation time for each of the samples was determined through experiments conducted on Brookfield DV–III Ultra Rheometer at 100 °C and 70 rpm. Viscosity reading for the sample was taken every five minutes and gelation point was identified as point of inflection on viscosity versus time. It was found for the samples prepared in fresh water that the gelation time decreased from 180 minutes to 110 minutes as the concentration of HPAM was increased from 4000 ppm to 6000 ppm (Fig. 43).

For the samples prepared in saline water (0.1 wt% NaCl solution), the gelation time was longer than for the samples prepared in fresh water. It was also found that as the concentration of HPAM was increased from 4000 ppm to 6000 ppm, the gelation time decreased from 280 minutes to 175 minutes (Fig. 44). Points of gelation have been highlighted in yellow in the figures below.

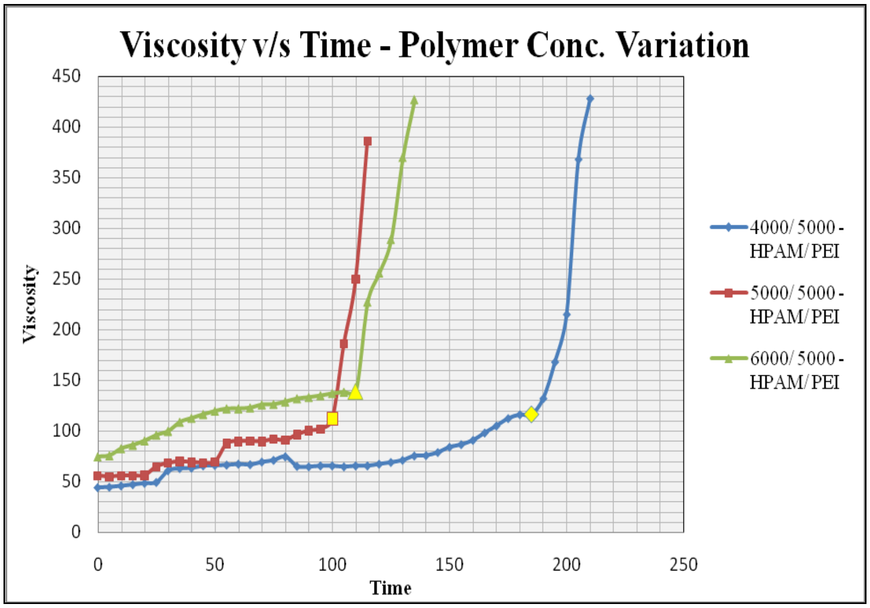


Fig. 43 – Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Fresh Water - Polymer Conc. Variation

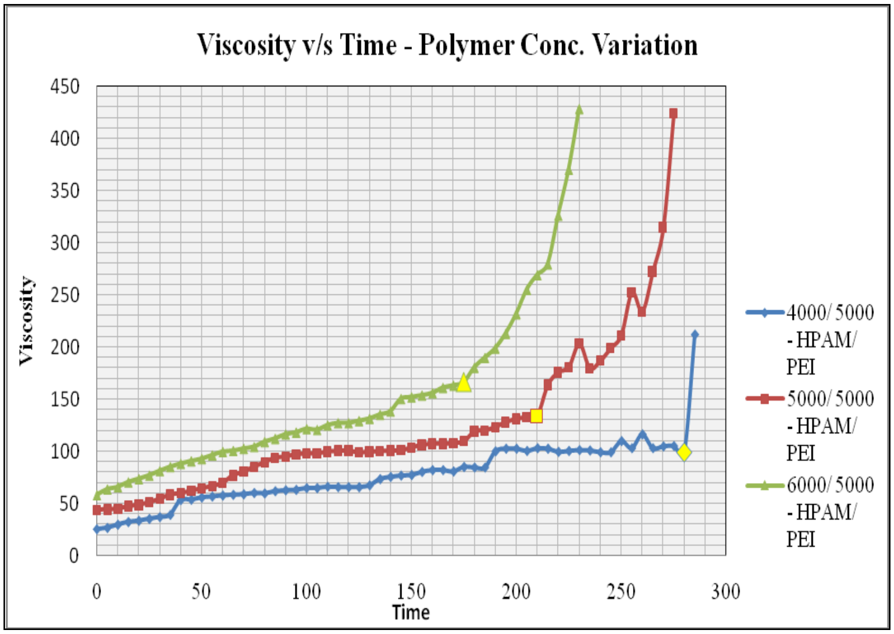


Fig. 44 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Saline Water - Polymer Conc. Variation

4.3.2 Crosslinker Concentration Variation

Crosslinker concentration's effect on gelation time of HPAM/ PEI (Research Grade) gelant solutions was studied by increasing the concentration of research grade PEI from 2000 ppm to 8000 ppm, while concnetration of HPAM was kept constant at 4000 ppm. The experiment was conducted at 100 °C and 70 rpm using Brookfield DV-III Ultra Rheometer. It was found that the gelation time of the sample prepared in fresh water decreased from around 145 minutes to 140 minutes (Fig. 45).

Similar behavior was observed for the gelant samples prepared in saline water (0.1 wt.% NaCl solution). Gelation time decreased from around 230 minutes to around 220 minutes as the concentration of PEI was increased from 2000 ppm to 8000 ppm

(Fig. 46). All the samples prepared in saline water were found to take longer time to gel than those prepared in fresh water.

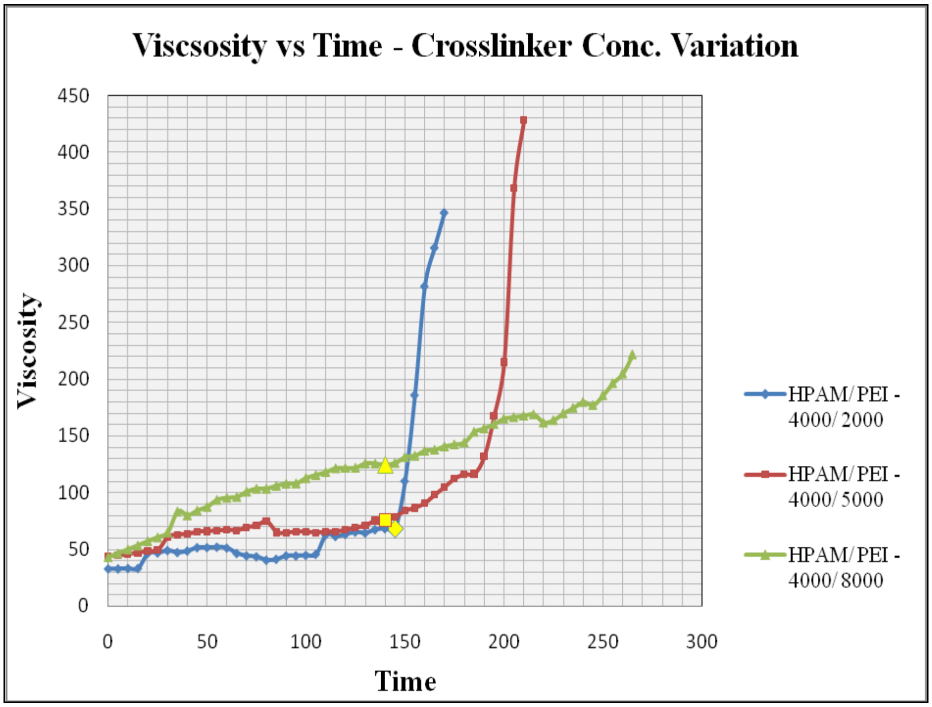


Fig. 45 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Fresh Water - Crosslinker Conc. Variation

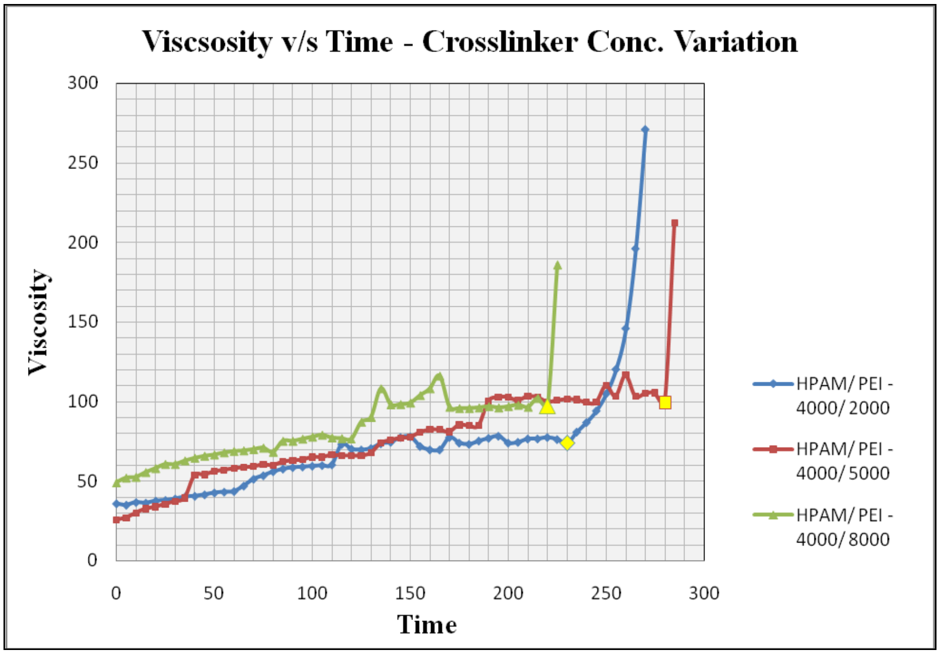


Fig. 46 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Saline Water - Crosslinker Conc. Variation

4.3.3 Temperature Variation

4000/ 4000 ppm, HPAM/ PEI (Research Grade) gelant samples prepared in fresh water and saline water (0.1 wt.% NaCl solution), were investigated for gelation time at 80 °C and 100 °C. Temperature of the gelant sample held inside the UL-Adapter was kept constant by using Brookfield TC-102 temperature bath. The temperature bath circulated mixture of ethylene glycol and water at set temperature, through the UL-Adapter causing temperature of the sample to rise to desired value.

Gelation time was found to decrease with increasing temperature for the gelant samples prepared in both fresh water and saline water. This has been explained in literature using Arrhenius type equation (Nasr-El-Din et.al. 2006). It was found that the gelation time of the 4000/ 4000 ppm, HPAM/ PEI (Research Grade) gelant sample prepared in fresh water decreased from around 320 minutes to around 150 minutes on raising temperature from 80 °C to 100 °C (Fig. 47).

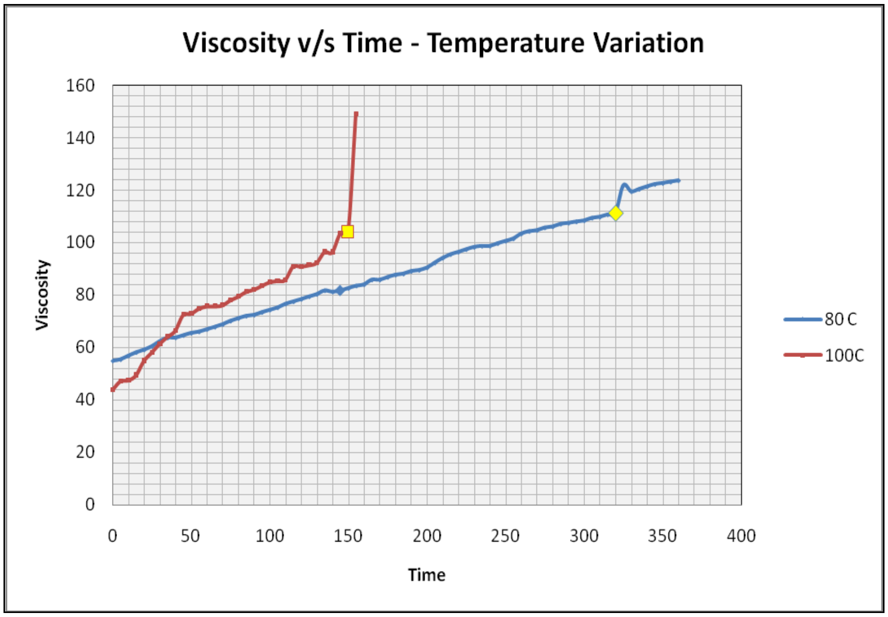


Fig. 47 - Gelation Time, HPAM/ PEI (Research Grade) in Fresh Water - Temperature Variation

Gelation time for the samples of same concentration prepared in saline water, decreased from around 385 to around 165 minutes on increasing the temperature from 80 °C to 100 °C (Fig. 48).

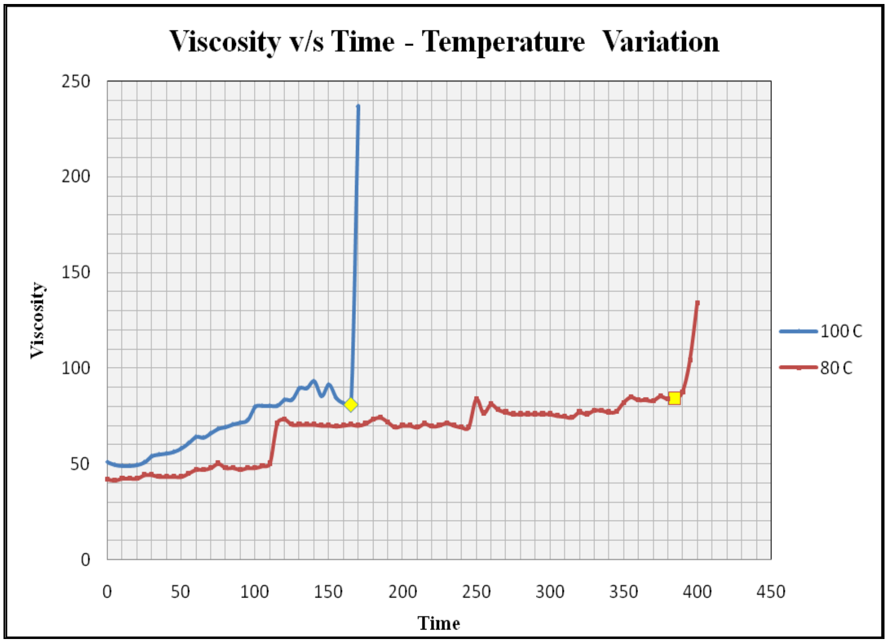


Fig. 48 - Gelation Time, HPAM/ PEI (Research Grade) in Saline Water – Temperature Variation

4.3.4 pH Variation

The HPAM/ PEI (Research Grade) gel system was found to be sensitive to pH. It was found that the gelation time of 4000/ 4000 ppm, HPAM/ PEI (Research Grade) gelant samples prepared in fresh water and in saline water decreased with increasing pH. One of the theories in literature (Al-Muntasheri et al., 2009) explains it to be a result of, increased hydrolysis at higher pH which leads to increase in concentration of negatively charged carboxylate ions. These ions, repel each other causing the polymer chain to expand faster, thereby decreasing the gelation time.

This study was conducted at 100 °C and 65 rpm using the Brookfield DV–III Ultra Rheometer. It was found that the gelation time of 4000/ 4000 ppm, HPAM/ PEI (Research Grade) gelant samples prepared in fresh water decereased from around 150 minutes to around 50 minutes on increasing the pH from around 10 to around 12 (Fig. 49).

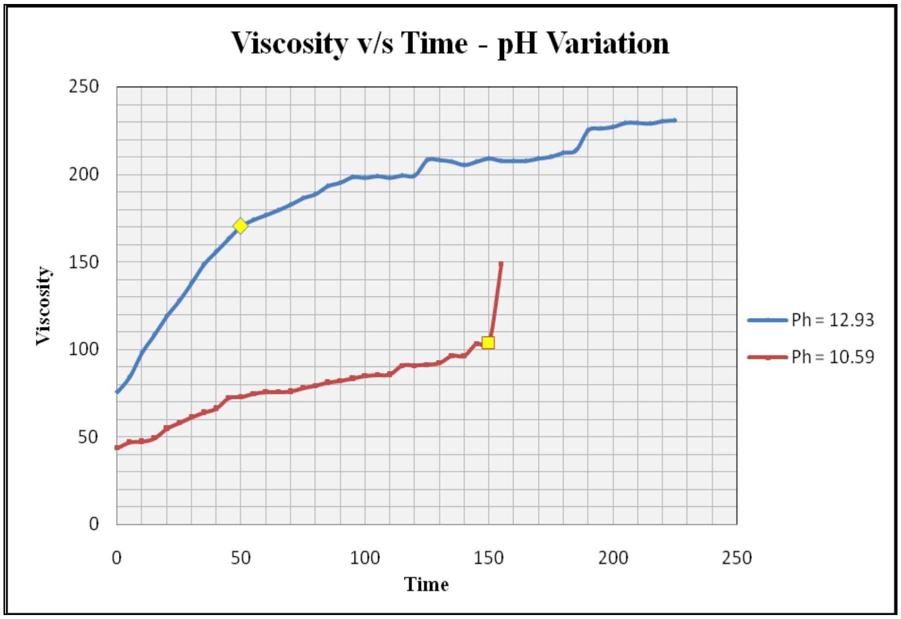


Fig. 49 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Fresh Water – pH Variation

Gelation time also decreased from around 165 minutes to around 85 minutes, for the gel sample of same concentration prepared in saline water (0.1 wt. % NaCl solution) on increasing the pH from around 10 to around 12 (Fig. 50).

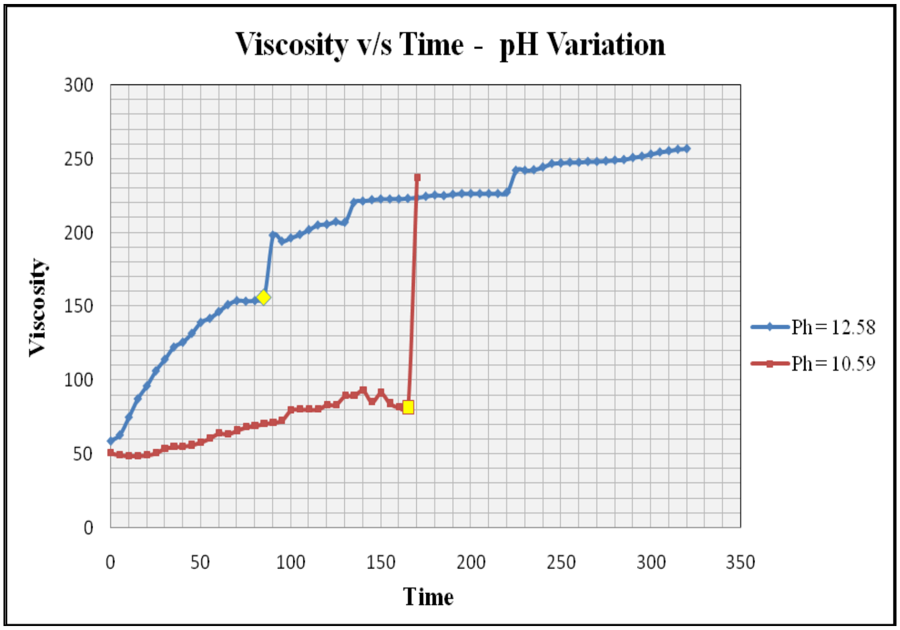


Fig. 50 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Saline Water – pH Variation

4.3.5 Salinity Variation

It was found from the experiments conducted on 4000/ 4000 ppm, HPAM/ PEI (Research Grade) gelant samples at 100 °C and 65 rpm, that the gelation time increased with increased salinity. This has been explained in literature (Zitha et al., 2008) to be a result of shielding of negatively charged carboxylate ions on the polymer chain by positively charged sodium ions.

It was found that the gelation time of around 150 minutes for the sample prepared in fresh water increased to around 220 minutes when the salinity was raised to 2 wt. % NaCl (Fig. 51). It was also found to increase from around 160 minutes to 235 minutes on increasing the salinity from 0.1 wt. % NaCl to 2 wt.% NaCl (Fig. 52).

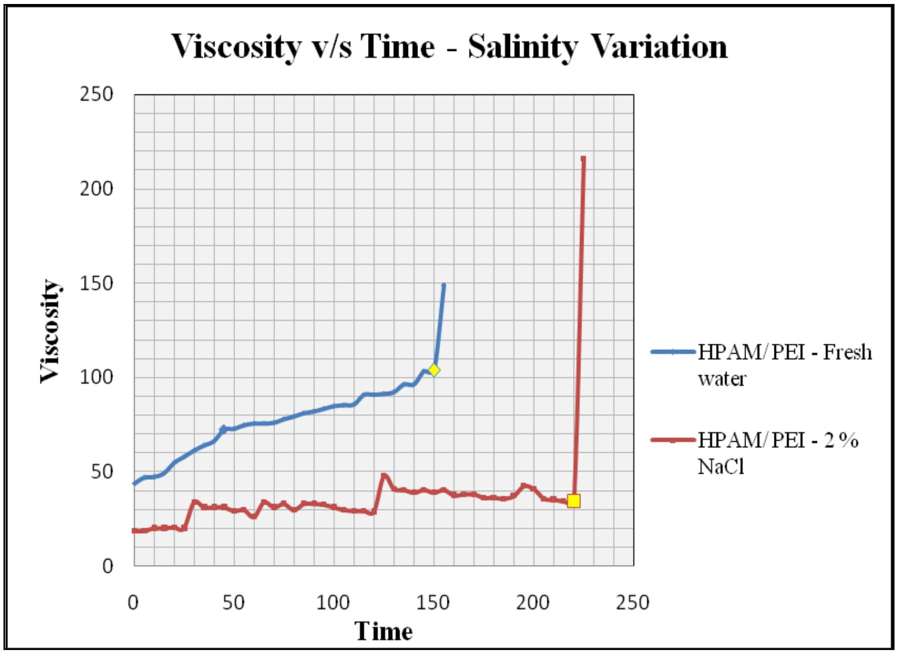


Fig. 51 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Fresh Water – Salinity Variation

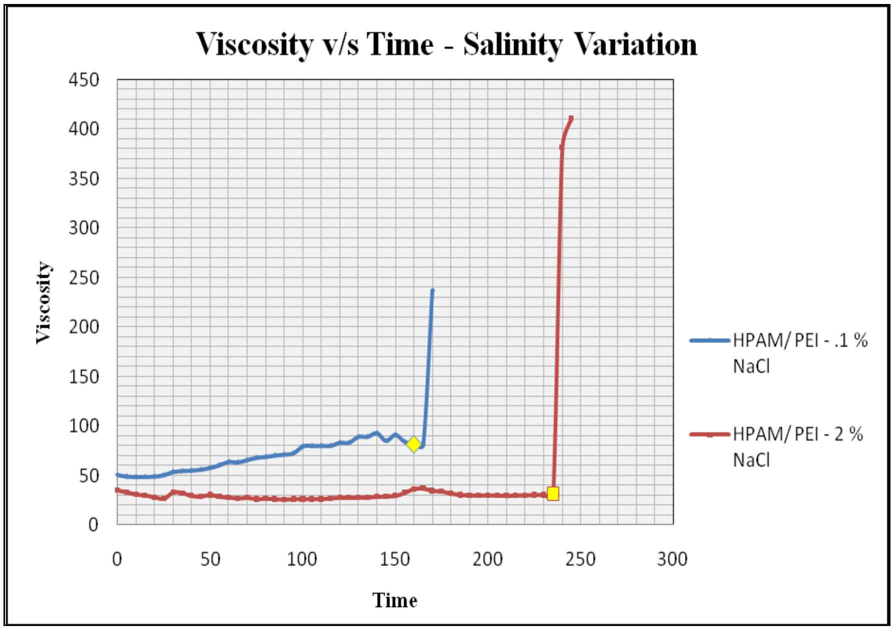


Fig. 52 - Gelation Time at 100 °C, HPAM/ PEI (Research Grade) in Saline Water – Salinity Variation

4.4 Results and Discussions – HPAM/ PEI (Commercial Grade) Gel System

The new environmentally benign polymer gel system based on HPAM and commercial grade PEI, was also characterized using the Brookfield DV–III Ultra Rheometer. Effects of varying polymer and crosslinker concentration, temperature, pH and salinity on geation time of HPAM/ PEI (commercial grade) gelant samples was studied. The new gel system was also also tested for viscosity at variable shear rates using Fann – 35 Viscometer. The gelant samples investigated were prepared in 0.1 wt. % NaCl solution. All experiments were repeated to confirm accuracy of the results.

4.4.1 Polymer Concentration Variation

HPAM/ PEI (commercial grade PEI) gelant samples were tested for the effect of HPAM concentration on gelation time. It was found from the study that like the gelant solutions based on research grade PEI, the gelation time for the HPAM/ PEI (commercial grade) gelant samples, decreased with increasing concentration of HPAM.

The experiment was carried out at 100 °C and 75 rpm using Brookfield DV–III Ultra Rheometer. The gelation time was found to decrease from 210 minutes to 35 minutes on increasing the concentration of HPAM from 4000 ppm to 6000 ppm while concentration of the crosslinker was kept constant at 5000 ppm (Fig. 53). The experiment was repeated under simillar conditions and for gelant samples with same concentration. It was found on reproducing the results, that gelation time decreased from around 225 minutes to around 40 minutes on increasing the HPAM concentration from 4000 ppm to 6000 ppm (Fig. 54).

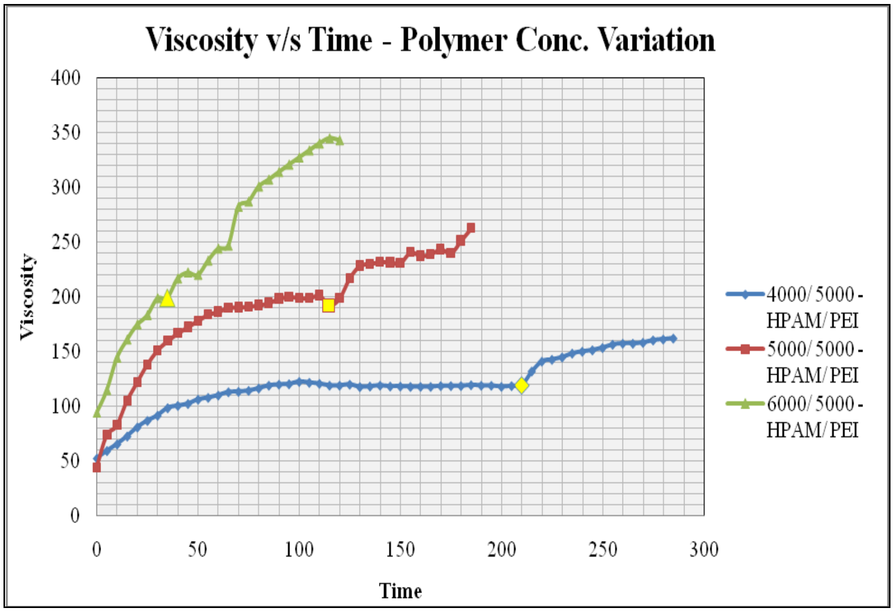


Fig. 53 - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Polymer Concentration Variation

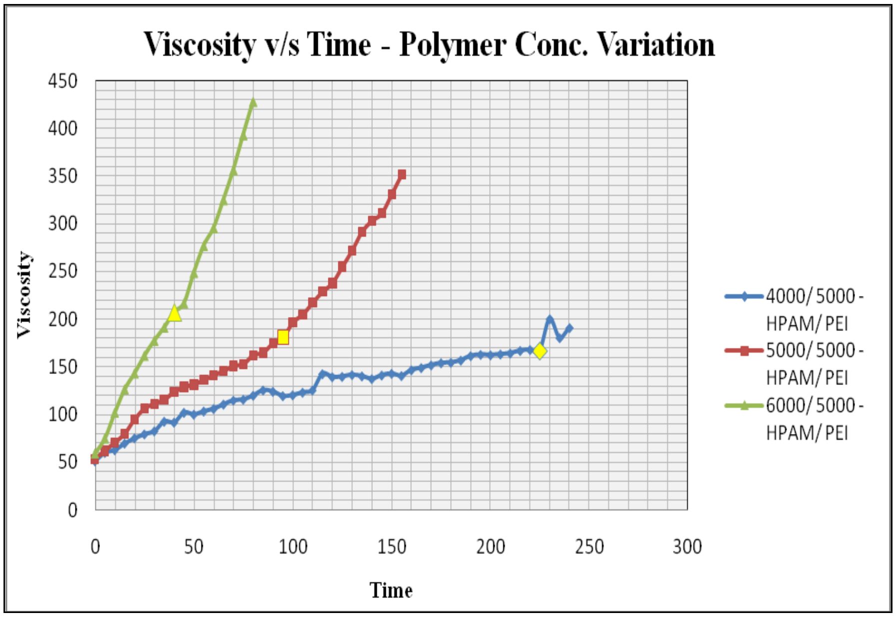


Fig. 54 - Results Reproduced - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Polymer Concentration Variation

4.4.2 Crosslinker Concentration Variation

Gelation time for HPAM/ PEI (Commercial Grade) gelant samples prepared in saline water (0.1 wt. % NaCl solution) was found to decrease with increasing concentration of PEI. The experiments were conducted on Brookfield DV–III Ultra Rheometer at 100 °C and 70 rpm. It was found that the gelation time decreased from around 205 minutes to around 35 minutes as the concentration of PEI was increased from 5000 ppm to 8000 ppm, while the concentration of HPAM was kept constant at 4000 ppm (Fig. 55). However, an anomolous behavior was observed for 4000/ 2000 ppm gelant sample. Its gelation time was found to be around 15 minutes, which was less than the gelation time of 4000/ 5000 ppm and 4000/ 8000 ppm, HPAM/ PEI (commercial grade) gelant samples.

Similar results were obtained on repeating the expriment. Gelation time decreased from around 225 minutes to around 150 minutes on increased concentration of PEI from 5000 ppm to 8000 ppm (Fig. 56). The gelation time of 4000/ 2000 ppm gelant sample was found to be around 10 minutes which was again less than that of gelant samples with 5000 ppm and 8000 ppm of commercial grade PEI.

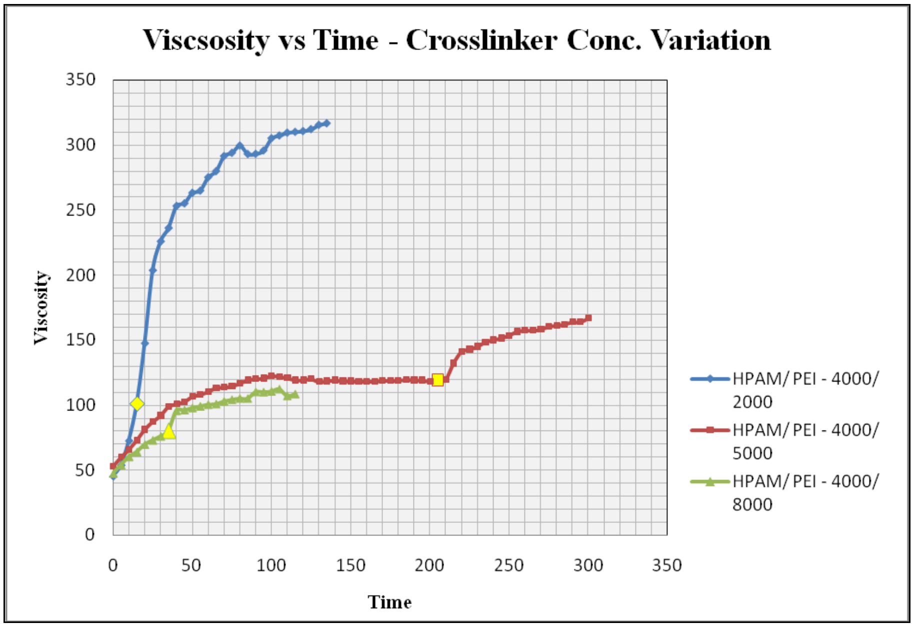


Fig. 55 - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Crosslinker Conc. Variation

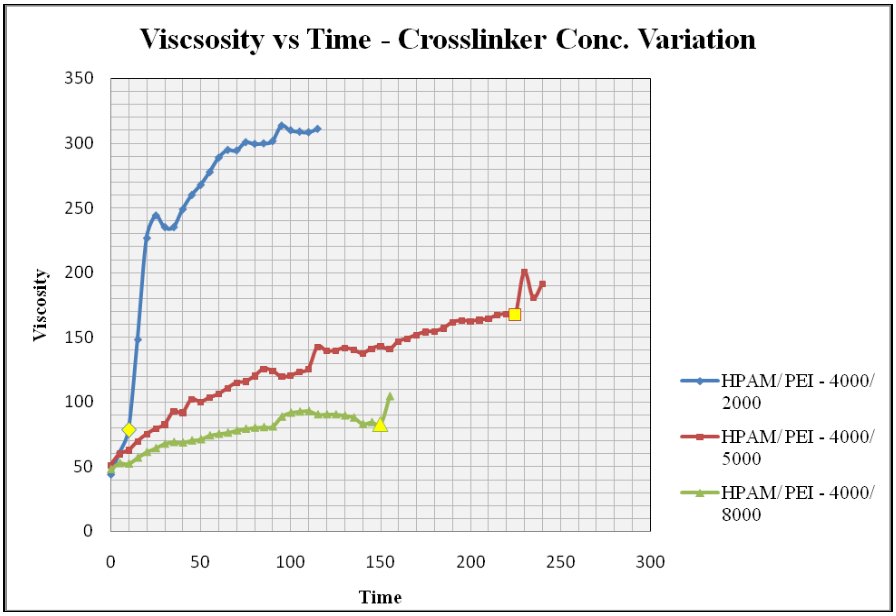


Fig. 56 – Results Reproduced - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Crosslinker Concentration Variation

4.4.3 Temperature Variation

Gelation time of 4000/ 4000 ppm, HPAM/ PEI (commercial grade) gelant sample prepared in saline water (0.1 wt% NaCl solution), was determined at 70 °C and 100 °C on a Brookfield DV–III Ultra Rheometer at 65 rpm. Gelation time was found to decrease with increasing temperature. This has been explained in the literature on the basis of Arrhenius type equation (Nasr-El-Din et.al. 2006).

It was found that the gelation time of the gelant sample decreased from around 375 minutes to around 25 minutes on increasing the temperature from 70 °C to 100 °C (Fig. 57). The experiment was repeated and a similar behavior was observed, the gelation time was found to decreased from around 325 minutes to around 15 minutes on increasing the temperature from 70 °C to 100 °C (Fig. 58).

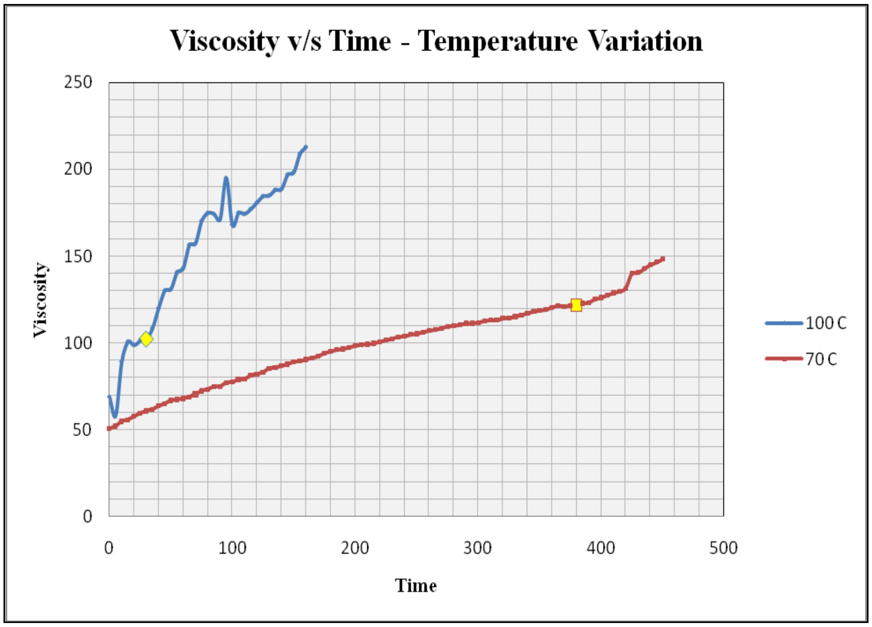


Fig. 57 - Gelation Time, HPAM/ PEI (Commercial Grade) – Temperature Variation

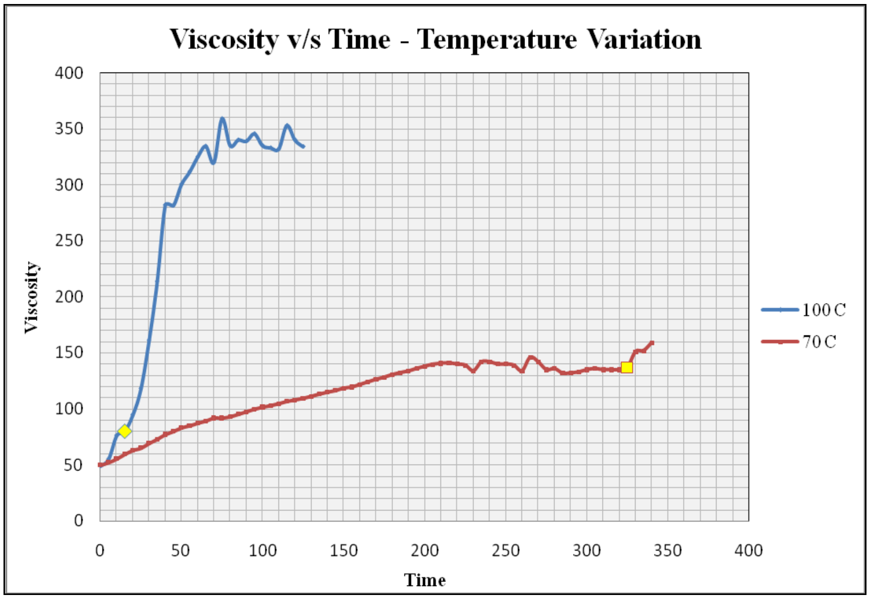


Fig. 58 – Results Reproduced - Gelation Time, HPAM/ PEI (Commercial Grade) – Temperature Variation

4.4.4 pH Variation

It was found from the experiments conducted on 4000/ 4000 ppm, HPAM/ PEI (commercial grade) gelant sample at 100 °C and 65 rpm, that the gelation time decreased with increasing pH. This behavior was identical to that observed in gelant samples based on research grade PEI. It has been explained in the literature (Zitha et al., 2008) to be result of increased repulsion by negatively charged carboxylate ions, formed on hydrolysis of PAM.

It was found that gelation time decreased from around 90 minutes to around 35 minutes when the pH was raised from 10.59 to 12.58 (Fig. 59). Similar results were obtained on repeating the experiment. It was found that the gelation time decreased from around 85 minutes to around 15 minutes when pH was raised from 11.6 to 11.8 (Fig. 60).

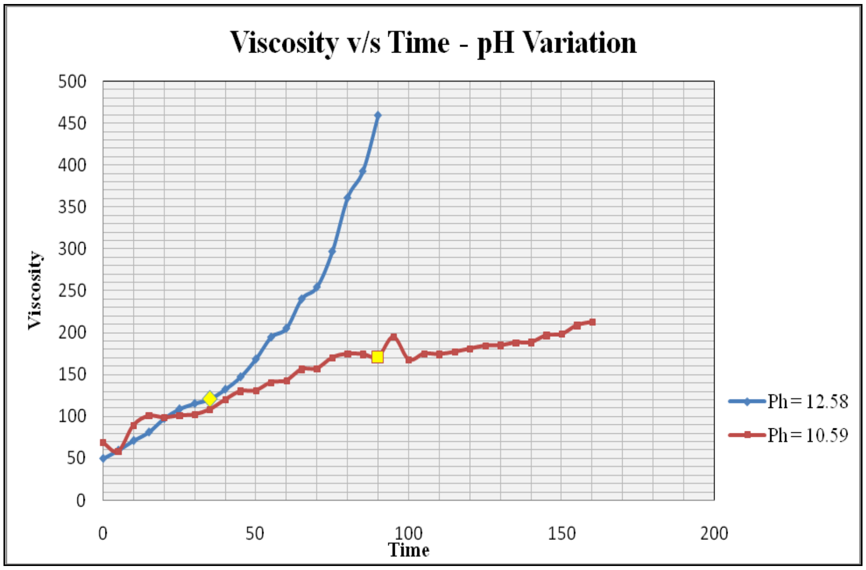


Fig. 59 - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – pH Variation

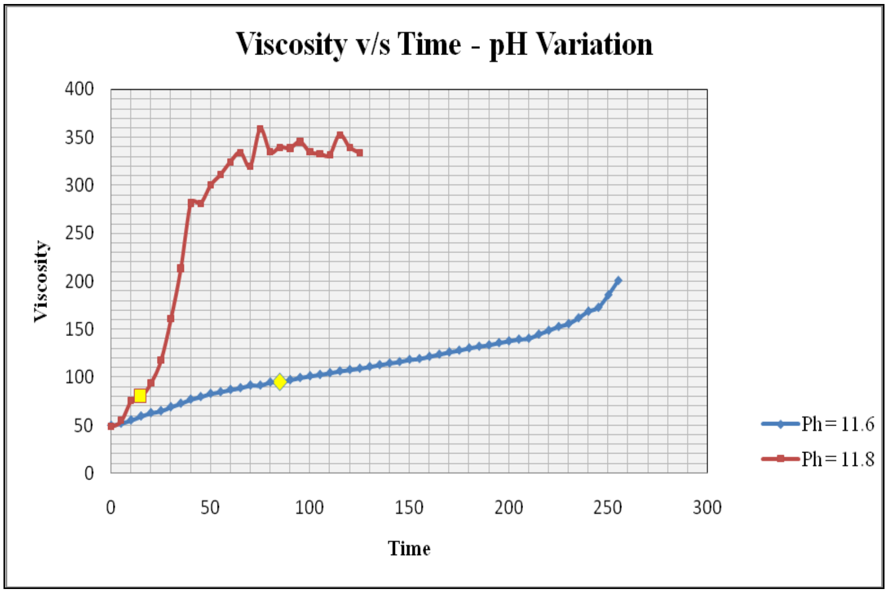


Fig. 60 – Results Reproduced - Gelation Time – HPAM/ PEI (Commercial Grade) – pH Variation

4.4.5 Salinity Variation

4000/ 4000 ppm, HPAM/ PEI (commercial grade) gelant sample was tested for the effect of salinity on gelation time at 100 °C and 65 rpm on Brookfield DV–III Ultra Rheometer. Gelation time was found to decrease with decreasing salinity. One of the reasons for such behaviour has been explained in the literature (Zitha et al., 2009), to be a result of shielding of the negatively charged carboxylate ions by positively charge sodium ions from repelling each other.

It was found that the gelation time of 4000/ 4000 ppm, HPAM/ PEI (Commercial Grade) gelant sample decreased from around 170 minutes to around 30 minutes with salinity decreasing from 2 wt. % NaCl to 0.1 wt. % NaCl (Fig. 61). On repeating the experiment under similar conditions, gelation time was found to decrease from around 115 minutes to around 25 minutes (Fig. 62).

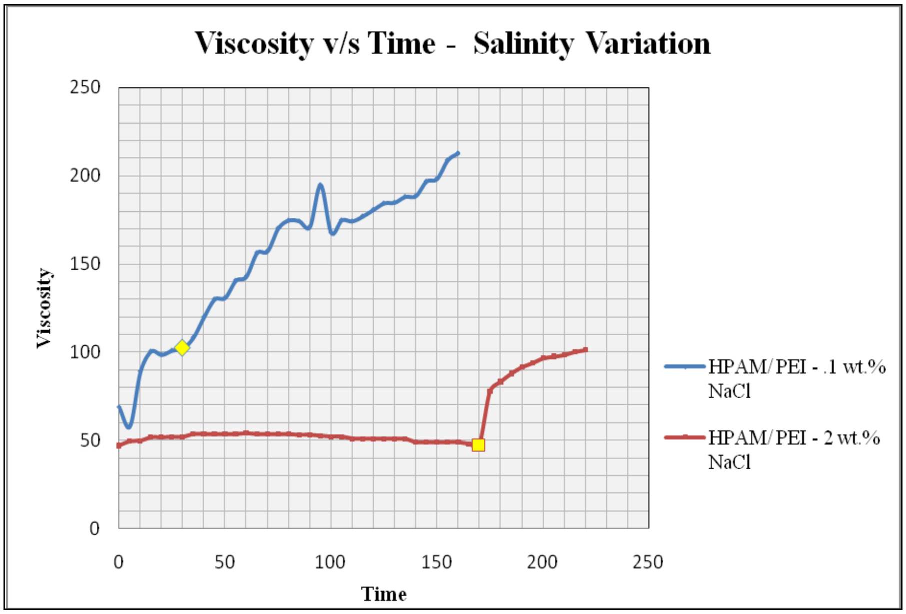


Fig. 61 - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Salinity Variation

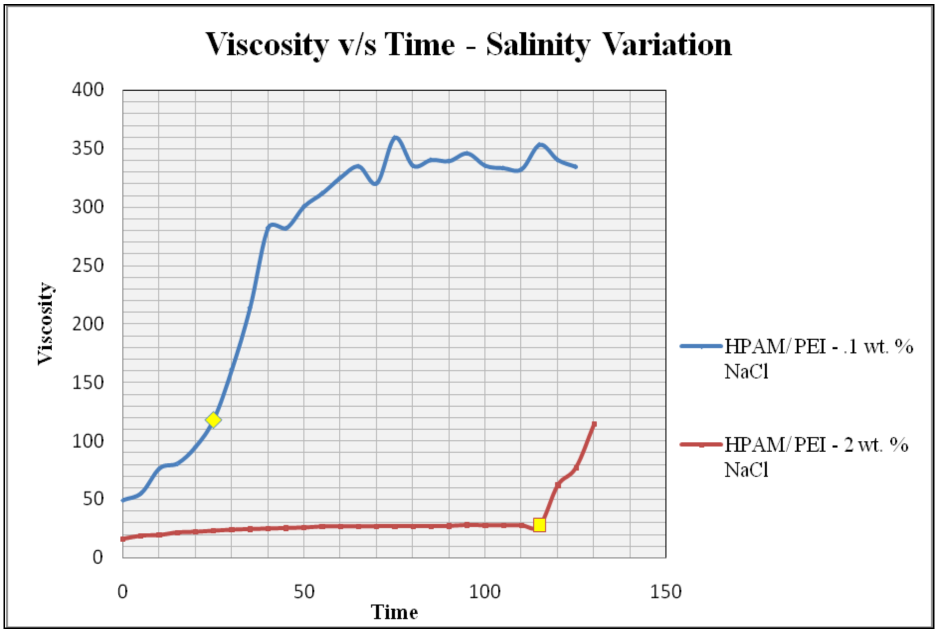


Fig. 62 – Results Reproduced - Gelation Time at 100 °C, HPAM/ PEI (Commercial Grade) – Salinity Variation

4.5 Gelation Time of Different Gelant Systems

Gelation time of different gel systems with similar concentration of base polymer at 100 °C and 65 rpm was investigated. All the gelant samples were prepared in 0.1 wt. % NaCl solution. Concentration of base polymers HPAM and PAM was 4000 ppm. Concentration of crosslinkers PEI (Research Grade) and PEI (Commercial Grade) was also 4000 ppm. For the gelant sample based on chromium(III) acetate as a crosslinker, the concentration of HPAM was 4000 ppm and that of crosslinker was 360 ppm. The amount of chromium(III) acetate for the gelant sample was, as prescribed by 'Margel' software from Marathon Oil Co. Gelation time of different gelant samples from the study are summarized in Table 8 below.

Table 8 – Gelation Time Comparison

Polymer/ Crosslinker	Concentration (ppm)	Gelation Time (minutes)
HPAM/ Chromium Acetate	4000/ 360	< 5
HPAM/ PEI (Commercial Grade)	4000/ 4000	30
PAM/ PEI (Commercial Grade)	4000/ 4000	160
HPAM/ PEI (Research Grade)	4000/ 4000	165

It was found from the experiments conducted that, the new 4000/ 4000 ppm - HPAM/ PEI (Commercial Grade) gelant sample took around 30 minutes to gel. The gelant system that was tested had a pH of around 11 and was prepared in 0.1 wt.% NaCl solution (Fig. 63). On the other hand the chromium(III) acetate based gelant sample took less than 5 minutes to gel under similar conditions of temperature, shear, salinity and HPAM concentration. This proved that the new gelant system takes longer than the existing chromium(III) acetate based system. This implies, a longer pumping time available to user for application on field. It was also found that gelant samples with similar concentration of PAM and HPAM, as base polymers and commercial grade PEI, as a crosslinker took around 160 minutes to gel under similar conditions of temperature and shear.

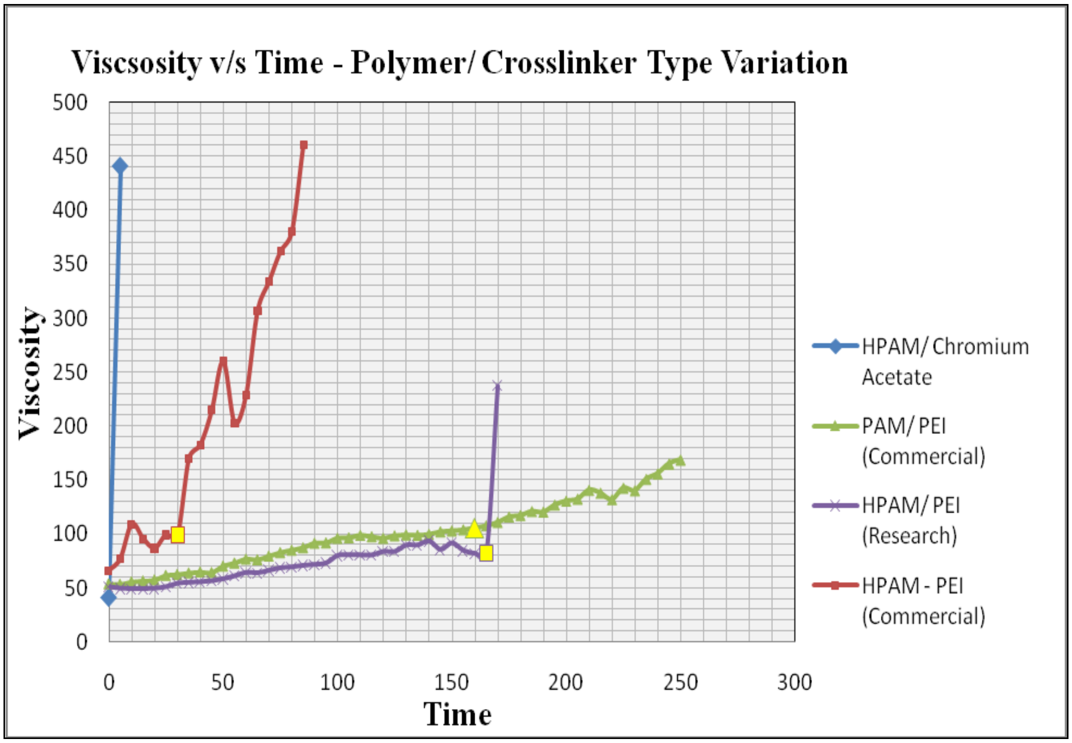


Fig. 63 – Gelation Time of Different Gelant Samples. 4000 ppm HPAM, 100 °C and 65 rpm

4.6 Shear Thinning Nature of the New HPAM/ PEI Gel

The new HPAM/ PEI (Commercial Grade) gelant samples of different concentrations were tested for the effects of variable shear rates on viscosity of the gelant system. The experiments were conducted using a Fann – 35 Viscometer (Fig. 64).

4.6.1 Fann – 35 Viscometer

Fann – 35 Viscometer is a rotational viscometer. The fluid that is being tested is contained in annular space between an outer cylinder and a bob. The viscometer is capable of operating at six different speeds of 3, 6, 100, 200, 300 and 600 rpm. During operation, the outer cylinder rotates at a set velocity, this causes the test fluid to exert viscous drag on bob. The bob is connected to a precision spring which measures its extent of deflection. The deflection measured is then correlated with instrument's constants to give a viscosity reading of test fluid on the display.

Fig. 64 - Fann – 35 Viscometer (Fann Instrument Company)

Shear rate to which test fluid is subjected, can be set by adjusting rotor and gear knobs. Different speed testing combinations for Fann-35 Viscometer have been summarized in Table 9 below.

Table 9 - Speed Testing Combinations, Fann – 35 Viscometer

Six – Speed Testing Combinations – Fann 35 Viscometer		
Speed RPM	**Viscometer Switch**	**Gear Knob**
600	High	Down
300	Low	Down
200	High	Up
100	Low	Up
6	High	Center
3	Low	Center

4.6.2 Experimental Procedure

The experimental procedure used to test the new HPAM/ PEI (Commercial Grade) gelant system at different shear rates is as follows:

Step 1. Gelant solution of required concentration was prepared.

Step 2. Around 300 ml of the test sample was then placed inside the double walled circulating cup, such that the sample was at least up to the level of 'minimum fill line'.

Step 3. Thermocouple connected to the circulating cup was then set switched on and temperature was set at 150 °F.

Step 4: Temperature of the sample was measured through a temperature probe. After the sample had reached the set point temperature, the motor was turned on. Rotor speed was then set by selecting appropriate motor speed and gear knob level combination. Different speed and shear rate options for the viscometer are summarized in Table 10 below.

Table 10 - Speed and Shear Rate Options on Fann–35 Viscometer

Motor Speed	Shear Rate
600	1021
300	511
200	340
100	170
6	10
3	5.1

Step 5. Shear stress value corresponding to the set shear rate was then noted from the viscometer dial.

Step 6: Shear stress value was then converted to viscosity value by using appropriate viscometer constants.

4.6.3 Results and Discussions

HPAM/ PEI gelant samples of different concentrations were subjected to six different shear rates at room temperature (80 °F) and at 150 °F using the Fann–35 Viscometer. It was found from the study that gelant samples based on both research grade and commercial grade PEI crosslinkers, exhibited shear thinning or pseudoplastic nature. Pseudoplastic or shear thinning fluids (Fig. 65) are known as the fluids that exhibit decrease in viscosity with increasing shear rate. Gelant samples of concentration 3000/ 3000, 5000/ 5000, 7000/ 7000 and 9000/ 9000 ppm - HPAM / PEI (research grade and commercial grade) were investigated at shear rates of 1021, 511, 340, 170, 10 and $5.1s^{-1}$. It was found from the study that viscosity of all the gelant samples decreased with increasing shear rate (Fig. 66 – Fig. 73).

Fig. 65 – HPAM/ PEI Gel – Pseudoplastic Nature

4.6.3.1 Shear Thinning Nature - HPAM/ PEI (Research Grade) Gels

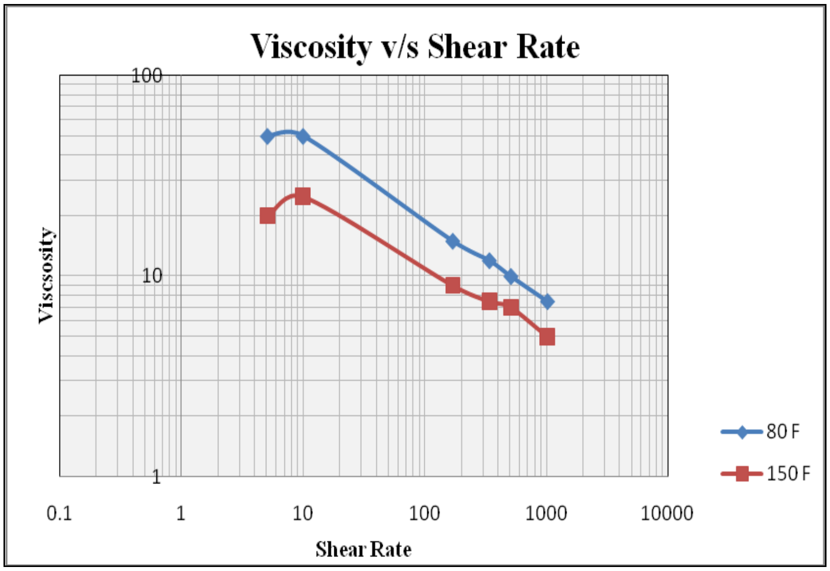


Fig. 66 – 3000/ 3000 ppm – HPAM/ PEI (Research Grade); Shear Thinning Gel

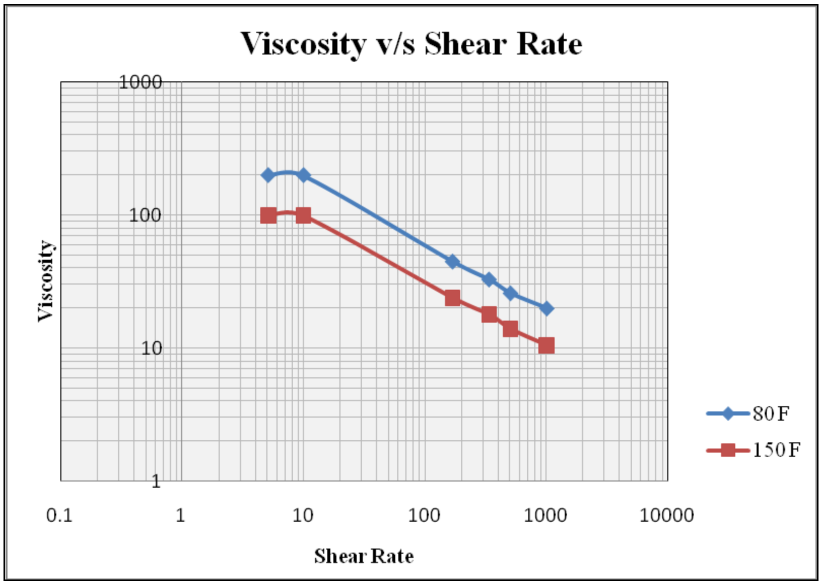


Fig. 67 – 5000/ 5000 ppm – HPAM/ PEI (Research Grade); Shear Thinning Gel

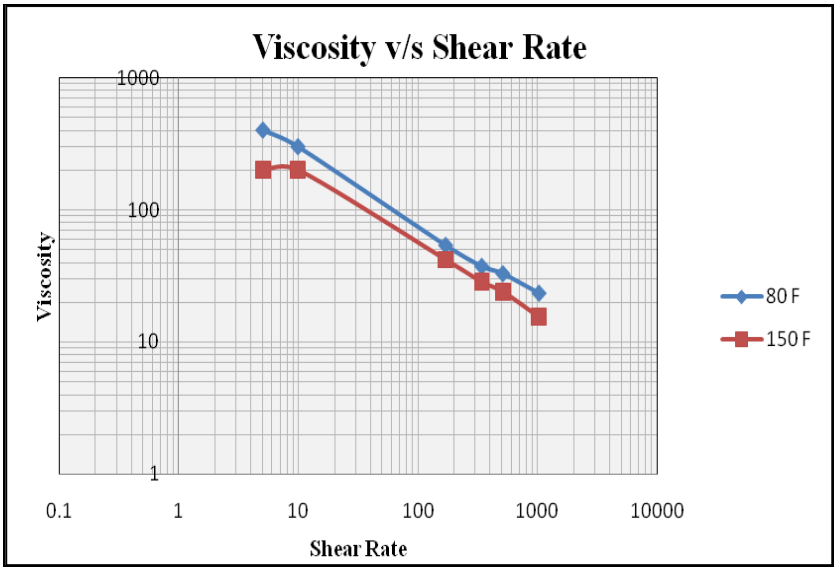


Fig. 68 – 7000/ 7000 ppm – HPAM/ PEI (Research Grade); Shear Thinning Gel

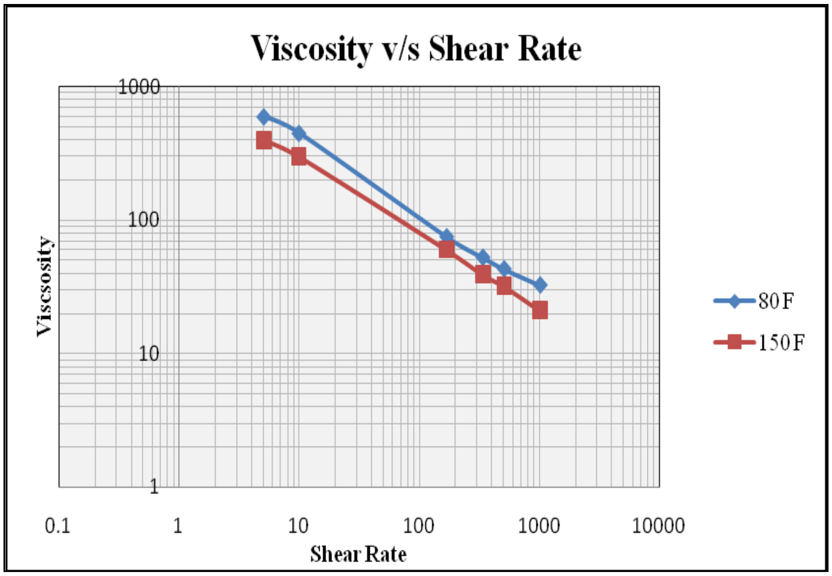


Fig. 69 – 9000/ 9000 ppm – HPAM/ PEI (Research Grade); Shear Thinning Gel

4.6.3.2 Shear Thinning Nature - HPAM/ PEI (Commercial Grade) Gels

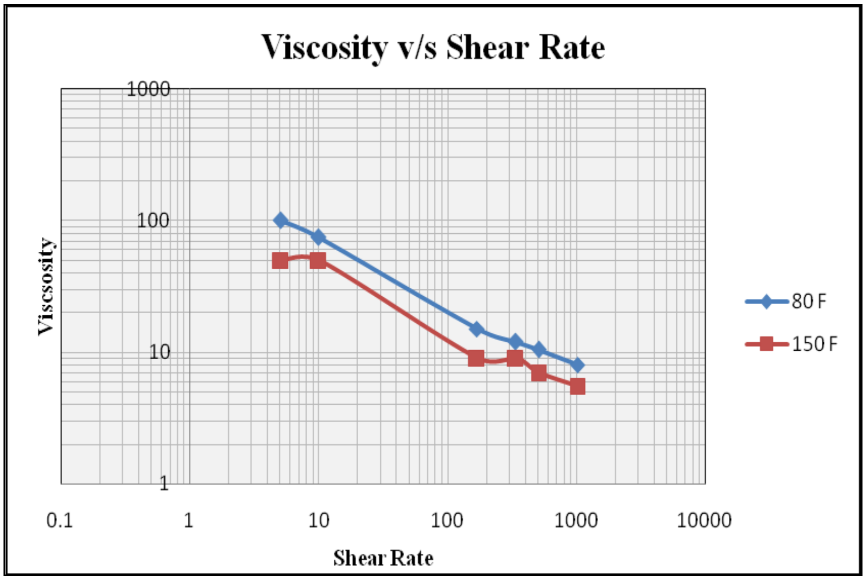


Fig. 70 – 3000/ 3000 ppm – HPAM/ PEI (Commercial Grade); Shear Thinning Gel

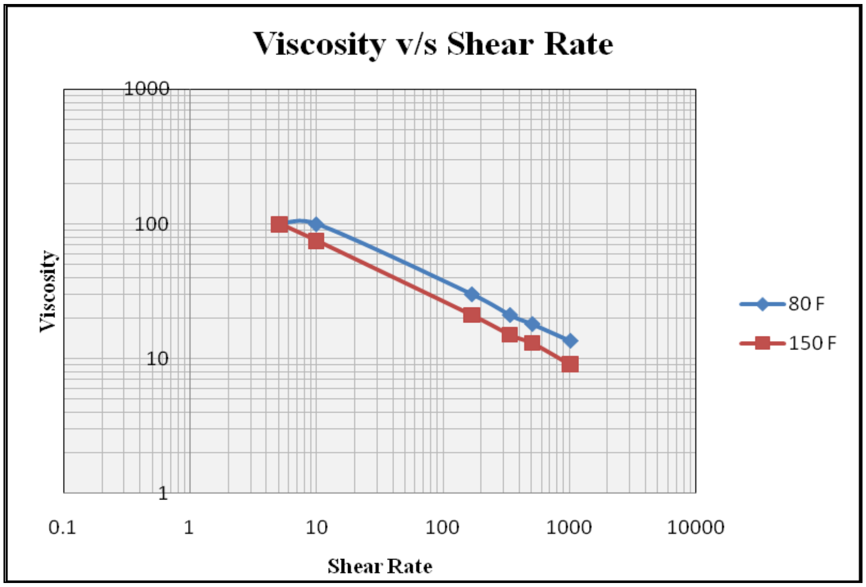


Fig. 71 – 5000/ 5000 ppm – HPAM/ PEI (Commercial Grade); Shear Thinning Gel

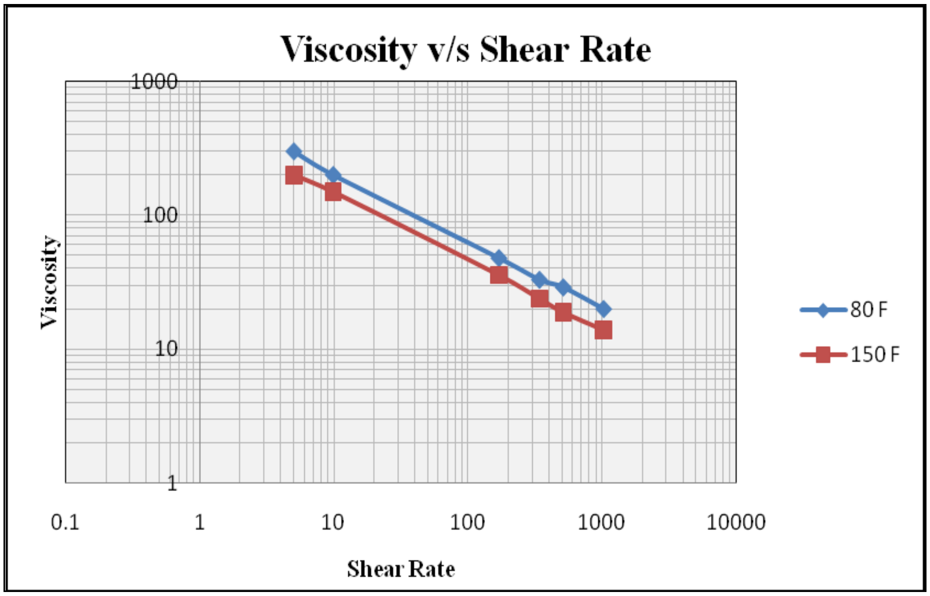


Fig. 72 – 7000/ 7000 ppm – HPAM/ PEI (Commercial Grade); Shear Thinning Gel

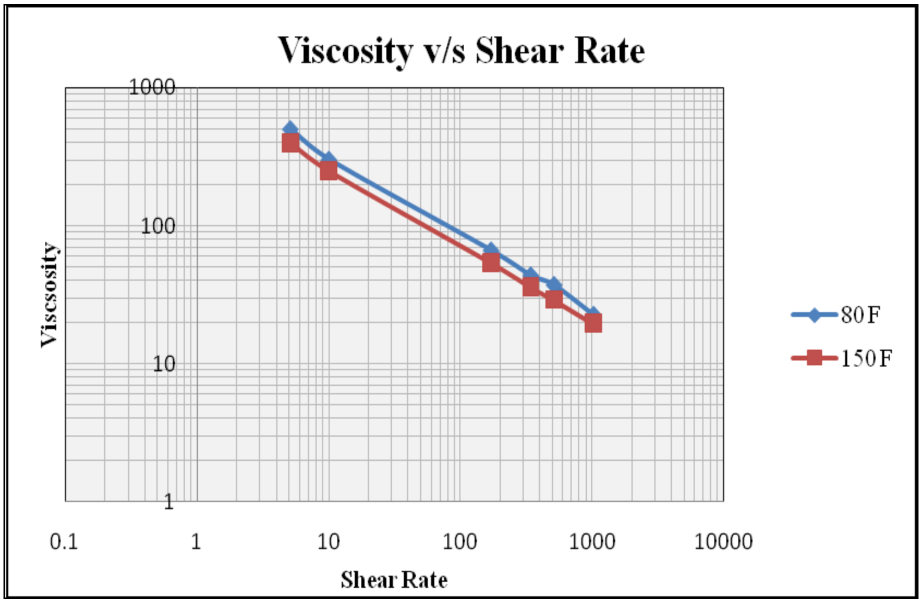


Fig. 73 – 9000/ 9000 ppm – HPAM/ PEI (Commercial Grade); Shear Thinning Gel

5. CONCLUSIONS

The objective of this study was to develop an environmentally benign polymer gel system for minimizing water production from shale and tight gas reservoirs by plugging narrow aperture fractures connected to a water source. The gel system was successfully developed, characterized and tested for its effectiveness in plugging narrow aperture fractures. Important findings from this study are concluded as:

1. An environmentally benign HPAM/ PEI polymer gel system based on a commercial grade PEI was succesfully developed. The gel system is based on high molecular weight, HPAM with molecular weight of 2 – 5 million Da. as a base polymer and commercial grade PEI of molecular weight 500,000 to 120,000 Da. as an organic crossliker.
2. The low cost of $ 2/ lb for the commercial grade PEI used as a crosslinker, makes the new HPAM/ PEI gel system a commercially viable product.
3. It was found that pH of the HPAM/ PEI (Commercial Grade) gelant solution had to be raised from around 7 to around 10, to obtain visually clear and stable gels.
4. Rheological characterization of the HPAM/ PEI gelant samples based on both research grade and commercial grade PEI was carried out using Brookfield DV–III Ultra Rheometer. It was found from the study that the gelation time of both types of gelant samples decreased with increasing polymer and crosslinker concentration, temperature, pH and decreasing salinity.
5. Gelation time of the new 4000/ 4000 ppm, HPAM/ PEI (Commercial Grade) gelant sample was also compared to the gelation time of other types of water

shutoff polymer gels of comparable concentrations like HPAM/ PEI (Research Grade), PAM/ PEI (Commercial Grade), HPAM/ Chromium(III) Acetate. The experiments were conducted under simillar temperature and shear conditions using the Brookfield DV–III Ultra Rheometer. It was found from the study that the new HPAM/ PEI (Commercial Grade) gelant samples took less time to gel than the HPAM/ PEI (Research Grade) and PAM/ PEI (Research Grade) gelant samples. However, it took substantially more time than HPAM/ Chromium(III) Acetate based gelants, which are used as standard water shutoff polymer gels in conventional formations.

6. Optimum concentartion ratios of the base polymer, HPAM and the crosslinker, PEI (Research/ Commercial Grade) were determined for preparing good gels. Around thirty five gelants samples each, based on research grade PEI and commercial grade PEI with concentration ranging from as low as 3000/ 2000 ppm to as high as 9000/ 10,000 ppm, HPAM/ PEI were prepared and stored at 200 °F for a period of three weeks. All of the seventy samples were assigned a Sydansk gel code on the basis of their appearance and flow characteristics for each of the twenty one days using the 'Bottle Testing' technique. The new HPAM/ PEI (Commercial Grade) gels were found to have a higher gel strength code than the existing chromium(III) acetate based gels. The new gel system was also found to be more stable at high temperature for long period of time than the existing gels.

7. Longer gelation time, higher gel strength at lower HPAM concentration and lower viscosity of the new HPAM/ PEI (Commercial Grade) gel system in comparison to the benchmark chromium(III) acetate based gels, make it better suited for application in shale and tight gas reservoirs which have fractures with narrower apertures. The longer gelation time will provide a longer pumping time to the user, making its field application much more easier. The longer gelation time also means that the new gel system will be partially crosslinked by the time it reaches target zone and thus will be able to penetrate the narrow aperture fractures with ease. Unlike the chromium(III) actetate based gels which would be completely crosslinked and would exert very high extrusion pressure to effectively penetrate the narrow aperture fractures in shale and tight gas reservoirs.
8. HPAM/ PEI gelant samples based on both research and commercial grade PEI were also tested for viscosity variation under variable shear rate at room temperature and at 150 °F using a Fann–35 Viscometer. It was found from the study that viscosity of all the gelant samples decreased with increased shear rate, both at room temperature and at 150 °F. This behavior confirmed the pseudoplastic or shear thinning nature of HPAM/ PEI (Research/ Commercial Grade) gels.

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