HYDROLYZED POLYACRYLAMIDE- POLYETHYLENIMINE- DEXTRAN SULFATE POLYMER GEL SYSTEM AS A WATER SHUT-OFF AGENT IN UNCONVENTIONAL GAS RESERVOIRS

A Thesis

by

SWATHIKA JAYAKUMAR

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

May 2012

Major Subject: Petroleum Engineering

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Approved by:

Co-Chairs of Committee,	Robert H. Lane
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ABSTRACT

Hydrolyzed Polyacrylamide- Polyethylenimine- Dextran Sulfate Polymer Gel System as
a Water Shut-off Agent in Unconventional Gas Reservoirs. (May 2012)
Swathika Jayakumar, B.Tech. Anna University, India
Co- Chairs of Advisory Committee: Dr. Robert H. Lane
Dr. Jerome Schubert

Technologies such as horizontal wells and multi-stage hydraulic fracturing have made ultra-low permeability shale and tight gas reservoirs productive, but the industry is still on the learning curve when it comes to addressing various production issues. Some of the problems encountered while hydraulically fracturing these reservoirs are the absence of frac barriers, thinner shales and the increased presence of geological hazards. Induced vertical fractures sometimes extend to an underlying aquifer and become a conduit to the well. We have developed a low-concentration, low-viscosity and delayed-crosslink polymeric gel system as a water shut-off agent for hydraulically-fractured tight gas and shale reservoirs, where some fractures might connect to water rich zones. The system also is a significant improvement over traditional flowing gels for fracture water shut-off in conventional reservoirs because of these features. The gel uses high molecular weight Hydrolyzed Polyacrylamide (HPAM) at low polymer concentrations with a delayed organic crosslinker. This crosslinker is more environmentally benign and provides much longer gelation time and stronger final gels than comparable polymer

loadings with chromium carboxylate crosslinkers at higher temperatures. The low viscosity system allows low-pressure extrusion of gelant into the narrow-aperture fractures present in unconventional gas reservoirs. The gelant can be pumped at low pressures due to lower polymer concentrations and delayed gelation point. This allows the potential to seal problem zones that are producing excess water, even when the fractures conducting water have very narrow apertures. By impeding water production, the gel system developed here can effectively delay water loading, thereby avoiding abandonment or installation of expensive equipment with increased operational costs, thus extending life and reserves of unconventional gas wells.

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And finally, I would like to thank my mother for always being there for me.

NOMENCLATURE

Ca	Calcium
Cl	Chlorine
cP	centipoise
DS	Dextran Sulfate
HCl	Hydrochloric Acid
HPAM	Hydrolyzed Polyacrylamide
K	Potassium
MW	Molecular weight
Na	Sodium
PAM	Polyacrylamide
PEI	Polyethylenimine
ppm	Parts per million
WGR	Water Gas Ratio
°C	Degree Celsius
°F	Degree Fahrenheit

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CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Unconventional gas wells are becoming a major energy source. Exploration, production, drilling and stimulation activities are prolific in shale gas plays such as the Barnett, Eagle Ford, Marcellus, Fayetteville, Haynesville and Woodford and in the tight gas plays in the Greater Green River Basin, Piceance Basin, San Juan Basin, Williston Basin, Appalachian Basin, Fort Worth Basin etc. Horizontal drilling and hydraulic fracturing are the two main technologies that have transformed these ultra-low permeability reservoirs into profitable ventures.

The hydraulically induced and natural fractures contribute towards increased gas productivity. However, if the fractures act as conduits between the well and an underlying aquifer or a water-bearing formation, it might cause incremental water production. Excessive water production renders the well uneconomical, leading to premature abandonment and large volumes of unrecovered reserves. Polymer gel technology is very effective at controlling the water influx in faulted and fractured reservoirs (Lane and Seright, 2000). However, there has been no specific gel system designed specifically for fractured unconventional gas reservoirs.

This thesis follows the *SPE Journal.*

The intent of this research was to develop and alter polymer gel chemistry to suit the unconventional gas formations. The new gelant formulation should be able to pass through the narrow fracture apertures and effectively seal the fractures connected to water sources.

1.2 Objectives of research

The objective of this research was to develop a solution to address the excessive water production problem in fractured unconventional gas wells. The proposed gel system will have a longer and controllable gelation time for proper placement of the gelant at the problem zone, a lower polymer concentration so the system is dilute enough for placement in narrow aperture natural and induced fractures and, stability at high temperatures and high salinity conditions so the gel treatment can retain strength for an extended period of time.

1.3 Background

A polymer gel typically consists of a water soluble polymer and a crosslinking agent. The low viscosity solution containing the polymer and the crosslinker, often called the gelant, is converted into a rigid structure because of the cross linking reaction. The polymer chains link together to form a three dimensional network (Sydansk, 2007). An inorganic crosslinking agent binds to the polymer through ionic bonds whereas an organic crosslinking agent binds through covalent bonds. An example of the inorganic gel system is Hydrolyzed Polyacrylamide (HPAM) with Chromium(III) acetate crosslinker(Sydansk, 1990) and that of the organic gel system is HPAM polymer with Polyethylenimine(PEI) crosslinker and, a copolymer of Polyacrylamide t-butyl acrylate(PAtBA) and Polyacrylamide(PAM) with PEI crosslinker (Al-Muntasheri et al., 2007; Eoff et al., 2006).

Gel treatments are the most effective means to reducing water channeling through fractures. In fractured reservoirs, formed gels can be extruded into fractures (Lane and Seright, 2000). But typical water shut-off gel formulations are too concentrated to extrude through the much narrower fractures prevalent in tight gas and shale formations. A typical gel formulation is 0.7-1% of polymer with about 500-2000ppm and the rest of the solution is water (Al-Muntasheri et al., 2007). Secondly, delaying the gelation time is the key to ensure proper treatment of the zone producing water. Gel systems with metallic crosslinkers have shorter gelation times and lower thermal stability. The commonly used metallic crosslinkers are multivalent cations such as $Cr^{3+,}$ Al^{3+} or Zr^{4+} (Ahmad, 2000). Early studies in delaying the gelation with metallic crosslinkers indicate that it was achieved by delivering the metallic ion in a complex molecule like acetate, propionate, malonate, glycolate and salicylate (Albonico et al., 1993; Lockhart and Albonico, 1994; Sydansk, 1990). Organic crosslinkers form covalent bonds with the polymer and hence are more stable at elevated temperatures and take longer to gel (Ahmad, 2000; Al-Muntasheri et al., 2008). The common organic crosslinkers include phenol and formaldehyde (Bryant et al., 1997a) and Polyethylenimine(PEI) (Al-Muntasheri et al., 2008). In the study by Al-Muntasheri et al. (2008), PEI was crosslinked with low molecular weight PAM (250-500 kg/gmol). The gelation times of this system was in the range of 20-100 minutes approximately at temperatures ranging from 140°C to 100°C. In general, organic crosslinkers result in gel systems with comparatively longer gelation time and increased stability at higher temperatures as compared to metallic crosslinkers.

1.4 Literature review

1.4.1 Development of unconventional gas resources

There are huge amounts of unconventional gas resources in the world and large exploration, drilling, stimulation and production activities are concentrated in United States. All kinds of unconventional energy resources such as tight gas sands, gas shales, coal bed methane and heavy oil are being developed in US more than in any other part of the world. This is because of the availability of both technology and capital investment. The two technologies that have brought about this development are horizontal wells and hydraulic fracturing. At reasonable gas prices and growing demand for clean fuel, unconventional gas reservoirs can be developed and produced at economic rates (Holditch, 2007).

Research is the key to sustained development of the above resources and to overcome various operational problems. According to EIA, some of the earliest research in this field dates back to mid-1970s when a group of operators, the U.S Department of Energy (DOE) and Gas Research Institute (GRI) developed technologies such as horizontal wells, multi-stage fracturing and slick water fracturing for commercial production of natural gas from Devonian shale in the eastern United States (*Review of Emerging Resources U.S. Shale Gas and Shale Oil Plays*, 2011). Recent research has been concentrating on improved fracturing fluids, mathematical models, three dimensional fracture simulators and fracture imaging methods to understand the science behind developing these resources in an efficient way. Solutions for associated water production problems have not been studied extensively for unconventional low permeability reservoirs because associated water production is usually minor in these reservoirs. Any excess production of water is usually from fractures connecting the well to an underlying aquifer. In our research we concentrate on excessive associated water production from shale and tight gas reservoirs and not on other types of unconventional gas resources like coal bed methane and gas hydrates. Stimulation and production techniques are similar in case of shale and tight gas reservoirs, as are the problems associated with them such as excessive water production. Mechanism of water production from coal bed methane and hydrate formations is also totally different.

The major shale plays in the lower 48 states include the Barnett, Eagle Ford, Marcellus, Fayetteville, Haynesville and Woodford **(Fig. 1)** and some of the tight gas plays are in the Greater Green River Basin, Piceance Basin, San Juan Basin, Williston Basin, Appalachian Basin and Fort Worth Basin **(Fig. 2)**.

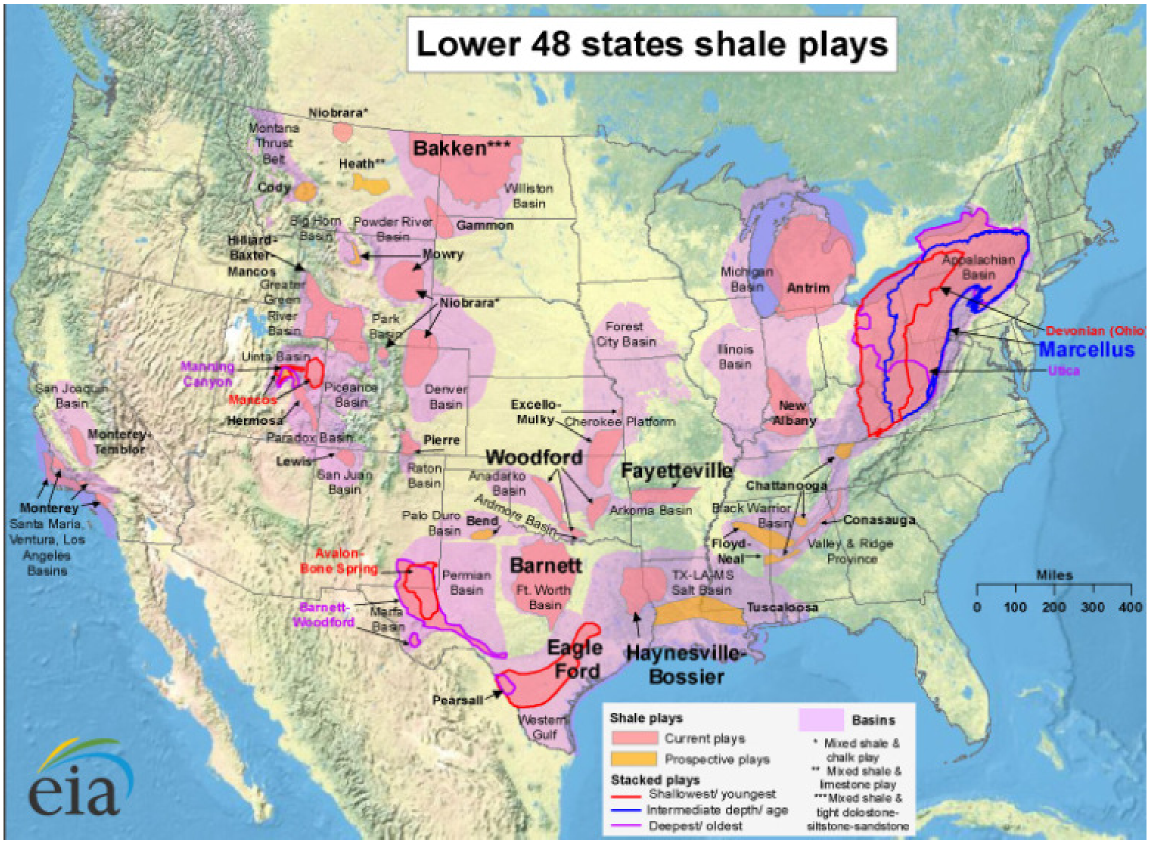


Fig. 1— Map of U.S. shale gas and shale oil plays (as of May 9,2011). Source U.S. Energy Information Administration.

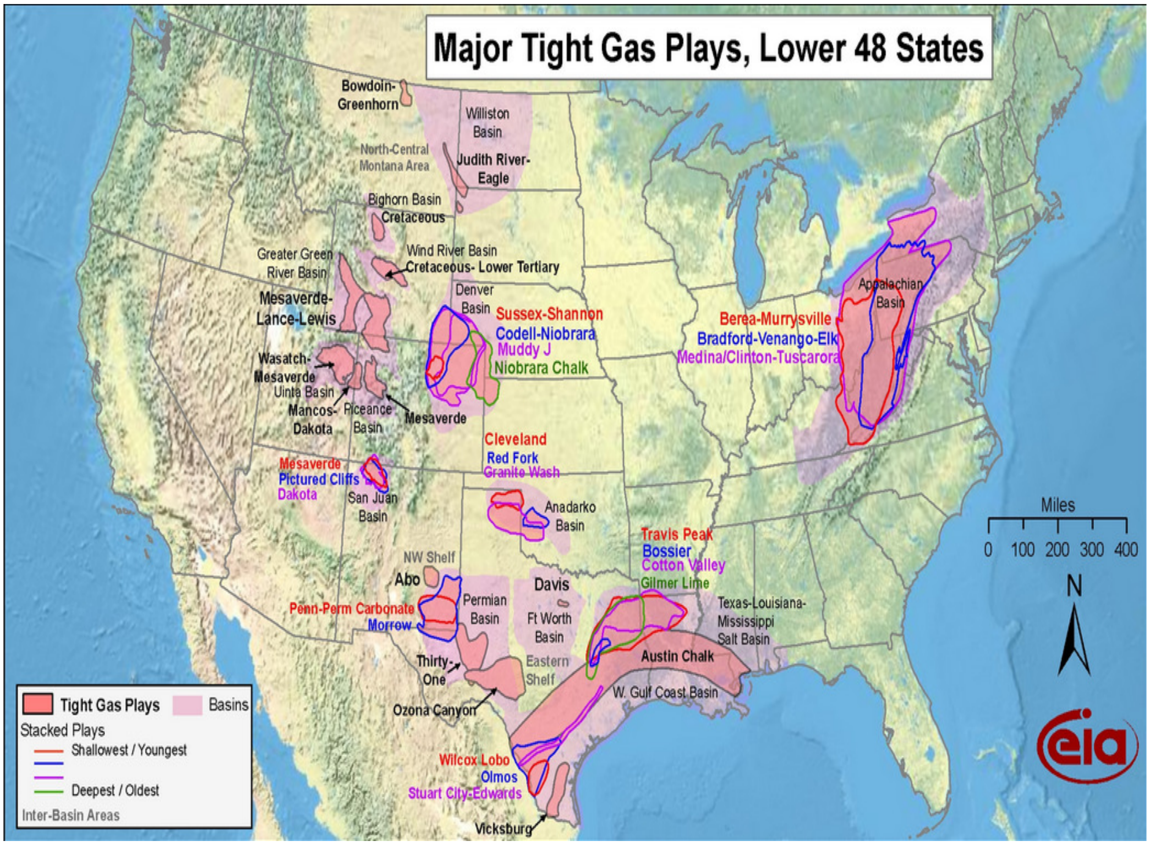


Fig. 2— Major tight gas plays in the lower 48 states. Source: Energy Information Administration based on data published from various published studies.

1.4.2 Hydraulic fracturing

Artificially inducing fractures is the key technique that has transformed previously unproductive ultra-low permeability reservoirs to economically viable projects. Hydraulic fracturing involves pumping large quantities of pressurized fluids into the wellbore which creates fractures and cracks in the reservoir, thereby increasing the effective permeability. The induced fractures become flow paths connecting the reservoir to the wellbore, thereby increasing gas flow rates. A hydraulic fracture treatment often starts with the pumping of Hydrochloric acid (HCl). This is done to clean the near wellbore area of cement and drilling mud. This is followed by slickwater, which is primarily water with a friction reducing chemical that allows the water to be pumped at higher rates into the shale. The next step is pumping another large volume of slickwater along with fine sand; this is followed by slickwater with coarser sand proppant. The proppant keeps the fractures open for gas to flow to the well. The last step is to clean the wellbore and equipment by flushing to remove the proppant from them. (Arthur et al., 2009).

The procedure described above is called a treatment stage. One horizontal well may have more than twenty treatment stages. Each stage is specifically designed based on reservoir properties such as thickness, total organic content, permeability and mechanical properties such as local stress conditions, Young's modulus and compressibility.

1.4.3 Excessive water production-unconventional gas reservoir case

Excess water production is a problem both environmentally and economically, especially for lower pressure reservoirs, leading to premature abandonment and large volumes of unrecovered gas reserves. In general, a high water-gas ratio (WGR) is economically detrimental because of the costs associated with separation, treatment and disposal of the produced water. Particularly at low reservoir pressures and/or low gas rates, a higher water-gas ratio (WGR) means huge costs in lifting the fluids to the surface. In most conventional reservoirs, the produced water is re-injected into the reservoir to keep the pressure up or for increased recovery. Disposal of produced water in shale gas reservoirs is an issue because of extremely low permeabilities. Produced water is usually taken to treatment plants in trucks which again leaves a footprint on the environment.

All the above factors limit the WGR up to which a well can be produced before treatment and disposal costs exceed per-well profits. An effective shut-off agent that reduces the amount of water produced without damaging the formation could add a huge amount to the proven reserves. There is no effective water shut-off agent specifically designed for shale and tight gas reservoirs.

1.4.4 Examples of excessive water production from shale and tight gas wells

Associated water production is usually very little in shale and tight gas reservoirs due to their ultra-low permeability. Excess water production is said to occur when the ratio of the water produced back to the water introduced in the formation through completion activities is greater than unity. Excessive water produced is most probably from fractures connecting an underlying aquifer to the producing well in most cases. Extensive hydraulic fracturing is what makes the shale and tight gas reservoirs productive but sometimes because of geological hazards such as the absence of fracture barriers and thinner shales, the induced fractures might extend to an underlying aquifer or a water bearing zone.

The first example is from the Barnett Shale, the most extensively explored shale gas play in the country; there have been claims of unsuccessful fracture treatments to the west of the Viola pinch out because of breakouts into the water-prone Ellenberger (King, 2011).

An extensive analysis of the water production dataset from nearly 11000 completions was done using conventional statistical techniques to study the water production mechanisms. The conclusions from this work are that 15% of the horizontal and vertical wells drilled in Denton County have a load water recovery factor greater than unity. Also, 15%/35% of the horizontal/vertical wells drilled in Parker County have a load recovery factor of greater than unity(Awoleke and Lane, 2010). This means that the Barnett Shale wells produce more water than was injected during drilling and completion. The data implies that the above percentages of wells are connected to an external water source.

The second example is from a tight gas reservoir. Ozobeme (2007) found that the wells completed in the Cotton Valley formation producing gas from tight sands are also producing very large volumes of water, in the order of 100-1000 bbls/MMcf. This is an exceedingly high rate of associated water production for a tight gas reservoir, where the rates are typically 10bbls/MMcf or less. In the above stated research, they analyze open-hole logs, core data, geologic maps and production data from the Cotton Valley sands in the Elm Grove and Caspiana fields to determine the source of the large volumes of water. Hydraulic fractures, natural fractures and faults could be the pathways that connect the water source to the wells **(Fig. 3)**. The study stated that it may most likely have been from large natural fractures and a poor fault sealing that is said to be the north of the field. Based on the simulation conducted in the study, it was concluded that the water source should be at a depth of 500ft from the edge of hydraulic fracture (Ozobeme, 2007).

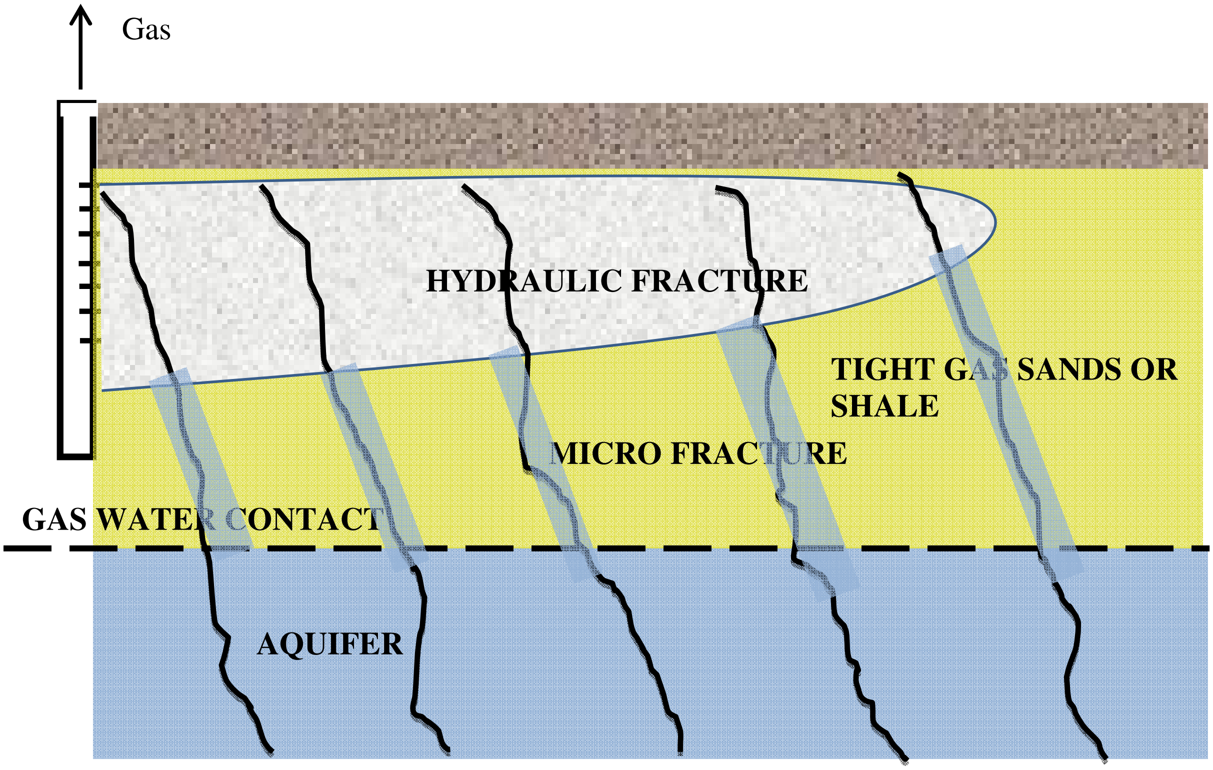


Fig. 3— A cartoon depicting a shale or tight gas reservoir with natural and hydraulic fractures connecting the aquifer to the well with flow of water.

1.5 Technologies to deal with excessive water production

Factors to be considered while designing a gel treatment for a fractured reservoir are the composition of the gel, gelation time, pressure gradient in the fracture, and the size, conductivity and the tortuosity of the fracture. Pressure gradients observed while placing gels in narrow fractures are related to fracture aperture(Seright, 1995). In fractured conventional reservoirs, gelant leakoff from fractures into the formation can be a major impediment to placement. To minimize this potential problem the polymer gel is partially crosslinked in order to reduce the gelant leakoff. However, in the narrow aperture fractures prevalent in unconventional gas reservoirs, a partially crosslinked, and high viscosity gelant would require very high extrusion pressures for proper placement.

1.6 Significance of a customized water shut-off agent

Assuming that the fractures in unconventional reservoirs are very narrow, a water shut-off agent for the fractured unconventional reservoir will need to be of lower initial viscosity than those of the higher concentration, partially crosslinked gels used in conventional fractured reservoir **(Table 1)**. If a gelant solution of higher initial viscosity is used to shut-off the narrow natural and induced fractures prevalent in shale and tight gas reservoirs, it would result in very high extrusion pressures. The extrusion pressure is related to the square root of the fracture aperture and it is thought that viscous gelant solutions, especially when partially crosslinked, would not be able to enter the narrow aperture fractures (Seright, 1995). In this research, we work on polymer concentrations from 3000ppm to 5000ppm which have a much lower initial viscosity.

The second most important property of a gel system that is to be used as a water shut-off system in deep and high temperature unconventional gas reservoirs is a delayed gelation point. This delayed gelation point addresses the problem of early partial crosslinking before the gelant reaches the fractures. The gelant solution retains its lower viscosity for an extended period of time. This ensures that the polymer will not be partially crosslinked during extrusion which further decreases the pressure requirements for proper placement.

Organic crosslinkers provide both relatively longer gelation time along with stability at elevated temperatures (Broseta et al., 2000). In order to delay the gelation even further, a controlled release approach is used. This involves binding the crosslinker, by mixing Polyethylenimine and Dextran Sulfate (Cordova et al., 2008). An electrostatic interaction between the sodium salt of Dextran Sulfate and PEI leads to a polyelectrolyte complex. PEI is a polycation and DS is a polyanion, the oppositely charged polymers self-assemble through phase separation to form nanoparticles at room temperature (Cordova et al., 2008; Tiyaboonchai et al., 2003). Initial increase in viscosity is due to the residual free PEI and at higher temperatures; the PEI-DS bonds break and release the crosslinker into the gel system. The PEI-DS system offers a significant delay in the gelation point, allowing enough time for proper placement of the gelant in the narrow fractures producing water. The customized water shut-off agent has a low initial concentration, longer gelation time, stronger final gel strength and most importantly is made of commercial available products **(Table 2)**.

Table 1— Comparison of properties of fractured reservoirs relevant to gel treatments.

Problem	Conventional Reservoirs	Unconventional Gas Reservoir requirement
Fracture aperture	Both wide and narrow	Mostly narrow
Leakoff into matrix	Higher gelant leakoff rate	Minimal gelant leakoff owing to ultra-low permeabilities

Table 2—Comparison of gel properties in existing systems and the new system developed for unconventional gas reservoir.

Parameters	Existing systems	New gel system
Gel type used for treatment	Partially crosslinked by the time it reaches the fractures	Needs to be of lower viscosity to avoid high extrusion pressures in narrow fractures
Polymer loading (HPAM)	Higher concentrations of 7000-10000 ppm	Lower concentrations of 4000-7000 ppm
Gelation point	In the order of few mins to few hours	The delayed crosslinker has a longer gelation point of up to 24 hours
Type of crosslinker	Metallic and Organic	Organic with a delaying additive, Dextran Sulfate

1.7 Delaying the gelation time

One of the objectives of this research was to achieve significant delay in gelation, allowing enough time for proper placement of the gelant solution in the narrow fractures. This will ensure the success of the treatment. Typically gel systems with metallic crosslinkers such as Cr^{3+}, Al^{3+} or Zr^{4+} have shorter gelation times and lower thermal stability (Ahmad, 2000). Earlier attempts at delaying the gelation time included delivering the trivalent metallic ion in a complex molecule (Sydansk, 1990), so as to reduce the rate of reaction. A few examples of this mechanism include attaching the chromium to complex molecules such as propionate and malonate (Lockhart and Albonico, 1994), glycolates, salicylate (Albonico et al., 1993). Additionally, the effectiveness of metallic crosslinkers reduces when used for treating high temperature reservoirs. This is because of the weak ionic bonds between HPAM and the metallic cross linker.

Organic crosslinkers form covalent bonds and these are much stronger at higher temperatures and have longer gelation times (Ahmad, 2000). The common organic crosslinkers include phenol and formaldehyde (Bryant et al., 1997b). The toxic nature of phenol and formaldehyde's carcinogenicity renders this particular organic crosslinking system unusable(Moradi-Araghi, 1994). So other chemicals were tested to be used in place of phenol and formaldehyde. The replacements for phenol include *o*- and *p*-aminobenzoic acids, *m*-aminophenol, phenyl acetate, phenyl salicylate, salicylamide, salicylic acid and furfuryl alcohol and HMTA for formaldehyde (Moradi-Araghi, 1994).Another organic crosslinking system is a combination of hydroquinone(HQ) and hexamethylenetetrmine(HMTA) (Hutchins et al., 1996).

The organic crosslinking systems already studied for their stability at high temperatures include terephtalaldehyde, terephthalic acid, dihydroxynaphthalene, glutaric acid, gallic acid and dibasic esters. These cross linkers are classified into primary and secondary crosslinkers, where primary crosslinkers produce unstable gels with the polyacrylamide polymer and the secondary cross linker stabilize the gel at higher temperatures. The primary crosslinkers are HMTA, terephtalaldehyde, terephthalic acid and glutaric acid and the secondary crosslinkers are while HQ, dihydroxynaphthalene and gallic acid(Dovan et al., 1997).

The cross linker extensively studied for high temperature application is Polyethyeleninime (PEI). Earlier research concentrated on using it with low molecular weight HPAM for matrix shut-off purposes. Low molecular weight HPAM is used for matrix shut-off purposes to block thief zones producing excessive water. PEI as a crosslinker has also been evaluated with polymers like PAM (Allison and Purkaple, 1988) and with a copolymer comprising of PAtBA and PAM (Al-Muntasheri et al., 2008). However, high molecular weight HPAM is used for fracture shut-off and its reaction mechanism with PEI crosslinker has not been studied extensively. Our research group studied with high molecular weight HPAM polymer with both research grade and commercial grade PEI as a crosslinker. The HPAM-PEI was intended to be a low cost water shut-off agent for fractured reservoirs.

All the systems stated above have gelation time ranging from a few minutes to about 100 minutes at temperatures above 100° C (Al-Muntasheri et al., 2007; Al-Muntasheri et al., 2008). For proper and successful gel treatments at elevated temperatures and deep problem zones in shale and tight gas plays, the gelation time should be at least in the order of 2-12 hours. A delayed gelation system was developed by Cordova et al. (2008). The mechanism for the delayed crosslinking was adapted from Tiyaboonchai et al.

(2003). Dextran Sulfate and Polyethylenimine, a polyanion and polycation respectively are mixed to form a polyelectrolyte nanoparticle suspension (**Fig. 4**)**.** This complex swells and acts as a nanoparticle shell which can be used as a delayed delivery vehicle of the crosslinker, when the bonds between PEI and DS break and release the entrapped molecule within. In Cordova et al. (2008), Chromium(III) acetate was entrapped within the nanoparticle created by mixing PEI and DS. Upon adding the crosslinker to the polymer solution, the PEI-DS bonds break slowly, thereby releasing the Chromium(III) acetate into the gelant system. The gelation time was around 5 hours at 80°C with HPAM- nanoparticle crosslinker delivery system as opposed to few minutes with just HPAM-Chromium(III) acetate crosslinker (Cordova et al., 2008). In this research, the Chromium(III) acetate was eliminated as the primary crosslinker. The nanoparticle suspension of PEI-DS was used as the crosslinker. The bonds between PEI-DS break slowly, releasing PEI into the gelant system and causing significant delay in the gelation point **(Fig. 5**).

Fig. 4— Polyelectrolyte nanoparticle suspension of Polyethylenimine and Dextran Sulfate.

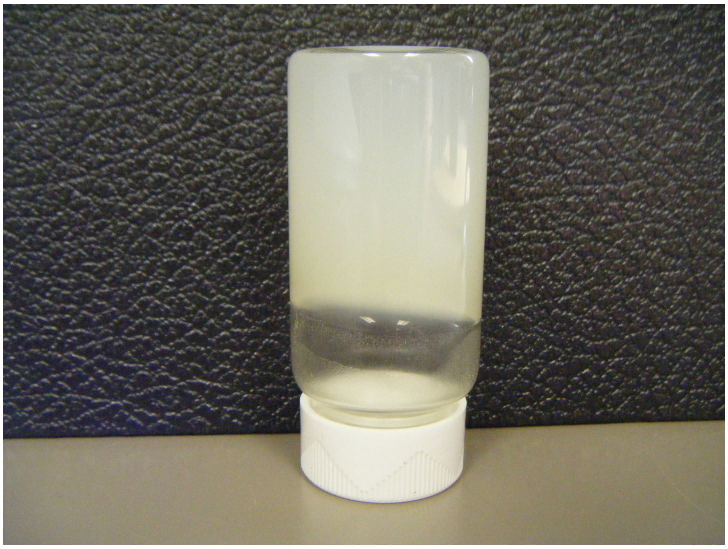


Fig. 5—A Hydrolyzed Polyacrylamide- Polyethylenimine- Dextran Sulfate gel with 7000ppm HPAM, 7000ppm PEI and 3500ppm Dextran Sulfate.

CHAPTER II

MATERIALS AND METHODS

2.1 Chemicals used

The polymer used in this study was high molecular weight (~2 – 5 million Daltons) Hydrolyzed Polyacrylamide (HPAM) obtained from a commercial supplier and used without further purification. Dextran Sulfate obtained from Fisher Scientific was used without further purification (Molecular weight = 400,000 - 600,000 Daltons). Two grades of Polyethylenimine (PEI), research and commercial were used **(Table 3)**. The research grade PEI obtained from Fischer Scientific was also used without further purification. Commercial grade PEI was obtained in liquid form from a supplier. It was described by the supplier as "approximately" 25% by weight solids in aqueous solution. No molecular weight was provided. The pH of the commercial grade pH had to be increased to 9 and above in order to obtain gels of good strength. The properties of both types of PEI are tabulated below.

Table 3— Physical properties of research and commercial grade Polyethylenimine (PEI).

Properties	Research Grade PEI	Commercial Grade PEI
Physical form	50% w/v aqueous solution	Approximately 25% w/v solution
Molecular weight (Daltons)	50000-100000 (average)	Not specified
Density (g/ml)	1.07	1.06
pH	10.5-11 @1% solution	7-8 @ 5% solution
Viscosity	Approximately 10000-20000 cP (20℃, 20 rpm)	150-350 cP (23℃)

2.2 Equipment used

A magnetic stirrer was used for making polymer solutions and mixing gelant solutions, 20 ml scintillation vials were used for Sydansk bottle testing, Orion 3-Star Plus pH meter for pH adjustments, DV-III Ultra Rheometer and UL adapter from Brookfield with a temperature bath were used for rheological characterization of the gel samples, and Zeta Potential Analyzer Utilizing Phase Analysis Light Scattering (ZetaPALS) for measuring particle size and zeta potential of the nanoparticle suspension.

2.2.1 DV-III ultra rheometer

The DV-III Ultra has the capability of measuring viscosity over an extremely wide range. This range is achieved through the use of several spindles over many speeds. The process of selecting a spindle and speed for an unknown fluid is a trial and error process. The general rule that helps in this trial and error process is that the viscosity range is inversely proportional to both the size of the spindle and the rotational speed. For example, to measure a high viscosity, choose a small spindle and/or a slow speed. In our case, we consistently used the 62 spindle at a speed of 20 rpm for multiple data point collection. The multiple viscosity data points are used to determine gelation time. Gelation time is defined as the inflection point of the viscosity- time graph.

2.2.2 Small sample adapter with circulating water bath for temperature control

The Brookfield UL Adapter can be used with a Brookfield rheometer for temperature control while measuring viscosity. The UL Adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube. Its rheologically correct cylindrical geometry provides accurate viscosity measurements and shear rate determinations which enables detailed product analysis. With the cap in place, the closed tube can be immersed in a temperature bath or used with a ULA-40Y water jacket for precise temperature control. The working temperature range is from -15°C to 100°C. This device has been used to determine initial viscosity and exact gelation points of samples in a controlled temperature.

The gelant solution is transferred into a UL adapter. The temperature is adjusted in the adjacent water bath from which hot water is circulated through the jacket surrounding the UL adapter for temperature control. An appropriate spindle is used based on the viscosity range of the solution to be tested. Since the solutions we test are from a viscosity range of 60-500 rpm, we use a No. 62 spindle at 20 rpm throughout all our experiments for uniformity in results. Viscosity and torque values are measured every 10 minutes. Gelation point is defined as the time corresponding to the inflection point on the viscosity vs. time curve.

2.2.3 Zeta potential analyzer utilizing phase analysis light scattering (ZetaPALS)

A ZetaPALS is used to study the size and the Zeta potential of nanoparticles. A dilute solution of the polyelectrolyte nanoparticle suspension obtained by mixing research grade PEI and DS was used in this study.

2.2.4 Orion 3-Star plus benchtop pH meter

The pH meter with a probe is used to adjust the pH of the PEI to study its effect on gelation time. It can be programmed for automatic temperature compensation for more accurate results. The attached electrode is inserted in the solution for simultaneous display of pH and temperature on the LCD display.

2.3 Experimental procedure

2.3.1 Preparation of polymer solution

A magnetic stirrer was used to prepare polymer solutions. Typically, polymer was weighed and added slowly to the edge of a vortex created in the water by the magnetic stirrer. The water is typically a 1% NaCl or 1% KCl solution. The solution is stirred for at least 3 hours until it forms a uniform clear solution.

2.3.2 Preparation of the polyelectrolyte nanoparticle suspension for delayed gelation

A 10 percent weight/ volume solution of research grade PEI was added to a volumetrically appropriate amount of 10 percent solution of the Sodium salt of Dextran

Sulfate. The solution was allowed to stir for a few minutes on the magnetic stirrer until a homogeneous solution was formed. A translucent mixture containing nanoparticles was obtained. This mixture was used as the crosslinking agent in this study and is known as the polyelectrolyte nanoparticle suspension. Light scattering experiments were performed on the polyelectrolyte suspension to study the size and zeta potential of the particles.

2.3.3 Preparation of the gelant solution

To prepare a HPAM solution, the polymer was dissolved in 1% Potassium Chloride solution. The 1% salt solution was in a beaker on a magnetic stirrer set at a speed sufficient to maintain a vortex during HPAM addition and initial polymer hydration. A measured amount of high molecular weight HPAM was slowly added to the outer edge of the vortex. The solution was then allowed to stir gently for at least 3-5 hours or until a clear solution was formed. This ensures proper dissolution and prevents the formation of clumps known as fisheyes. Fisheyes occur when the polymer particles stick together and do not dissolve properly. This result in wastage of polymer and in actual field conditions, it can cause plugging of the surface pumping equipment, piping, perforations and/or reservoir rock. Then, a nanoparticle suspension containing the appropriate amount of PEI crosslinker was added to the solution. The resulting gelant solution was allowed to stir for a few minutes until a homogeneous solution was formed.

2.3.4 Size and zeta potential of nanoparticle polyelectrolyte suspension

Zeta Potential Analyzer Utilizing Phase Analysis Light Scattering (ZetaPALS) was used in this study. A 0.1% weight/volume solution of PEI and a 0.1% weight/volume solution of DS were mixed in a ratio of 1:1 and 3:1. A translucent mixture was obtained which is indicative of presence of Nano or colloidal size particles. This solution was then transferred to a specially designed container to be used in a light scattering device to study the size and zeta potential of the nanoparticles in solution.

2.4 Sydansk bottle testing method

Bottle testing is a highly cost-effective and straightforward technique to obtain a semi-quantitative measure of gel strength and gelation rate. It is also a convenient means to evaluate long term stability at a given test temperature. Bottle testing in the laboratory is used to rapidly screen a large number of gel samples and to select a few of the gel samples for more costly and rigorous testing such as the dynamic-oscillatory-viscosity measurements. The gel strength code is set up such that two observers, who view the same gel sample, should be able to assign to the sample a gel strength code that differs by no more than one letter code **(Table 4)**. For gel strength comparison using Sydansk gel code, same volumes of gelant should be placed in identical bottles or ampoules (Sydansk, 2007).

Table 4—Sydansk gel code classification.

Code	Gel type	Gel behavior in the bottle
A	No detectable gel formed	The gelant solution appears to have the same viscosity(fluidity) as the original polymer solution, and no gel structure is visually detectable
B	Highly flowing gel	The gel appears to be only slightly more viscous than the initial polymer solution
C	Flowing gel	Most of the obviously detectable gel flows to the bottle cap on inversion of the bottle
D	Moderately flowing gel	A small portion(approximately 5 to 15%) of the gel does not readily flow to the bottle cap on inversion-usually characterized as a “tonguing” gel (i.e., after hanging out of the bottle, the gel can be made to flow back into the bottle by slowly turning the bottle upright).
E	Barely flowing gel	The gel slowly flows to the bottle cap and/or a significant portion (>15%) of the gel does not flow to the bottle cap on inversion.
F	Highly deformable nonflowing gel	The gel does not flow to the bottle cap on inversion (gel flows to just short of reaching the bottle cap).
G	Moderately deformable nonflowing gel	The gel flows approximately halfway to the bottle cap on inversion.
H	Slightly deformable nonflowing gel	Only the gel surface slightly deforms on inversion.
I	Rigid gel	There is no gel-surface deformation on inversion.
J	Ringing rigid gel	A tuning-fork-like mechanical vibration can be felt after the bottle is mechanically tapped.

In this study we use 20 ml scintillation vials which seal well, preventing the entry of extraneous oxygen. They also withstand high temperatures for an extended period of time. Bottle testing was done to understand the difference in gel strength and the approximate gelation time between various samples prepared with different polymer, crosslinker, cation concentrations at different temperatures and pH. The gelant solution was transferred to the vials such that it occupies 50% of the volume of the bottle. The bottles were then kept at a desired elevated temperature in an industrial oven. The bottles were taken out periodically and a Sydansk gel code was assigned (**Fig. 6**). The Sydansk gel code is indicative of the strength of the gel system, and this also gives an estimate of the gelation time which we use later in our research to narrow down the gelation time, when we attempt to delay the gelation process.

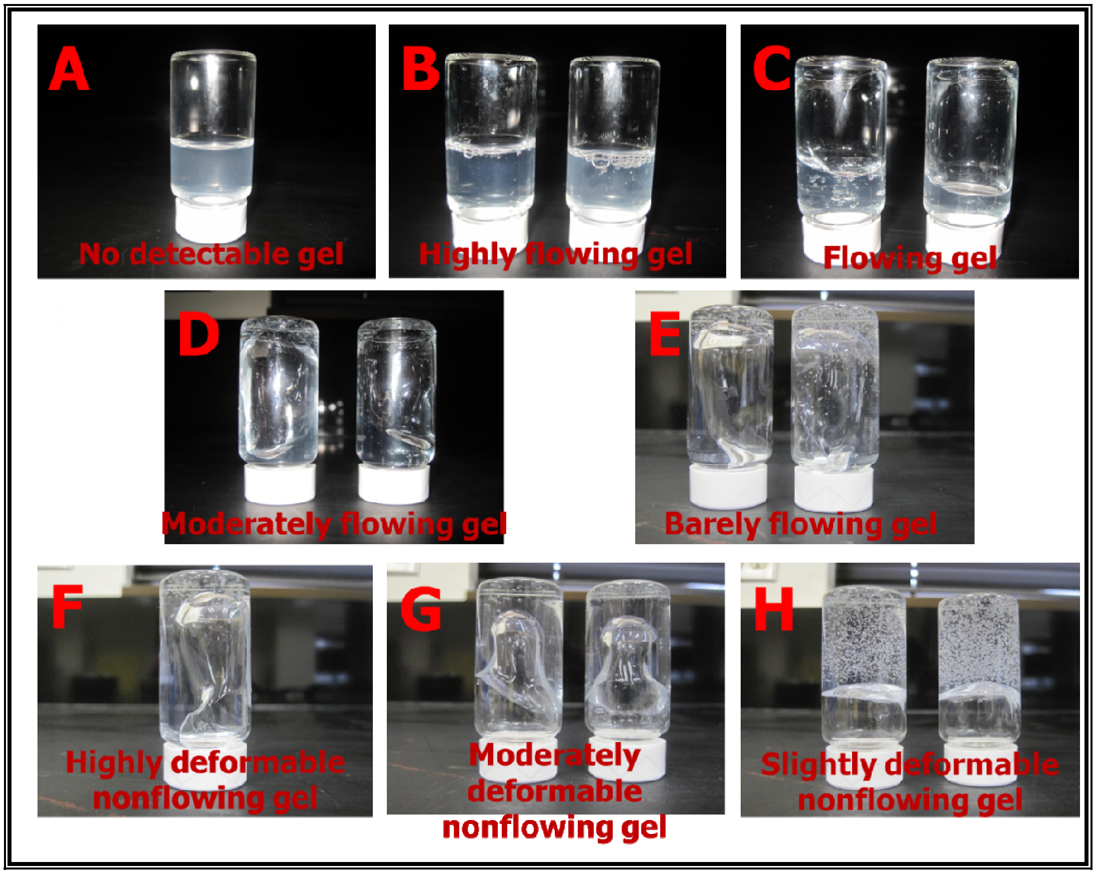


Fig. 6—Sydansk gel code assigned to gel samples.

2.5 Gelation time curves

The DV-III Ultra Rheometer (Brookfield) with LV spindle No.62 was used to measure the viscosity to determine the gelation time. The gelation time is the time taken for the gelant viscosity to increase sharply with time at a constant temperature. It is the inflection point of the viscosity- time graph. The various controlling factors studied were the concentrations of polymer, crosslinker (PEI), and delaying agent (DS), DS: PEI volume ratio, temperature, pH and salt concentration.

2.6 Comparison between gelation time curves and bottle testing method

Commercially available PEI gives a longer delay in gelation when used in the form of polyelectrolyte nanoparticle suspension (by mixing it with Dextran Sulfate) for delayed crosslinking. However, to find the exact gelation point, the gelant solution has to be maintained at an elevated temperature in an oxygen-free environment for up to 36-48 hours and the viscosity has to be measured using a rheometer periodically. In this study, the gelant solution was stored in a high density polyethylene bottle and placed in an industrial oven. It was taken out periodically to measure the viscosity using the DV-III Rheometer. The system did not gel properly within the same time range it had gelled during the Bottle testing method. Hence it was difficult to determine the gelation time with the viscosity-time curve. This is consistent with the temperature and developing gel structure being disturbed too often and yielding the inconsistent results. Therefore it was concluded that the approximate time taken to attain gelation using the nanoparticle suspension should be determined using the Sydansk bottle testing method. The gelation time, the inflection point on the viscosity-time graph, was correlated to the Sydansk gel code at the same time and temperature. The gelation time of a gelant solution of HPAM polymer with PEI and DS was determined using a DV-III Rheometer. A part of the same solution was used for Bottle testing where Sydansk gel code of the sample was noted down periodically. The gelation time from the graph was correlated to the Sydansk gel code change at that time. For ease of plotting, codes A through J of the Sydansk gel code are represented here with the numbers 1 through 10 respectively. This is referred to as Sydansk gel code- Numerical in the graphs (**Table 5**).

Table 5—Numerical Sydansk gel code for plotting data.

Code	Numerical Sydansk gel code
A	1
B	2
C	3
D	4
E	5
F	6
G	7
H	8
I	9
J	10

2.7 Measurement of gel time under various conditions-controlling variables

2.7.1 Effective polymer concentration

Polymer solutions of various concentrations such as 3000ppm, 4000ppm, 5000ppm, 7000ppm and 9000ppm were prepared by dissolving the polymer in a 1% Sodium Chloride solution. These polymer solutions were then used to prepare gelant solutions to study the effect of polymer concentration on gelation time.

2.7.2 Effective PEI concentration

The effect of PEI concentration on the gelation point was studied by varying the concentrations of PEI for the same concentration of polymer (7000ppm). The amount of PEI was varied with each sample keeping the polymer concentration same and the DS: PEI ratio was kept at 1:2.

2.7.3 Effective Dextran Sulfate concentration in crosslinker

To study the delaying effect of Dextran Sulfate on gelation time, gelant solutions with and without Dextran Sulfate were prepared. The delaying effect the addition of DS has on the system was studied through this experiment.

2.7.4 Effective DS to PEI ratio

The PEI and DS ratio is the important factor that controls the delay of the gelation point as DS binds with the crosslinker, PEI and slowly releases it into the gelant system. The ratio is controlled by varying the amount of DS added to a given amount of PEI, while preparing the nanoparticle crosslinker solution. The crosslinking agent thus prepared is used to study the effect of DS: PEI ratio on the gelation point.

2.7.5 Effective temperature

Experiment temperature was controlled using an UL adapter with a circulating water bath. A temperature probe attached to the DV-III Ultra Rheometer was used to check the temperature of the system.

2.7.6 Effective pH

In this study, pH of the system was controlled by controlling the pH of the Polyethylenimine solution. The pH of the research grade PEI was 10-11 and was used as received. The pH of the commercial grade PEI was 7-8 and the pH had to be increased in order to obtain strong gels. The commercial grade PEI was tested under two different pH values; 9.65 and 10.65. A 5N solution of NaOH was freshly prepared and used to control pH. The pH is adjusted to the desired point using a Thermo Scientific Orion Benchtop pH meter.

2.7.7 Effective salt concentration

The influence of both monovalent and divalent cations on the polymer gel was studied by preparing both 1% and 2% solution of the salts and using that solution to dissolve the polymer. In this study, we used chloride salts of Sodium, Potassium, Calcium and Magnesium. The dissolved polymer is then used to prepare the gelant to study and the effect of cations on the gelation time.

2.7.8 Effective polymer molecular weight

Low molecular weight Hydrolyzed Polyacrylamide is generally used to prepare gels intended for matrix shut-off. The effect of the delaying agent on the strength of final gel systems with low molecular weight polymer was studied. Polymer solutions of concentrations, 30000ppm and 40000ppm were dissolved in 1% NaCl and 6000ppm and 800oppm of PEI: DS crosslinking agent was added in a 3:1 ratio respectively.

2.7.9 Effective molecular weight of Polyethylenimine (PEI)

Three different types of PEI were evaluated in this study. The two types of research grade PEI differ by molecular weight and a commercial grade PEI. These were used to prepare the polyelectrolyte nanoparticle suspension with Dextran Sulfate, which is the delayed crosslinking agent in this study. The effect of the PEI molecular weight on gelation time was studied.

CHAPTER III

RESULTS

3.1 Hydrolyzed Polyacrylamide-Chromium(III) acetate system

Sydansk bottle testing and gelation time determination was done for the gel system comprising of high molecular weight HPAM and Chromium(III) acetate crosslinker **(Table 6)**. Initial screening of the gel system was done based on gelation time and final gel code. At comparable polymer loadings, the HPAM-PEI-DS system resulted in a stronger final gel than the HPAM-Chromium(III) acetate system. For example, at 4000 ppm HPAM concentration, the final Sydansk gel code with the Chromium(III) acetate crosslinker is C, whereas the Sydansk gel code with the PEI-DS crosslinker is a G. This denotes a stronger gel at the same polymer concentration. Low polymer concentrations translate to low initial viscosity and therefore, low extrusion pressure through the fractures as compared to the Chromium(III) acetate-HPAM system. The additional delay in gelation offered by the PEI-DS crosslinker helps maintain the low viscosity long enough for placement in high temperature, deep reservoirs.

Table 6—Comparison of properties between the Chromium(III) acetate crosslinker the PEI-DS crosslinker.
***- With DV-III Ultra Rheometer and LV spindle 62.**

Parameters	HPAM- Chromium(III) acetate gel		HPAM-PEI-DS gel	
HPAM concentration, ppm	4000	7000	4000	7000
Crosslinker type	Chromium(III) acetate		Commercial grade PEI	
Crosslinker concentration, ppm	400	560	4000	7000
DS concentration, ppm	N/A	N/A	800	1400
DS: PEI Ratio	N/A	N/A	1:2	1:2
pH of PEI	N/A	N/A	10.65	10.65
Temperature	100° C	100 °C	100 °C	100 °C
Salt concentration	1% Potassium Chloride	1% Potassium Chloride	1% Potassium Chloride	1% Potassium Chloride
Gelation time	7 minutes	5 minutes	12 hours	8 hours
Initial gelant viscosity*, @ 20rpm, 100° C	27 cP	28.5 cP	24.0 cP	25.5cP
Final Sydansk gel code	C	G	G	I

3.2 Comparison of gelation times between various crosslinking systems

Unconventional gas reservoirs are usually deep with high formation temperatures. For example, the average well depth in the Haynesville is 11800feet with an average bottom hole temperature of 300 °F (U.S. Shale Gas, 2008). Longer gelation times are required for proper placement of the gel in identified problem zones that may have fractures and faults that connect a water source to the well. A controlled release approach was used to delay the gelation process(Cordova et al., 2008). Mixing of PEI and DS at room temperature results in a polyelectrolyte nanoparticle suspension (Tiyaboonchai et al., 2003). The bonds between PEI and DS break over time and at higher temperatures, slowly releasing PEI (the crosslinker) into the gel system. This mechanism causes the delay in the gelation process. **Fig. 7** indicates that a considerable delay was achieved in the onset of gelation by adding Dextran Sulfate to PEI at 100 °C **(Table 7)**.

Table 7—Comparison between various crosslinkers based on gelation time, Sydansk gel code at 100°C.

Polymer concentration, HPAM, ppm	Crosslinker with concentration, ppm	Gelation time	Sydansk gel code	pH
4000	Chromium(III) acetate 400	Less than 5 min	B	10.22
4000	Research grade PEI 4000	100 min	I	10.21
4000	Research grade PEI+DS 4000+2000	160 min	I	10.22
4000	Commercial grade PEI+DS 4000+2000	8 hours	G	10.65

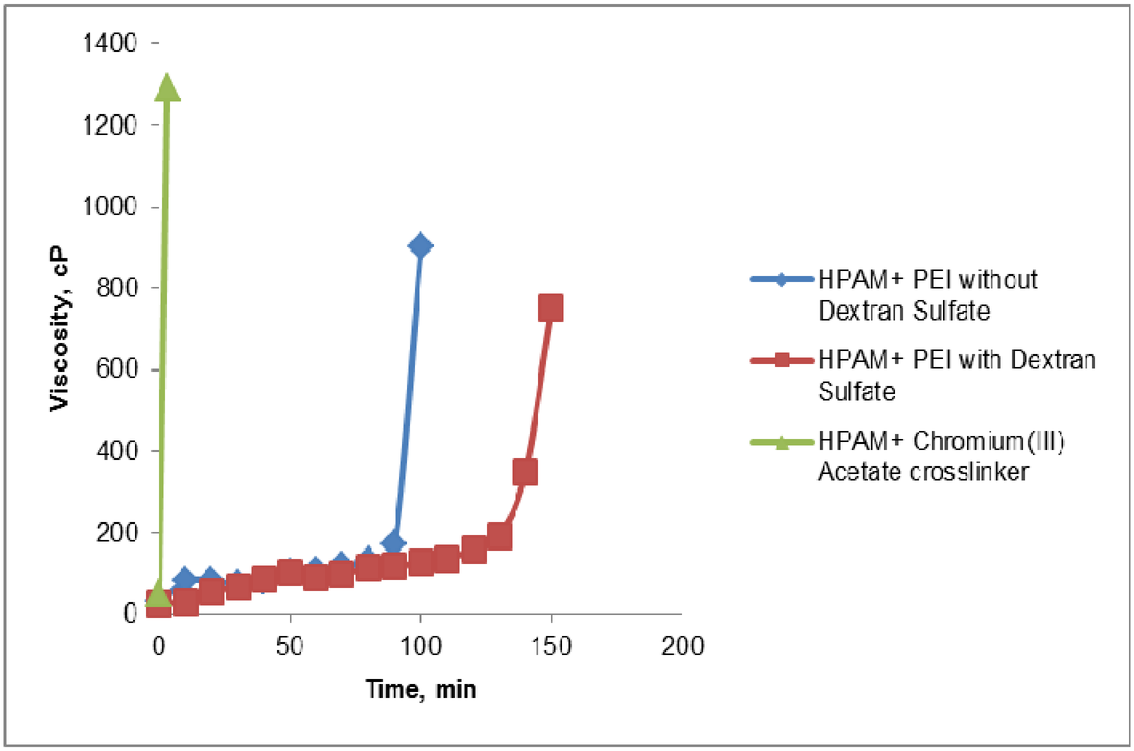


Fig. 7— Comparison of gelation times between Chromium(III) acetate, PEI and PEI-DS crosslinking system on 7000ppm HPAM solution with 1% KCl at 100°C.

3.3 Comparison between gelation time curves and bottle testing method

Commercial grade Polyethylenimine (PEI) had a delay in gelation of up to 8-15 hours depending on various conditions such as polymer concentration, temperature, pH etc. Using the DV-III Ultra Rheometer for that period of time at elevated temperatures to determine the gelation time was not deemed practical. To overcome this problem, a method was developed to correlate the gelation time to Sydansk gel code change with time. This was used to determine the approximate gelation time when commercial grade PEI was used in the delayed crosslinking system. **Fig. 8** below indicates that the gelation time of a 7000ppm HPAM/7000ppm PEI system was approximately the same amount of time required for the Sydansk gel code to change from A to B. In samples prepared with the commercial PEI and DS, the gelant was kept in a 20ml glass vial in an oven. It was taken out periodically and the Sydansk gel code was noted. For ease of plotting, codes A through J of the Sydansk gel code are represented here with the numbers 1 through 10 respectively. This is referred to as Sydansk gel code- Numerical in the graphs **(5).**

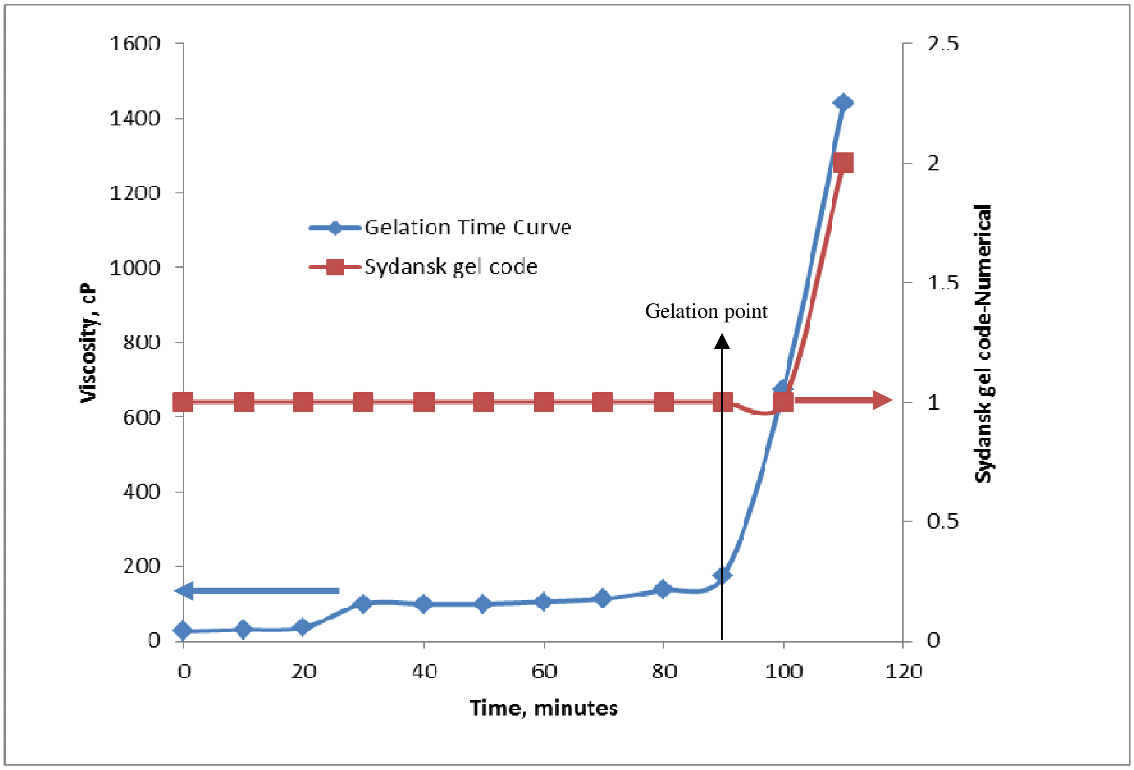


Fig. 8— A comparison of gelation time between viscosity- time graph and change in Sydansk gel code with time.

3.4 Effect of various controlling factors on gelation time

The gelation time can be controlled by altering factors such as polymer concentration, crosslinker concentration, DS: PEI volume ratio, temperature, pH and, salt concentration in the polymer solution. The effect of the above controlling factors on gelation time was studied both with research grade PEI and commercial grade PEI (**Table 8**). The viscosity time graph was used to determine the gelation time with research grade PEI. For commercial grade PEI, the gelation time was determined based on the change in Sydansk gel code. The responses of the gelation time to change in the above parameters are tabulated below.

Table 8 —Effect of various parameters on gelation time.
***- When pH was maintained in the 9-10.65 range.**

Parameter	When the parameter	Gelation time
Polymer concentration	Decreases	Increases
PEI concentration	Decreases	Increases
Ratio of DS: PEI	Increases	Increases
pH of PEI	Increases	Increases slightly*
Temperature	Increases	Decreases
Salt concentration	Increases	Increases

3.5 Size and zeta potential of the nanoparticle

A Zeta Potential Analyzer Utilizing Phase Analysis Light Scattering (ZetaPALS) was used in this study for conducting the light scattering experiments. A 0.1percent weight/volume solution of PEI and a 0.1 percent weight/volume solution of DS were mixed in ratios of 1:1 and 3:1. A more dilute composition was used for this experiment as the equipment's (ZetaPALS) accuracy decreased at higher concentrations. The translucent mixture obtained was indicative of presence of Nano or colloidal size particles. This solution was then transferred to a specially designed container to study the size and zeta potential of the nanoparticles in solution. The effective diameter of the particles on the basis of weight percentage of solution and PEI: DS ratio is shown in the graph below **(Fig. 9- Fig. 13)**. **Table 9** shows effective diameter of the nanoparticles in the suspension of varying PEI and DS weight/volume percentages and PEI: DS ratios.

Table 9—Effective diameter of nanoparticles in the suspension for varying PEI, DS weight/volume percentages and PEI: DS ratios.

PEI weight/volume %	DS weight/volume %	PEI:DS ratio	Effective diameter, nm
0.1	0.1	1:1	203
0.1	0.1	3:1	197
1	1	1:1	717
1	1	3:1	581

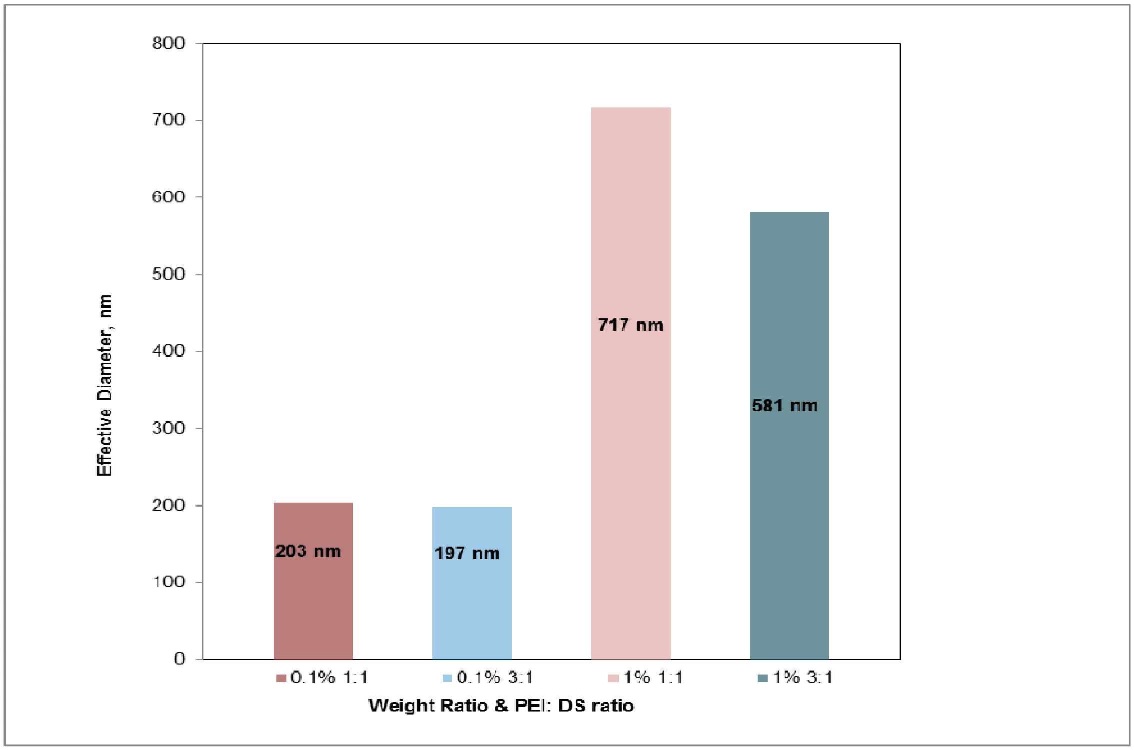
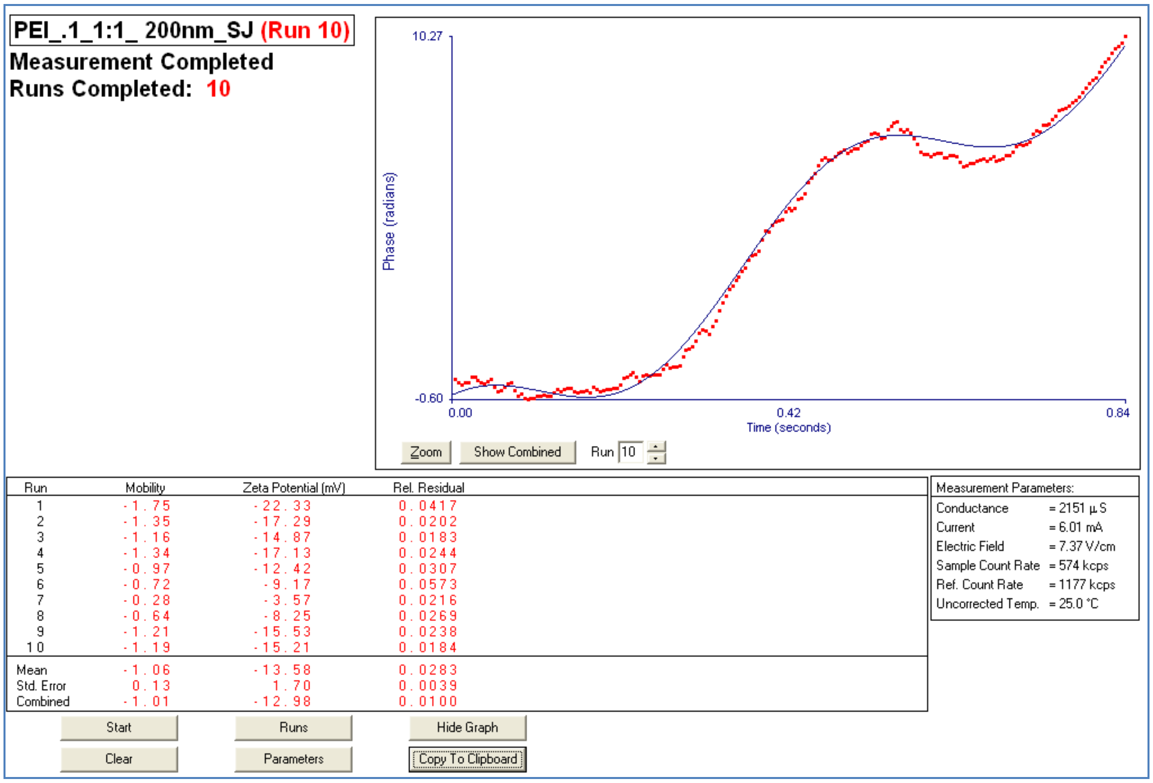


Fig. 9—Effective diameter of nanoparticle suspension of various concentration and PEI: DS ratios.



PEI_.1_1:1_ 200nm_SJ (Run 10)

Measurement Completed

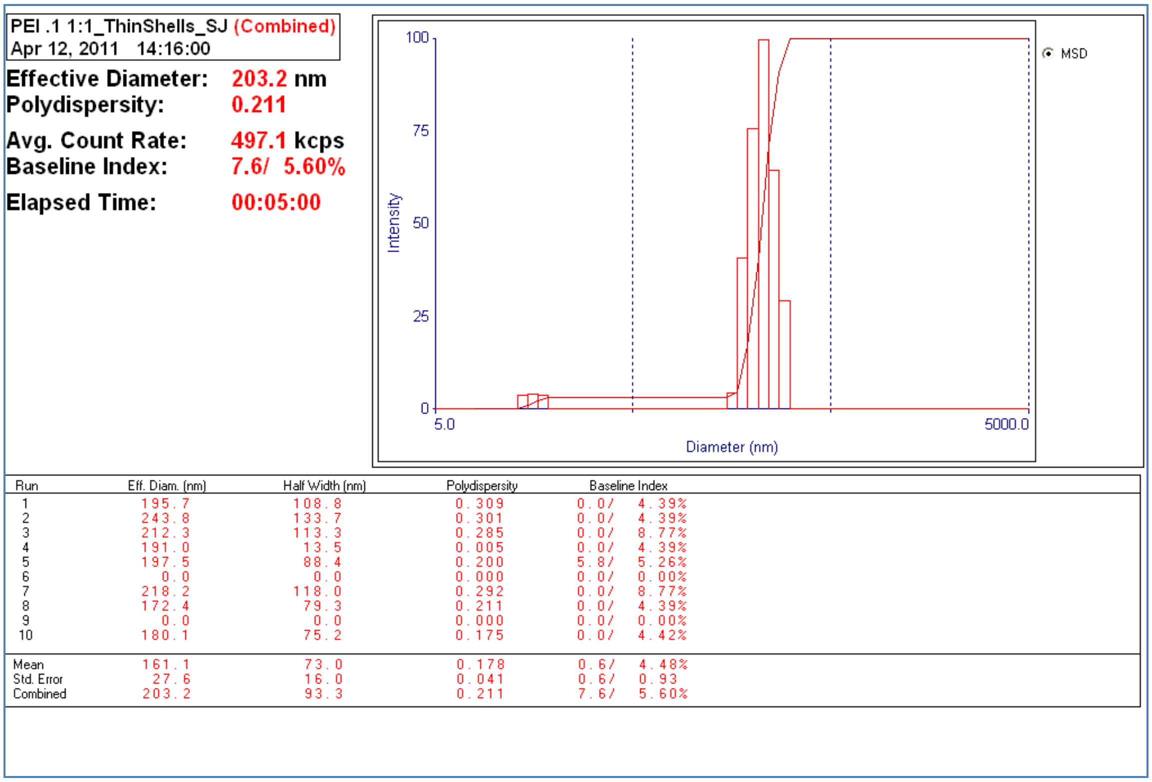
Runs Completed: 10

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-1.75	-22.33	0.0417
2	-1.35	-17.29	0.0202
3	-1.16	-14.87	0.0183
4	-1.34	-17.13	0.0244
5	-0.97	-12.42	0.0307
6	-0.72	-9.17	0.0573
7	-0.28	-3.57	0.0216
8	-0.64	-8.25	0.0269
9	-1.21	-15.53	0.0238
10	-1.19	-15.21	0.0184
Mean	-1.06	-13.58	0.0283
Std. Error	0.13	1.70	0.0039
Combined	-1.01	-12.98	0.0100

Measurement Parameters:

Conductance = 2151 µS
Current = 6.01 mA
Electric Field = 7.37 V/cm
Sample Count Rate = 574 kcps
Ref. Count Rate = 1177 kcps
Uncorrected Temp. = 25.0 °C

Fig. 10—Zeta potential distribution of 0.1% 1:1 PEI-DS nanoparticle suspension.

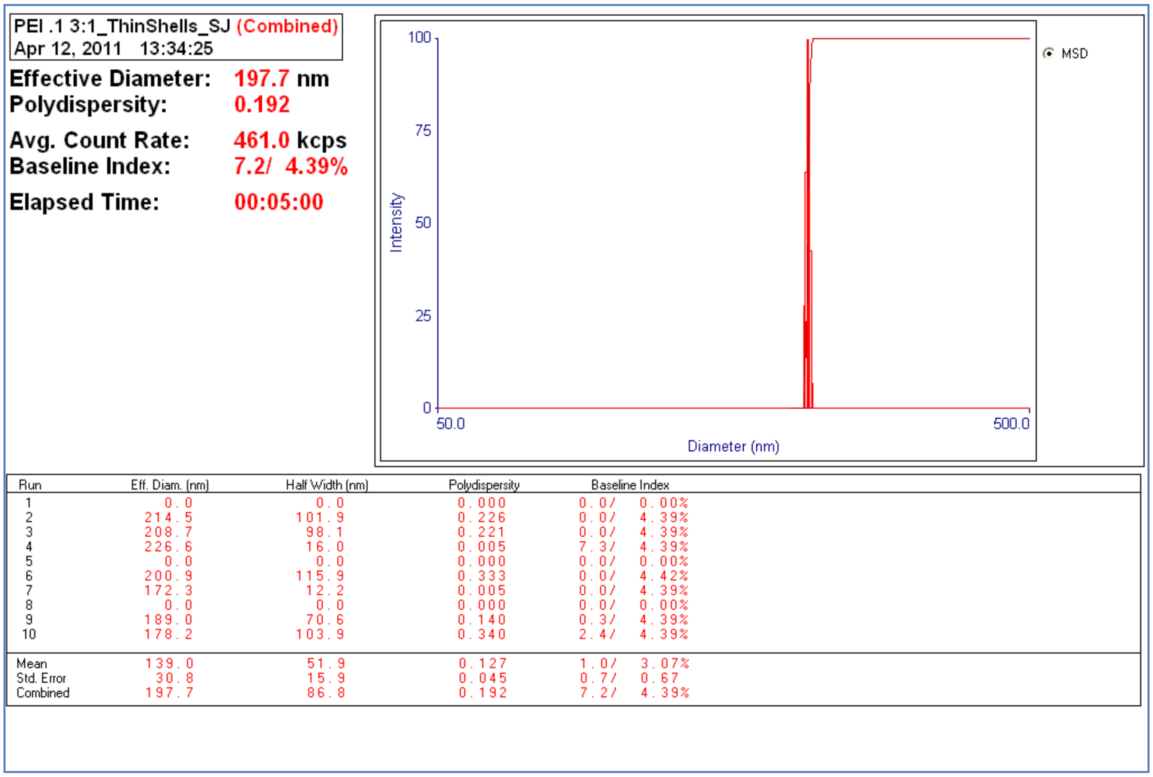


PEI .1 1:1_ThinShells_SJ (Combined)
Apr 12, 2011 14:16:00

Effective Diameter: 203.2 nm
Polydispersity: 0.211
Avg. Count Rate: 497.1 kcps
Baseline Index: 7.6/ 5.60%
Elapsed Time: 00:05:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	195.7	108.8	0.309	0.0/ 4.39%
2	243.8	133.7	0.301	0.0/ 4.39%
3	212.3	113.3	0.285	0.0/ 8.77%
4	191.0	13.5	0.005	0.0/ 4.39%
5	197.5	88.4	0.200	5.8/ 5.26%
6	0.0	0.0	0.000	0.0/ 0.00%
7	218.2	118.0	0.292	0.0/ 8.77%
8	172.4	79.3	0.211	0.0/ 4.39%
9	0.0	0.0	0.000	0.0/ 0.00%
10	180.1	75.2	0.175	0.0/ 4.42%
Mean	161.1	73.0	0.178	0.6/ 4.48%
Std. Error	27.6	16.0	0.041	0.6/ 0.93
Combined	203.2	93.3	0.211	7.6/ 5.60%

Fig. 11—Size distribution of 0.1% 1:1 PEI-DS nanoparticle suspension.



PEI .1 3:1_ThinShells_SJ (Combined)
Apr 12, 2011 13:34:25

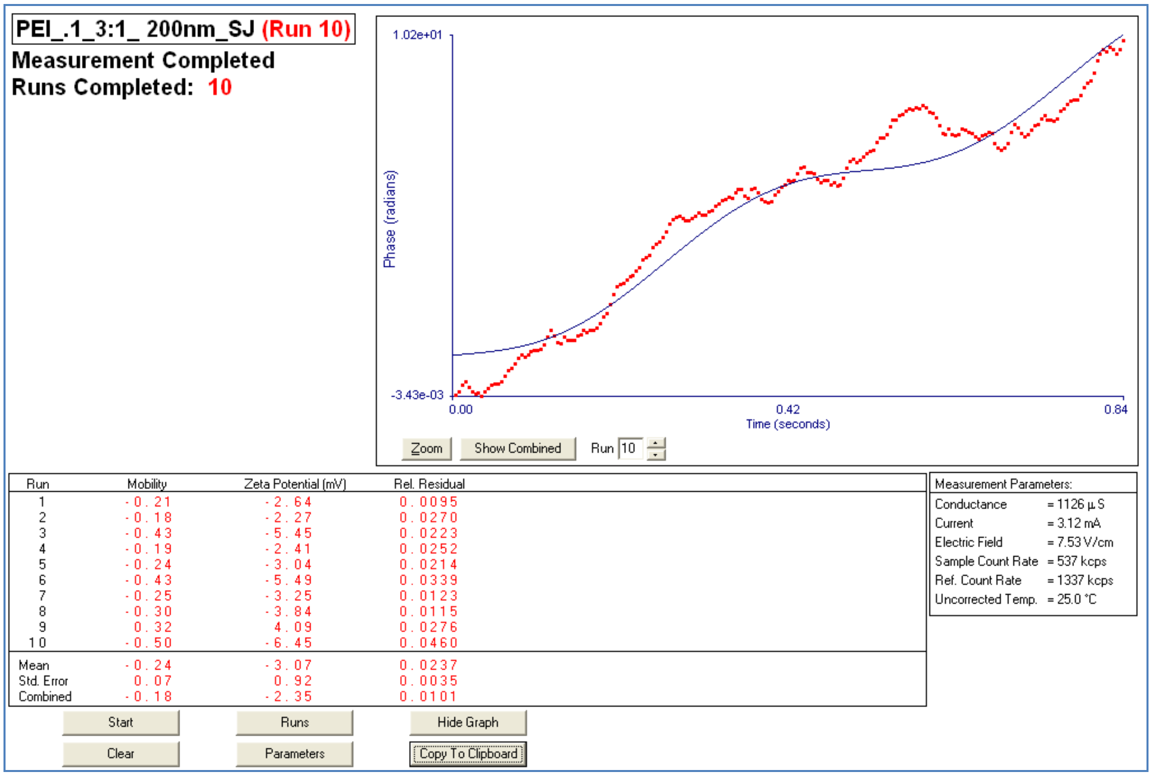
Effective Diameter: 197.7 nm
Polydispersity: 0.192

Avg. Count Rate: 461.0 kcps
Baseline Index: 7.2/ 4.39%

Elapsed Time: 00:05:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	0.0	0.0	0.000	0.0/ 0.00%
2	214.5	101.9	0.226	0.0/ 4.39%
3	208.7	98.1	0.221	0.0/ 4.39%
4	226.6	16.0	0.005	7.3/ 4.39%
5	0.0	0.0	0.000	0.0/ 0.00%
6	200.9	115.9	0.333	0.0/ 4.42%
7	172.3	12.2	0.005	0.0/ 4.39%
8	0.0	0.0	0.000	0.0/ 0.00%
9	189.0	70.6	0.140	0.3/ 4.39%
10	178.2	103.9	0.340	2.4/ 4.39%
Mean	139.0	51.9	0.127	1.0/ 3.07%
Std. Error	30.8	15.9	0.045	0.7/ 0.67
Combined	197.7	86.8	0.192	7.2/ 4.39%

Fig. 12— Zeta potential distribution of 0.1% 3:1 PEI-DS nanoparticle suspension.



PEI_.1_3:1_ 200nm_SJ (Run 10)

Measurement Completed

Runs Completed: 10

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-0.21	-2.64	0.0095
2	-0.18	-2.27	0.0270
3	-0.43	-5.45	0.0223
4	-0.19	-2.41	0.0252
5	-0.24	-3.04	0.0214
6	-0.43	-5.49	0.0339
7	-0.25	-3.25	0.0123
8	-0.30	-3.84	0.0115
9	0.32	4.09	0.0276
10	-0.50	-6.45	0.0460
Mean	-0.24	-3.07	0.0237
Std. Error	0.07	0.92	0.0035
Combined	-0.18	-2.35	0.0101

Measurement Parameters:

Conductance	= 1126 µS
Current	= 3.12 mA
Electric Field	= 7.53 V/cm
Sample Count Rate	= 537 kcps
Ref. Count Rate	= 1337 kcps
Uncorrected Temp.	= 25.0 °C

Fig. 13— Size distribution of 0.1% 3:1 PEI-DS nanoparticle suspension.

CHAPTER IV

RESULTS-CONTROLLING VARIABLES

4.1 Effect of polymer concentration on gelation time

Fig. 14 shows the changes in gelation time with polymer concentration. For a gelant with 4000ppm polymer concentration, 4000ppm of PEI was used and the DS: PEI volume ratio was maintained at 1:2 in the nanoparticle crosslinking solution. It can be observed that the gelation time increases with decrease in polymer concentration. Hence, using a low- viscosity, low polymer concentration would result in a considerable delay in gelation. This would be an added advantage while treating deep, high temperature formations.

Fig. 15 shows the change in gelation time with polymer concentration when commercial grade PEI was used in the crosslinking solution. The gelation time is the point of transition of the Sydansk gel code from A to B. The gelation time of a 4000 ppm HPAM gelant is close to 14 hours with the commercial grade PEI and DS. For both sets of experiments, the temperature of investigation was 100°C and the polymer was prepared in 1% Potassium Chloride solution.

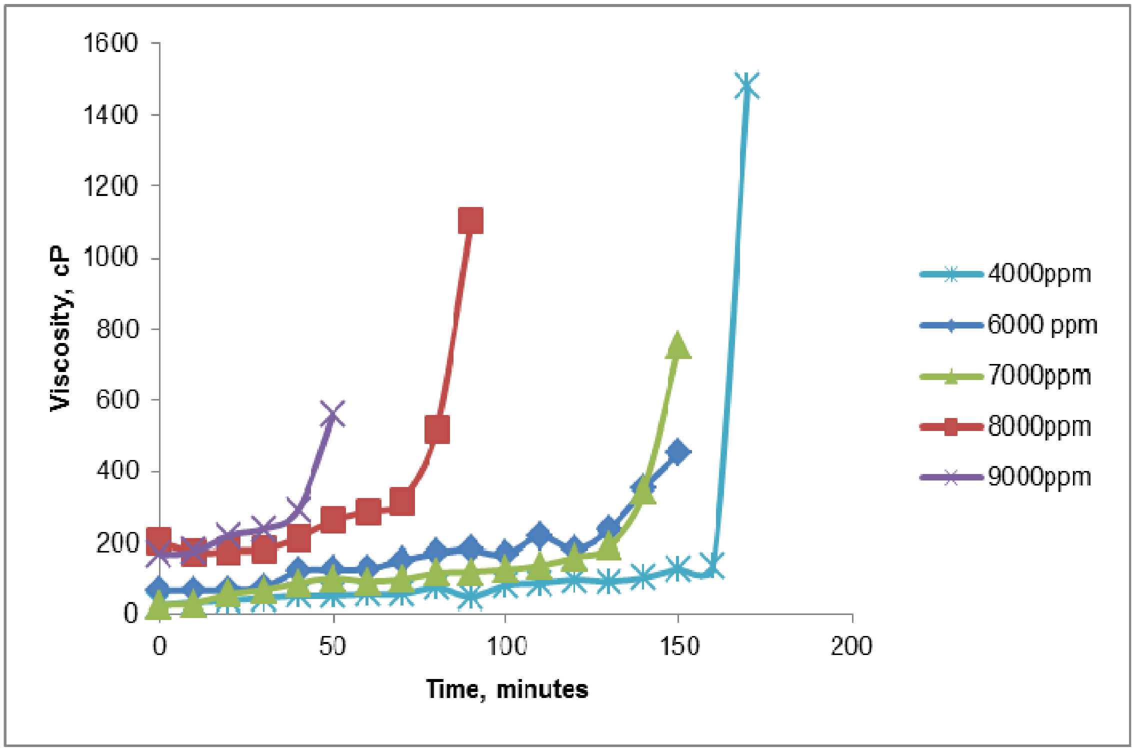


Fig. 14—Effect of polymer concentration on gelation time. Research grade PEI was used with DS: PEI ratio kept at 1:2. The samples were maintained at 100°C.

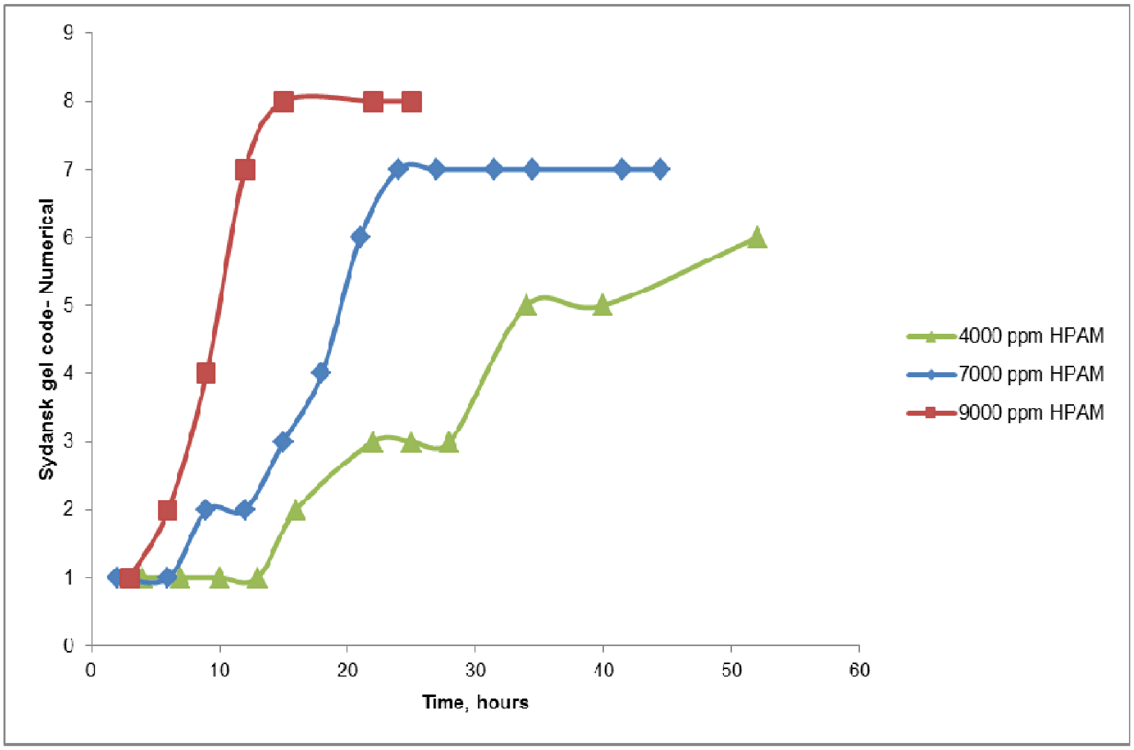


Fig. 15— Effect of polymer concentration on gelation time when commercial grade PEI was used in the delaying crosslinker. The DS: PEI ratio was kept at 1:2 and the samples were maintained at 100 °C. The pH of commercial grade PEI used was 10.65.

4.2 Effect of PEI concentration on gelation time

Fig. 16 shows the change in gelation time when the PEI concentration in the delayed crosslinking agent was varied while holding the polymer concentration and temperature constant. Also, the volumetric ratio of DS: PEI was kept constant at 1:2 in both samples. Decreasing PEI concentration led to a delayed onset in gelation. A 7000 ppm solution of HPAM polymer dissolved in 1% weight/volume Potassium Chloride solution was used as the stock solution throughout this study unless specified otherwise.

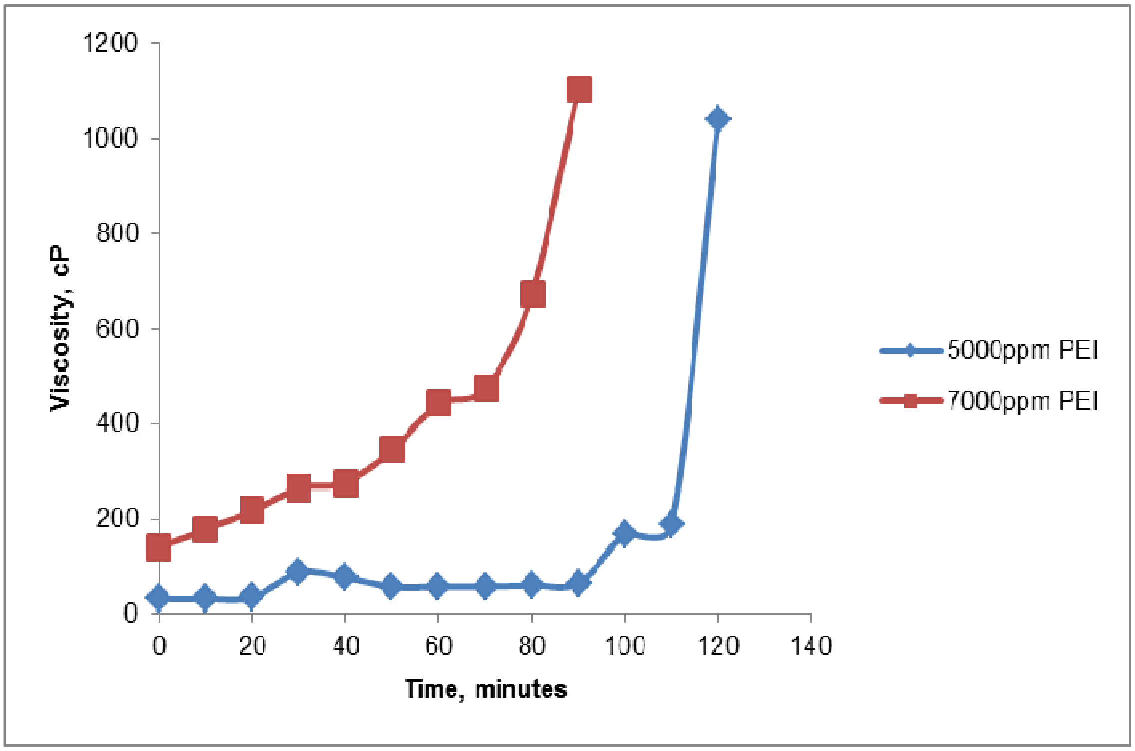


Fig. 16— Effect of research grade PEI concentration on gelation time. The polymer concentration was 7000ppm HPAM in both samples with DS: PEI volume ratio kept at 1:2. The samples were maintained at 100°C.

The effect of the concentration of commercial grade PEI on gelation time can be observed in the graph below (**Fig. 17**). It can be seen that the decrease in the PEI concentration in the delayed crosslinker increased the gelation time when the polymer concentration and temperature were maintained constant.

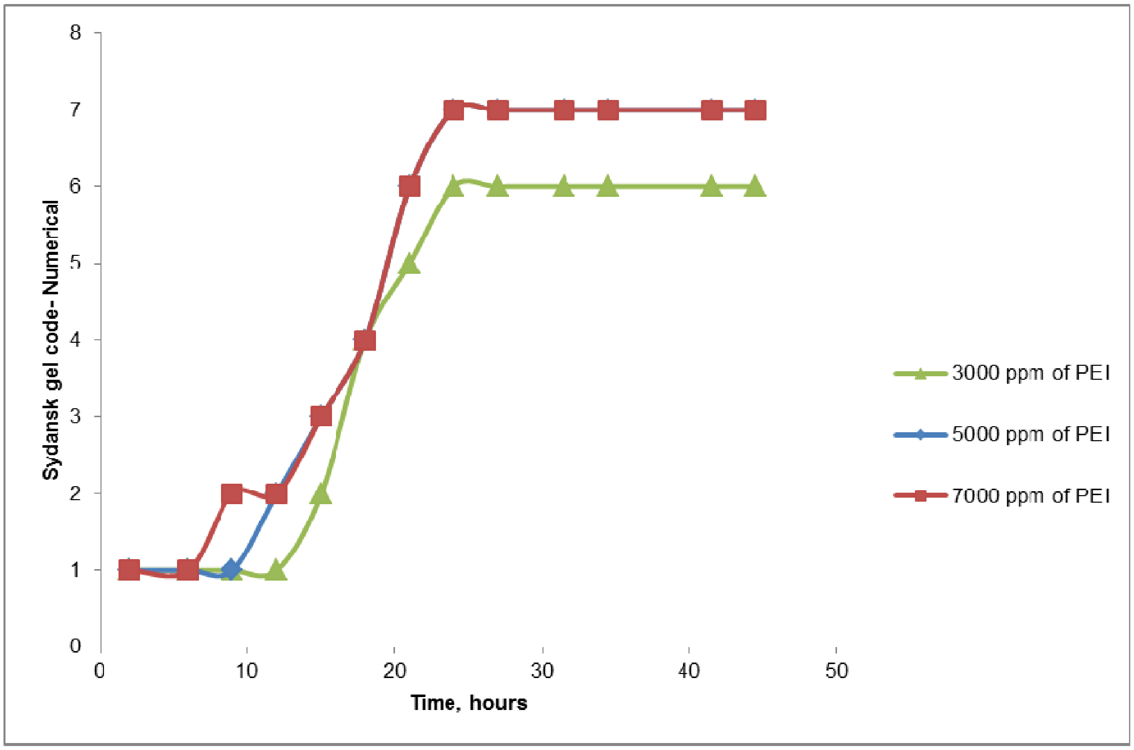


Fig. 17—Effect of commercial grade PEI concentration on gelation time. The gelant had 7000ppm HPAM polymer with DS: PEI volume ratio at 1:2. The samples were maintained at 100°C. The pH of commercial grade PEI used was 10.65.

4.3 Effect of DS: PEI concentration ratio on gelation time

The effect of DS: PEI volume ratio on gelation time can be seen in **Fig. 18 and Fig. 19**.The delay in gelation time was achieved by transiently binding the PEI crosslinking sites with DS, and making it temporarily unavailable for crosslinking with the HPAM polymer. To better control the delay in gelation time, the ratio of DS: PEI can be adjusted. For a shorter delay in gelation, the DS: PEI should be as low as 1:5 and for a longer delay in gelation time, it could be 1:2. The mechanism of faster gelation at low concentrations of DS can be explained by the availability of free PEI in the beginning of the reaction. This contributed to the steady increase in viscosity.

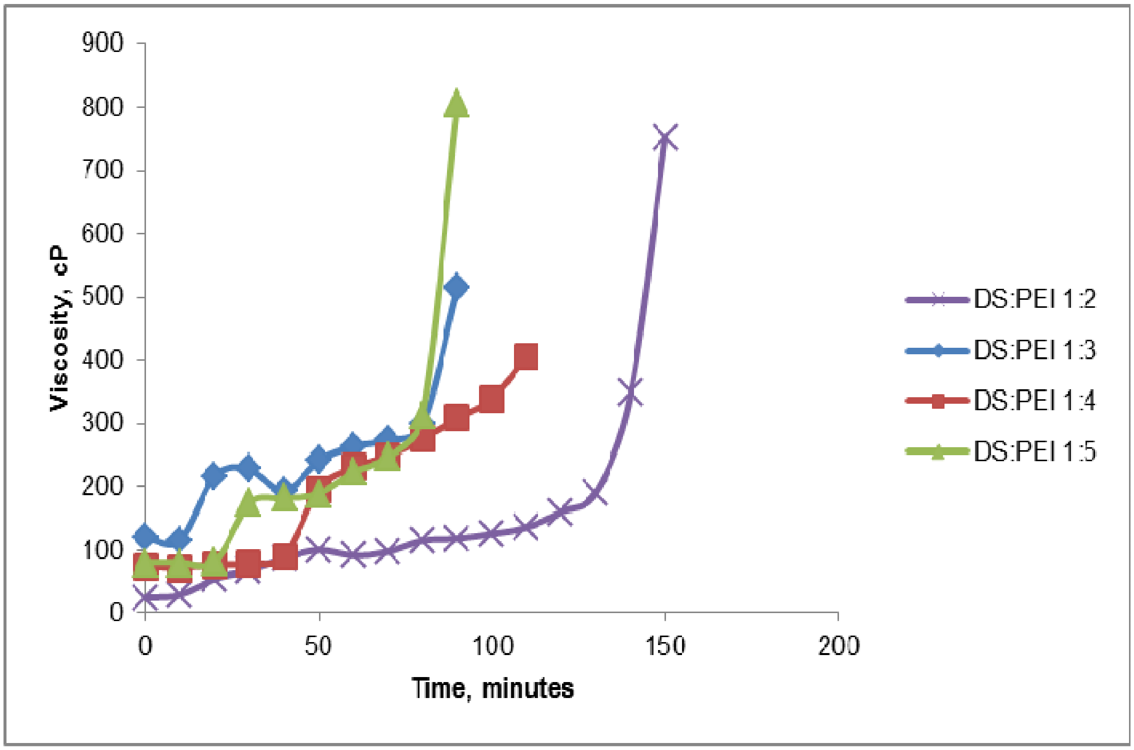


Fig. 18—Effect of DS: PEI volume ratio on gelation time. The gelant had 7000ppm HPAM polymer dissolved in 1% Potassium Chloride solution, with 7000 ppm of research grade PEI. The temperature was maintained at 100°C.

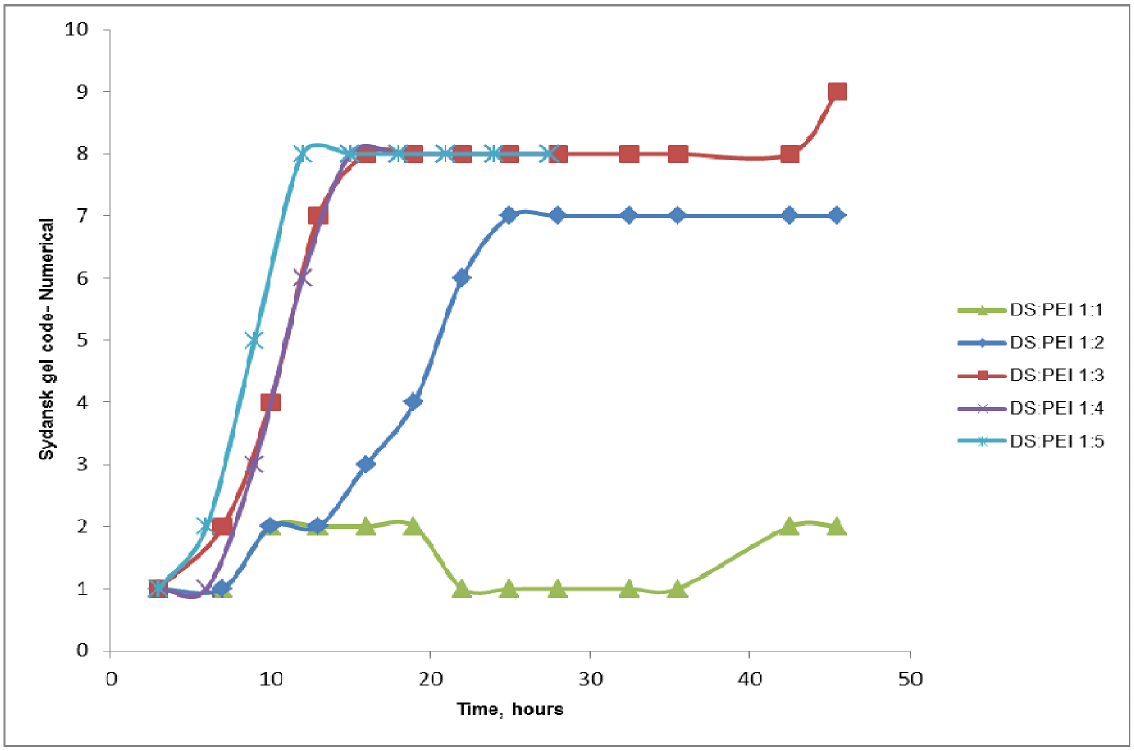


Fig. 19—Effect of DS: PEI volume ratio on gelation time with commercial grade PEI. The gelant had 7000ppm HPAM dissolved in 1% Potassium Chloride solution with samples maintained at 100°C. The pH of commercial grade PEI used was 10.65.

4.4 Effect of temperature on gelation time

Temperature has a dramatic effect on gelation time. **Fig. 20** shows the effect of temperature on a 7000 ppm HPAM, 7000 ppm PEI gelant system. The ratio of DS: PEI was maintained at 1:2. The graph below shows that the gelation time is strongly dependent on the temperature and at the lower temperature of 75 °C; the gelant took longer to gel.

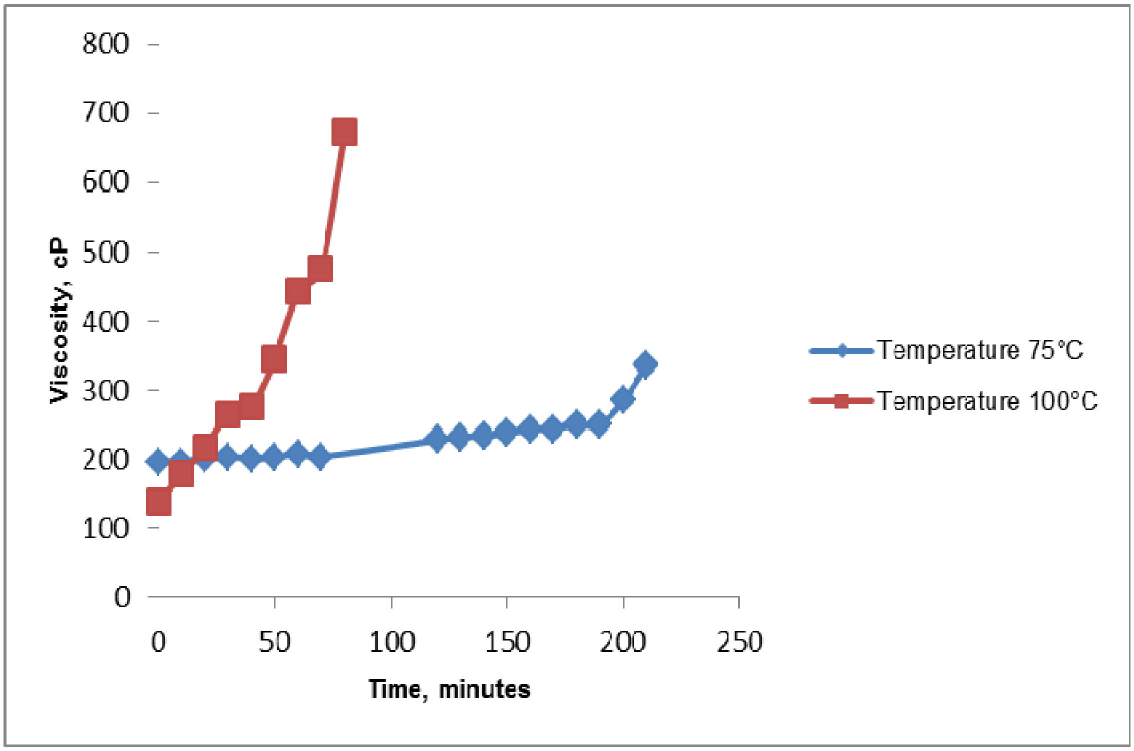


Fig. 20—Effect of temperature on gelation time. The gelant consisted of 7000ppm HPAM polymer dissolved in 1% Potassium Chloride solution with 7000ppm research grade PEI and DS: PEI volume ratio of 1:2.

4.5 Effect of pH of PEI on gelation time

The pH of the research grade PEI was 10.5-11 and was used as received. However, the commercial grade PEI was obtained at a pH of 7-8. It was found that the PEI could not be used as received to prepare the polyelectrolyte nanoparticle suspension, as it precipitated immediately upon addition of Dextran Sulfate. This could not be used as an effective crosslinker without increasing the pH. The pH of the system was then increased to 9. At that pH, it formed a nanoparticle suspension when mixed with Dextran Sulfate. No precipitation was observed. The gel obtained from using this crosslinker with HPAM resulted in strong gels with adequate delay in crosslinking. The effect of pH on gelation time was studied at the pH of 9.61 and 10.65. The figure (**Fig. 21**) indicates that the gelation time based on pH does not change much when maintained in the range of 9-10.65. Hence the optimum working range of pH of this system would be from 9-10.65.

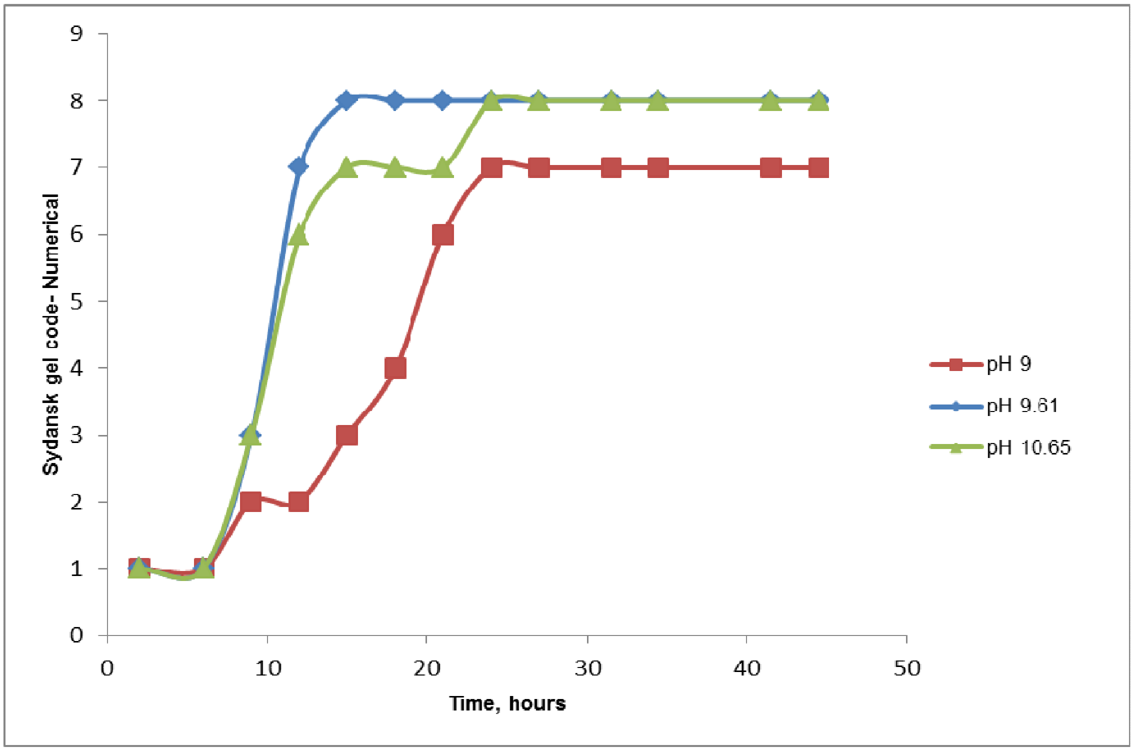


Fig. 21—Effect of pH of commercial grade PEI on the gelation time. The gelant had 7000ppm HPAM polymer dissolved in 1% Potassium Chloride with 7000ppm PEI and DS: PEI volume ratio was maintained at 1:2 at 100°C.

4.6 Effect of salt concentration in polymer solution on gelation time

Sodium Chloride (NaCl) and Potassium Chloride (KCl) were used to prepare the brine solutions that were used to dissolve the HPAM polymer. The cations and anions from the dissolved salts shield the cationic PEI from anionic sites on the polymer, thereby decreasing the tendency of PEI to associate with HPAM prior to gelation. This results in delay of gelation. A similar phenomenon occurs with the PEI-DS nanoparticle crosslinker causing a further delay in gelation point (Cordova et al., 2008) The presence of ions in the polymer solution had a significant effect on gelation time. It has previously been suggested that the presence of cations stabilized the PEI-DS crosslinking system, which resulted in a delayed release of the PEI, thus causing a further delay in the gelation time (Cordova et al., 2008). The gelation point of 1% KCl and 1% NaCl differ by no more than 20 minutes. Additionally, a 4% NaCl solution was prepared to study the gelation time at salt concentrations similar to seawater. It can be seen in **Fig. 22** that the presence of additional ions further delayed the gelation point. **Fig. 23** shows the effect of salts on gelation time when commercial grade PEI was used in the crosslinker.

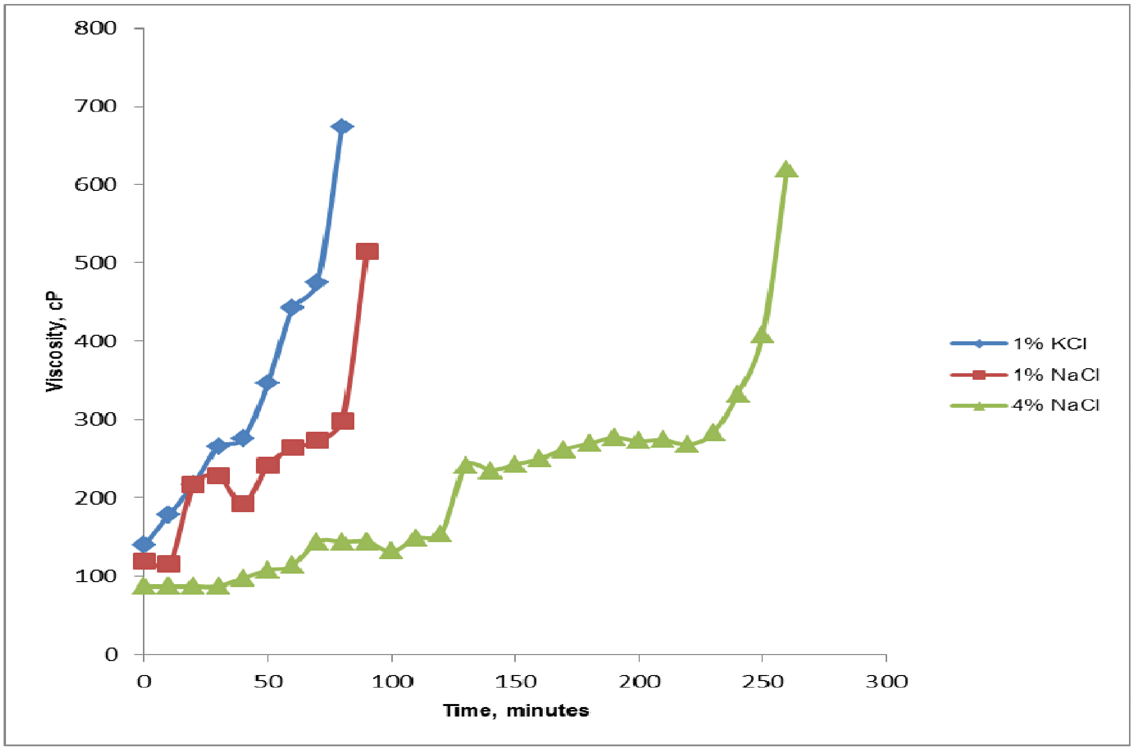


Fig. 22—Effect of cation concentration in polymer solution on gelation time. The gelant had 7000ppm HPAM polymer with 7000ppm research grade PEI and DS: PEI volume ratio was maintained at 1:2 at 100°C.

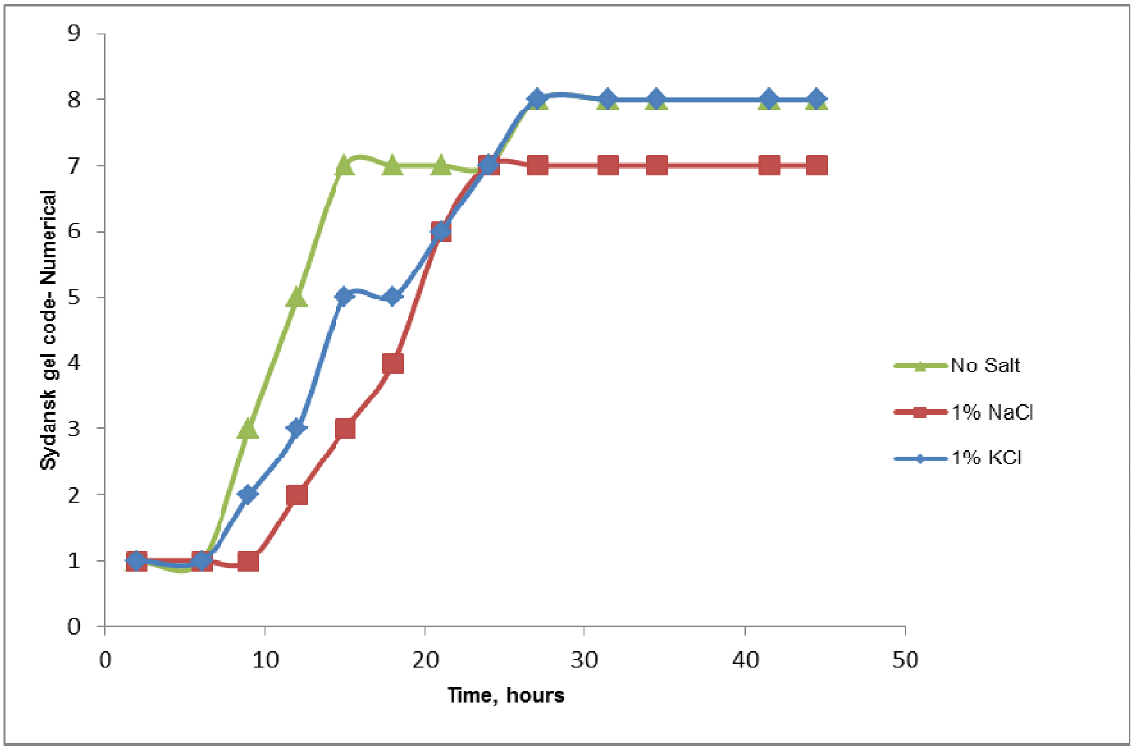


Fig. 23—Effect of cation concentration in polymer solution on the gelation time. The gelant had 7000ppm HPAM with 7000ppm commercial grade PEI and DS: PEI volume ratio was maintained at 1:2 at 100°C.The pH of PEI was 10.65.

4.7 Effect of polymer molecular weight

Throughout this research, high molecular weight HPAM has been used as the polymer with a molecular weight of 2 – 5 million Daltons. A low molecular weight HPAM (250-500 thousand Daltons) was crosslinked with the PEI- DS polyelectrolyte nanoparticle suspension to study the effect of polymer molecular weight. Usually the low molecular weight HPAM is used in gel systems intended for matrix shut-off. Final gel strength was studied using the Sydansk gel code. Gel systems prepared with the PEI: DS crosslinker had the same gel strength code as the gel systems with just PEI **(Fig. 24)**

(**Table 10**). This indicates that the new crosslinking solution did not have any effect on the final gel strength of gels formed low molecular weight HPAM. However, further studies on gelation time and influence of various factors were not done in this study.

Table 10—Sydansk gel code of low molecular weight HPAM when maintained at 100°C.

Polymer, ppm	Crosslinker, ppm	Sydansk Code
50000	10000	J
40000	8000	J
30000	6000	I
20000	4000	E

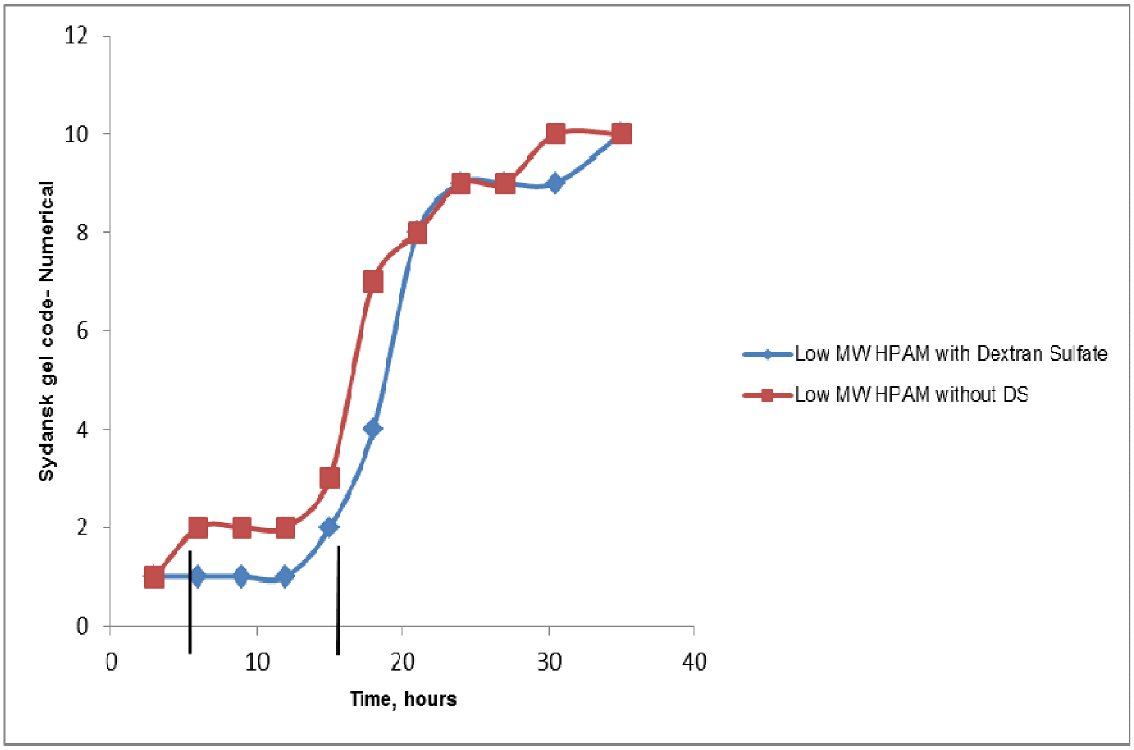


Fig. 24—Delaying effect of Dextran Sulfate on low molecular weight Hydrolyzed Polyacrylamide- Polyethylenimine polymer gel system. A 40000ppm concentration of HPAM, 8000ppm of PEI and 2667 ppm of Dextran Sulfate at 100°C.

4.8 Effect of Polyethylenimine molecular weight

The molecular weight of PEI had a strong influence in the gel strength. The gelation time of the sample with high molecular weight PEI was considerably longer than the one with low molecular weight PEI (**Fig. 25**). This could be because of a faster reaction with the high molecular weight due to stronger association of PEI with HPAM.

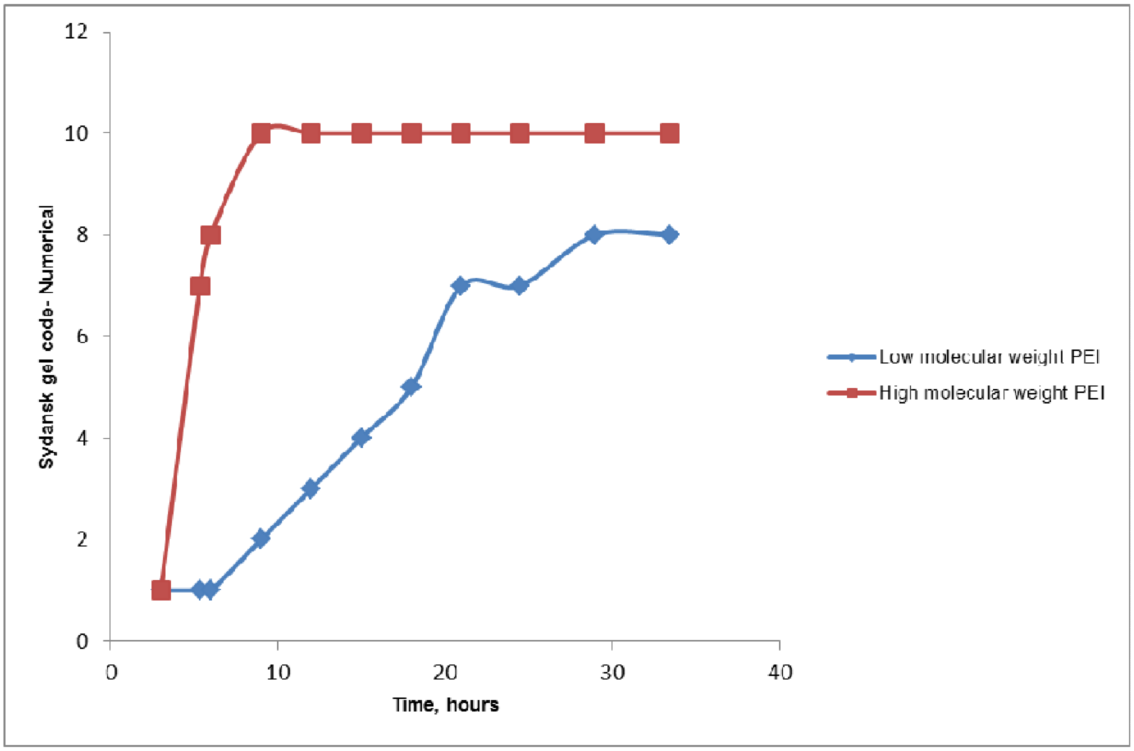


Fig. 25—Effect of PEI molecular weight on gelation time of 7000ppm HPAM and 7000ppm PEI and 3500DS gelation solution at 100°C.

CHAPTER V

DISCUSSION

Gelant and subsequent gel prepared from high molecular weight HPAM crosslinked with DS: PEI clearly have properties desirable for a gel system designed to extrude at low pressure into narrow aperture fractures, yet still form a gel with reasonable strength. At HPAM concentrations (~4,000 ppm) where Chromium(III) acetate-crosslinked HPAM formed a very weak gel (Sydansk code C), the DS:PEI system formed a gel with strength approximating that of 4,000 ppm HPAM crosslinked with Chromium(III) acetate (Sydansk code G).

Polymer concentration, PEI concentration, pH, DS: PEI ratio in the crosslinker and salt concentration all have an impact on the delay in gelation. Most importantly, the ratio of DS: PEI in the crosslinker can be used to actively control the delay in gelation for a given polymer concentration, temperature, pH, etc. If the ratio of DS: PEI is kept low, then less PEI is bound to DS than when the ratio is higher, resulting in a modest delay in gel time. The pH of the gelant is an additional means to control the change in the viscosity profile of the system. The pH of the PEI affects its charge density. At lower pH, PEI has a higher positive charge density (protonated amine nitrogen) and easily ion pairs with the carboxylate groups in the HPAM polymer (Cordova et al., 2008). Ion pairing presumably increases the time (or effective concentration) of close proximity of reactive amines on the crosslinker with transamidation sites on HPAM. A very slight delay in gelation was observed as the pH was increased from 9 to 10. However, this delay was not significant as the pH studied in this experiment was kept in the range of 9-

10.65. Lastly, increasing salinity increased the delay in gelation. We believe this is due to salinity shielding the positively charged PEI from crosslinking sites in HPAM, decreasing crosslinker-polymer ion pairing.

Commercial grade PEI was used to prepare the polyelectrolyte suspension used for the delayed gelation process. With the commercial grade PEI, considerable delay was observed in the onset of the gelation process compared to the research grade product. Up to 12 hours of delay was achieved by adjusting the various controlling factors at 100 °C. The difference in delay caused by using commercial grade instead of research grade PEI could be because of the presence of impurities which further retard the gelation process. The type or concentrations of these impurities are not known at this time. This phenomenon is under continuing investigation.

5.1 Optimum gel system for an unconventional gas reservoir

The most suitable gel system for an unconventional gas reservoir would have a low polymer concentration, low initial viscosity and a considerable delay in gelation time to allow proper placement in deep, high temperature problem zones and in narrow aperture fractures (**Table 11**). This work has demonstrated that such a gel with a range of properties and gelation times can be prepared with the system comprising of HPAM, PEI and DS. The various controlling factors can be tuned to better adjust the gelant viscosity and gelation time as required.

Table 11—An optimum water shut-off gel system for an unconventional gas reservoir.

Property	Research Grade PEI+DS	Commercial Grade PEI+DS
Polymer Concentration	4000ppm HPAM	4000ppm HPAM
Initial viscosity	Around 27 cP at 100℃	Around 27 cP at 100℃
PEI Concentration	4000ppm PEI	4000ppm PEI
DS: PEI ratio	1:2	1:2
pH of PEI	10.5-11	9-10.65
Temperature	100℃	100℃
Salt concentration	1% Potassium Chloride	1% Potassium Chloride
Gelation time	160 minutes	8 hours
Final Sydansk gel code	I	G

CHAPTER VI

CONCLUSIONS

1. An effective, environmentally benign delayed crosslinking system for HPAM polymer has been demonstrated in the laboratory. The delayed crosslinker is composed of nontoxic PEI and biodegradable Dextran Sulfate.
2. Polyethylenimine (PEI) and Dextran Sulfate (DS) form a polyelectrolyte nanoparticle suspension which is an effective delayed crosslinking agent for Hydrolyzed Polyacrylamide (HPAM) polymer.
3. Use of PEI as crosslinker for high molecular weight HPAM resulted in stronger gels at lower polymer concentration than is observed when Chromium(III) acetate is used as crosslinker. This allows placement of a stronger gel at lower viscosity, and hence lower extrusion pressure, than is possible with the Chromium(III) acetate crosslinked system.
4. Two different sources of PEI were studied in this research. Considerable delay in gelation of up to 12 hours was achieved while using the commercial grade PEI in the delayed crosslinker.
5. The longer gelation time allows for the low viscosity to be maintained long enough for proper placement in deep, high temperature reservoirs, both conventional and unconventional.
6. Strong final gels were obtained with this system at low polymer concentrations. This would help effectively plug the narrow aperture fractures prevalent in unconventional gas reservoirs.

7. The gelation time of the gelant could be controlled by adjusting various factors such as the HPAM concentration, PEI concentration, DS: PEI volume ratio, temperature, pH and salt concentration.
8. A new method was developed to determine the gelation time of a gel system using Sydansk bottle testing method.

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APPENDIX

Table 12— Properties of 4000ppm high molecular HPAM and commercial grade PEI with gelation time and final gel code dependence on controlling factors.

	Changing DS: PEI ratio			**Changing Crosslinker concentration**			**Changing Salt Concentration**		**Changing pH Concentration**	
Polymer concentration, ppm	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000
Crosslinker concentration, ppm	4000	4000	4000	4000	3000	2000	4000	4000	4000	4000
DS: PEI Ratio	1:2	1:3	1:4	1:2	1:2	1:2	1:2	1:2	1:2	1:2
pH of PEI	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	9.61
Salt concentration	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% KCl	1% NaCl	1% NaCl
Temperature, °C	100	100	100	100	100	100	100	100	100	100
Gelation time, hours	12	9	6	12	15	18	12	9	12	6
Final Sydansk gel code	F	G	G	F	C	C	F	F	F	G

Table 13— Properties of 7000ppm high molecular HPAM and commercial grade PEI with gelation time and final gel code dependence on controlling factors.

	Changing DS: PEI ratio			Changing Crosslinker concentration			Changing Salt Concentration		Changing pH Concentration	
Polymer concentration, ppm	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
Crosslinker concentration, ppm	7000	7000	7000	7000	5000	3000	7000	7000	7000	7000
DS: PEI Ratio	1:1	1:2	1:3	1:2	1:2	1:2	1:2	1:2	1:2	1:2
pH of PEI	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	9.61
Salt concentration	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	1% NaCl	No Salt	1% NaCl	1% NaCl
Temperature, °C	100	100	100	100	100	100	100	100	100	100
Gelation time, hours	12	9	6	9	12	15	9	7	9	8
Final Sydansk gel code	D	G	I	G	G	F	G	H	G	I

Table 14— Properties of 9000ppm high molecular weight HPAM and commercial grade PEI with gelation time and final gel code dependence on controlling factors.

	Changing DS: PEI ratio			Changing Crosslinker concentration				Changing Salt Concentration		Changing pH Concentration	
Polymer concentration, ppm	9000	9000	9000	9000	9000	9000	9000	9000	9000	9000	9000
Crosslinker concentration, ppm	9000	9000	9000	9000	8000	7000	5000	9000	9000	9000	9000
DS: PEI Ratio	1:1	1:2	1:3	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2
pH of PEI	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	10.65	9.61
Salt concentration	1%NaCl	1%NaCl	1%NaCl	1%NaCl	1%NaCl	1%NaCl	1%NaCl	1%NaCl	1%KCl	1%NaCl	1%NaCl
Temperature, ℃	100	100	100	100	100	100	100	100	100	100	100
Gelation time, hours	8	6	6	6	6	6	6	6	5	6	4
Final Sydansk gel code	J	J	J	J	J	I	I	J	J	J	J

Table 15— Properties of 40000ppm low molecular weight HPAM and commercial grade PEI with gelation time and final gel code dependence on controlling factors.

	Changing Crosslinker Concentration			With and Without Dextran Sulfate	
Polymer concentration, ppm	40000	40000	40000	40000	40000
Crosslinker concentration, ppm	8000	7000	6000	8000	8000
DS: PEI Ratio	1:3	1:3	1:3	1:3	NO DS
pH of PEI	10.65	10.65	10.65	10.65	10.65
Salt concentration	1% KCl	1% KCl	1% KCl	1% KCl	1% KCl
Temperature, ℃	100	100	100	100	100
Gelation time, hours	15	18	18	15	6
Final Sydansk gel code	J	J	J	J	J

Table 16— Properties of 30000ppm low molecular weight HPAM and commercial grade PEI with gelation time and final gel code dependence on controlling factors.

	Changing Crosslinker Concentration			With and Without Dextran Sulfate	
Polymer concentration, ppm	30000	30000	30000	30000	30000
Crosslinker concentration, ppm	6000	5000	4000	6000	6000
DS: PEI Ratio	1:3	1:3	1:3	1:3	NO DS
pH of PEI	10.65	10.65	10.65	10.65	10.65
Salt concentration	1% KCl	1% KCl	1% KCl	1% KCl	1% KCl
Temperature, °C	100	100	100	100	100
Gelation time, hours	16	18	21	16	6
Final Sydansk gel code	J	I	H	J	J

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