LABORATORY INVESTIGATION ON GELATION BEHAVIOR OF XANTHAN CROSSLINKED WITH BORATE INTENDED TO COMBAT LOST CIRCULATION

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LABORATORY INVESTIGATION ON GELATION BEHAVIOR OF XANTHAN CROSSLINKED WITH BORATE INTENDED TO COMBAT LOST CIRCULATION

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ABSTRACT

LABORATORY INVESTIGATION ON GELATION BEHAVIOR OF XANTHAN CROSSLINKED WITH BORATE INTENDED TO COMBAT LOST CIRCULATION

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This thesis addresses the application of xanthan/borate gel for lost circulation treatment. Steady shear viscometry method was applied in which the gel system was under constant shear rate while apparent viscosity was being recorded. The apparent viscosity was constant up to initial gelation time in which viscosity started to build up. Four parameters: initial and final gelation times as well as initial and final viscosities are defined and a correlation is derived between those parameters and four variables: polymer blended with crosslinker, pH-controller, and magnesium chloride concentration as well as temperature. These correlations can help the drilling industry to manage the lost circulation treatment job in a way to have enough time and pressure to pump the fluid and to optimize the time and quality required for final gel. The effects of those variables besides mixing time and shear history on gelation were also investigated. Temperature and pH-controller shortens initiation of gelation. Poly-cross shifts viscosity upward. Retarder postpones the final gelation time. Shear history does not affect initial gelation time and increase of mixing time reduces initial gelation time.

This thesis also investigates the rheological model behavior of this gel system before initial gelation time which is the time allowed for pumping the fluid. Shear stress was measured at 0.1,1,50, and 450 rpm besides the conventional readings. Then residual mean squares for six common rheological models were obtained. Sisko was found to be the best fitting model based on this statistical approach. Moreover a modified Bingham-plastic and low shear yield point model are suggested.

Keywords: Gel, Lost Circulation, Borate, Xanthan, Rheological Model

ÖZ

SİRKÜLASYON KAYBI İYİLEŞTİRMELERİ İÇİN BORAT İLE ÇAPRAZBAĞLI XANTHA'NIN JELLEŞME DAVRANIŞI

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Çapraz bağlı polimer jeller petrol üretim endüstrisinde su kesimi, profil modifikasyonu ve hidrolik çatlaklarda kullanılmaktadır. Başarılı bir geçmişe sahip olan bu uygulamalar en ağır sondaj sorunlarından biri olan sirkulasyon kaybın çözümü için yeni bir çığır açılmasına öncülük etmiştir. Uygun pH koşullarında jelleşme kayıp bölgede başlar ve bölgeyi tıkayabilecek bir üç boyutlu jel yapısı ile sonuçlanır.

Sabit hızlı kayma viscometry bir metodur ki onda jel sistemi 3rpm´li sabit bir kayma hızı oranın altındaydi. Görünür viscidity, visciditynin oluşmaya başladığı jel derecesine kadar sabitkalmıştır. İlk jelleşme zamanı, son jelleşme zamanı, ilk viscidity ve son viscidity jel sisteminin davranışlarını tanımlayabilen parametrelerdir ve bu çalışmada belirtilmişlerdir.

Her ne kadar karıştırma zamanındaki artış ilk jelleşme zamanını düşürüyor olsa da, karıştırma zamanı ve ilk jelleşme zamanının toplamı belirli bir örnek için sabit kalmıştır. Diğer bir deyişle jelleşme, karıştırma zamanının uzatılmasıyla ertelenememektedir. Kesme tarihçesi ve hızı ilk jelleşme zamanın etkilememektedir. Sabit bir oranda polimer artı çapraz-bağlayıcı konsantrasyonunun artması viscidity grafiğini yukarı doğru kaydırmakta ancak ilk jelleşme zamanını değiştirmemktedir. Sıcaklık ve pH denetleyicisi çarpaz bağlanma için hazır olan daha yüksek konsantrasyonda borat iyonu sağlayarak jelleşmenin başlamasını hızlandırmaktadır. Diğer taraftan, magnezyum klorid son jelleşme zamanını çoğaltır ve viskositeyi azaltır. Ampirik modeller de bu değişkenlerin bir fonksiyonu olarak jel özelliklerinin tahmini için önerilmektedir.

Ayrıca reolojik model belirlenmesi de araştırılmıştır. Kesme stresi, (3, 6, 100, 200, 300, ve 600) kesme oranlarının yanı sıra geleneksel kesme oranları olan 0.1, 1, 50, and 450 rpm oranlarında da ölçülmüştür. Artık kareler ortalaması her örnek için ayrı ayrı hesaplanmış ve Box-Whisker grafiğinde sunulmuştur. Bu reolojik veri kümesine Sisko ‘nun uygun olduğu bulunmuştur. Ayrıca, değiştirilmiş bingham plastik ve değişilmiş “low shear yeild point” modelleri öneriliyor.

Anahtar kelimeler: Jel, Sirkülasyon Kaybı, Borat, Xanthan, Reolojik Model

To My Family

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NOMENCLATURE

ACC	Accelerator
BHA	Bottom Hole Assembly
bopd	barrel of oil per day
bgpd	barrel of gas per day
BP	Bingham Plastic
CMG	Carboxymethyl Guar
CMHPG	Carboxymethyl Hydrapropal Guar
DMA	Dynamic Mechanical Analysis
DPR	Disproportionate Permeability Reduction
DR	Dial Reading
ECD	Equivalent Circulating Density
EOR	Enhanced Oil Recovery
GAG	Gel Alternating Gas
GC	Gas Chromatography
H-B	Herschel Bulkley
HMTA	Hexamethylene Tertramine
HPG	Hydroxypropyl Guar
HQ	Hydroquinone
KGM	Konjac Glucomannan
LCM	Lost Circulation Material
LSYP	Low Shear Yield Point
MHHPA	Expoxy-hexaanhydro-4-methylphthalic-anhydride
MCC	Magnesia Crosslinked Cement
NMR	Nuclear Magnetic Resonance

OBM	Oil Based Mud
PAM	Polyacrylamide
PAtBA	Polyacrylamide teributyl Acrylate
PEI	Polyethyleneimine
PHPA	Partially Hydrolyzed Polyacrylamide
P-L	Power Law
Poly-Cross	Polymer-Crosslinker: Form-A-Plug II
RCC	Regular Crosslinked Cement
Reg	Regression
RMS	Residual Mean Squares
RRF	Residual Resistance Factor
R-S	Robertson Stiff
RSS	Residual Sum of Squares
SBM	Synthetic Based Mud
WGR	Water Gas Ratio
WBM	Water Based Mud
YP	Yield Point
σ	Tensile stress
ε	Tensile strain
τ	Shear stress
μ	Viscosity
$\dot{\gamma}$	Shear rate
δ	Phase lag
G'	Storage modulus
G''	Loss modulus
G^*	Complex modulus
η^*	Complex viscosity
η'	Viscous part of complex viscosity
η''	Elastic part of complex viscosity

α	Shift factor of frequency
τ_y	Yield stress
μ_p	Plastic viscosity
k	Consistency factor
n	Flow behavior index, number of data points
$\dot{\gamma}_0$	Shear rate corrector of Robertson-Stiff model
θ_{600}	Dial reading at 600 rpm
θ_{300}	Dial reading at 300 rpm
τ_m	Measured shear stress
τ_p	Predicted shear stress by rheological models
p	Number of parameters
R	Resistance, gas constant
t_c	Sol-gel transition time
μ_i	Initial viscosity
C_{pc}	Poly-cross concentration
μ_f	Final viscosity
E	Young's modulus, Activation energy
C_A	Accelerator concentration
C_r	Retarder concentration
T	Temperature
t	time
t_i	Initial gelation time
t_f	Final gelation time
τ_3	Shear stress at 3 rpm
τ_6	Shear stress at 6 rpm

CHAPTER 1

INTRODUCTION

Polymer chains can be connected to each other by a crosslinker to make a three dimensional gel structure. Gels represent an intermediate state between liquid and solid that exhibit viscous behavior due to its major portion of solvent as well as elastic behavior due to its network structure. Gels are pumped down in fluid state. Then after a certain time which is called initial gelation time, they are converted to a product that can block subsurface zones for several applications such as: 1. blocking water producing zones due to water coning of oil wells. 2. blocking high permeable zones that prevent low permeable zones of being swept in enhanced oil recovery operations. 3. enhancing hydraulic fracturing by improving the viscosity of fracturing fluid which can increase proppant carrying capacity. In this case, a breaker like an enzyme should accompany the gel system in order to destroy the crosslinking after hydraulic fracturing job for allowing back flow of fluids.

Lost circulation is flow of drilling fluid to subsurface formations due to the natural phenomena like vugular, cavernous or high permeable zones; or due to induced fractures because of high hydraulic pressure on wellbore. It is a big problem which imposes considerable costs on drilling operations. In this thesis, the crosslinking of xanthan with borate has been investigated for blocking the thief zones.

As the best of author's knowledge, for the first time a comprehensive study on gelation behavior of xanthan/borate gel for lost circulation treatment is presented. This thesis will help to understand the effect of key factors on gelation behavior.

Empirical models will help the drilling industry to manage the concentration of materials required for a well with specific depth and temperature in order to have enough time to pump the fluid, optimize the time for waiting on gel to set, monitor the initial viscosity of gel and final gel quality. In addition rheological model determination helps to understand the fluid flow properties and use it in pressure loss calculation.

CHAPTER 2

LITERATURE REVIEW

In this chapter, a review of publications related to the application of gels for the lost circulation treatment will be given as well as the general studies on gel properties. Then papers on statistical approach for determination of rheological model are presented.

The publications on application of gels for lost circulation treatment are quite rare. Moreover there are some similarities between lost circulation problem and other applications that can help to develop the proposed gel system according to some previous achievements in other areas. For this purpose the literature review of gel applications for water shut-off, profile modification and hydraulic fracturing are given in appendix C.

Sydansk (1988) proposed a qualitative method to examine gelation process. This method is based on observation of inversed bottle flow at different time intervals. Based on these observations, Sydansk proposed a table which appoints a code to any state of flow.

Dawson (1991) employed ^{11}B NMR analysis as well as steady and oscillatory measurements in order to examine the crosslinking of galactomannan and borate. He observed that the gel is reversible, thermal and shear thinning. Moreover just at the concentrations higher than 300 lb/gal, di-diol complexes were formed; boric acid does not react with polymer and the primary crosslinking is due to ionic association of anionic borate and absorbed cations on second polymer.

Basta et al. (1991) demonstrated the relation between gel kinetics and electrical conductivity referring to geometrical percolation theory. They concluded that there is a correlation between electrical resistance and sol-gel transition time (t_c): $R\alpha(t-t_c)^{\alpha}$.

Kesavan and Prud'humme (1992) measured the rheological properties of guar and hydraoxypropyl guar (HPG) crosslinked with borate ions. Measurements were conducted on 0.48 wt% polymer and temperatures between 15 to 65°C and pH from 6.35 to 9.5. The storage and loss modulus obeyed time-temperature and time-pH superposition. Moreover the activation energy of this reaction was obtained to be from 90 to 115 kJ/mol.

Harris (1993) elucidated the chemistry of borate-crosslinked fluids. Two types of crosslinking are 1:1 complexes which are very predominant but do not change viscosity and 2:1 complexes which are real crosslinking and raise viscosity. Gelation is a function of polymer and borate ion concentration, temperature and pH. He proposed a diagram for borate ion fraction versus pH at different temperatures for 7.2 lb/1000gal boric acid in 2% KCL. It shows that with increasing pH, borate ion fraction increases and with increasing temperature, borate ion decreases.

Kruijf et al. (1993) also investigated the chemistry of borate crosslinking fracturing fluids. They described that crosslinking occurs in three steps. First, boric acid dissociates in water and produces borate ion. Then, when enough borate ions are available, 1:1 complex (monodiol) is produced. Finally it will react further with another polymer chain and produces 2:1 complex. This final complex forms a network that increases the fluid viscosity.

Kolnes et al. (1997) studied the effect of pH on gelation time of xanthan crosslinked with three different sources of chromium (chromium nitrate, chromium triacetate and basic chromium acetate). pH was kept at a constant value by autotitrator. The effect of pH was lower when autotitrator was used compared to pH control by buffer or no control at all. Moreover, gelation time decreased by factor of 4 and 1.5 for one unit of pH increased in chromium nitrate and chromium triacetate respectively. However with basic chromium acetate as crosslinker, when pH was less than 5.5, the gelation time increased by the pH rise but decreased for pH values above 5.5.

Shah et al. (1997) were the first to investigate the shear history of borate-crosslinked fracturing fluid by fracturing fluid characterization facility. They observed that gel behavior is dependent on shear history. However an optimum gel at a certain pH and temperature was found to be shear history independent.

Quinn et al. (1999) explained three methods to solve the lost circulation: 1. the traditional method of solving lost circulation is carried out by employing the lost circulation materials (LCM). If it does not work, cement plugs can be used. However cement plugs cause the formation damage and are expensive due to wait on cement time as well as materials cost. 2. gunk: In this method one fluid is injected through drill pipe and another one through annulus. They are squeezed in to the lost zone by pressure. Then the fluids react and build a rubbery solid material in lost zone which consequently blocks the zone. 3. crosslinked polymer gels: these gels mostly have enough strength to seal formations. They also mentioned that the drawback of gels is that gelation may set in bottom hole assembly (BHA) since gels are mixed on the surface. A new drilling fluid was designed to solve lost circulation. It is an invert emulsion (water in oil) in which a crosslinker is encapsulated inside oil phase. This encapsulation is shear sensitive. As a result it breaks at a minimum shear encountered in BHA. It takes from 30 seconds to 30 minutes for a rigid gel to be obtained which can mitigate lost circulation.

Boey and Qiang (1999) determined the gel point of an expoxy-hexaanhydro-4-methylphthalic anhydride (MHHPA) by dynamic viscometry method. It was concluded that the common $G^{|} - G^{||}$ crossover is not appropriate for finding a gel point. Instead $\tan\delta$ can estimate gel point since it is frequency-independent. In addition the activation energy for crosslinking reaction was obtained to be 75.1 kJ/mol.

Harris and Batenburg (1999) compared fresh water borate base gel with the one prepared with sea water. Magnesium ion available in sea water reacts with hydroxide and precipitates. In other words it consumes the hydroxide which results in less borate ion available for complexation. The effect of different breakers on viscosity reduction after proppant transportation, the fracture face damage due to leak off of fracturing fluid as well as the damage due to remained polymer in fractures were also studied.

Nishinari et al. (2000) stated that gel represent an intermediate state between liquid and solid states. Gels exhibit fluid like properties since they contain major liquid state as well as solid like behavior because they have a network.

Douglas et al. (2002) described some case studies of applying a crosslinking pill in deepwater of Gulf of Mexico to combat the lost circulation and gave some recommendation for this operation. They suggested the use of 100% excess slurry volume besides the volume across thief zone as well as explaining the lessons learned from this lost circulation treatment job.

Romero-Zeron et al. (2004) employed low-field nuclear magnetic resonance (NMR) in order to investigate crosslinking of partially hydrolyzed polyacrylamide chromium acetate gel. They found that this method was reliable for finding gel point since it did not affect gelation process at all. The results of NMR were compared with bottle testing method and dynamic viscoelastic method but the steady shear viscometry was not included.

Mata and Veiga (2004) reported the use of crosslinked cement to combat lost circulation. Two types of crosslinked cement were suggested: 1. magnesia crosslinked cement (MCC). This cement is a blend of magnesium, calcium oxides, carbonates and sulfate besides carboxy-methyl hydraoxy-ethyl-celulose as a gallant and fluid loss control, a borax based retarder, and zirconium as crosslinker. MCC is designed for the lost circulation in productive zone and is 98% acid soluble. 2. regular crosslinked cement (RCC): it is 73% soluble with acid. As a result it can be used in non-productive zones.

Lecolier et al. (2005) reported the use of a nanocomposite gel to solve the lost circulation problem. However the composition of this gel is not clear. The rheological studies have been conducted using Haake RS 150 viscometer in a controlled shear stress manner. It was observed that the gel system is environmentally friendly, does not degrade after 16 hours at 120°C, and can effectively plug high permeable zone.

Zhang et al. (2008) investigated crosslinking of partially hydrolyzed polyacrylamide with phenolic aldehyde. They observed three stages of crosslinking: first, in an induction period, intra-molecular crosslinking occurs which leads to a small decrease of viscosity. In the second period as viscosity increases rapidly, inter-molecular cross-linking happens. Finally, a long period in which networks is strengthened. It was also concluded that increasing concentration of polymer or crosslinker makes gel stronger due to increasing probability of crosslinking bonds.

Gao et al. (August 2008) examined crosslinking of konjac glucomannan (KGM) with borax at different concentration of konjac and borax as well as strain and temperature by dynamic viscoelastic measurement. At low frequencies, the gel system behaves like liquid but it demonstrates elastic relaxation response at higher frequencies. A plateau of storage modulus as well as a maximum and minimum of loss modulus were obvious at this relaxation period. In another study, Gao et al. (December 2008) investigated sol-gel transition time of KGM crosslinked with organic borate using Winter-Chambon criterion. The sol-gel transition time decreased when concentrations of KGM or organic borate as well as temperature increased.

2.2. Rheological models

Gucuyener (1983) proposed the following rheological model:

$$\tau^{1/m} = \tau_y^{1/m} + \eta\gamma^{1/2}, \tau \rangle \tau_y \quad \text{and} \quad \gamma = 0, \tau \le \tau_y \tag{2.1}$$

The proposed model is analyzed for 71 drilling fluid and cement samples and it was found that it can describe the behavior of that set of data better than previous models.

Ratkowsky (1990) emphasized that use of R^2, goodness of fit, is misleading for evaluating non-linear models. "R^2 has no role to play in such evaluation and need never be calculated".

Okafor and Evers (1992) studied Robertson-Stiff model accuracy in comparison to power law and Bingham Plastic. They concluded that Robertson-Stiff could predict rheological behavior of two types of clay drilling fluids better than those of conventional models.

Weir and Bailey (1996) conducted an extensive statistical study on 414 Fann viscometer data sets in order to find the most fitted rheological model. Twenty rheological models were compared based on residual mean square values shown on box-whisker plots. It was found that several other rheological models can exhibit better fitting than conventional models. Moreover interval of confidence and test of significance were calculated.

Bailey and Weir (1998) investigated the best rotational viscometer readings for direct parameter estimation of rheological models. Based on residual mean squares, it was concluded that conventional readings were not appropriate and they suggested new default readings such as: 600/30 combination instead of 600/300 for Bingham Plastic model or 600/100 combination for power law model etc. They also found Sisko as the best fitted model.

Davison et al. (1999) investigated the rheological behavior of drilling fluids which experience cold temperatures in riser for deepwater drilling. They concluded that Herschel-Bulkley and Casson models fit the data for oil based mud (OBM) and synthetic based mud (SBM). For water based muds (WBM), Herschel-Bulkley fitted salt/polymer fluids and unweighted bentonite while Casson was the best for weighted bentonite muds. Since in deepwater drilling the gap between fracture pressure and pore pressure is very narrow, mud weight should be designed very carefully. Therefore equivalent circulating density (ECD) was compared between the proposed model and the one without considering temperature effect. It was found that ECD is underestimated 6.1% for SBM and overestimated 3.1% for a WBM which confirmed the importance of accurate rheological model estimation.

Kok et al. (2000) studied the effect of different type of bentonite and concentration on rheological properties. Three bentonite types (karakaya1 and 2, API) bentonite types at 6 concentrations (20-22.5-24-26-28-30) were analyzed. Higher rheology and wall building behavior was observed when cation exchange capacity (CEC) and clay content was increased. It was found that the samples exhibited pseudoplastic behavior at low concentrations while they showed yield pseudoplastic behavior at higher concentrations.

Power and Zamora (2003) studied yield stress by vane rheometer type. They concluded that among 6 candidates for yield stress measurement: shear stress at 3 rpm, shear stress at 6 rpm, low-shear yield point $(2\tau_3 - \tau_6)$, zero gel strength, initial gel strength, and 10 minute gel strength, the third one can best represent yield stress based on comparison with vane rheometer results.

Kok and Alikaya (2004) examined 45 KCL/polymer samples in variety of concentrations in order to find the best rheological model. The selection was based on residual mean squares. However R^2 was also calculated in order to give a rough estimation. It is concluded that power law model can best fit rheograms of KCL/ Polymer drilling fluids.

Kelessidis et al. (2006) employed the golden section search method to find yield stress since non-linear regression of shear stress versus shear rate for finding Herschel-Bulkley parameters may results in unrealistic (negative) values for yield stress. Then the other two parameters by linear regression were calculated. Moreover they demonstrated the effect of these parameters on pressure drop, velocity profile and penetration rate estimation.

Lachement et al. (2008) studied rheological behavior of raw cements as a function of concentration and particle size. Herscehl-Bulkley best fitted the set of data and yield stress was correlated as exponential function of concentration. The rheological behavior depended on both concentration and particle size.

Gucuyener proposed a model for calculating of yield point:

$$\tau_y = \frac{\tau_3 \tau_{600} - \bar{\tau}^2}{2\bar{\tau} - \tau_3 - \tau_{600}} \tag{2.2}$$

In which $\bar{\tau}$ is shear stress at shear rate of $72.3\,\mathrm{sec}^{-1}$.

CHAPTER 3

STATEMENT OF THE PROBLEM

Drilling fluids circulation is a crucial parameter in drilling operation and any induced fracture or a natural event that leads to loss of drilling fluids is quite costly or even may lead to some dangerous consequences. Cost of lost circulation depends on both non-productive time (NPT) spent for treatment and cost of materials. Lost circulation may lead to kick if the hole can not be filled while there is flow of fluid from another formation.

In this thesis, a comprehensive study on a gel behavior was carried out with respect to lost circulation treatment. Gelation behavior of xanthan crosslinked with borate was studied. Initial gelation time, final gelation time, initial viscosity, and final viscosity are necessary parameters for managing a successful lost circulation treatment job by gels. By steady viscometry method, these values were obtained for different polymer blended with cross-linker concentration, pH-controller concentration, magnesium chloride concentration, temperature, mixing time, shear rate and shear history. Knowledge of initial gelation time and viscosity helps us to have enough time and power to pump the fluid down. As a result, blockage of mixer or drillpipe with gel can be prevented. Moreover knowledge of final gelation time and viscosity can help to manage time required for waiting on gel as well as gel final quality to be high enough to resist pressure.

Rheological model determination of this gel was also carried out since it affects several factors in drilling operation. For instance, hydraulics or pressure loss calculation is a function of rheological model. A rheological model that best fitted to available data was proposed. Since some models are easier and more popular in industry, some modifications to more common rheological models (Bingham Plastic, and Herschel Bulkley) were sought. This part will help to understand flow of fluid in drillpipe.

As the best of author’s knowledge, it is for the first time that xanthan/borate gel system is used for combating lost circulation and effect of variety of parameters are investigated with respect to this high concentration solution. Besides the initial gelation time, three other parameters are defined (final gelation time, initial viscosity, and final viscosity) and the proposed empirical models will fully predict the gel behavior. Therefore, this thesis will help the drilling industry to rely more on this solution to lost circulation problem and manage the job effectively in order to prevent problems and decrease the price by optimizing the concentrations.

CHAPTER 4

THEORY

This chapter explains the chemistry of xanthan crosslinking with borate. Then it will go through the rheological models and the statistical approach to find the best rheological model.

4.1. Chemistry of crosslinking

The crosslinking of xanthan gum with borax is a function of borax/borate ion equilibrium. First, Borax ($Na_2B_4O_7.10H_2O$) dissociates into equal amount of boric acid and monoborate ion (Gao, 2007)

$$B_4O_7^{2-} + 7H_2O \rightarrow 2B(OH)_3 + 2B(OH)_4^- \qquad (4.1)$$

Then there is equilibrium between boric acid and monoborate generation depending on pH and temperature. (Sinton et al., 1987)

$$B(OH)_3 + H_2O \xleftrightarrow{K_A} B(OH)_4^- + H^+ \qquad pk_A = 9 - 9.2 \qquad (4.2)$$

Figure 4.1 illustrates the dependency of borate ion generation from boric acid on pH and temperature (Harris and Batenburg, 1999). At a constant temperature, as pH increases the borate ion fraction increases as well. On the other hand, at a constant pH, as temperature increases, the fraction of borate ion decreases. The Figure also reveals that if the solution is not basic, no borate ion will be produced. Figure 4.2 shows borate ion fraction represented by Kruijf et al. (1993). The borate ion fraction increases with increasing pH till a peak at about 11. This part is similar to the study by Harris and Batenburg; and the pH in this thesis is also in this range. However, Kruijf shows the rise of borate ion with increase of temperature in the left section which is in opposition to Harris and Batenburg.

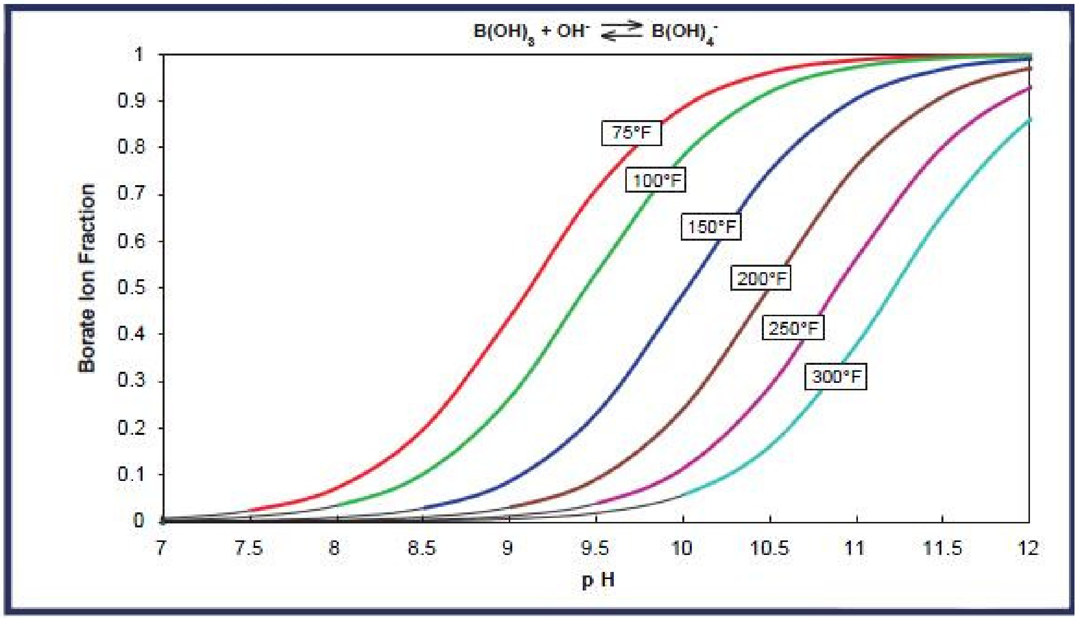

Figure 4.1: Boric acid equilibrium in 5% KCL [Harris and Batenburg, 1999]

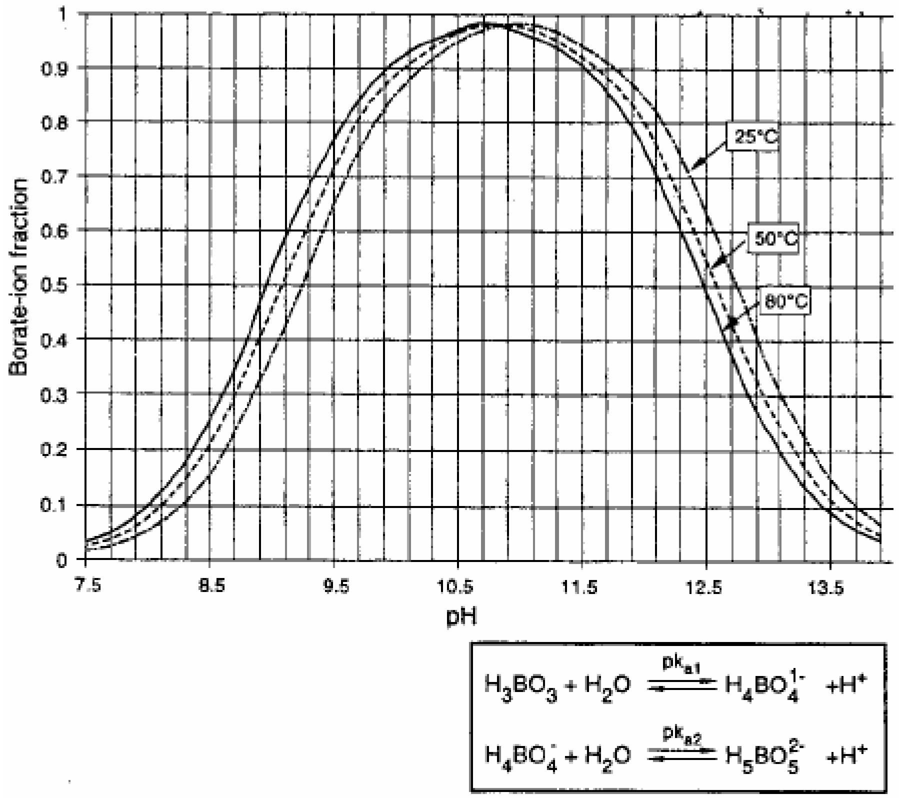

Figure 4.2: Borate ion fraction vs. pH [Kruijf et al., 1993]

4.2. Rheological models

Several models have been suggested to describe the shear stress versus shear rate behavior of fluids. Some of them are reviewed below.

1. Bingham Plastic Model (1957)

Bingham plastic is one of the most common models in petroleum industry. This model defines yield stress (τ_y), the stress below which there is no flow, and plastic viscosity (μ_p.).

$$\tau = \tau_y + \mu_p . \dot{\gamma} \tag{4.3}$$

2. Power law model(de waele 1923, Ostwald 1925)

This is another two parameter model which also called Ostwald-de Waele. The parameters of this model, k and n, are called consistency index and flow behavior index respectively.

$$\tau = k\,\dot{\gamma}^{n} \tag{4.4}$$

3. Herschel-Bulkley model(1926)

This is a three-parameter model. It is similar to the Power Law with yield stress term included.

$$\tau = \tau_y + k\,\dot{\gamma}^{n} \tag{4.5}$$

4. Robertson-Stiff model(1976)

It is also a three parameter model with $\dot{\gamma}_0$ as a shear rate corrector.

$$\tau = A(\dot{\gamma}_0 + \dot{\gamma})^{B} \tag{4.6}$$

5. Casson model(1959)

$$\tau = (\sqrt{\tau_y} + \sqrt{(\mu\,\dot{\gamma})^2} \tag{4.7}$$

6. Sisko model(1958)

$$\tau = a\,\dot{\gamma} + b\,\dot{\gamma}^{c} \tag{4.8}$$

For two-parameter models, it is possible to find the coefficients directly since there are two unknowns and it is possible to write two equations with two combinations of data. For Bingham Plastic and power law model, shear stress at 600 and 300 rpm is usually used to find the coefficients. Bingham Plastic coefficients can be calculated as:

$$\mu_p = \frac{\tau_2 - \tau_1}{\dot{\gamma}_2 - \dot{\gamma}_1} \tag{4.9}$$

$$\tau_y = \tau_1 - \mu \dot{\gamma}_1 \tag{4.10}$$

In FANN rotational viscometer with bob/rotor geometry of 1/1, yield stress and plastic viscosity can be obtained directly as a function of shear stress at 600 and 300 rpm:

$$\mu_p = \theta_{600} - \theta_{300} \tag{4.11}$$

μ_p = plastic viscosity in centipoises (cp)

$\theta_{600}, \theta_{300}$ = dial readings of viscometer at 600 and 300 rpm

$$\tau_y = 2\theta_{300} - \theta_{600} \tag{4.12}$$

or

$$\tau_y = \theta_{300} - \mu_p \tag{4.13}$$

τ_y = yield stress in $lb/100ft^2$

In the same way, power law coefficients can be obtained as:

$$n = 3.3219 \log\left(\frac{\theta_{600}}{\theta_{300}}\right) \tag{4.14}$$

$$k = \frac{510.88(\theta_{300})}{(511)^n} \tag{4.15}$$

Flow behavior index is dimensionless and consistency index has unit of cp.

In Herschel-Bulkley method, it is possible to estimate yield stress in some ways, then find other two parameters by linear regression. In regression analysis, any model predicts a shear stress for any shear rate. The sum of square of difference between measured shear stress (τ_m) and predicted shear stress (τ_p) for one set of shear rates is called residual sum of squares (RSS).

$$RSS = \sum_{i=1}^{n} \left[\tau_{mi} - \tau_{pi}\right]^2 \tag{4.16}$$

Then residual mean square (RMS) can be calculated as a criterion for accuracy of models.

$$RMS = \frac{RSS}{(n-p)} \tag{4.17}$$

n= number of data points (10 points in this study)

p= number of parameters which are two for Bingham Plastic, Power Law and Casson and three for the other models.

RMS calculations are carried out by Statistica software. The range of RMS values for each model can be depicted in Box-Whisker plots and best model can be chosen based on the smallest median RMS.

CHAPTER 5

EXPERIMENTAL WORK

One of the first tasks of this study was to elucidate the function of each material and obtain a reasonable concentration range for the following experiments. Steady shear viscometry method was chosen and some experiments were conducted to approve that this method can be suitable. The procedure of conducting the experiments is explained in detail at the end of this chapter.

5.1. Materials

Turkish Petroleum Corporation generously donated the materials for this thesis. The preliminary purpose of this thesis was to find the theory behind this kind of gelation. After several experiments, this could be obtained and a reasonable concentration range for each material was appointed. Consequently this information is mentioned in Table 5.1. The composition of tap water of METU used in the experiments is given in Table 5.2.

Table 5.1: Materials used in the experiments and their functions

Name	Composition	Function
Poly-cross	Xanthan/Borax/ Starch	Increasing viscosity (primary polymer and crosslinker)
Retarder	Magnesium Chloride	Decreasing the rate of gelation and lowering viscosity
pH controller (Accelerator)	Inorganic salt/ Alkali	Increasing crosslinking rate by manipulating pH

Table 5.2: Composition of tap water of METU (Personal communication with Prof. Dr. Filiz B. Dilek, Environmental Engineering Department, METU)

Parameter	Concentration(mg/l)
Cr	<0.02
Pb	<0.001
As	<1.0
Se	<1.0
Cyanide	<1.0
Cd	<0.001
Fluoride	0.34
Nitrate	1.12
Chloride	54.6
Cl	<0.02
Sulfate	147
Fe	0.042
Mn	<0.03
Cu	<0.001
Zn	0.011
Ag	<0.005
Ca	151
Mg	26.3
Detergent	<0.01
Phenol	<0.01
pH	7.21

Borax as the raw material of crosslinker and xanthan, primary polymer, are available in a blend called poly-cross to show that it is a blend of polymer and crosslinker. There was no direct access to control the effect of cross-linker or polymer separately. However, the effect of increasing the polymer and cross-linker concentration at a contact ratio was studied.

Accelerator is a pH-controller agent. When it was not added to the drilling fluid, no gelation occurred even after some days. However, when different concentrations of pH controller are added, there was no significant change in pH. As it was explained in the chemistry of xanthan/borate crosslinking, pH controller is used to convert borax to borate ions. Therefore, by increasing the amount of this material, the pH can be adjusted easier and more borate ions will be available for complexation.

Retarder is magnesium chloride. This material reduces pH and consequently the amount of borate ions available for complexation. In addition, it decreases the viscosity of primary polymer. Therefore, when the concentration of poly-cross is too high such as 25 wt%, Retarder should be used as the thinner of the drilling fluid.

5.2. Experimental method

Model 900 OFITE viscometer was used for the experiments which is a coquette coaxial rotational viscometer. The speed range of motor is between 0.006 to 1000 rpm. The R1B1 geometry combination was employed in this equipment in which bob radius is 1.7245 cm, bob height is 3.8 cm and rotor radius is 1.8415 cm. As a result, the shear gap is 0.117 cm and the ratio of bob radius to rotor radius is 0.9365. Rotation of rotor exerts a shear stress on bob. This stress results in an angle change of bob and a transducer measures it.

A PC software was accompanied with the viscometer. Therefore, all the operations were controlled from computer. The temperature unit was adjusted to centigrade, shear stress to dial reading (DR). However shear stress was later converted to Pascal (Pa) by multiplying with 0.5107 for analysis and shear rate converted to S^{-1} by multiplying with 1.7023.

A thermocup with thermocouple was applied for heating the drilling fluid and measuring the temperature. The maximum allowed temperature was 88°C. Therefore the effect of temperature was studied in the range of room temperature up to 80 °C.

5.3. Experimental procedure

The mixing time for the comparison experiments was 10 minutes and for the empirical model determination was 7 minutes. Since the mixing time affects the gelation time, this value was measured carefully. Later for the rheological model determination part, 10 minutes mixing time was applied. The mixer was MULTIMIXER model (Sterling Multi-Products Inc.). Besides the mixer, manually mixing was also done to make sure that mixing was homogenous. The procedure of conducting the experiments is given in below:

1. Weight the materials
2. Turn on the heater of viscometer and set the temperature
3. Pour the water in the mixer cup
4. Add the retarder
5. Start the mixing. Simultaneously start measuring time.
6. Add the poly-cross and mix properly
7. Add the accelerator rapidly at the end
8. Pour the fluid in the viscometer cup
9. Put the cup in the heater of viscometer
10. Start shear rate at 3 rpm and heating simultaneously
11. Observe the apparent viscosity changes with time.
12. Confirm the end of gelation with the results and observation

Thirty six samples at different concentrations and temperatures are prepared by 10 minutes mixing. The concentrations were chosen by trial and error in order to give a reasonable range of initial gelation time, initial viscosity, final gelation time and final gel quality. Therefore if some samples had some deficiencies like: very thick initial viscosity, very short gelation time, very long gelation time or very weak final gel, they were removed from the list. Temperatures used are mostly at 60° and 80° in order to simulate behavior of gel at lost zone which depends on depth and location. Table 5.3 shows the composition of those samples.

The shear stress was monitored and recorded while the rotor was rotating at steady shear rate of 3 rpm. Shear rate at three rpm was chosen since it is the lowest shear rate available in conventional viscometers in order to avoid gel rupture by rotation. However experiments conducted later on lower shear rates like 1 rpm and gel at rest determined similar initial gelation time.

Table 5.3: Composition of samples used for empirical models

C_{pc} Wt%	C_A Wt%	C_r Wt%	T °C
15	5	0.25	80
15	5	0.25	60
15	5	0	60
15	5	0	80
15	5	1	80
15	10	0.5	80
15	10	0.25	80
15	10	0	60
15	10	0	80
15	15	0.5	80
15	15	0.25	80
20	5	0.5	60
20	5	0.25	80
20	5	0	60
20	5	0	80
20	5	1	60
20	10	0.5	40
20	10	0.5	60
20	10	0.5	80
20	10	0.25	40
20	10	0.25	60
20	10	0	80
20	10	1	60
20	15	0.5	40
20	15	0	60
20	15	1	80
25	5	0.5	80
25	5	0.25	80
25	5	0	60
25	5	0	80
25	5	1	80
25	10	0.5	80
25	10	0.25	80
25	10	0	60
25	10	1	80
25	15	1	40

In the rheological model studies, twenty samples were prepared at different concentrations and temperatures. The compositions of samples are depicted in Table 5.4. Shear stress was measured at 10 different shear rates (0.1, 1, 3, 6, 50, 100, 200, 300, 450, 600 rpm). The experiments were conducted at different shear rates before initial gelation time. If the initial gelation time was long enough, the experiments were conducted two times, once in decreasing order of shear rate and then in increasing order. Otherwise the experiments were conducted two times and the average value was appointed to it. There is increasing of viscosity due to 1:1 comlexation. On the other hand there is decreasing of viscosity due to thixotropic behavior of xanthan especially in presence of magnesium chloride. There is also error of measuring. The graphs in appendix B show that there is no significant difference between the rheograms. Therefore time independent behavior is assumed.

Table 5.4: Composition of samples for rheological model determination

	C_{pc}	C_A	C_r	T
Sample	wt%	wt%	wt%	°C
1	15	10	0	80
2	15	5	0	60
3	15	5	0	80
4	15	5	1	80
5	15	10	0	40
6	15	10	0	60
7	15	10	1	40
8	15	10	1	60
9	15	10	1	80
10	15	10	0	80
11	15	7.5	0	80
12	20	5	0.5	40
13	20	5	0	40
14	20	5	0	60
15	20	5	0	80
16	20	5	1	40
17	20	5	1	60
18	20	5	1	80
19	20	10	1	40
20	20	10	1	80

Figure 5.1 shows a typical result of steady shear viscometry experiment. It demonstrates four parameters measured: 1. Initial gelation time which is the time of sudden viscosity build up. 2. Initial viscosity which is the viscosity at the first period in which viscosity is almost constant. In this period, there are two opposite effects of 1:1 comlexation and thixotropic effect of xanthan especially in presence of magnesium chloride which results in a little change of viscosity. 3. Final gelation time which is the time when viscosity reaches its peak and the observation confirms this phenomenon as well. Measuring this time is difficult and not accurate since when the final gel is about to produced; the readings are fluctuating and not any more meaningful. 4. Final viscosity is the viscosity at its peak, at the time of final gelation time. Moreover the rate of crosslinking is the slope of line (or the trend of the curve) between the initial gelation time and final gelation time. Figure 5.2 shows the viscometer and the final gel.

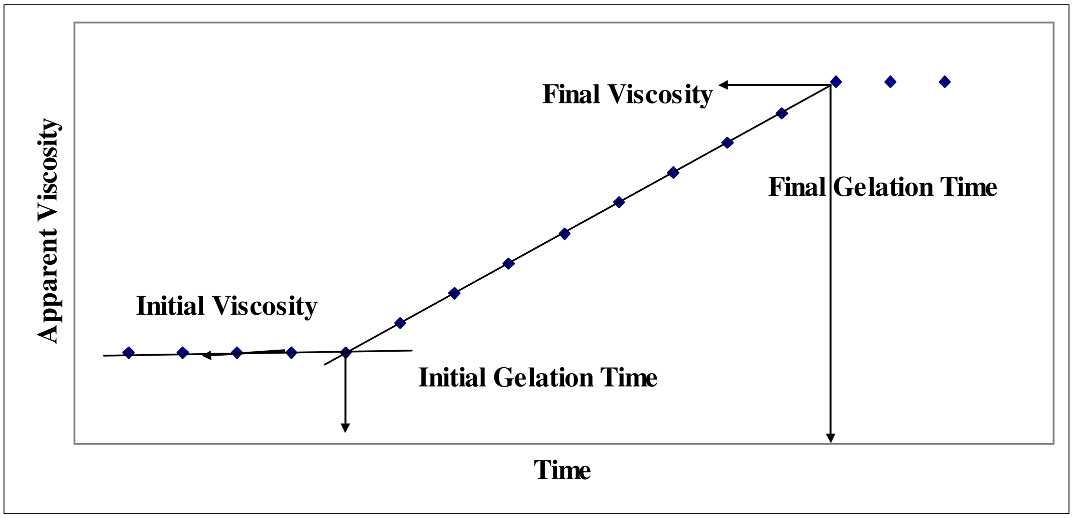

Figure 5.1: Typical steady viscometry method result

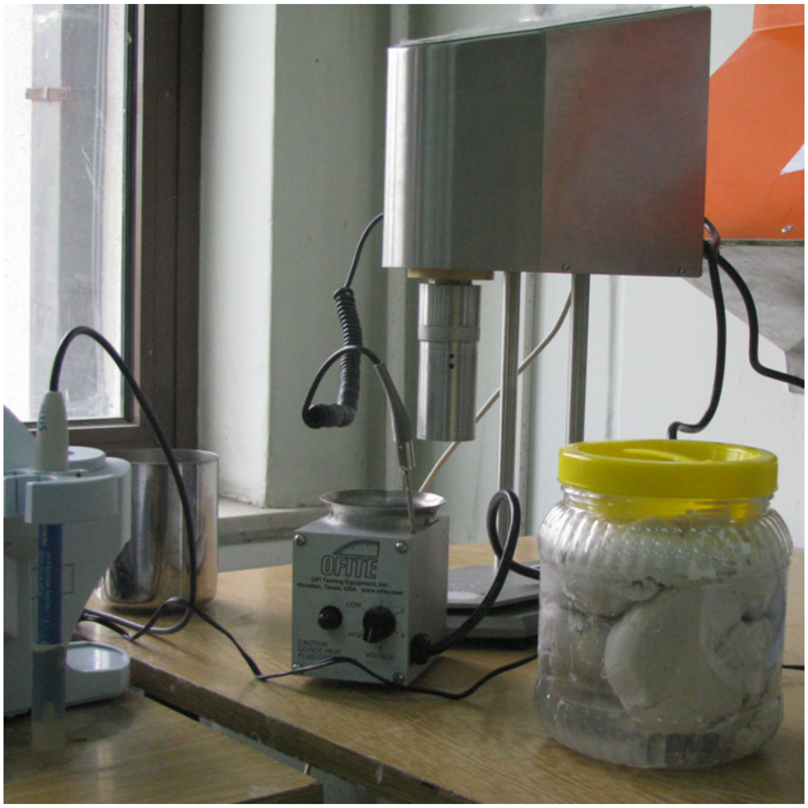

Figure 5.2: viscometer and gel

CHAPTER 6

RESULTS AND DISCUSSIONS

This chapter is divided into three sections: In the first section, the effect of variety of parameters (pH controller, magnesium chloride, poly-cross, temperature, shear rate and history, and mixing time) on initial gelation time, final gelation time, initial viscosity, and final viscosity are discussed. In the second section, empirical models for initial gelation time, final gelation time, initial viscosity and final viscosity are given. In the last section, rheological models studies based on shear stress versus shear rate data were conducted and the best fitted rheological model is obtained by a statistical approach. Finally modified Bingham Plastic and yield point models are suggested for this gel system to facilitate use of the rheological model in field operations.

The unit of time is minute, unit of apparent viscosity is cp and the unit of concentration is wt% throughout this thesis. Otherwise it will be mentioned.

6.1 Effect of pH-controller on gelation

It was observed that without adding the pH-controller (accelerator), no gelation occurred even after several days. By adding of accelerator in concentrations of 2.5, 5, 7.5, and 10 wt%, (these concentrations were selected by trial and error in order to have a reasonable range of initial gelation time) the pH rose to 10.20, 10.30, 10.40, and 10.40 respectively. Therefore the accelerator is a necessary part of this system for making an alkaline environment for solution to release borate ion from borax. In other words, without adding accelerator, no gelation occurs since no crosslinker (borate ions) can exist without having appropriate pH. Although pH does not change significantly by adding accelerator, more borate ions can be released by increasing concentration of accelerator. Moreover the amount of borate ion can be more than enough for crosslinking. Therefore initiation of gelation can be accelerated since the possibility of complexation increases. The rate of crosslinking also increases when the ph-controller concentration increases from 2.5 to 5 wt%. Figure 6.1 depicts the effect of pH-controller on gelation.

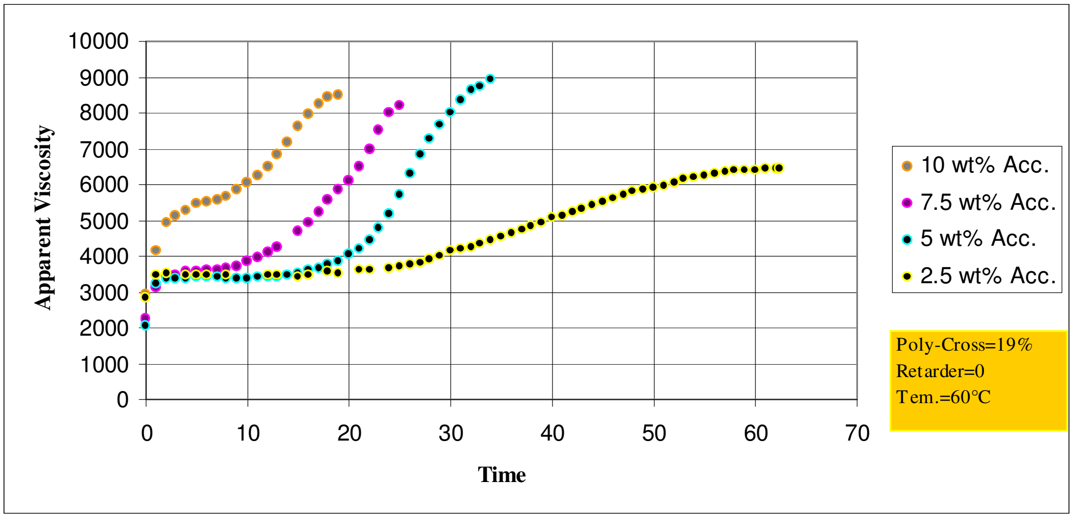

Figure 6.1: Effect of pH-controller on gelation

Initial viscosity depends on xanthan properties. Figure 6.1 reveals that pH-controller has negligible effect on initial viscosity. For 10 wt% pH-controller, initial viscosity is not clear since the gelation is very rapid.

Final gel viscosity can represent final gel quality. Figure 6.1 also shows the effect of pH-controller on final gel viscosity. Since by adding more pH-controller, more borate ion is available for crosslinking, the final gel network will be stronger. This is clear when 2.5 wt% is compared with 5 wt% with 6450 and 8900 cp final viscosities respectively. However there is negligible difference between 5, 7.5, and 10 wt%. It can be explained in this way that after a certain pH-controller concentration, more borate ion simply helps initiation of crosslinking, however the final number of crosslinkings do not change. This idea can be strengthened by observing almost constant slope for the first three lines and lower slope for the lowest concentration. Therefore after a certain pH concentration, the borate ion concentration will be constant. As a result the rate of crosslinking and final viscosity will be constant but initiation of gelation is always accelerated by increasing pH controller concentration since the possibility of initial attack increases.

Moreover, the final gelation time increases with decreasing pH-controller concentration. Again there is little difference for the first three high concentrations while there is a major increase for the lowest concentration.

Since the main function of pH-controller is to decrease the initial gelation time, the effect of pH-controller on initial viscosity is derived from Figure 6.1 and is depicted in Figure 6.2.

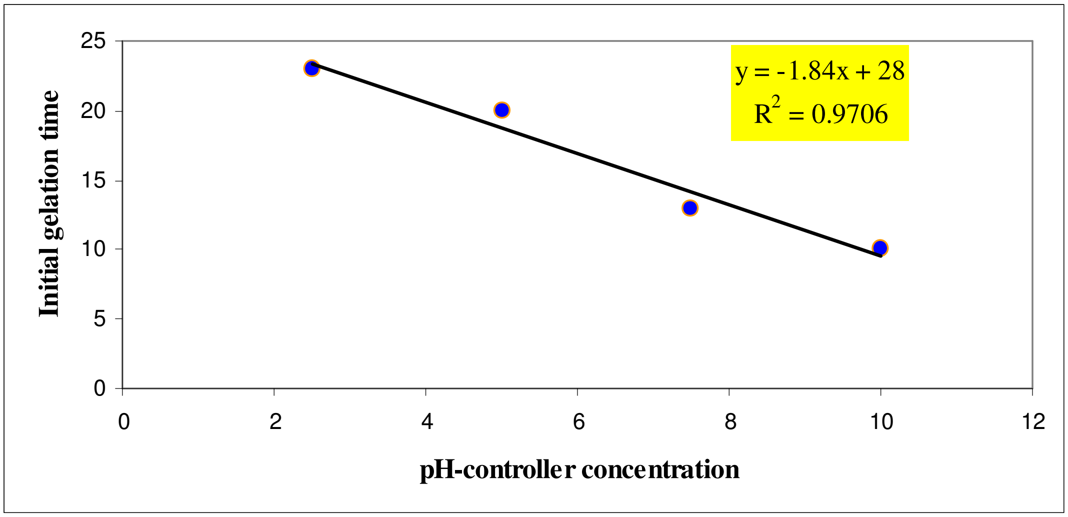

Figure 6.2: Effect of accelerator on initial gelation time

6.2. Effect of poly-cross concentration on gelation

Poly-cross is a blend of polymer, xanthan, and raw crosslinker, borax. (if the concentration of poly-cross is changed, the ratio of polymer to crosslinker remains constant). Figure 6.3 illustrates the effect of poly-cross on gelation. The initial gelation time is almost constant when poly-cross concentration increases.

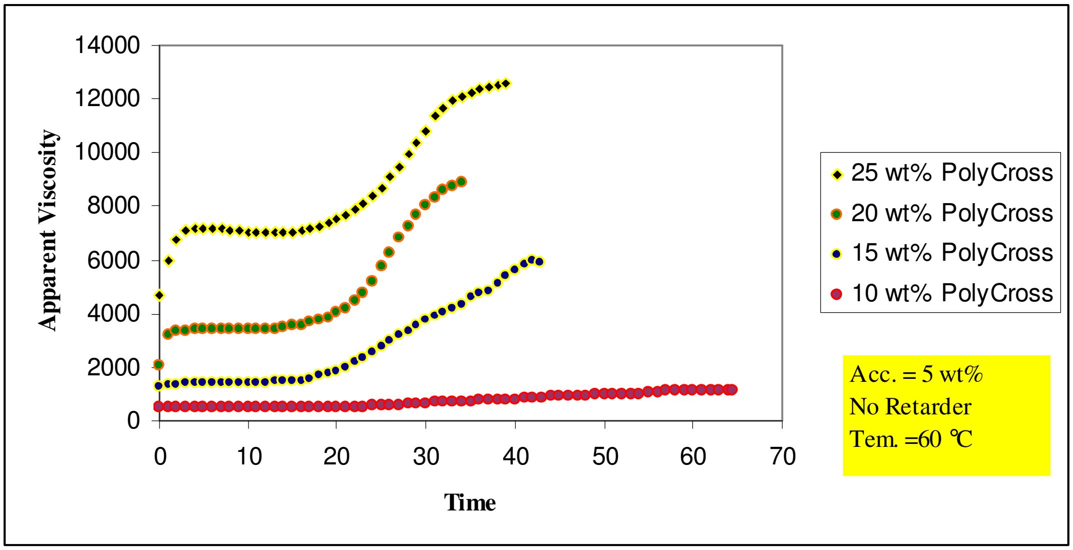

Figure 6.3: Effect of poly-cross on gelation

Final gelation time increases very rapidly when poly-cross concentration drops from 15 wt% to 10 wt% since there is not enough borax and xanthan for crosslinking reaction in 10 wt% poly-cross. However after a certain concentration, the number of crosslinking will be constant and the poly-cross concentration contributes to solution just by increasing viscosity.

The initial gelation time for the 10 wt% poly-cross is not clear since it has lower viscosity in comparison with others. Therefore, it is shown in a Figure 6.4 separately.

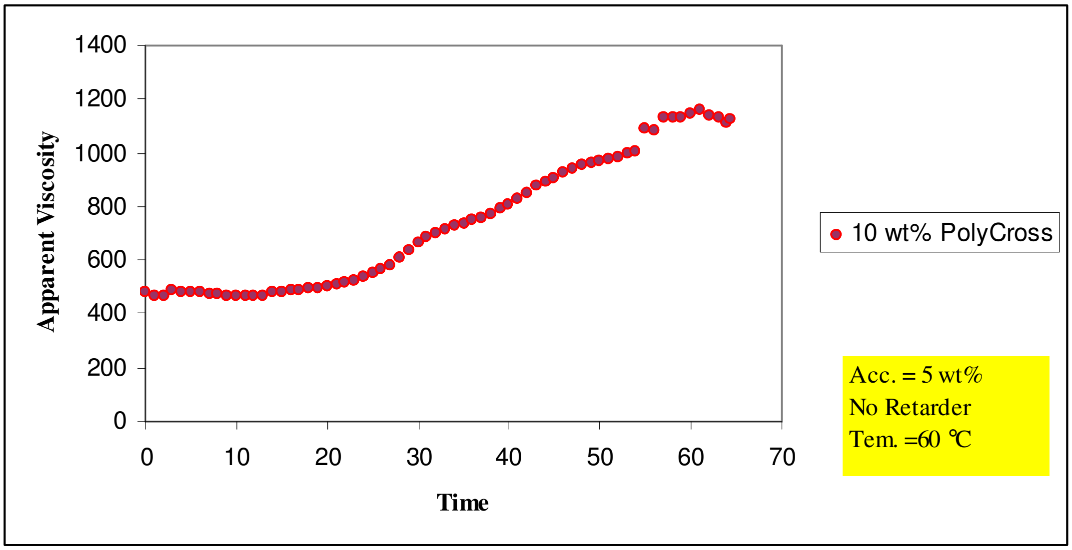

Figure 6.4: Gelation behavior of 10 wt% poly-cross

The main function of poly-cross is increasing of viscosity. Therefore the initial viscosity of sample in Figure 6.3 is obtained and depicted in Figure 6.5.

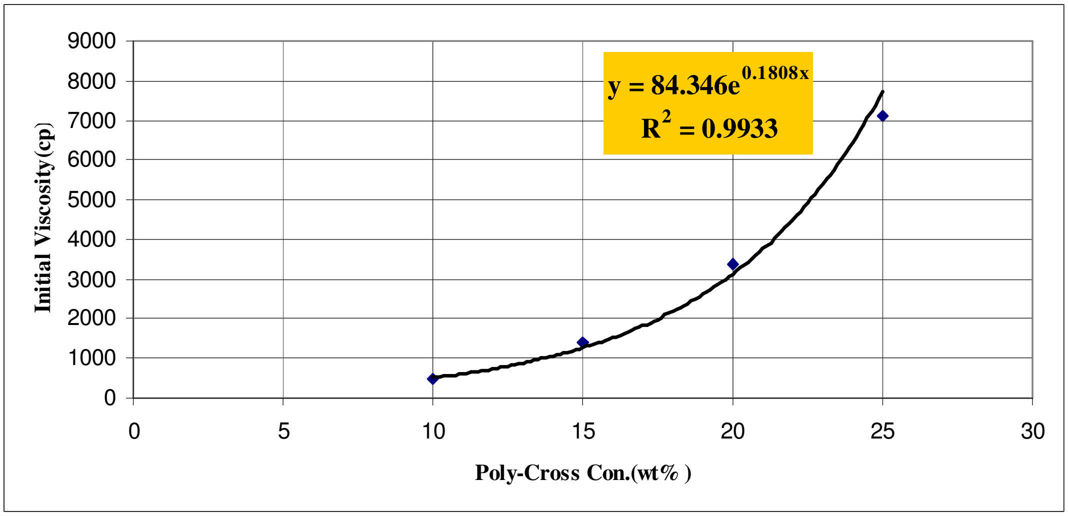

Figure 6.5: Effect of poly-cross on initial viscosity

According to Figure 6.5, initial viscosity is a significant function of poly-cross concentration and it grows up in an exponential manner but final viscosity is a kind of a linear function of poly-cross concentration (Figure 6.6).

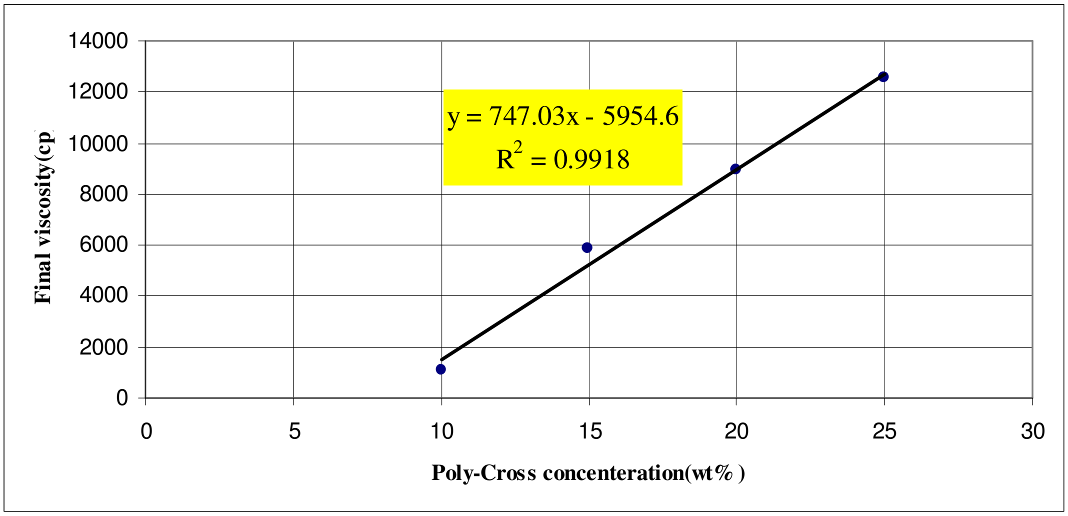

Figure 6.6: Effect of poly-cross on final viscosity

Finally, for this sample initial and final viscosity equations can be obtained from correlating of the data points in Figure 6.5 and 6.6.

$$\mu_i = 84.346e^{0.181C_{pc}} \qquad (6.1)$$

$$\mu_f = 747.03C_{pc} - 5954.6 \qquad (6.2)$$

μ_i =initial viscosity (cp)

C_{pc} =Poly-cross concentration (wt %)

μ_f = final viscosity (cp)

6.3. Effect of magnesium chloride on gelation

Magnesium chloride or Retarder contributes to solution by reducing borate ions. Magnesium ions react with OH^- ions and precipitates as insoluble $Mg(OH)_2$.

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad \text{[Harris and Batenburg]} \qquad (6.3)$$

Therefore hydroxide ions of solution are consumed with magnesium ions which results in less borate ions available for crosslinking. Figure 6.7 illustrates the effect of magnesium chloride concentration (0, 0.25, 1and 2 wt %) on gelation process.

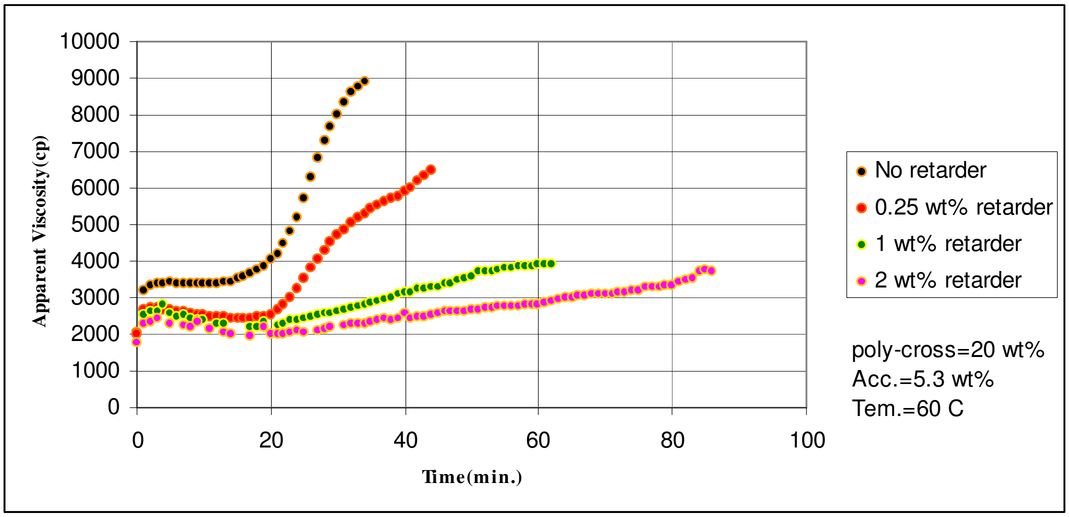

Figure 6.7: Effect of magnesium chloride on gelation

At more than 2 wt%, the solution becomes very dilute and a weak gel will be produced in a long period of time which is not appropriate for lost circulation purposes in which a strong gel in a shortest time after placement in thief zone is reasonable. Initial gelation time changes negligibly with increasing retarder concentration. However rate of crosslinking is significantly higher at lower magnesium chloride concentration.

Consequently the final gelation time is longer (Figure 6.8). Initial viscosity is a function of xanthan viscosity and xanthan viscosity decreases with the attacks of magnesium chloride on this biopolymer. The final gel is also weaker due to less networks generation shown by lower viscosity (Figure 6.9).

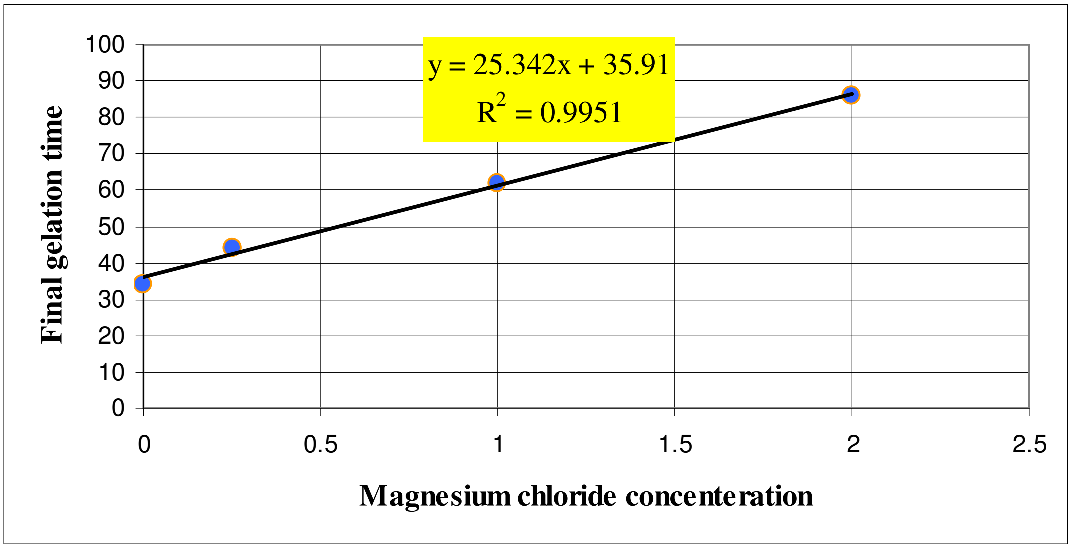

Figure 6.8: Effect of magnesium chloride on final gelation time

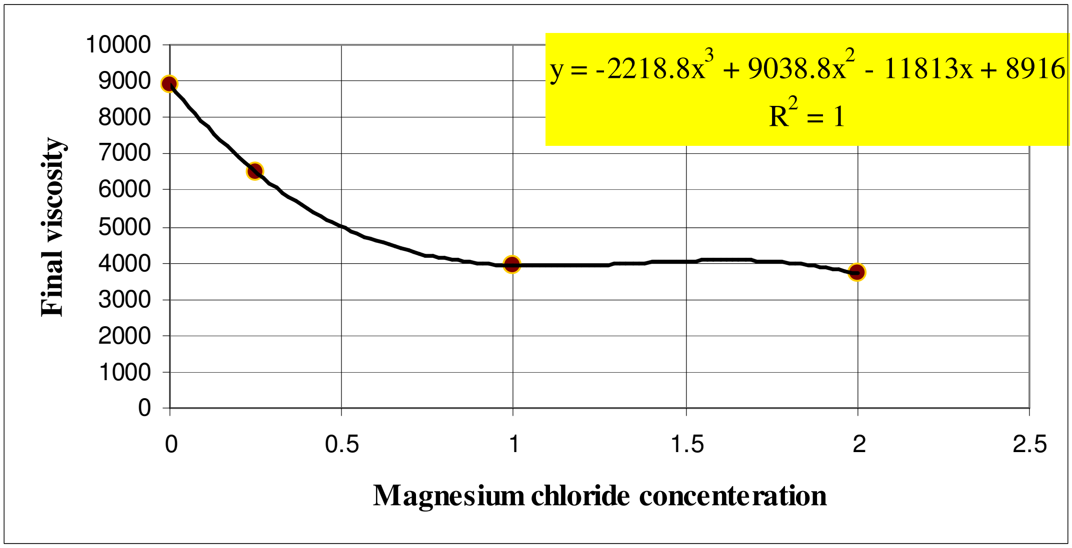

Figure 6.9: Effect of magnesium chloride on final gel viscosity

6.4. Effect of temperature on gelation

This effect is much more complicated. According to borate ion equilibrium by kruijf, more borate ions are available at higher temperature at a constant pH (however it is in contradiction with what Harris et al. (1993) concluded). Crosslinking is a function of borate ion concentration as well as activation energy of crosslinking. Therefore at higher temperatures, more borate ions are available as well as more energy to overcome enthalpy of crosslinking (according to Harris less borate ions are available at higher temperature. However it can be explained in the way that enthalpy is dominant here).Figure 6.10 shows the effect of temperature on the progress of gelation.

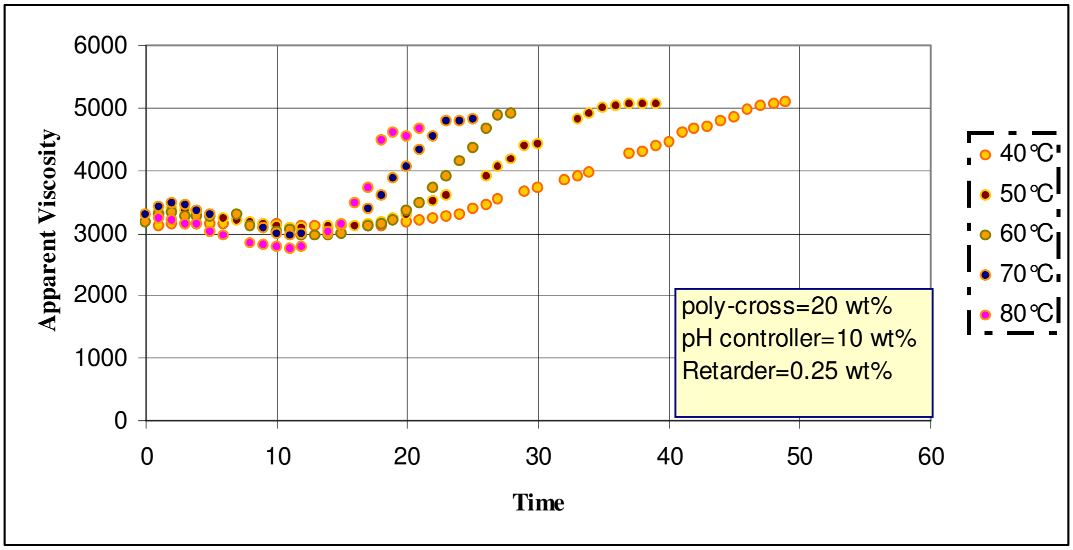

Figure 6.10: Effect of temperature on gelation

Initial gelation time decreases with increasing temperature since more borate ions as well as energy are available for crosslinking reaction. The major effect of temperature is on initial gelation time. Therefore the initial gelation time is obtained from the Figure 6.10 is depicted below in Figure 6.11. Final gelation time is longer at lower temperatures. The effect is shown in Figure 6.12.

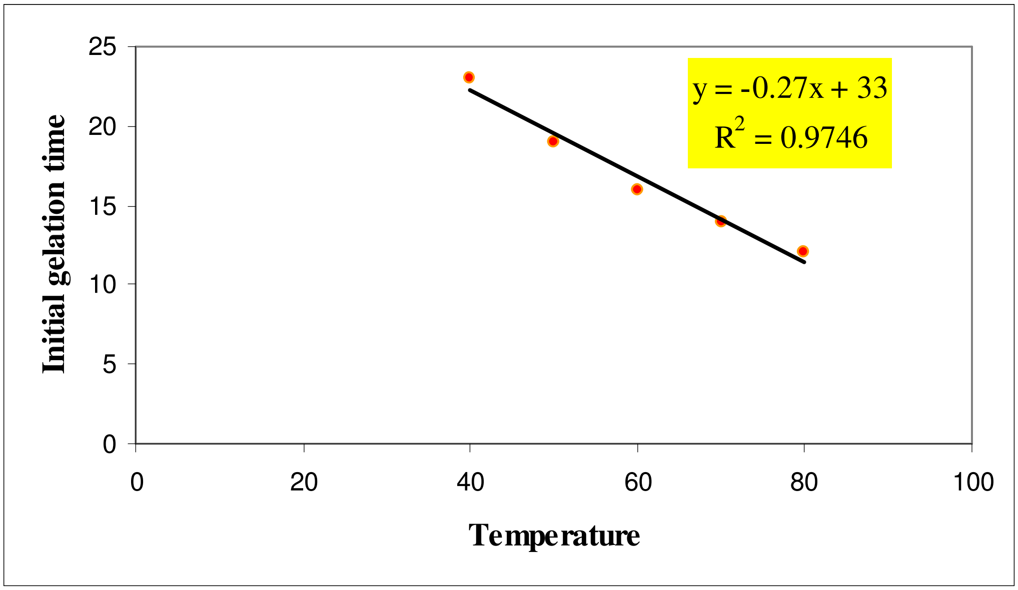

Figure 6.11: Effect of temperature on initial gelation time

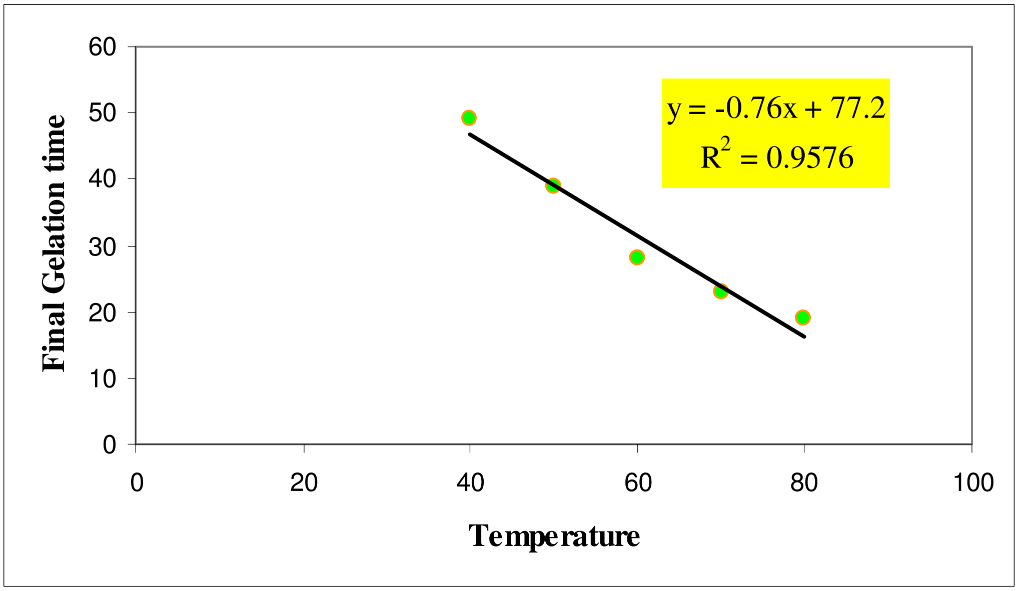

Figure 6.12: Effect of temperature on final gelation time

The effect of temperature on gelation can be represented by Arrhenius plot of ln(1/t) against 1/T in which t is time in seconds and T is temperature in Kelvin.

$$\frac{1}{t} = Ae^{-E_a/RT} \tag{6.4}$$

$$\ln(1/t) = \ln A - \frac{E_a}{R} \times \frac{1}{T} \tag{6.5}$$

The slope is equal to –E/R in which E is activation energy and R is gas constant (8.314 J/K.mol). As a result activation energy calculated is 14.792 kJ/mol. Figure 6.13 shows the Arrhenius plot for calculating activation energy. When activation energy is known then it is possible to correlate the initial gelation time at other temperatures.

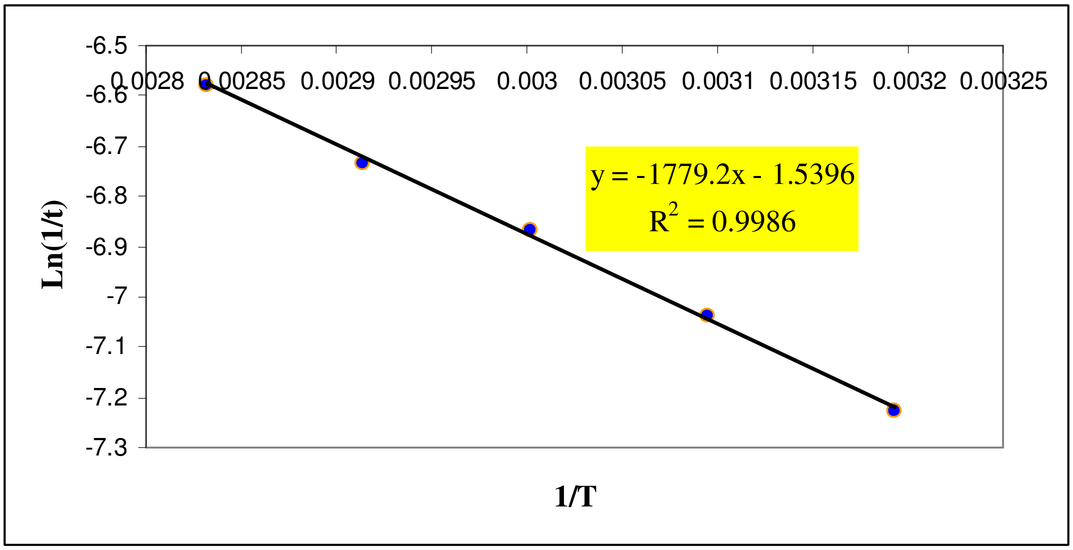

Figure 6.13: Determination of activation energy

6.5. Effect of mixing time on gelation

In this case, solutions (poly-cross= 20 wt%, accelerator= 5.3 wt%, no retarder, temperature= 60°C) were prepared during different mixing periods (7, 10,15,20,30 minutes). Then a constant shear rate of 3 rpm was employed. In the end of mixing, the drilling fluid temperature was measured as it is illustrated in Figure 6.14. It increases linearly with increasing mixing time.

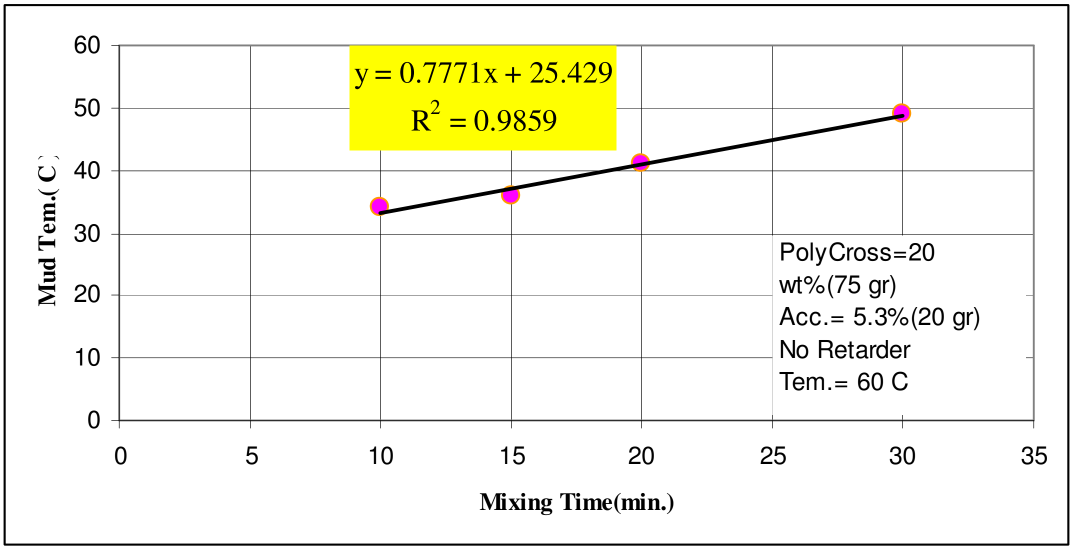

Figure 6.14: Effect of mixing time of solution temperature

Increasing of mixing time, decreases initial gelation time .For the fluid prepared by 30 minutes mixing, a sharp increase of viscosity is observed from the early beginning. Decreasing of initial gelation time can be attributed to increase of fluid temperature as well as to the fact that from beginning of mixing crosslinking starts. Other parameters such as initial viscosity, rate of cross-linking, and final viscosity are almost not affected by mixing time. The gelation behavior can be observed in Figure 6.15.

However when initial gelation time was added to mixing time, all of samples with different mixing time periods had almost the same total time of mixing plus gelation time. It proves that from beginning of mixing, time is counted. In other words, gelation can not be delayed by mixing the solution for a longer period of time. Figure 6.16 shows that addition of initial gelation time and mixing time is almost constant.

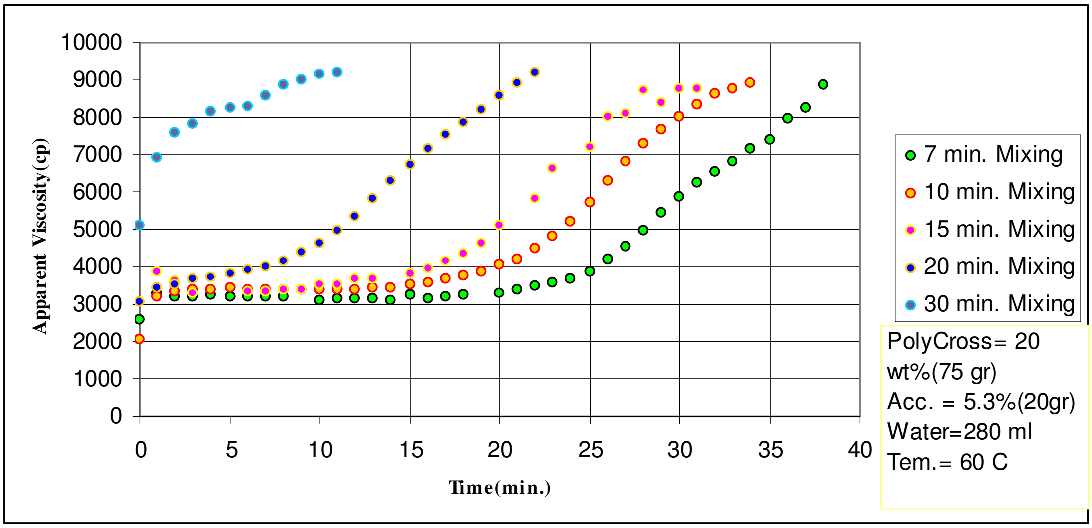

Figure 6.15: Effect of mixing time on gelation

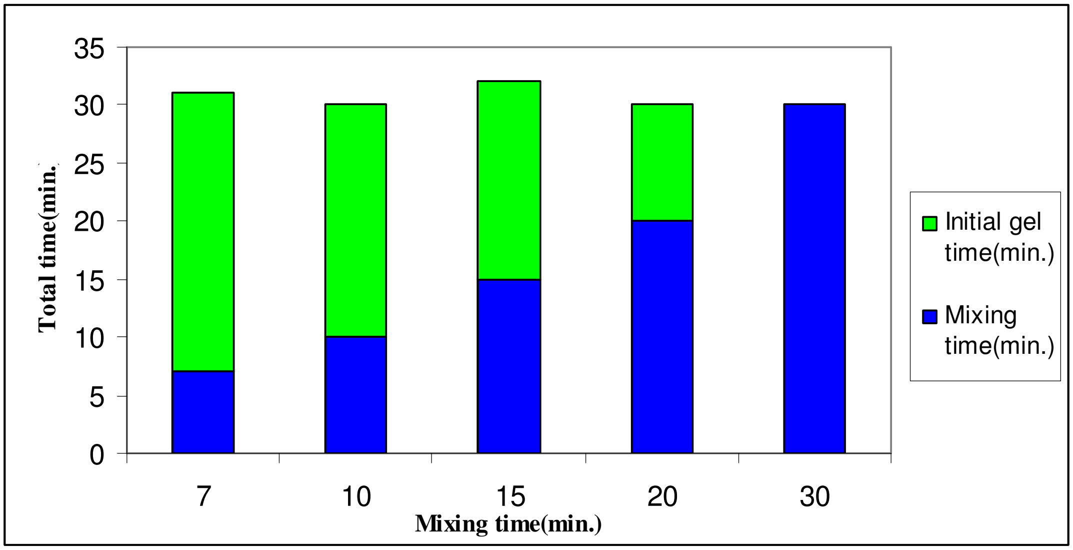

Figure 6.16: Total gelation time

6.6. Effect of Shear history on gelation

Since there is some criticizes from supporters of dynamic viscometry method that shear may cause dissociation of some crosslinks in steady shear viscometry method, the effect of shear on gelation was also investigated.

For a sample, initial gelation time was measured with normal procedure of steady shear viscometry as explained before. Later a similar sample was prepared and put in rest for 15 minutes before initiation of gelation that was obtained from previous experiment (the flat pink line in Figure 6.17 shows this rest time). Then the shear rate at 3 rpm was applied. Figure 6.17 shows that both samples exhibited almost similar gelation time. Thus, the shear did not have any effect on initial gelation time determination. However, the viscosity after initiation of gelation is little higher for the sample being at rest for 15 minutes.

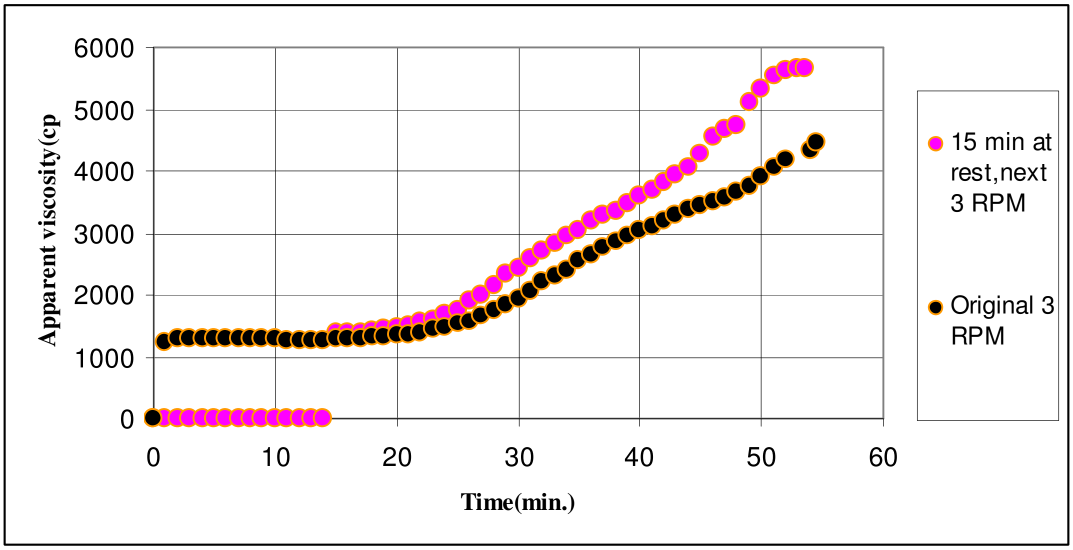

Figure 6.17: Effect of shear on gelation

In order to simulate what happens to gel during its flow inside drillpipe in field operation, experiments were conducted at high shear rates. Two samples were under 100 and 300 rpm for 10 minutes in order to simulate fluid flow in drillpipe. Then the shear rate switched to 3 rpm to simulate rest condition at thief zone. Figure 6.18 illustrates that this high shear rate history does not affect initial gelation time. (The time for shear is not counted in initial gelation time. In other words gelation is postponed here). However the viscosity is higher in this case. Time zero shows the time that the shear rate was switched from 100 or 300 rpm to 3 rpm for the last two samples. It should be noticed that gel can be produced near the wall since the velocity is low there.

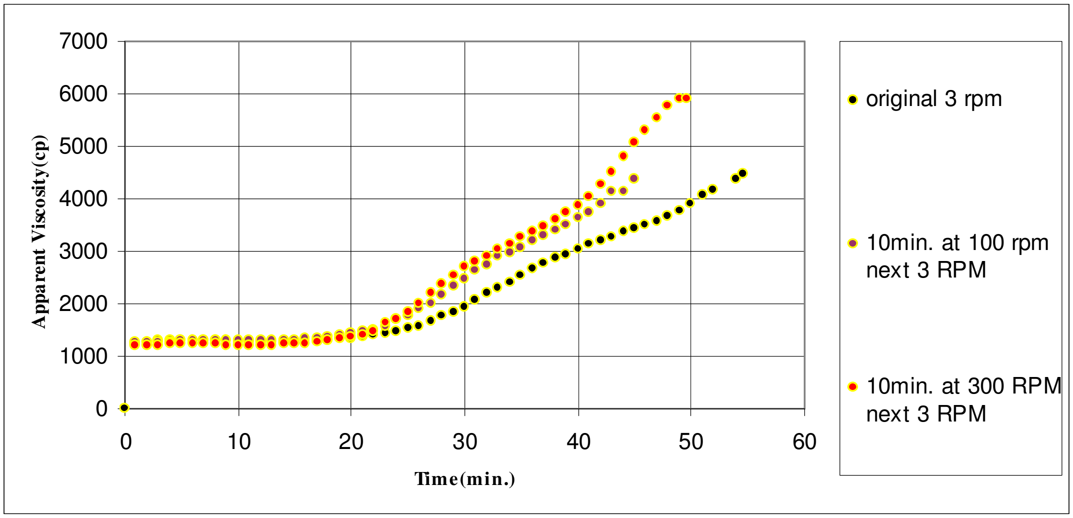

Figure 6.18: Effect of shear history on gelation

Finally an experiment was conducted at shear rate of 1 rpm to see whether lower shear rates(in comparison to 3 rpm) may change initial gelation time or not. Figure 6.19 shows that the sample at 1 rpm has similar initial gelation time as one at 3 rpm depicted before in Figure 6.17.Therefore it also confirms that rotation at 3 rpm does not have effect on gel destruction on gel. As a result, it is better to conduct experiments at a common 3 rpm shear rate instead of very low ones.

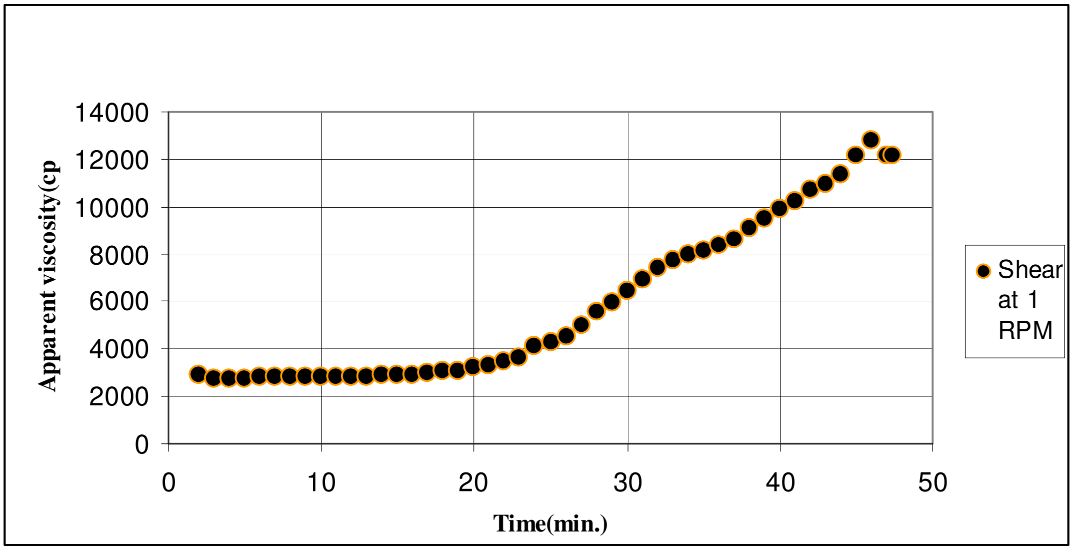

Figure 6.19: Gelation at 1 rpm

6.7. Empirical models for gelation behavior estimation

In this section, an empirical model for initial gelation time prediction is suggested. Similar models for final gelation time, initial viscosity and final viscosity estimation are given. However the initial gelation time is much more of quantitative importance.

Regression analysis by Statistica software was used to generate empirical models. The models are linear function of four parameters: poly-cross concentration, accelerator concentration, retarder concentration and temperature. By regression analysis and least square method the coefficients were obtained. Then the results from the models and what was obtained from experiments were compared to see the how well they are correlated. The results are depicted in Table 6.1.

Table 6.1: The results for empirical model determination

C_{pc} Wt%	C_A Wt%	C_r Wt%	T °C	t_i Min.	t_f Min.	μ_i cp	μ_f cp
15	5	0.25	80	17	35	1000	1795
15	5	0.25	60	21.5	60	950	2185
15	5	0	60	23	50	1370	6723
15	5	0	80	17	36	1200	6015
15	5	1	80	18	51	750	1138
15	10	0.5	80	15	27	1200	1800
15	10	0.25	80	15	23	1500	2076
15	10	0	60	16.5	28	1660	3100
15	10	0	80	11.5	20	2300	4200
15	15	0.5	80	11	23	1500	2200
15	15	0.25	80	11	21	1625	2765
20	5	0.5	60	25	60	2400	4300
20	5	0.25	80	19	31	2700	5200
20	5	0	60	22	45	3170	10600
20	5	0	80	17	23	4000	8300
20	5	1	60	22	75	1900	4200
20	10	0.5	40	22	53	3700	5400
20	10	0.5	60	16	27	3400	4800
20	10	0.5	80	14	23	3850	5050
20	10	0.25	40	20	50	3150	5250
20	10	0.25	60	18	43	3100	7200
20	10	0	80	9	15	6200	9400
20	10	1	60	19	59	2100	5900
20	15	0.5	40	18	48	6200	7700
20	15	0	60	10	17	7350	8230
20	15	1	80	10	17	3300	4300
25	5	0.5	80	19	40	5030	11600
25	5	0.25	80	19	27	6000	9930
25	5	0	60	20	44	8280	17900
25	5	0	80	15	21	9600	14385
25	5	1	80	19	36	5170	6900
25	10	0.5	80	13	20	9000	9580
25	10	0.25	80	12	18	9100	10600
25	10	0	60	14	25	11500	20000
25	10	1	80	13	26	7600	8500
25	15	1	40	17	35	9600	11500

The following model was obtained for initial gelation time:

$$t_i = 40.65 - 0.15C_{pc} - 0.94C_A + 2.62C_r - 0.20T \qquad (6.6)$$

t_i : Initial gelation time (min.)

C_{pc} : Poly-cross concentration (wt %)

C_A : Accelerator concentration (wt %)

C_r : Retarder concentration (wt %)

T : Temperature (°C)

In equation 6.6, the negative sign of poly-cross, accelerator and temperature coefficients show that they decrease the initial gelation time. On the other hand, retarder with positive coefficient sign increases initial gelation time.

The range of input of these parameters is as follows: poly-cross (15-25 wt %), accelerator (5-15 wt %), retarder (0-1 wt %) and temperature (40-80). Therefore if they are substituted in the formula, they can contribute to the equation in this way:
Poly-cross (-2.25 to -3.75), accelerator (-4.75 to -14.1), retarder (0 to +2.62) and temperature (-8 to -16).

Therefore if they are compared with the constant of equation, it can be concluded that retarder and poly-cross has negligible effect while accelerator and temperature have major effect on initial gelation time. This is in absolute agreement with what was explained before during the investigation of effect of parameters on gelation.

Figure 6.20 compares the results from the model with what was measured for initial gelation time. The line is almost passing through y=x and R^2 of 0.875 shows that the model is fairly good.

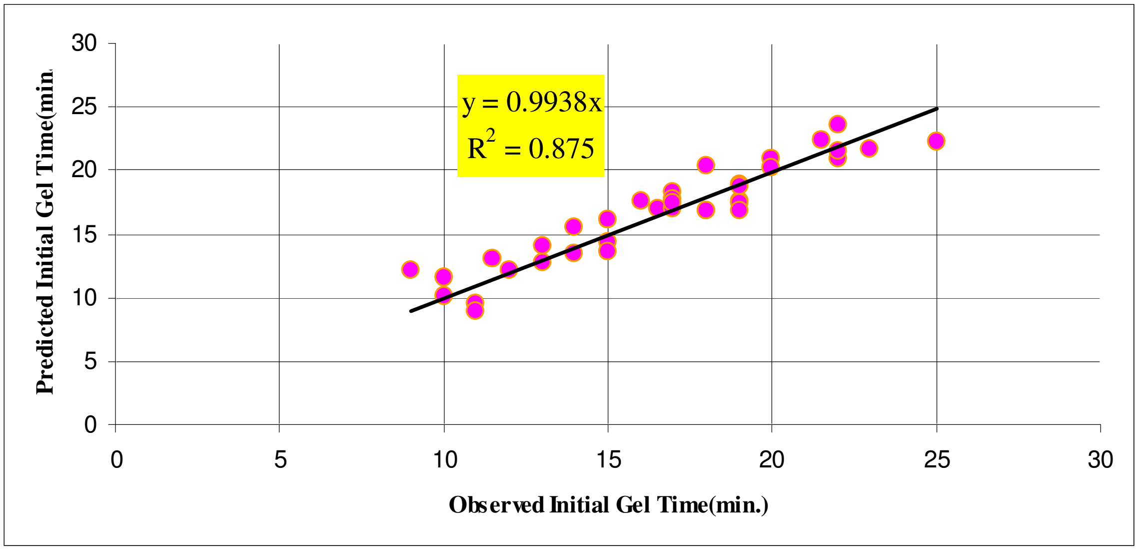

Figure 6.20: Comparison of predicted initial gelation time with measured values

Similar regression analysis on final gelation time was conducted. The following equation was obtained for prediction of final gelation time.

$$t_f = 130.47 - 1.20C_{pc} - 2.81C_A + 19.20C_r - 0.80T \tag{6.7}$$

Due to the sign of coefficients, only retarder increases final gelation time. According to their range of input, the following range of contribution is obtained: Poly-cross (-18 to -30), accelerator (-14.05 to -42.15), retarder (0 to +19.2), temperature (-32 to -64).Therefore temperature and accelerator has major effect on decreasing of final gelation time while retarder increases final gelation time.

Figure 6.21 shows the comparison of results from the model with the measurements of experiments.

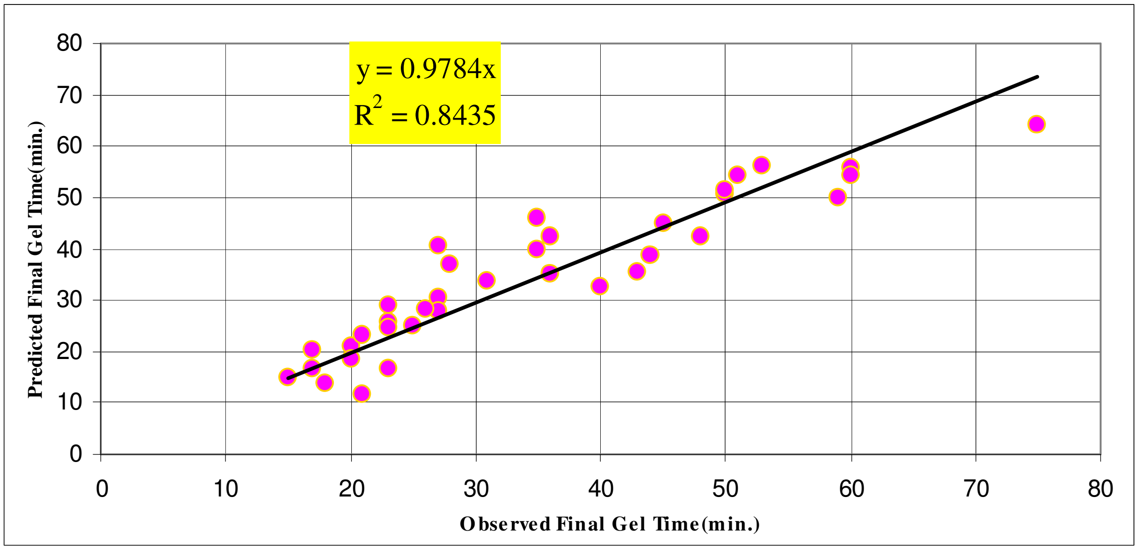

Figure 6.21: Comparison of predicted final gelation time with measured values

Initial viscosity is criteria of fluidity of fluid before start of gelation which is the time for pumping the fluid. Equation 6.8 was obtained after regression analysis as follows:

$$\mu_i = -11887.7 + 729.24C_{pc} + 249.40C_A - 2480.28C_r + 5.87T \qquad (6.8)$$

From the coefficient analysis, it can be obtained that retarder decrease initial viscosity while others have positive effect. Temperature effect is negligible and poly-cross has a major effect on increase of initial viscosity. The results from experiments and the model are compared in Figure 6.22.

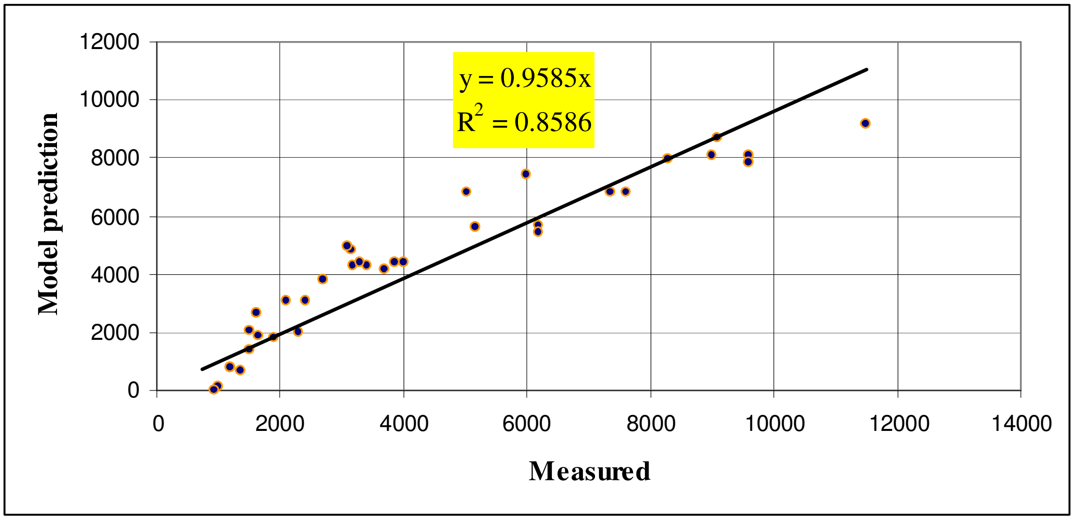

Figure 6.22: Comparison of predicted initial viscosity with measured values

Final viscosity can be criteria for final gel quality. Equation 6.9 is suggested for prediction of final viscosity.

$$\mu_f = -8695.86 + 985.77C_{pc} + 14.22C_A - 5472.57C_r - 28.34T \qquad (6.9)$$

According to the coefficients, poly-cross has a major effect on increase of final viscosity. On the other hand, retarder has a significant effect on decrease of final viscosity. Temperature decrease final viscosity while accelerator has negligible effect. The results from the model and measured values from experiments are compared in Figure 6.23.

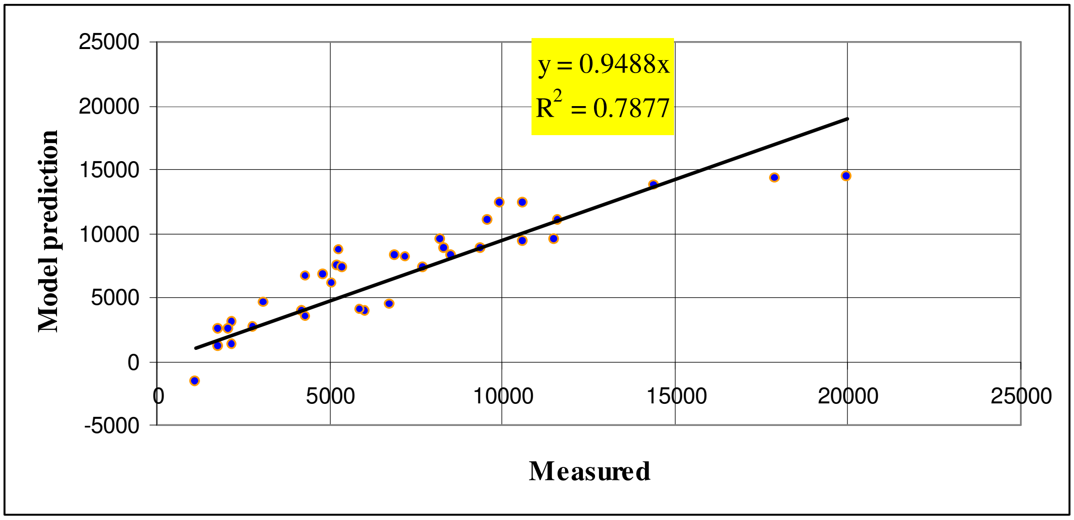

Figure 6.23: Comparison of predicted final viscosity with measured values

6.8. Empirical models for field application

For facilitating the use of empirical models in field application, the conversion of units was done and the following models are suggested in which the unit of concentrations is lb/bbl and unit of temperature is °C. Table 6.2 shows the composition of materials in these units. These equations are obtained by statistical approach and the units of opposite sides are not similar. It should be mentioned that the values obtained from these experiments may be different from what exactly happens in the field. This can be due the mixing procedure (the mixer heats the drilling fluid and accelerates the gelation), the water composition (the gelation is dependent on ions such as magnesium chloride, etc.), the temperature of water and environment, the period of mixing, etc. Moreover these equations have also some amount of errors.

$$t_i = 38.309 - 0.013C_{pc} - 0.168C_A + 0.590C_r - 0.205T \tag{6.10}$$

$$t_f = 120.820 - 0.167C_{pc} - 0.483C_A + 3.940C_r - 0.808T \tag{6.11}$$

$$\mu_i = -7900.430 + 118.209C_{pc} + 20.673C_A - 561.517C_r + 8.105T \tag{6.12}$$

$$\mu_f = -4056.740 + 165.393C_{pc} - 28.997C_A - 1146.090C_r - 27.816T \quad (6.13)$$

Table 6.2: Composition of materials in field unit

C_{pc} lb/bbl	C_A lb/bbl	C_r lb/bbl	T °C
65.83	21.94	1.09	80.00
65.83	21.94	1.09	60.00
65.63	21.88	0.00	60.00
65.63	21.88	0.00	80.00
66.46	22.15	4.43	80.00
70.47	46.98	2.35	80.00
70.23	46.82	1.17	80.00
70.00	46.67	0.00	60.00
70.00	46.67	0.00	80.00
75.54	75.54	2.51	80.00
75.27	75.27	1.25	80.00
93.96	23.49	2.34	60.00
93.64	23.41	1.17	80.00
93.33	23.33	0.00	60.00
93.33	23.33	0.00	80.00
94.59	23.65	4.73	60.00
100.72	50.36	2.51	40.00
100.72	50.36	2.51	60.00
100.72	50.36	2.51	80.00
100.36	50.18	1.25	40.00
100.36	50.18	1.25	60.00
100.00	50.00	0.00	80.00
101.45	50.72	5.07	60.00
108.52	81.39	2.70	40.00
107.69	80.77	0.00	60.00
109.38	82.03	5.47	80.00
125.90	25.18	2.51	80.00
125.45	25.09	1.25	80.00
125.00	25.00	0.00	60.00
125.00	25.00	0.00	80.00
126.81	25.36	5.07	80.00
135.66	54.26	2.70	80.00
135.13	54.05	1.35	80.00
134.62	53.85	0.00	60.00
136.72	54.69	5.47	80.00
148.31	88.98	5.93	40.00

6.9. Rheological model determination

In this section, rheological model determination was intended to analyze behavior of drilling fluid during its flow. Twenty samples were prepared at different concentrations and temperatures. The shear stress was measured at 10 shear rates (0.1, 1, 3, 6, 50, 100, 200, 300, 450, 600 rpm).

The experiments were conducted at different shear rates before initial gelation time. The experiments are conducted once in decreasing order of shear rate, then in increasing order or conducted two times if initial gelation time is not enough and average value is assigned to them. The graphs in appendix B shows that the samples are almost time independent since the 1:1 comlexation starts from beginning while the thixotropic behavior of xanthan especially in presence of magnesium chloride is also present. It is assumed that the fluid shows time independent behavior in order to find the rheological models.

Rheograms shows shear stress versus shear rate behavior of fluids. From this piece of information, rheological models can be obtained. Figure 6.24 shows the rheograms of all the samples. Each color represents a sample (the number is appointed on the right of diagram) and the sample composition can be found in table 6.2. Interception with y axes, shear stress axes, determines yield stress of drilling fluid and the slope determines plastic viscosity of drilling fluid in Bingham-Plastic model. All the rheograms are illustrated below for the comparison.

Residual mean square (RMS) values were obtained for two-parameter models (Bingham Plastic, Power Law, and Casson) and three-parameter models (Robertson-Stiff, Herschel-Bulkley, and Sisko). Since the RMS values for two-parameter models are much higher than three-parameter models, they are shown in two separate charts.

Column charts for two-parameter models (Figure 6.25) reveals that Bingham Plastic model has the highest RMS values (least fitting) and Power Law has the lowest one (except the samples 1 and 20). Moreover samples 17 and 18 have unusual high RMS values. According to Box-Whisker plots (Figure 6.26), Power Law model has the least median RMS value (Power law: 11.13, Casson: 43.99, Bingham Plastic: 140.37). Therefore Power Law is the best fitted model among two-parameter models. Other information obtained from this plot (sample minimum, sample maximum, lower quartile, and upper quartile) also confirms this superiority.

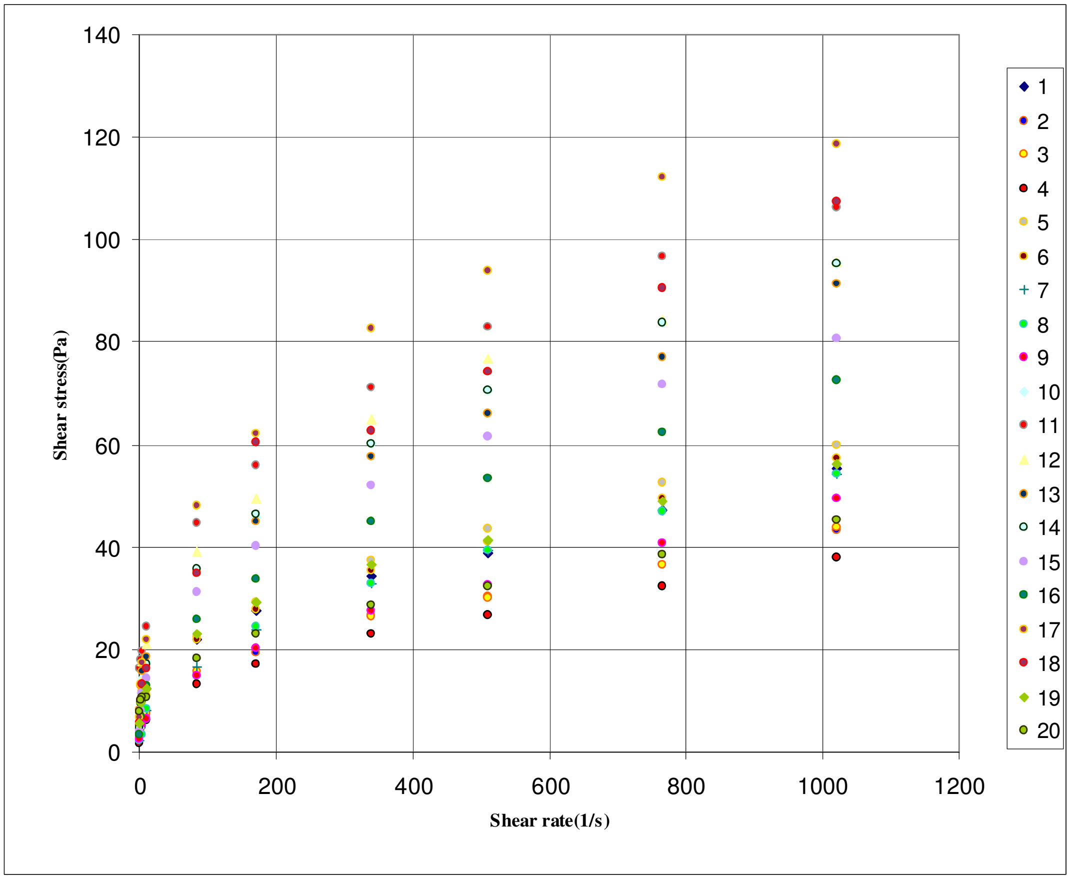

Figure 6.24: Rheograms of all samples

In three-parameter models, again samples 17 and 18 have very high values of RMS. Mostly Sisko models have the least RMS values according to column chart (Figure 6.27.). However sample number 11 shows very high RMS values for Sisko model. Figure 6.28 shows that Sisko is the best model to represent this gel system.

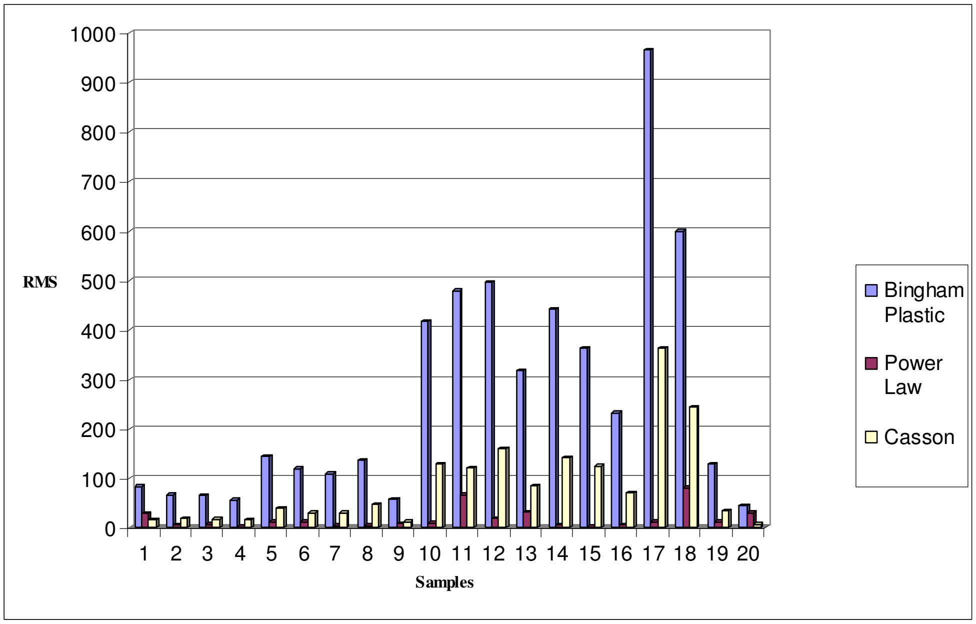

Figure 6.25: Residual mean squares of two-parameter models

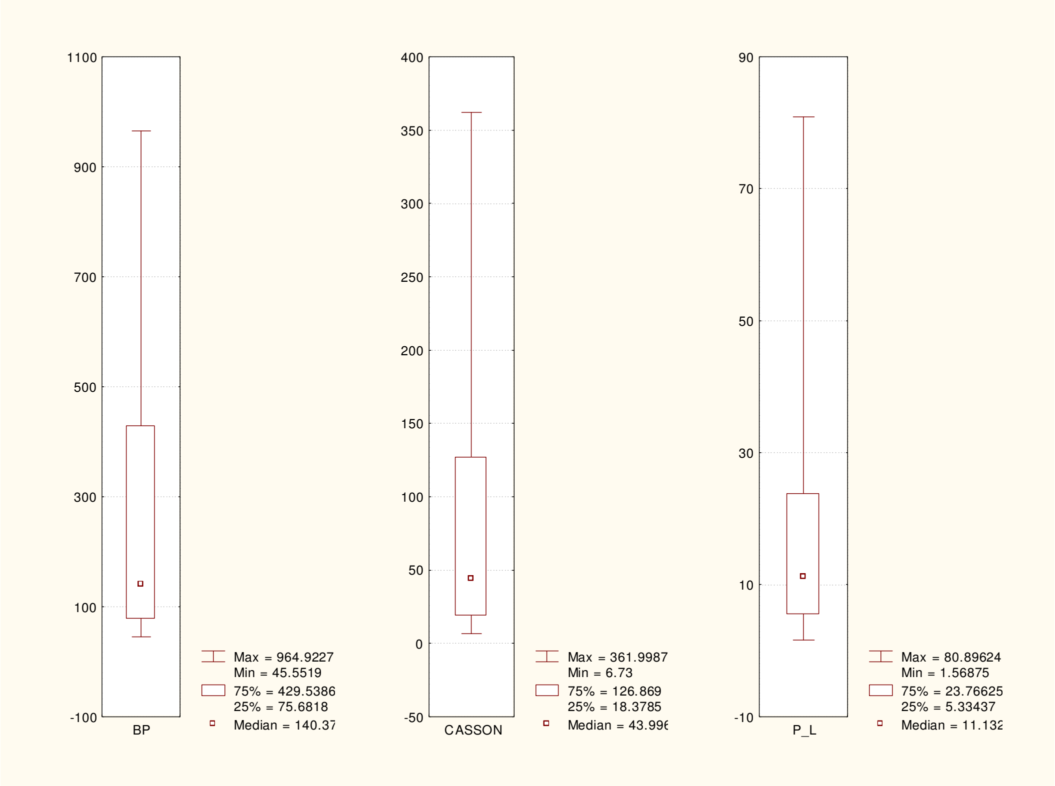

Figure 6.26: Box-whisker plot of two-parameter models (Bingham-Plastic, Casson, Power-Law)

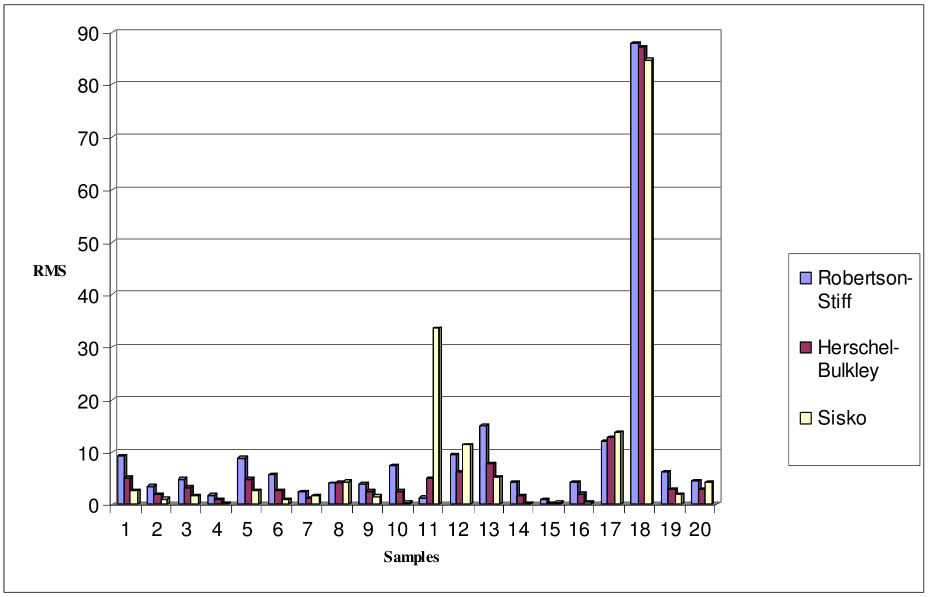

Figure 6.27: RMS values of three-parameter models

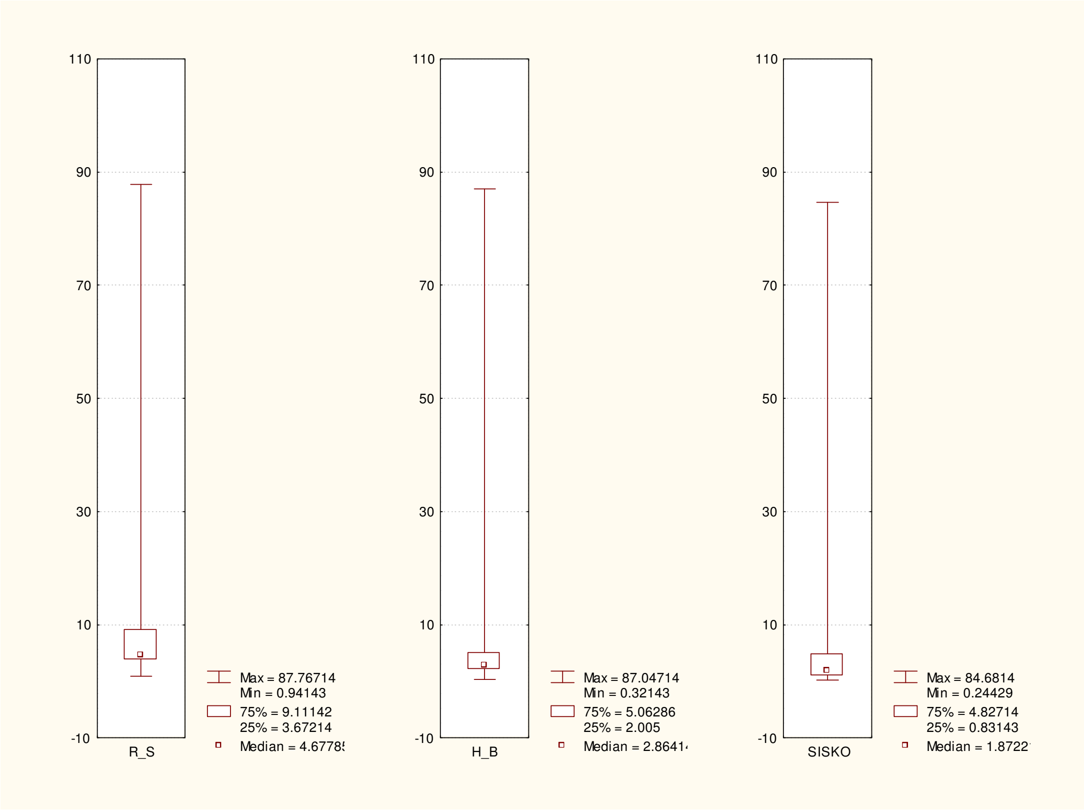

Figure 6.28: Box-Whisker plot of three-parameter models (Robertson-Stiff, Herschel-Bulkley, Sisko)

6.10. Modified Bingham-Plastic model

Direct estimation of rheological model parameters is more popular in petroleum industry. However this method usually does not give reasonable results. That is why a modified Bingham-Plastic model using just reading shear stress at 600 and 300 rpm was considered.

First yield point and plastic viscosity were obtained by direct calculation from 600/300 rpm combination. Then the parameters were obtained from regression analysis of all data points. By comparing these two values, some shift factors were suggested in order to minimize RMS.

Bingham-Plastic model is:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{6.14}$$

τ = Shear stress ($lb/100ft^2$)

τ_0 = yield stress ($lb/100ft^2$)

μ_p = Plastic viscosity ($lb.s/100ft^2$)

$\dot{\gamma}$ = Shear rate (1/s)

And the modified one is suggested as follows:

$$\tau = \alpha\tau_{0(600/300)} + \beta\mu_{p(600/300)} \dot{\gamma} \tag{6.15}$$

α =0.435

β =1.707

Table 6.3 shows Bingham-Plastic parameters obtained in three conditions: regression of all data, direct calculation from 600/300 combination, and modified model.

Table 6.3: Bingham-Plastic parameters (Total data points regression, direct calculation from 600/300 combination, modified model)

Sample	τ_0 Total	μ_p Total	τ_0 600/300	μ_p 600/300	τ_0 Modified	μ_p Modified
1	26.680	0.087	43.500	0.063	18.923	0.108
2	15.680	0.075	34.450	0.049	14.986	0.084
3	16.420	0.074	31.900	0.053	13.877	0.090
4	13.380	0.066	30.550	0.042	13.289	0.072
5	24.970	0.102	53.500	0.062	23.273	0.106
6	24.260	0.096	48.600	0.062	21.141	0.106
7	17.670	0.098	47.400	0.058	20.619	0.099
8	17.311	0.098	48.600	0.056	21.141	0.096
9	14.710	0.087	31.200	0.064	13.572	0.109
10	37.230	0.166	89.800	0.094	39.063	0.160
11	54.030	0.170	116.700	0.089	50.765	0.152
12	45.300	0.161	112.700	0.073	49.025	0.125
13	39.810	0.151	79.500	0.097	34.583	0.166
14	36.840	0.167	89.850	0.095	39.085	0.162
15	32.010	0.142	83.150	0.073	36.170	0.125
16	26.670	0.127	66.850	0.070	29.080	0.119
17	50.880	0.213	135.600	0.095	58.986	0.162
18	39.080	0.185	80.900	0.126	35.192	0.215
19	27.030	0.091	51.300	0.057	22.316	0.097
20	23.997	0.069	37.700	0.050	16.400	0.085

Figure 6.29 shows that RMS values obtained from modified model are close to the RMS values obtained from regression analysis for all the samples. Moreover RMS values for three conditions are shown in Box-Whisker plots for the 20 samples in Figure 6.30. It shows that the median of RMS values as a measure of accuracy of models has improved from 805.87 in direct estimation model to 156.83 in modified model. As a result, the simple modified model proposed can predict the rheological properties almost similar to what regression analysis of all data points can do. (Median of total regression= 144.06, median of modified model=156.83).Therefore the proposed model can be attractive for field application due to its simplicity.

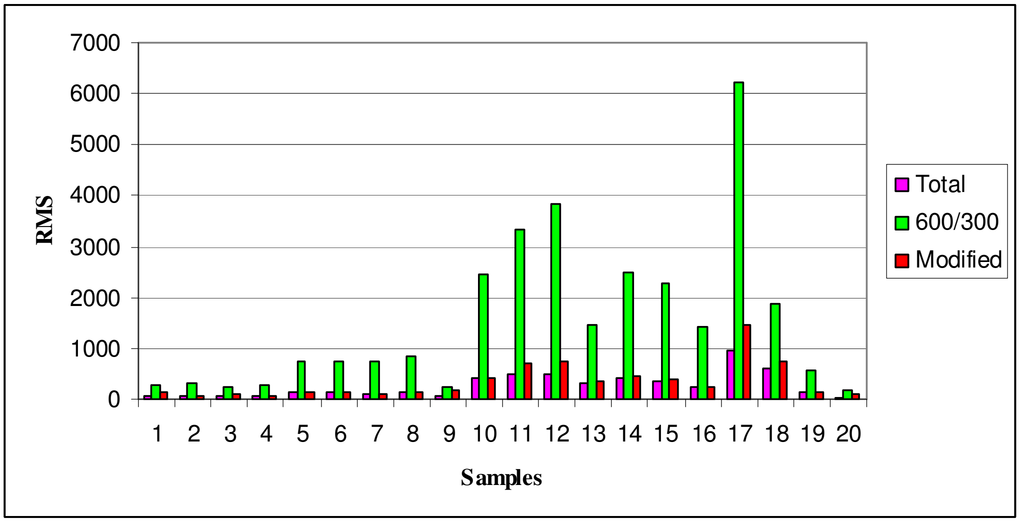

Figure 6.29: RSM values for Bingham-Plastic model (Total regression, direct calculation from 600/300 combination, and modified model)

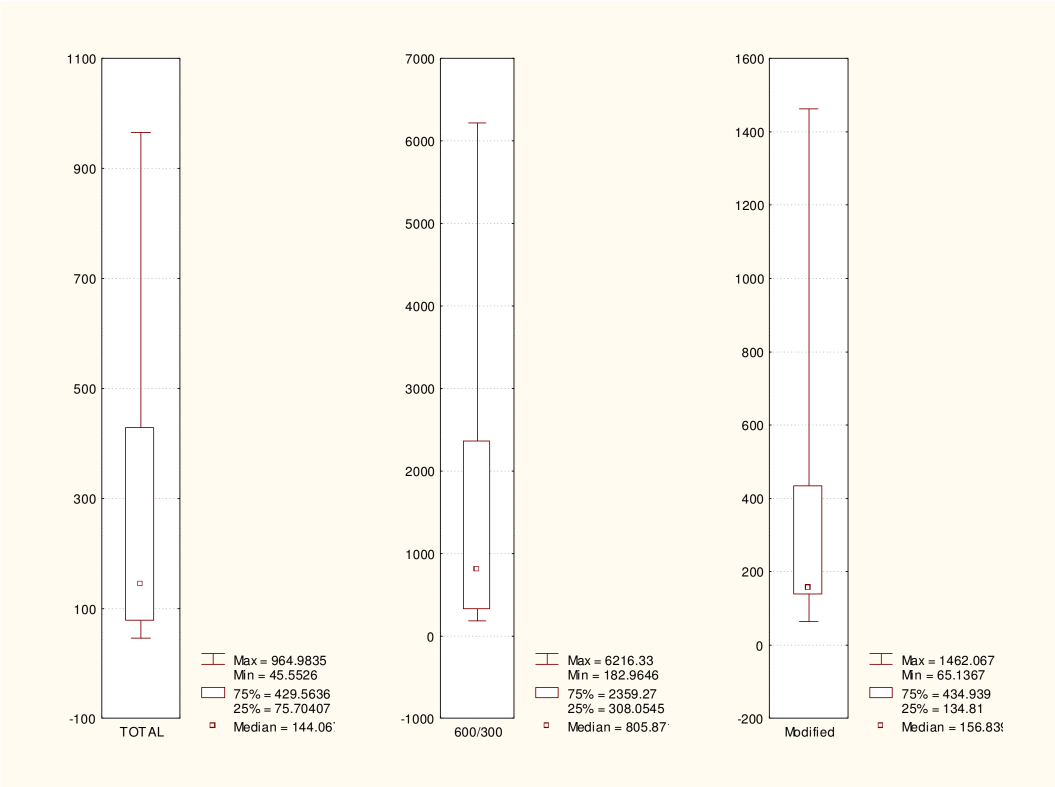

Figure 6.30: Box-Whisker plot of Bingham-Plastic model (Total regression, direct calculation from 600/300 combination, and modified model)

6.11. Modified Herschel-Bulkley model

Herschel-Bulkley is one of the best rheological models that can describe rheological behavior of drilling fluids. In the gel system that is used in this study Herschel-Bulkley also showed reasonable results. Since Herschel-Bulkley is not a two-parameter model, it is not possible to find its parameters directly. Moreover, regression analysis sometimes gives non-meaning negative values for yield stress. Therefore there are some methods to estimate yield stress. Then with a known yield stress, the other two parameters can be obtained by regression analysis.

Shear stress at very low shear rate, 0.1 rpm, was assumed as yield point which later was proved to be a good estimation of yield stress. It is called true yield stress (YP) and it is compared with four other methods of yield stress estimation:

1. Shear stress at 3 rpm (τ_3)
2. Shear stress at 6 rpm (τ_6)
3. Low Shear Yield Point (LSYP=$2\tau_3 - \tau_6$)
4. Yield point obtained from regression analysis of all data points

Yield points obtained from regression analysis were compared to what was measured at 0.1 rpm in Figure 6.31. There is a moderate correlation between these two parameters.

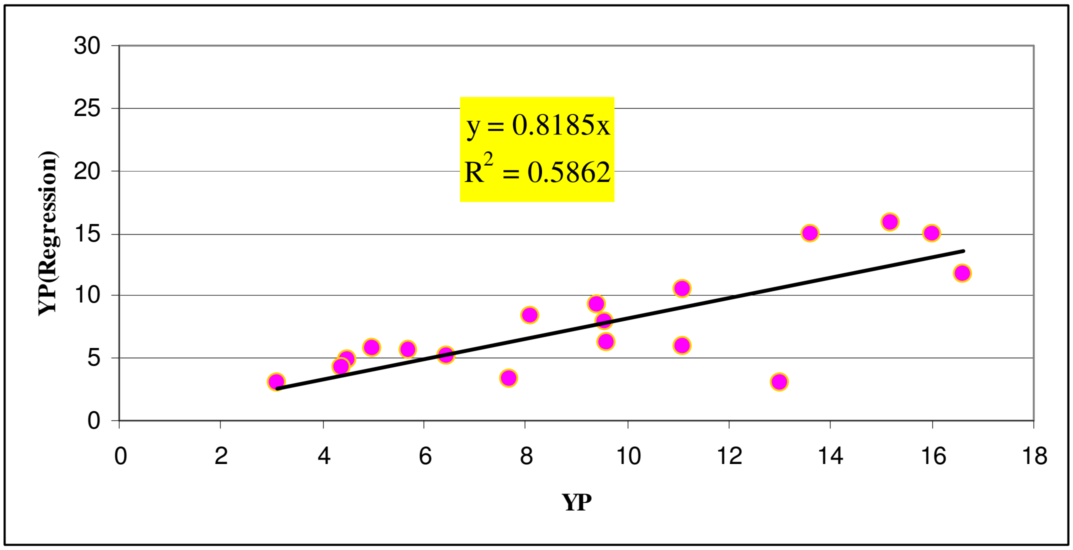

Figure 6.31: Yield point obtained from regression analysis correlation with true yield point

Figure 6.32 and Figure 6.33 show low correlation between shear stress at 3 and 6 rpm respectively with true yield point since the correlated line obtained from least square method shows almost two times of yield point for shear stress at 3 and 6 rpm. This situation is worse for 6 rpm; that is why it was omitted from further studies.

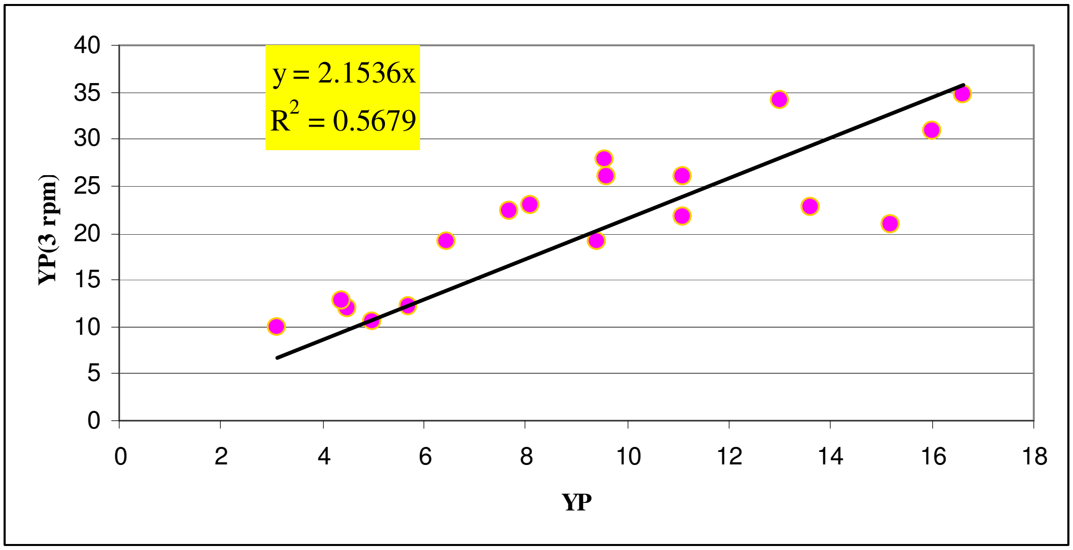

Figure 6.32: shear stress at 3 rpm correlation with true yield point

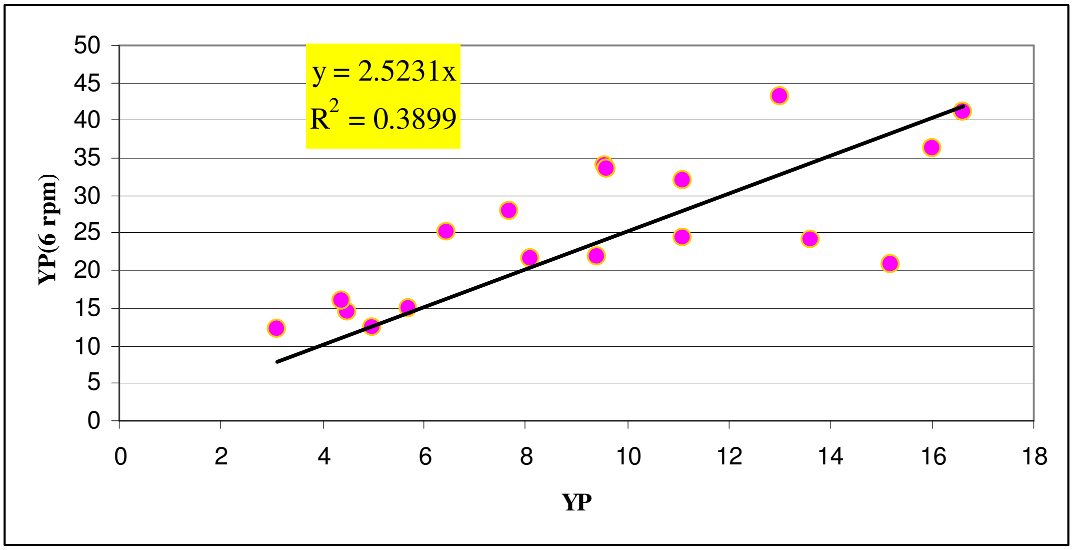

Figure 6.33: Shear stress at 6 rpm correlation with true yield stress

Low shear yield point is one of common methods of direct yield stress estimation but it did not exhibit reasonable results for this drilling fluids. Figure 6.34 shows the correlation between LSYP and the true yield point.

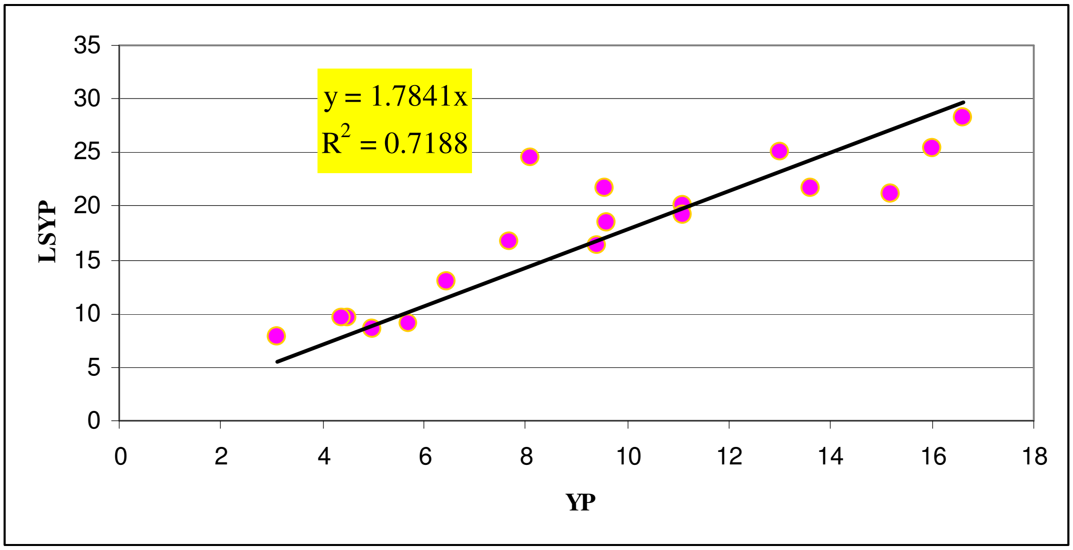

Figure 6.34: Low shear yield point correlation with true yield point

Many new models based on low shear rate data points combination were investigated for yield point determination. Then the results from those models were compared to true yield stress and residual values were calculated. Finally the following model could demonstrate the best behavior:

$$YP = \tau_3 - 0.5\tau_6 \tag{6.16}$$

Figure 6.35 shows the relation between the modified yield point and the true yield point.

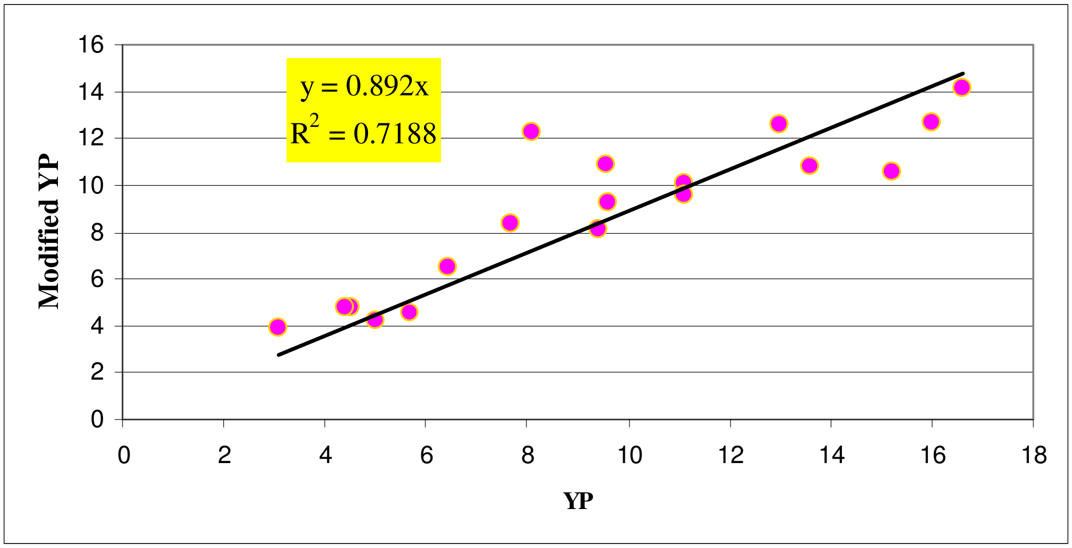

Figure 6.35: Modified yield point correlation with true yield point

Then yield points obtained from shear stress at 3 rpm, LSYP, and the proposed model, were substituted in the Herschel-Bulkley model. The other parameters were obtained by regression. Then residual sum of squares were calculated and were divided by (n-p), 8, to get RMS values.

RMS values of four cases are compared in the Figure 6.36. The modified yield point gives almost similar median of RMS value to what was obtained from regression analysis (3.251 for the proposed model in comparison to 2.39 for regression analysis). The good behavior of proposed model also confirms that assumption of shear stress at 0.1 shear rate to be a good criterion. Finally rheological model of this gel system can be predicted very well with direct estimation of yield point by the proposed model.

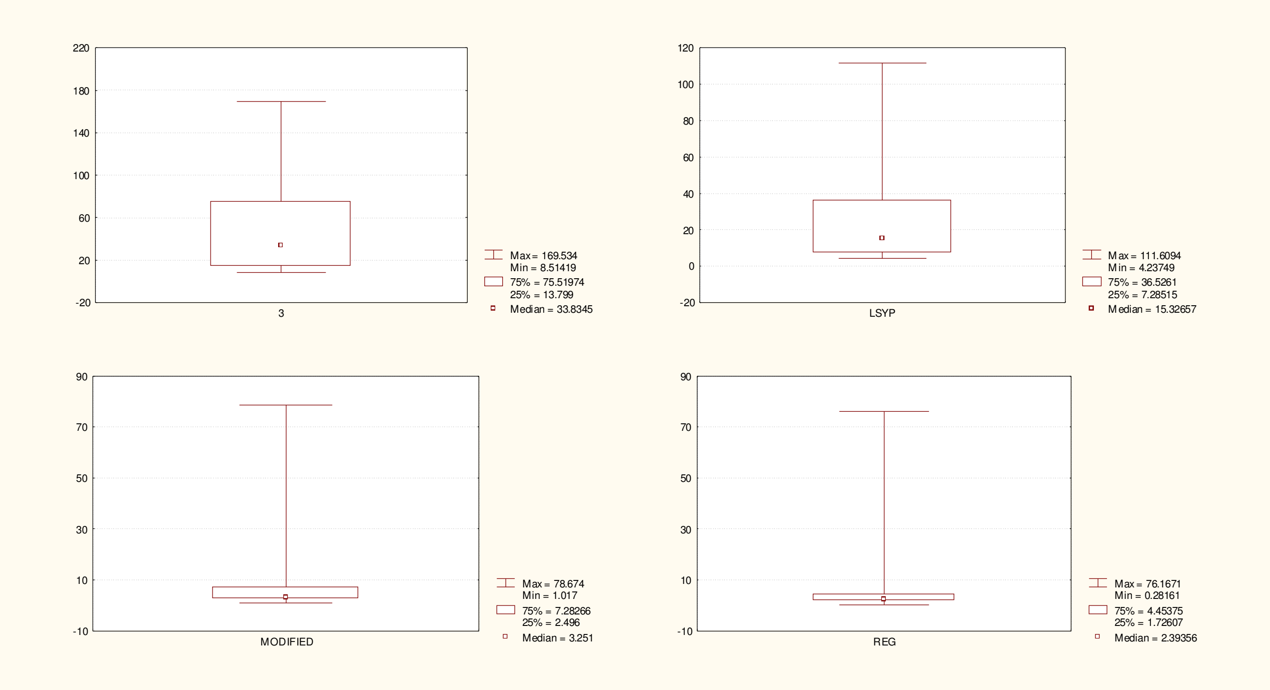

Figure 6.36: Box-Whisker illustration of RMS values for LSYP (yield point by 3rpm, modified model, yield point by LSYP, yield point by regression)

CHAPTER 7

CONCLUSIONS

In this thesis, use of a gel system for combating lost circulation was investigated. A system composed of xanthan, borax, accelerator, and retarder was prepared and steady shear viscometry method was employed to study the gel behavior. A main parameter, initial gelation time, besides three other parameters: final gelation time, initial viscosity and final viscosity were obtained at different concentrations of poly-cross, accelerator, retarder as well as temperature. With the knowledge of initial gelation time, the time allowed for pumping of gel system can be obtained. With a rough estimation of final gelation time, the time required for waiting on gel can be found. The gel system should be pumped in the first period of gelation, before initial gelation time, as a fluid; therefore initial viscosity helps to have a comparative knowledge on gel behavior in this period. Finally final gel viscosity is a comparative measure of gel quality. The following conclusions can be obtained from this study:

1. Poly-cross concentration contributes significantly to the system by increasing initial and final viscosity. Consequently final gel quality improves. Initial and final gelation times are insignificantly affected.

2. Accelerator shortens initial and final gelation times by manipulating pH, consequently release of more borate ions. Initial viscosity is not affected. Final viscosity is also not affected unless the amount of pH-controller is not enough for the amount of poly-cross. It also contributes to rate of crosslinking.

3. Retarder, magnesium chloride, decreases the initial viscosity and final viscosity. Therefore it is useful for high-polymer-concentration samples. It does not almost change initial gelation time but postpones the final gelation time. It reduces the rate of crosslinking significantly.

4. Increasing mixing time does not postpone the initiation of gelation. In other words it does not help to gain time since the summation of initial gelation time and mixing time is constant for a specific sample. Final gelation time is also decreased by increasing the mixing period. Initial and final viscosities are not affected.

5. Shear history of the conducted experiments at 3 rpm does not change initial gelation time or final one.

6. Decreasing temperature postpones initiation of gelation and final gelation time. The initial and final viscosities are affected insignificantly.

7. Good empirical models were obtained that can estimate initial gelation time, final gelation time, initial viscosity and final viscosity. Therefore lost circulation treatment job can be managed to optimize time and materials for a specific well.

8. Sisko model is the best representative of the rheological data of this gel system in comparison to other available models analyzed since it showed lowest median of RMS values.

9. Modified Bingham-Plastic model and yield point model were suggested for this gel system as they are simpler and almost the same accurate as regression and complicated models. Therefore they can be more suitable for field applications.

CHAPTER 8

RECOMMENDATIONS

The following recommendations for further study are suggested:

1. Acid solubility of this gel system can be studied. Then if the results are reasonable, the gel system can be applied for combating lost circulation in productive zones.

2. Effect of pressure on the gel system can be studied. Then the resistance of gel system against wellbore pressure can be thoroughly understood.

3. The mixing system employed on rig is different from mixing method in the laboratory in this thesis. Therefore it should be considered.

4. Viscoelastic properties can be obtained by oscillatory method. Then gelation time obtained from oscillatory method can be compared with the results of this study.

5. Using enzymes for breaking of gel when it is used for lost circulation treatment in productive zone can be investigated.

6. Experiments can be conducted on more popular drilling fluids to investigate modified Bingham-Plastic and yield point models.

7. More polymer/ crosslinker combinations can be studied to determine which one has better gel quality required for lost circulation treatment.

8. More investigation is needed for control over initial gelation time. For instance, crosslinker encapsulation can be considered.

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APPENDIX A

POLYMERS

Polymers are long molecular structures composed of one or more elementary units. Hundred of thousands or millions of such units can exist in a single polymer chain. These units are called monomers. When a polymer is made up from just one type of monomer, it is called homopolymer and it is called copolymer when two or more types of monomers make a polymer. The length of chains or number of monomers in a chain is expressed by the degree of polymerization. Molecular weight is also another way of characterizing polymers. However an average value is appointed to them since they can exhibit molecular weights in a range due to the length of chains. Polyacrylamides and polysaccharides are two most common groups of polymers in petroleum industry.

A1. Polyacrylamides

The monomer of polyacrylamides, acrylamide, is made up of carbon, hydrogen, oxygen, and nitrogen (C_3H_5NO). Partially hydrolyzed polyacrylamide (PHPA) is a copolymer in which some amide groups of polyacrylamide are substituted with carboxyl groups. The degree of hydrolysis is defined as ratio of carboxyl groups to the total number of carboxyl and amide groups. This copolymer can be generated from heating of homopolymer with dilute sodium hydroxide or by copolymerization of acrylamide (non-ionic) and acrylate (ionic).

A2. Polysaccharides

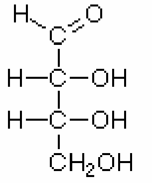
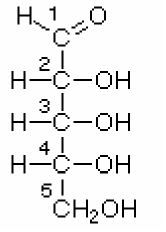
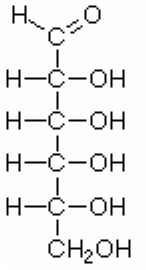
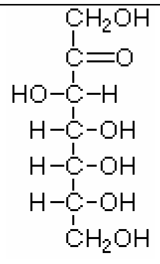
The polymer used in this study, xanthan, is a polysaccharide. That is why the description of this type of polymer is given in more detail below. Basic forms of carbohydrates are sugars or monosaccharides. Carbohydrates with two to ten sugars are defined as oligosaccharides and those with larger number of sugars are called polysaccharides. They are composed of carbon (C), hydrogen (H), and oxygen (O) in which there are two times hydrogen in structure than oxygen and carbon.

Monosaccharides or sugars are water soluble crystalline carbohydrates that are classified according to their number of carbons. Table B.1 gives the classification of sugars and table B.2 shows chemical structure of some of these sugars.

Table A.1: Classification of monosaccharides [www.scientificphysics.com]

Number of carbons	Name	Examples
4	Tetrose	Erythtrose, Threose
5	Pentose	Arabinose,Ribose, riboluse,Xylose, Lyxose
6	Hexose	Allose, Altrose, Fructose, Galactose, Glucose, Gulose, Idose, Mannose, Sorbose, Talose, Tagatose
7	Heptose	Sedoheptulose

Table A.2: Chemical structure of some linear sugars [www.scientificphysics.com]

D-Erythrose	D-Ribose	D-Allose	D- Sedoheptulose
			

Sugars exist in chain as well as in a ring form. Figure B.1 illustrates glucose in these two forms. However orientation of hydroxyl groups (-OH) can also make difference. In alpha glucose, hydroxyl group is in the opposite side of $-CH_2OH$ group, but in beta glucose it is on the same side.

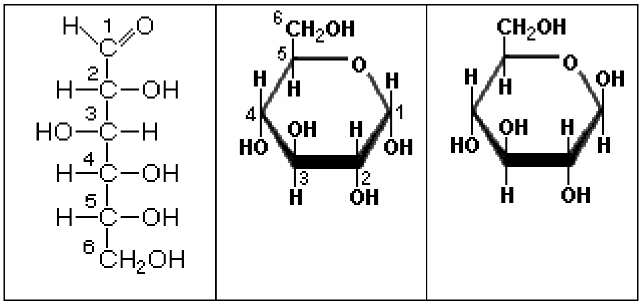


Figure A.1: D-Glucose, α-D-Glucose, β-D-Glucose [www.scientificphysics.com]

Starch is a very common material in drilling fluids. It is a mixture of 10-20% amylase and 80-90% amylopectin. Both of them are composed of α-D-Glucose. However amylase is a linear polysaccharide and amylopectin is a branched one.Figure B.2 shows these two components of starch.

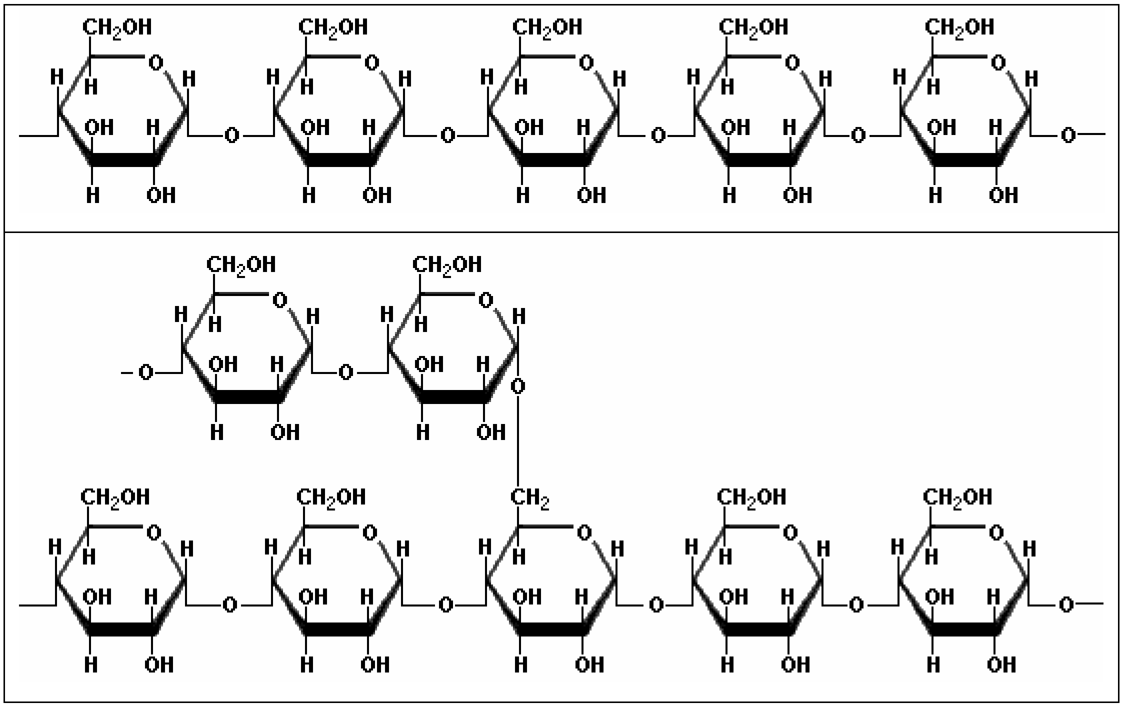


Figure A.2: Chemical structure of amylase (top) and amylopectin (bottom) [www.scientificphysics.com]

Cellulose is composed of β-D-Glucose with $-CH_2OH$ alternating in the top and bottom of structure. It is an unbranched polymer which exists in plant like cotton and which is almost totally cellulose. Figure B.3 depicts cellulose structure.

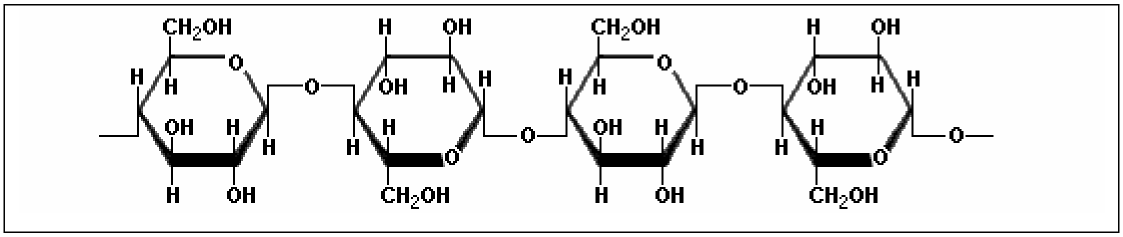


Figure A.3: Cellulose structure [www.scientificphysics.com]

Xanthan gum is a polysaccharide with a backbone of β-D-Glucose similar to cellulose. However every other glucose is linked to a trisaccharide composed of a mannose, glucuronic acid, and again another mannose. Figure B.4 shows xanthan gum structure. It is produced by a bacterium available at cruciferous vegetables like cabbage called Xanthomonas Campestris.

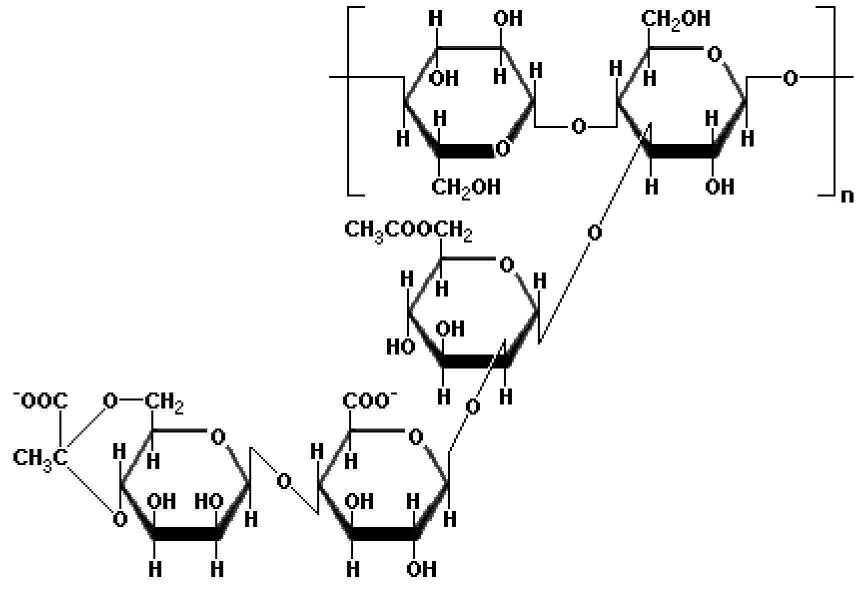


Figure A.4: Xanthan gum structure [www.scientificphysics.com]

Chromium, aluminum, and boron are among common crosslinkers in petroleum industry. Since heavy metal ions cause environmental concerns, there have been some efforts to replace them. Organic crosslinkers like polyethyleneimine are also suggested by some authors (Vossoughi, 2000).

Borax ($Na_2B_4O_7.10H_2O$) is the raw crosslinker used in this thesis. Borax at certain pH can release boric acid and borate ion. Boric acid also will be converted to borate ion. Therefore concentration of borate ion (B^-) is function of borax, pH and temperature.

$$B_4O_7^{2-} + 7H_2O \rightarrow 2B(OH)_3 + 2B(OH)_4^- \qquad \text{(B.1)}$$

$$B(OH)_3 + H_2O \xleftrightarrow{K_A} B(OH)_4^- + H^+ \qquad pk_A = 9 - 9.2 \qquad \text{(B.2)}$$

APPENDIX B

RHEOGRAMS

The unit of shear rate is rpm and the unit of shear stress is dial reading (DR).

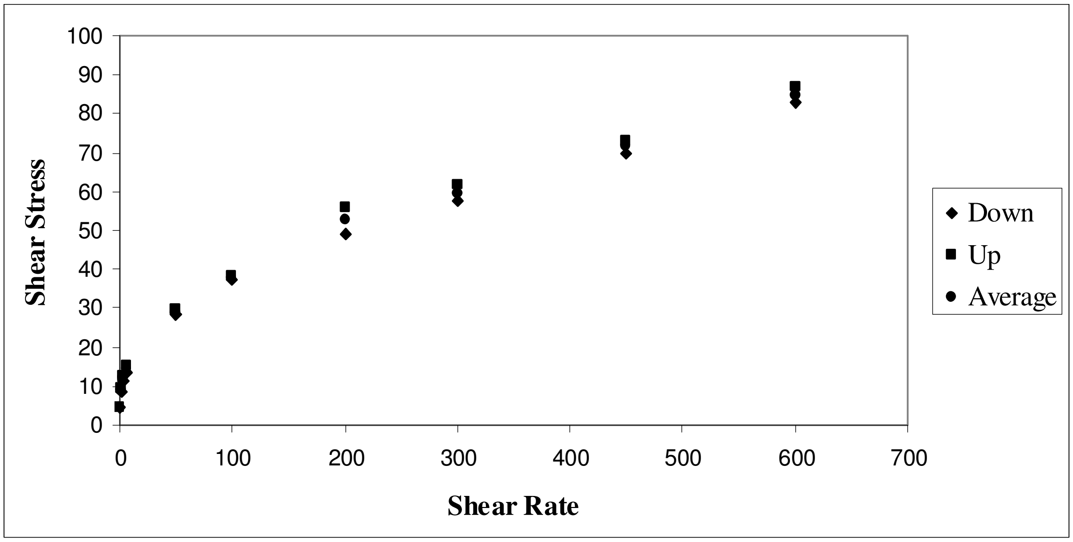


Figure B.1: Sample No. 2

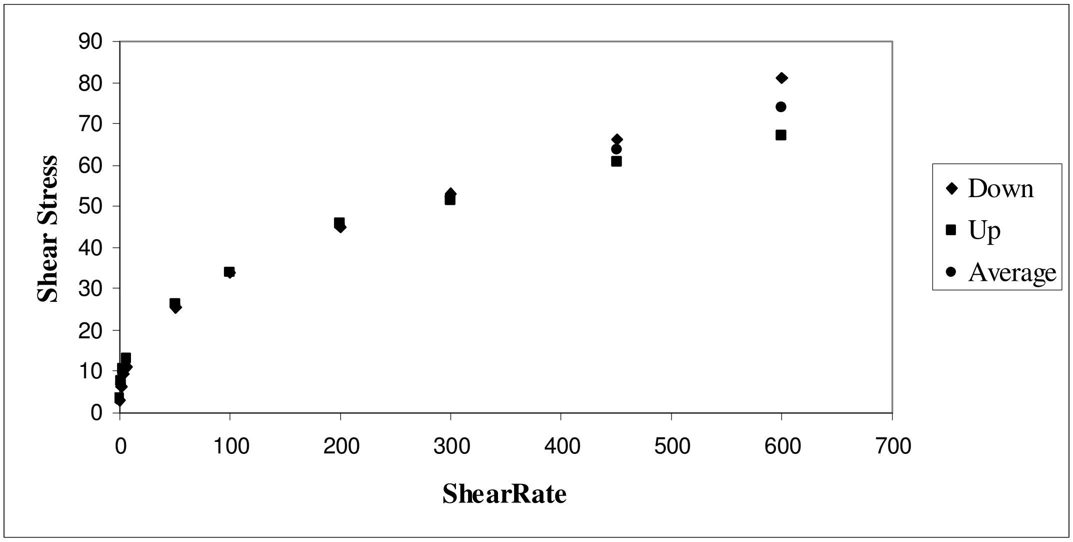


Figure B.2: Sample No.4

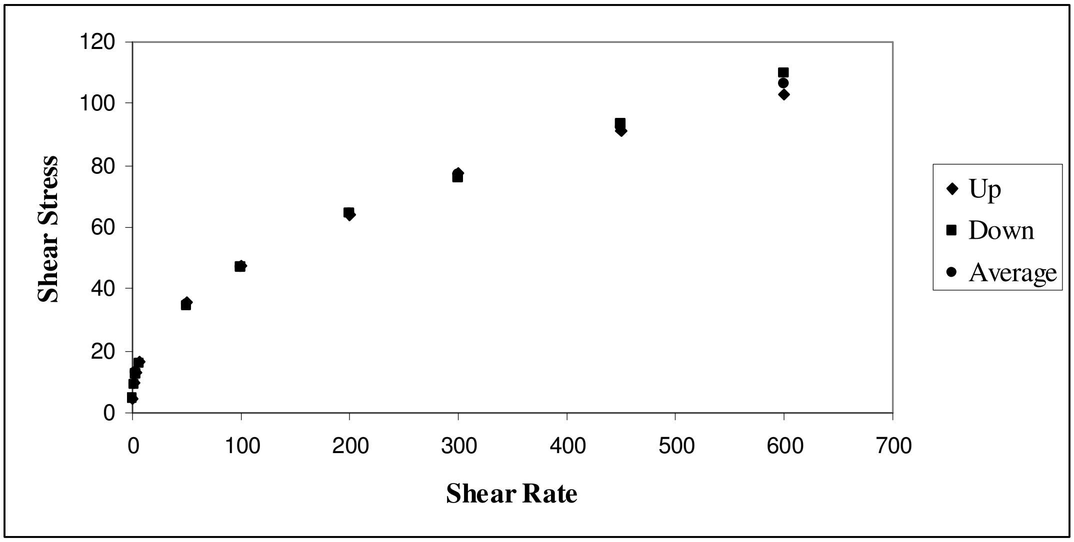


Figure B.3: Sample No.7

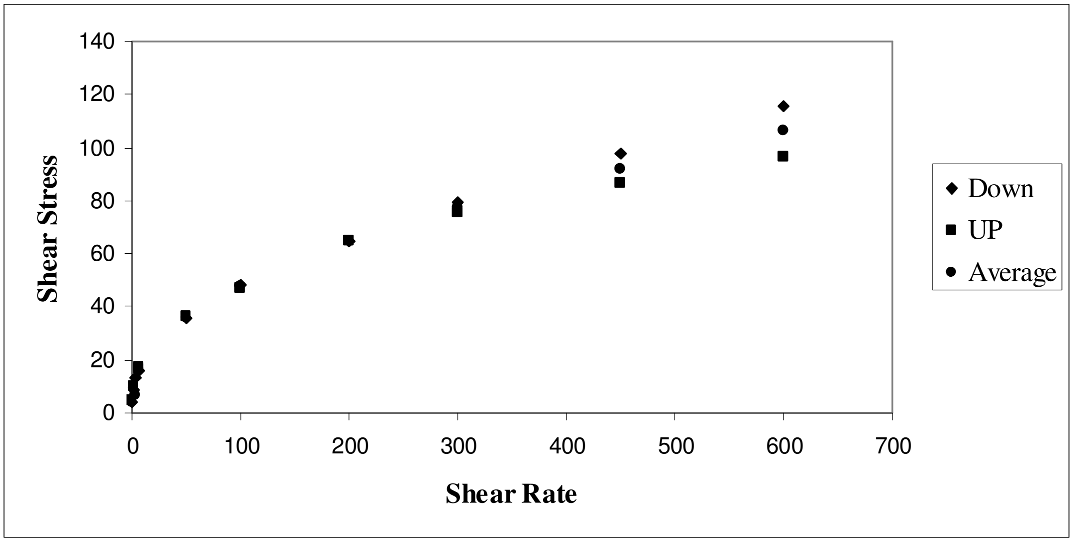


Figure B.4: Sample No.8

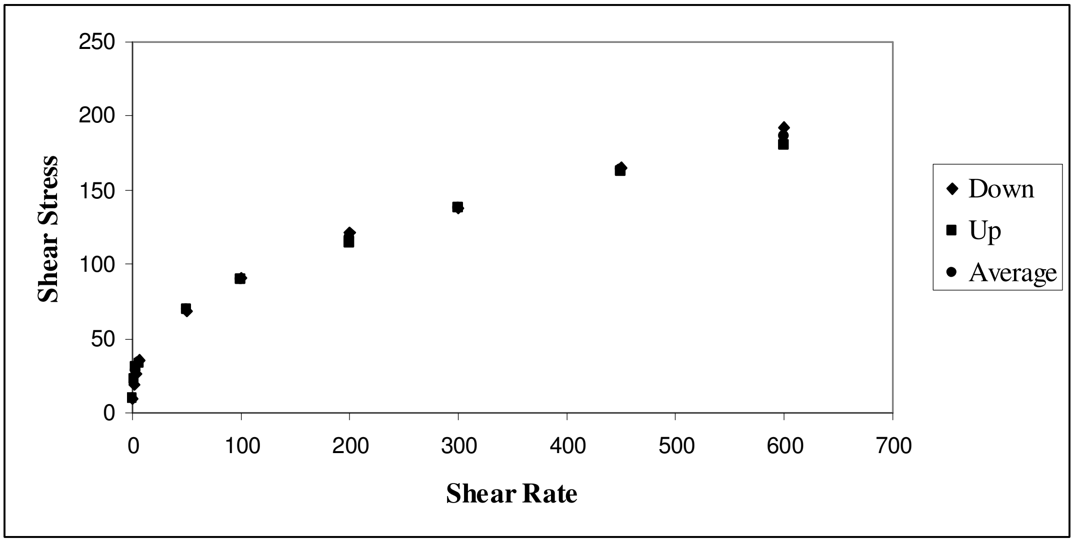


Figure B.5: Sample No.12

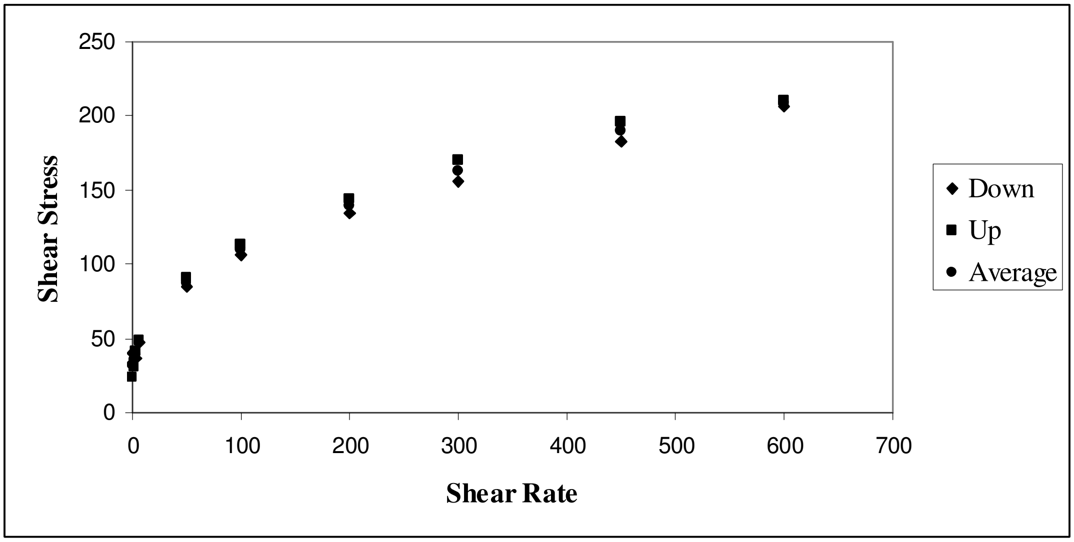


Figure B.6: Sample No.13

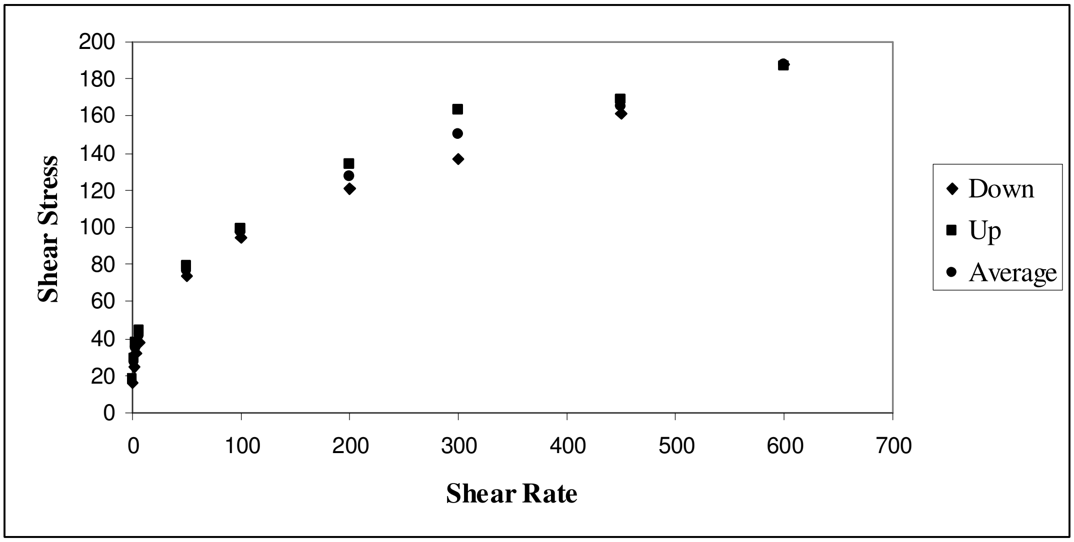


Figure B.7: Sample No.14

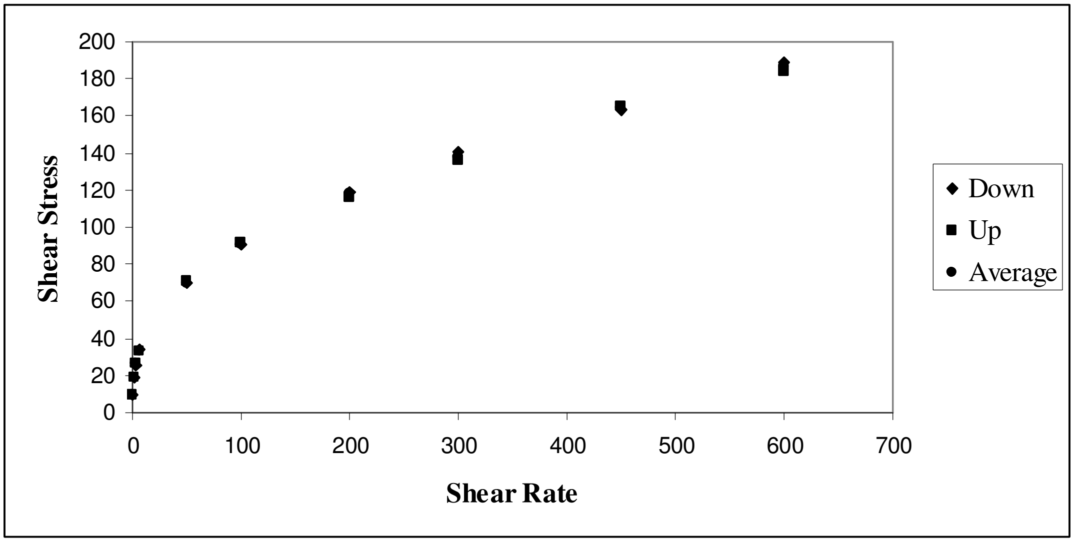


Figure B.8: Sample No.16

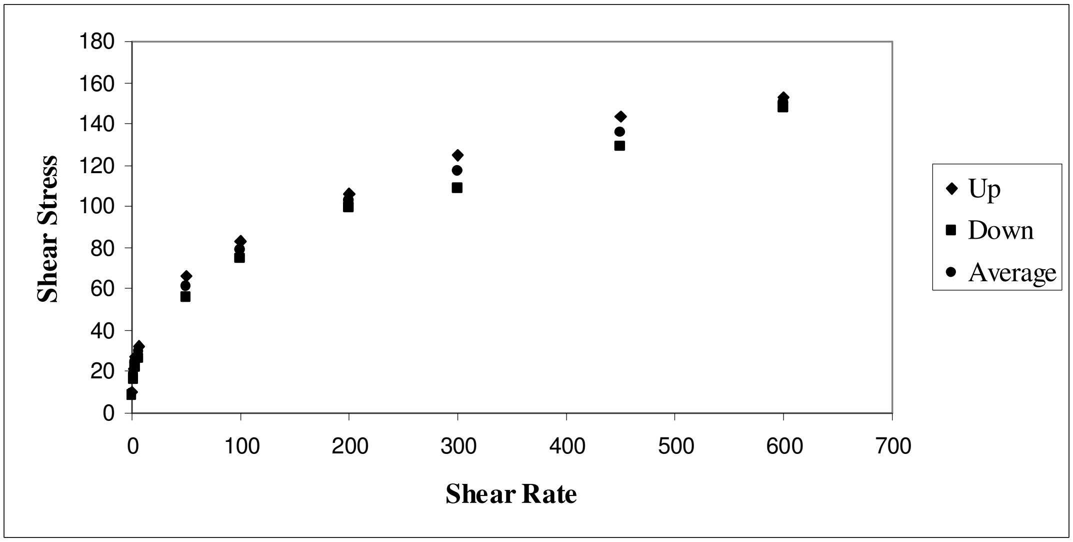


Figure B.9: Sample No.17

APPENDIX C

OTHER APPLICATIONS OF GELS IN PETROLEUM INDUSRY

Although application of gels for lost circulation treatment is new and there are quite few papers in this subject, gels have been widely used in petroleum industry for three other purposes: water shut-off, profile modification, and hydraulic fracturing. The successful history of these operations and some similarities between them and lost circulation problem have led the petroleum industry to the opening of a new solution to the problem of lost circulation during drilling. The understanding of these applications can help to develop the application for lost circulation treatment easier as well as to distinguish the differences of this study from other studies. For instance, most of studies on gel applications in hydraulic fracturing have used xanthan/borate system. Therefore they should be reviewed to understand the gel system of this thesis, although the concentration range in hydraulic fracturing is very low and physical gel structure is not necessary. In addition, the use of gels for water shut-off and profile modification has similar purpose as the lost circulation treatment has: blocking flow from or to a zone. However the initial gelation time should be faster for the lost circulation treatment in comparison to profile modification or water shut-off. In general, they are all studies on gel properties and have been useful in conducting this thesis or giving ideas for recommendations for further studies. For instance, breaking of a gel after hydraulic fracturing is well established. It can be also useful in recovery of gels used for the lost circulation treatment in productive zones.

C1. Application of gels for water shut-off

For producers, oil production is desirable. However some amount of water is associated with this oil. The rising of water production leads to oil production decline as well as a considerable increase in cost of production due to treating and disposal of the water. Since water has higher density than oil and gas, it increases the hydrostatic pressure inside wellbore. Consequently oil production rate decreases or cease at the end. Gels can be used to reduce water production.

Kakadjian et al. (1999) studied gel strength of three gels systems, two polyacrylamide/ chrome (III) and one polyacrylamide/ organic crosslinker using the dynamic rheology method. Sodium acetate was proved to make gel system weaker and more viscous. Moreover, the elastic and loss modulus were the functions of gelling time and final consistency as well as frequency.

Wawro et al. (2000) studied the use of gel alternating gas (GAG) for reducing water production from a naturally fractured gas well. Since the injection of gel in to gas wells displaces the gas in near wellbore zone to residual amount, alternative gas injection can recover the gas permeability reduction while water permeability falls down (Dovan and Hutchins, 1994). In this case, water gas ratio (WGR) decreased 75% after treatment while gas rate increased 20 to 70%. Moreover the cost of treatment operation was compensated by 4 months extra gas production.

Broseta et al. (2000) studied the rheological behavior of low-molecular-weight polyacrylamide crosslinked with chromium (III) acetate for water shut-off purposes by steady viscometry method. The gel system was observed to be a strong function of temperature with activation energy of 115 kJ/mol. Moreover it was a weak function of crosslinker in comparison to polymer concentration. On the other hand, it was independent of shear rate. In addition polymers with lower hydrolysis degree had longer gelation.

Awang and Seng(2003) intended to make a link between bottle testing results and permeability reduction in porous media. It is concluded that for a specific polymer and crosslinker, Sydansk codes can be used to estimate permeability reduction.

Sydansk et al. (2004) compared partially formed(less than 8-hr-old) chromium(III)-carboxylate/acrylamide-polymer with fully formed gel(higher than 15-hr-old). The former had less effective viscosity during its placement in 1-mm-wide fracture than fully formed with the same composition.

Al-Muntasheri et al. (2004) stated the four mechanisms for water production:

1. Water coning: in this mechanism, the water is produced from the aquifer beneath the oil reservoir since the rate of oil production is very high.
2. There are some fractures that connect the aquifer to reservoir.
3. There is an aquifer above the reservoir and a leakage in casing results in water production.
4. There is a breakthrough of water injected for pressure maintenance or enhanced oil recovery.

Llamedo et al. (2005) explained the effect of salinity of formation water on performance of a gel system for water shut-off. Residual resistance factor (RRF) was lower when the water used for preparation of gel and formation water had similar salinity. On the other hand RRF increased when formation water had higher salinity.

Eoff et al. (2006) reported eight-year successful application of acrylamide/t-butyl acrylate copolymer (PAtBA) crosslinked with polyethyleneimine (PEI) for water shut-off which included over 200 jobs reviews.

Al-Muntasheri et al. (2007) demonstrated the use of acrylamide and t-butyl acrylate crosslinked with polyethyleneimine for water shut-off treatment. Polymer concentration was 3-7 wt.% and crosslinker concentration is in range of 0.3 to 1.2%. The properties of the gel were studied by dynamic mechanical analysis (DMA).

Al-Muntasheri (2007) demonstrated a comparative study on crosslinking of polyacrylamide teributyl acrylate (PAtBA) copolymer and polyacrylamide (PAM) homopolymer with polyethyleneimine (PEI) by steady shear viscometry. Gas chromatography (GC) showed isobutene release when PAtBA reacts with PEI in the temperature range of 60-130°C. Sodium chloride increased gelation time of both systems and lower initial pH postponed gelation time of PAM with PEI.

C2. Application of gels for profile modification

Oil reservoirs have mostly a natural driving force to produce oil in the beginning of reservoir age. However the depletion of oil rate begins and makes oil production uneconomical while a major part of oil is still remained in the reservoir. Water injection is a method aimed at maintaining the reservoir pressure. In this method, water is injected to a well nearby in order to compensate the pressure drop due to oil production. Enhanced oil recovery (EOR) methods are the variety of methods used to push the oil toward wellbore while they were not able to be moved by natural driving force. In these methods, a fluid such as a gas or water in combination with some chemicals are injected to an injection well nearby to push the oil toward production well. Two kinds of sweep efficiency are effective in EOR: volumetric sweep efficiency and microscopic sweep efficiency. In the former one, the portion of reservoir that is affected by injected fluid is evaluated. In the later one, the amount of oil moved due to interaction with injected fluid is taken in to account.

Volumetric sweep efficiency is the subject of profile modification by gels. Since reservoirs are heterogeneous, the injected fluid looks for the most permeable parts and goes through those layers. Consequently some parts remain unswept by injected fluid. Mostly the permeability variation is in vertical direction since the sedimentary layers could occur in this way. Therefore, some reservoirs are multilayer reservoirs with permeability variation in vertical axes or in some cases mostly in fractured reservoirs; there are some fractures that connect the injection well to production well. As a result, a breakthrough can occur when large part of oil is still unswept.

Gels are a solution to this problem. Cross-linked polymeric materials are injected to block the high permeable zones. Consequently, the fluids injected later will be diverted to low permeability zones. Application of crosslinked polymer gels for profile modification started in early 1980s (Avery et al., 1986) and Vossoughi(1999) gave a comprehensive review of profile modification by in situ gelation.

Avery et al. (1986) explained the use of xanthan gum/ trivalent chrome gel system for profile modification. They presented successful field result (75-80%) and the advantages of xanthan/Cr (III) gel system.

Buller et al. (1990) developed a gel system called KUSP1 in which a B-1,3-polyglucan as a biopolymer is produced from fermentation of a bacterial called Alcaligenes Faecalis and certain species of Agrobacterium. The gelation starts when pH reduced to 10.8 or lower. Therefore, the gel system can be used in porous media by using acid (Vosoughi et al. 1991), by CO_2 (Raje et al. 1999), or by hydrolysis of an ester (Raje et al. 1999).

Eggert et al. (1992) conducted experiments on sandpack in order to investigate the persistence of permeability reduction by xanthan/Cr (III) gel system. Samples were prepared with 2,000 ppm xanthan concentration and 25 to 200 ppm Cr (III). The gel system was injected to the sandpack and they waited up to 4 months to set. The sandpacks were flushed by brine at a constant pressure drop of 13.3 psi/ft. Bulk-gel syneresis was not a right detector of the gel behavior in porous media since the best permeability reductions were obtained with gels that exhibited 35 to 60% shrinkage of volume due to syneresis.

Hejri et al. (1993) employed xanthan/ chromium (III) gel system for permeability reduction. At frontal velocity of 3 to 35 ft/D, the plugging of porous media was detected but at high frontal velocity of 83 to 118 ft/D which is typical for wellbore region, high flow resistance was not detected.

Hutchins et al. (1996) applied polyacrylamide with a combination of hydroquinone (HQ) and hexamethylenetetramine (HMTA) as crosslinker and demonstrated that it was stable at 149 °C for 12 months and at 176.7 °C for 5 months. By this system, oil production raised to 660 bopd from 340 bopd before treatment and water production fall to 1490 bwpd from 3760 before treatment.

Moradi-Araghi (1999) stated that a typical gel system for profile modification has 0.7-1.0% polymer concentration and 500-2000 ppm crosslinker concentration. He also reviewed and recommended some gel systems useful for high temperature reservoirs since gel systems with metallic cross-linker (Cr, Al, Zr) have low thermal stability.

Vossoughi (1999) elucidated two types of gel placement: 1. near wellbore 2. in-depth. If there is a cross-flow between layers, in depth placement or injection of gel to a large radius should be performed. Gao et al. (1990) demonstrated the inadequate gel sweep efficiency occurred due to near wellbore gelation of cross-flowing wells since the injected flow diverts to high permeability zone again in this case. Sydansk et al. (1987) reported successful field testing of in-depth profile modification by gels and Rajeet al. (1995, 1999) reported 80% permeability reduction to brine and CO_2 for Berea sandstone cores.

Topguder (1999) compared profile modification by a weak gel with in-depth penetration and a strong gel with wellbore nearby penetration for CO_2 injection at Bati Raman heavy oilfield. The strong gel could resist 2000 psi in core flooding experiment without any breakthrough. The weak gel exhibited a breakthrough; however it could reduce permeability significantly.

Asghari et al. (2004) investigated in-depth gel profile modification for carbon dioxide flooding in carbonate reservoirs. AlcoFlood 935-Cr (III) gel system reduced the brine permeability from 2.43 Darcy to 21.9 md. Moreover the residual resistance factors were in the range of a few hundreds to a few thousands. The thinning effect of sodium lactate on the gel system was also confirmed.

Nguyen et al. (2004) studied the effect of composition of polyacrylamide/Cr (III) acetate on disproportionate permeability reduction (DPR) which is the measure of permeability reduction to water in comparison to oil. The effect of composition on dehydration of gel system was also studied. DPR was a strong function of composition and pressure gradient while gel dehydration was affected very weakly.

Wang et al. (2005) reported the successful application of compound ion gel for the profile modification in highly heterogeneous reservoirs of Daqing oilfield.

C3. Application of gels in hydraulic fracturing operation

Hydraulic fracturing is a stimulation technique for enhancing the production of oil/gas wells. A fracturing fluid is injected to wellbore which cause the reservoir to break and a solid agent, proppant, is used to hold the fracture open. Hydraulic fracturing creates a conductive path in reservoir which gives more area available for oil/gas toward well. A fracturing fluid should be designed in a way to facilitate the fracture creation and to increase proppant carrying capacity while the damage to the near fracture zone should be minimized. There are varieties of fracturing fluids in industry such as: water-based, oil-based, alcohol-based, foam-based, and emulsion based. Cross-linked polymer gels are one of the oldest fracturing fluids. Crosslinking initiation time is vital to have enough fracture penetration. Moreover, the cross-linked gels should be broken by a chemical agent in order to be back produced to surface.

Kruijf et al. (1993) elucidated the chemistry of guar or hydroxypropyl guar (HPG) crosslinked with borate for hydraulic fracturing application. The viscosity was dependent on borate ion equilibrium which was a function of pH while pH was a function of temperature.

Kenneth et al. (1997) reported unsuccessful application of low concentration gel systems for hydraulic fracturing in the past due to inability to control pH. However the proposed pH buffer technology could solve this problem even at temperatures up to 210 °F. Moreover due to low polymer concentration, the clean up of fractures was better than that of conventional systems and 10 to 25% higher conductivity was achieved based on laboratory conductivity experiments. Moreover duration of clean up reduced to half of that for conventional ones.

Harris et al. (1998) studied the rheological properties of low concentration borate gel, 15 to 25 lbm/1000 gal, instead of common 40 and 50 lbm/1000 gal gels. A turbulent flow-loop viscometer was used to simulate the fracturing fluid condition in surface equipments as well as in tubing. Then the fluid is heated under laminar flow in order to simulate the fluid condition in fracture. An appropriate proppant transport was observed in a transparent slot model. The gel system exhibited shear degradation resistance while it was transmitted in tubing.

Harris and Walters (2000) stated that lower polymer concentration in hydraulic fracturing jobs causes less residues in fractures. Consequently the damage decreases. As a result a low loading gel, 15-25 lbm/Mgal, was optimized as a function of preconditioning shear rate, temperature, pH, ionic strength, gel stabilizer, gel breaker, surfactant, and proppant type in order to have appropriate properties for a certain well.

Weaver et al. (2003) explained the gel breakers were used to lower the viscosity of fracturing fluids after the proppant placement and consequently in order to allow the reservoir pressure to force the fracturing fluid to go out of fracture. For this reason, a reverse cross-linking materials or an enzyme can be used.

Although less polymer concentration can place less polymer in fractures, it may also decrease viscosity to a level that is not suitable for proppant transportation. Therefore the use of carboxymethyl guar (CMG) instead of common carboxymethyl hydrapropal guar (CMHPG) was suggested since CMG can give the same viscosity with half concentration. Parks (2003) addressed the application of this gel system to the Mid-Continent region. By comparing the results of hydraulic fracturing using CMG with the offset well which used CMHPG, more production was observed with the later one.