NTNU
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A Comparative Analysis of Rheological Characteristics of Polymer Solutions Exposed to Temperature and Stress Over Time

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Preface

This Master thesis titled *"A Comparative Analysis of Rheological Characteristics of Polymer Solutions Exposed to Temperature and Stress Over Time"* is the final step towards a Master of Science degree in Petroleum Engineering at the Norwegian University of Science and Technology, NTNU.

The study has been carried out at the Department of Geoscience and Petroleum at NTNU in collaboration with Statoil Research Center Rotvoll. Supervisor for the project is Professor John-Morten Godhavn and co-supervisor Dr. Aminul Islam.

I must thank Professor John-Morten Godhavn and Dr. Aminul Islam for giving me the opportunity, planning and guidance throughout the project. Also I want to thank Noralf Vedvik for providing the necessary equipment for the experiments, and Statoil Research Center Rotvoll for acquiring chemicals for the project.

A special thank you to my family for all the support towards graduating.

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Jostein Dale Arnesen

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II

Abstract

The purpose of the thesis was to analyze how time, shear stress, and heat influence a polymer solutions rheology and what impact added salt can have. The basis for comparison is done in another thesis with extensive testing on how polymers degrade in time. The experimental part of the thesis was time consuming, and most of the time has been spent in the laboratory mixing samples and measuring each sample with a 24-hour interval. Acquiring comparable results to previous results has been challenging with a somewhat simple mixing set up since polymers are highly reactive to temperature and shear stress, especially the polymer xanthan gum.

A series of experiments with thixotropic fluids composed of polymers and salt, with various temperatures and in circulation were carried out to examine how it influenced the current polymers decompositioning. The results indicated that salt would increase the time a polymer, in relatively high concentrations, would maintain its initial rheological characteristics. Exposing a polymer solution to shear stress has revealed that the polymer undergoes viscoelastic creep where the polymer fails under stress and decreases in viscosity rapidly the first 24 hours, 2 cP in 2%PAC and 10 cP in 4%PAC, before flattening out. The rapid early decrease enhanced when the temperature was increased from 25℃ to 50℃ in both a 2%PAC solution and a 4%PAC solution with respectively 4 cP and 17 cP (plastic viscosity). The polymer xanthan gum appears to be more reactive to small changes in temperature and shear stress when dissolved in water than polyanionic cellulose.

Samandrag

Hensikta med denne oppgåva var å analysere korleis tid, skjærkrefter, og varme påverka rheologien til polymer, polyanionisk cellulose og xanthan gum, og korleis salt kan ha ein påverknad. Grunnlaget for å kunna samanlikne resultat er lagt i tidlegare oppgåver med omfattande testing av korleis polymerar degraderast over tid. Den eksperimentelle delen av denne oppgåva har vore tidkrevjande, og mesteparten av tida er brukt på laboratoriet ved miksing og måling av kvar prøve med eit 24 timars intervall. Å oppnå samanliknbare resultat har vore ei utfordring med ein noko enkel metode for miksing av prøver då polymer er særs lettpåverkeleg både temperatur og skjærkrefter, spesielt polymeret xanthan gum.

Ei rekke med eksperiment med thixotropiske fluid komponert av polymer og salt, med ulik temperatur og sirkulasjon, har vore utført for å undersøka korleis det påverkar dekomponering av den aktuelle polymeren. Resultata indikerer at salt forlenger tida eit polymer, i relativt høg konsentrasjon, ivaretar de originale rheologiske eigenskapane før de avtar. Når polymer vart utsatt for skjærkrefter så er det funne at i de fyrste 24 timane mistar væska viskositet i ei høg rate, 2 cP for 2%PAC og 10 cP i 4%PAC. Etter 24 tima byrjar degraderinga å avta og vert meir stabil. Når temperaturen vart auka frå 25℃ til 50℃ vart denne effekten tydeligare i både 2%PAC og 4%PAC løysningar og den tidlege hurtige degraderinga vart auka med henholdsvis 4 cP og 17 cP (plastisk viskositet). Polymeret xanthan gum verkar å væra særdeles lettpåverkeleg av små endringar i både temperatur og skjærkrefter når løyst i vatn samanlikna med polyanionisk cellulose.

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Nomenclature

Symbol

ft	Feet
cP	Centi Poise
lb	Pound
Pa	Pascal
ε	Creep Stress
t	Time

Abbreviations

CMC	Carboxmethyl cellulose
JDA	Jostein Dale Arnesen
NaCl	Sodium Chloride
NTNU	Norwegian University of Science and Technology
OJR	Ole Julius Rye
PAC	Polyanionic Cellulose
pH	Potential of Hydrogen
PHS	Priyad Harishini Saptharishi
PV	Plastic Viscosity
RPM	Revolutions Per Minute
YP	Yield Point
XG	Xanthan Gum

X

1 Introduction

This chapter involves the background for this project, why this study has been carried out, what are we likely to get from it, and the experimental procedures.

1.1 Drilling Fluids

Drilling fluid is first and foremost the primary well barrier, ensuring the integrity of a well. The functions of a drilling fluid are many and needs to fulfill numerous requirements to be efficient. The drilling fluid has exert a hydrostatic pressure that is within the mud window, meaning it has to withstand pore pressure, prohibiting formation fluids to enter the well at the same time as not exceeding the fracture pressure of subsurface formation and have a high enough mud weight to avoid well collapse. The drilling fluid also has to clean the wellbore, cool the drill bit, and suspend and transport cuttings out of the well. To be able to do all of this the drilling fluid rheology has to be compatible. Rheology is the study of the flow of primarily a liquid. A fluids ability to flow is characterized by its viscosity, and viscosity is affected by stress and temperature.

A drilling fluid has to be reliable and consistent to maintain the integrity of a well, and in this study we will observe the effects of temperature, time and constant circulation on water based drilling fluids.

1.2 Basis For The Project

This thesis is based on the previous works by Ole Julius Rye and Priyad Saptharishi, it is essential to study their results and limitations to ensure effective methods and relevant experiments are carried out.

Saptharishi started this line of projects with extensive testing, in the thesis entitled ***"Rheological characterization of Water-based Drilling Fluids- A Comparative Analysis of Manual and Automated measurements"***, of WBM containing PAC, XG, and barite. The tests were taken after mixing and particles had been properly dispersed and air had migrated out of the fluid. This project presents experimental rheological characterization of different concentrations of PAC along with selected commercial compositions of Water base mud (WBM) additives like Barite, sand

particles and xanthan gum in order to replicate wide drilling fluids portfolio. In addition to the primary rheology properties like density, viscosity, dynamic rheological properties like shear-thinning, visco-elasticity, thixotropy and yield stress of above said compositions are investigated. (Saptharishi 2016)

Ryes thesis entitled *"Statistical Analysis of Rheological characterization of Water-based Drilling Fluid"* is a follow up on Priyad Saptharishis study. In his report, results from Fann viscometer tests carried out for a selection of fluids containing poly-anionic cellulose (PAC), xanthan gum (XG) and barite were presented. Compositions were chosen on a comparable basis to Saptharishis study. By using an increased number of measurements, repeatability could be assessed, and used as a foundation to compare the previously obtained results from Saptharishi. (Rye 2017)

Rye studied the effects of time on a fluid by storing the samples in a glass flask at room temperature. It can be discussed whether or not this is applicable since a drilling fluid is circulated in a well, with high temperatures and dynamic forces applied to it as well as being static in both the wellbore and pits. This project will take the same compositions of fluids and run them in a small scale flow loop, both at room temperature and in a heated cabinet, to compare with the results from Ryes study to see if there is a measureable difference. This will require a significant amount of time spent in a laboratory to be able to go through all the fluid compositions and different temperatures.

1.3 Objectives

- The first task of the project is to observe the effects of NaCl on samples containing PAC and PAC + Xanthan Gum.
- Compare aging on flask with circulated aging at 25℃.
- Compare samples circulated at 25℃ with samples circulated at 50℃.
- Compare previously heated, when mixed, samples to new continuous heated and circulated samples at 50℃.

1.4 Hypothesis

The effect of salt added in the samples is expected to result in a longer life span, and continuity in its rheological characteristics. Salt should nullify the bacteria effectiveness and therefore prevent degradation of mud properties.

As both OJR and PHS showed, the viscosity decreased over time, as expected. By continuously circulating the fluid we expect to see a more significant and rapid decrease in viscosity in time due to the stresses applied.

When circulated samples are measured we will most likely observe that the samples circulated when exposed to heat will have a greater factor of degradation.

OJR heated some samples when mixing and let them rest in glass flasks to see if it affected its characteristics over time, and if they were reversible. When we circulate the samples in a constant heated environment, rather than let them cool, it is interesting to see if there is a connection between a sample that has been heated and one at a constant heated temperature.

2 Relevant Theory

In drilling fluids a polymer is added to mainly work as a viscosifier, control fluid loss and shale stabilizer. Polymers have limitations at high temperatures, salinity and hardness (Jr., Chenevert et al. 1972). The most common naturally occurring polymers are the polysaccharides, which include carboxmethyl cellulose (CMC), starches, xanthan gum, and guard gum (Hughes, Jones et al. 1993). There are several CMC products; one of them is polyanionic cellulose, which is used, along with xanthan gum, in the experiments in this thesis.

2.1 Polyanionic Cellulose

In this experiment polyanionic cellulose (PAC) will be used as to increase viscosity of a fluid. PAC comes from cellulose, which is a component in plant material and it is not soluble in water. PAC has added components to give it the wanted properties, reduce filtrate loss and being water soluble and therefore viscosity. PAC has a high grade of inhibition with options for high and low viscosity, it reduces fluid loss in wells and is stable up to 150°C (Arnesen and Virak 2014) and is not subjected to bacterial degradation (Lummus and Azar 1986).

The structure of a polymer consists of many threads, and these threads make bonds which gives viscosity. When the polymer is exposed to stress these threads starts to separate from the bonds and make the polymer less viscous. The threads can be altered by temperature, and at increasing temperature the threads can be stretched. When exposed to very high temperature the threads can break, and the viscosity will decrease (Kalur, Frounfelker et al. 2005).

2.2 Xanthan Gum

Xanthan gum (XG) is a microbial polysaccharide secreted by Xanthomonas campestris, it is pseudoplastic, highly soluble and viscous, and stable over a wide range of pH and temperature (Saleh, Annuar et al. 2017).

Xanthan gum is a polymer applied within petroleum production as a lubricant or in friction reduction in wellbore and it reduces water mobility by increasing viscosity and decreasing permeability. The concentration of XG on petroleum production varies from 0,05 to 0,4(% w/w) (Garcıa-Ochoa, Santos et al. 2000).

Solutions of xanthan obtained by dissolution at moderate temperatures tend to be highly viscous. The dissolution temperature greatly affects viscosity by controlling the molecular conformation and appearance of ordered structures (Garcıa-Ochoa, Santos et al. 2000).

2.3 Temperature Behavior of Mud in Well

The way a drilling fluids temperature alters during a cycle downwards the drill string and upwards in the annulus compared to the natural temperature gradient in the ground is presented in Figure 1. The fluid is not directly exposed to the formation; it is isolated inside the drill string. When the fluid is exposed to the formation it rapidly increases in temperature before the increase is compensated by the decreasing temperatures in the formation travelling up the annulus, eventually returning to initial temperature. A drilling fluid is not circulated at a constant temperature, and is exposed to shear forces and various temperatures (Skalle 2017).
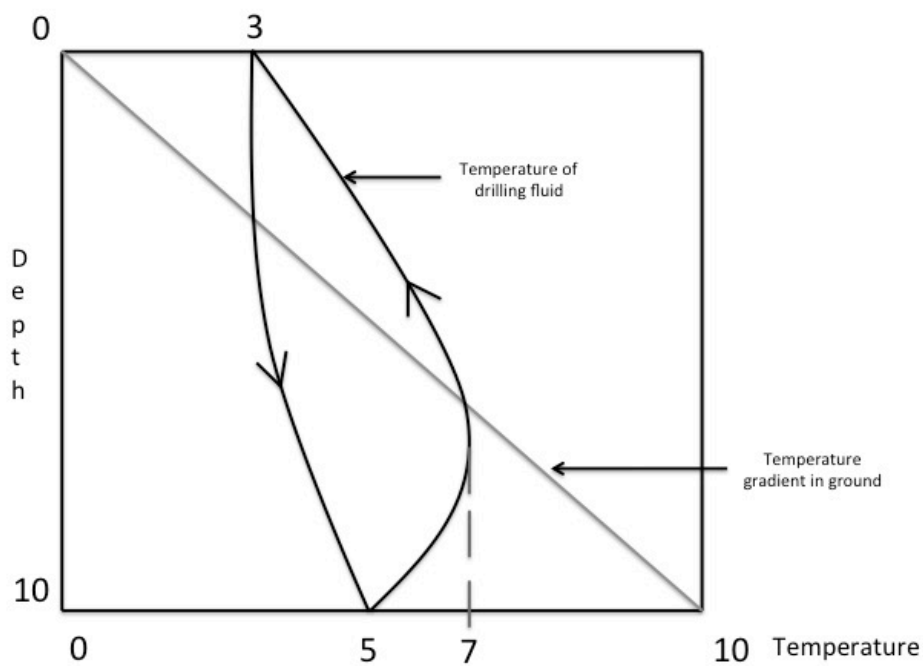
Figure 1: Temperature Behavior of Circulated Drilling Fluid in Well

2.4 Thermal Polymer Degradation

Polymers are sensitive to temperatures; Figure 2 presents how polymers degrade at a higher rate with increased temperatures. For a polymer to be able to live for an adequate time 80°C is a critical point, temperatures above this point will most likely result in a fluid loosing its rheological properties rapidly (Skalle 2017). CMC can be used in temperatures up to 150°C while thermal degradation begins at about 95°C for starch (Jr., Chenevert et al. 1972).
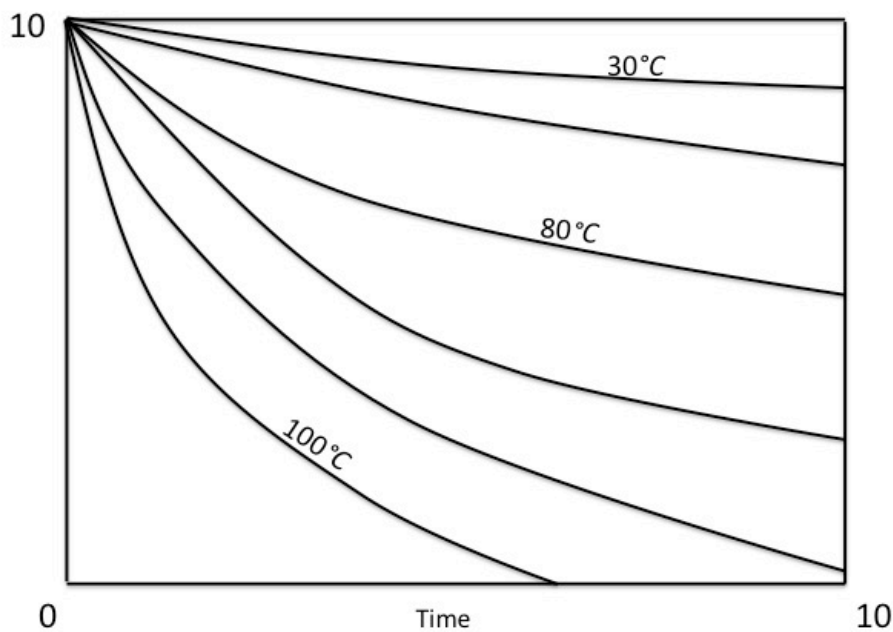
Figure 2: Thermal polymer degradation in time

Adding salt to a polymer solution will hopefully result in a prolonged state where the polymer is able to maintain the original rheological characteristics.

CMC has a low efficiency in salt concentrations above 50,000 ppm (Jr., Chenevert et al. 1972). When a xanthan gum and salt solution structure is disrupted by high shear or temperature, the recovery of dynamic properties is slow and incomplete in low salt concentrations, and fast and complete in high salt (0,5%NaCl) environments (Rochefort and Middleman 1987).

2.5 Shear Stress Effect on Fluids

Fluids behave differently when stress is applied. Shear thickening fluids increase in viscosity with increased stress, and shear thinning fluid decrease in viscosity with increasing stress. In science, stress means that a force is applied to body, and the result of that stress is called strain. A liquid is thixotropic when the viscosity of the fluid is decreasing with time. (Hub 2010) A drilling fluid is often a thixotropic liquid and will decrease in viscosity when stress is applied. To be able to suspend cuttings in the wellbore when circulation is stopped, the fluid has to be able to behave elastic and return to its original state where it has a gelling effect. The gel effect means that the fluids ability to flow decreases and prohibits particles to travel downwards the well. As well as the fluid has to start flowing again when circulation is commenced.

Materials that exhibit both viscous and elastic characteristics when a force is applied are called viscoelastic. Viscoelastic materials resist shear flow and strain linearly with time when exposed to stress. When the stress is removed it returns to its initial state. (Meyers and Chawla 1999)

Long time exposure to dynamic load can result in fatigue of the material. The two most important types of long-term material behavior are stress relaxation and viscoelastic creep. (Rosato and Rosato 2013)

2.6 Viscoelastic Creep

When a material is subjected to constant stress, it undergoes a time dependent increase in strain, an irreversible deformation called creep (Rosato and Rosato 2013). A deformation is a change in shape and size of a body due to applied forces. An irreversible deformation is when a matter is not reverted back to its initial form when the force is removed. Creep may continue over the entire life of a structure. (Debrecen 2009)

A polymer material that is subjected to a constant stress for a sufficient time will respond to the stress with a strain (deformation) that increases until it ultimately fails. This is shown in Figure 3 below, where ε = creep strain and t = time. (Rosato and Rosato 2013)
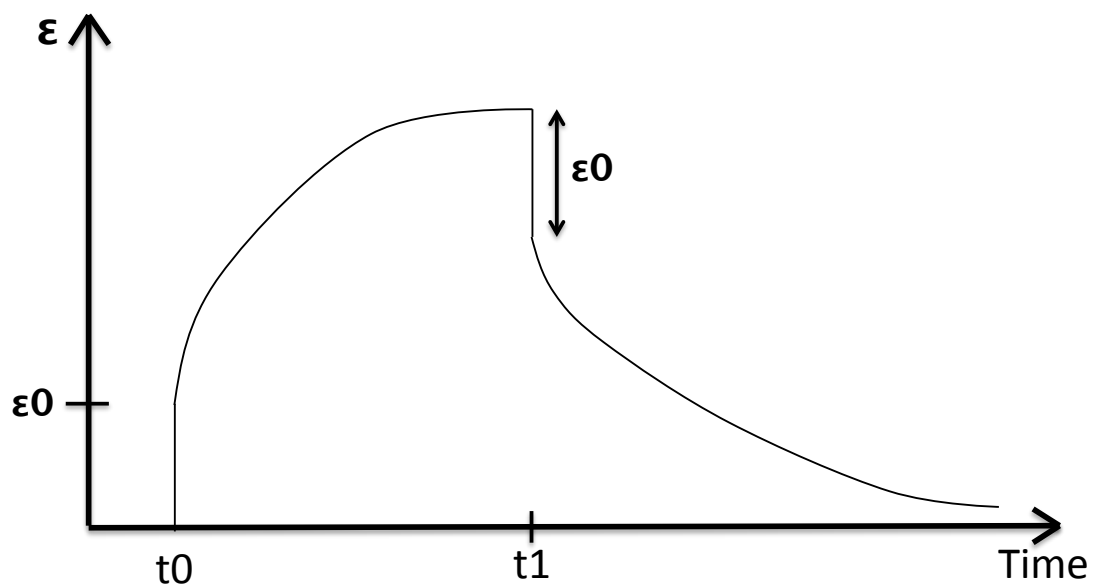
Figure 3: Induced Stress as Functions of Time for a Viscoelastic Material

2.7 Potential of Hydrogen

Potential of Hydrogen (pH) is a measure of acidity and the pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (mol/L) (Chang 2007):

$$pH = -\log[H_3O^+]$$

or

$$pH = -\log[H^+]$$

pH is a way of expressing hydrogen concentration, and a solution can be determined by its pH value if it is acidic or basic:

Acidic solutions: pH < 7.00

Basic solutions: pH > 7.00

Neutral solutions: pH = 7.00

In non-ideal behavior in reality ion-pair formation and other types of intermolecular interactions may affect the actual of species in a solution (Chang 2007).

3 Experimental Work

The experiments for this thesis have been carried out in the reservoir laboratory at the Department of Geoscience and Petroleum at NTNU. The institute has provided equipment and necessary materials have been handed down from previous student Ole Julius Rye.

The works of Priyad Saptharishi and mainly Ole Julius Rye have set the basis for this thesis. The experiments can be divided in to two; seeing the effects of salt added in samples containing PAC and XG, and observing the change in viscosity when samples are circulated in both room temperature and in a heated environment.

The methods of mixing samples have been discussed, but to be able to compare results, all samples are mixed as done by OJR.

3.1 Equipment Used

A variety of instruments have been used to measure weights, mixing samples and measuring. A detailed list of the equipment used in the experiments can be seen in Appendix A Equipment.

3.2 Mixing Procedure

All samples were mixed with both a Janke & Kunkel and a Heidolph magnet mixer. First the salt was dissolved into tap water, and then PAC and/or xanthan gum was dispersed into the salt water little by little to avoid clumping. Xanthan gum is added through a fine meshed sieve, otherwise it gathered immediately and was hard to disperse. The mixing procedure was time consuming because the particles took time to dissolve and disperse properly in the water. Some lumps of additives did not dissolve and had to be broken up with a stirring spoon. The samples were mixed at 480 RPM, same as OJR used, so the results are comparable with previous tests. A picture of a sample being mixed is shown in Appendix D - Additional Photos.

After mixing the pH values are measured simultaneously with testing the viscosity of the sample.

3.4 Measuring Procedures

Tap water is measured using a Sartorius 1 scale, while additives like PAC, NaCl and xanthan gum is measured with the more accurate Sartorius CP 4202 S scale.

3.4.1 Fann 35 Viscometer Procedure

The standard procedure for measuring viscosity and gel strength with a Fann 35 Viscometer is to let it run at max revolutions for 1 minute. Then measure for each revolution from 600 RPM down to 3 RPM. When testing gel strength the viscometer should run at max revolutions for 1 minute between each testing interval. Measure gel strength by letting the sample rest for the current time interval, and then read the max value at 3 RPM. This is done for 10 seconds, 1 minute and 10 minutes.

Dial readings from Fann 35 viscometer are read and converted in to shear stress [Pa]. Gel strength [lb/100 ft^2] can be read off the viscometer without any conversion. Equations for calculating Plastic viscosity (PV) and yield point (YP) are shown in the equations below and are calculated by subtracting the 300 RPM dial reading from the 600 RPM dial reading for PV [cP], and subtracting PV from the 300 RPM dial reading for YP [lb/100 ft^2] (Company 2016).

$$PV = \theta600 - \theta300 \ [cP]$$

$$YP = \theta300 - PV \ [lb/100ft^2]$$

3.5 pH Measurements

In addition to measuring viscosity, pH measurements are obtained for every sample at the same time as viscosity. This additional information will hopefully contribute in understanding why the changes in the samples occur.

3.6 Effects of Salt in Samples

Drilling fluids that are being used on-site are designed to last as long as possible. In the works of OJR the life span of the samples were short, and it lost its rheological properties rapidly. Adding salt to the water and then the additives may prolong its life span by decreasing the bacterial effectiveness and hence keep its properties for a longer time period.

3.7 Test Matrix for Non-Circulated Samples

The tests that are carried out without circulation are the same as done before by OJR, but with NaCl added. Samples are stored on airtight glass bottles in between tests. Temperature will vary in the laboratory, and is measured every day.

Sample Data			Fann Viscometer RPM					
Time hrs	Test temp	pH	3	6	100	200	300	600

Sample Data			Gel strength lb/100 ft2			PV	YP
Circulated	Test temp [°C]	pH	10sec	1min	10min	[cP]	[lb/100 ft2]

The different compositions of samples to be tested un-circulated:

- o 2%PAC+1%NaCl
- o 4%PAC+1%NaCl
- o 2%PAC+1%XG+1%NaCl
- o 2%PAC+2%XG+1%NaCl
- o 4%PAC+2%NaCl

3.8 Flow Loop

A flow loop has been manufactured using a circulation pump shown in Appendix A Equipment. To complete the loop there is a container, working as a reservoir for the sample, and two types of hoses. The pump can run with temperatures as high as 110℃ and over a long period of time. This means that samples can be circulated to simulate the mud system on a rig site and measure the effects on the mud instead of storing it in a flask.

The circulation loop will run in both room temperature and in a heated cabinet. It is a closed system to ensure that fluids are not lost to evaporation during circulation in high temperatures. The loop is built in small scale to be able to fit inside a Termaks heating cabinet so tests can be done in temperatures up to $100°C$.

3.9 Test Matrix for Circulated Samples

Fluid samples that are circulated are tested the same way as non-circulated samples.

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [C	pH	3	6	100	200	300	600

Sample Data			Gel strength lb/100 ft2			PV	YP
Circulated	Test temp [°C	pH	10sec	1min	10min	[cP]	[lb/100 ft2]

The different compositions of samples to be tested circulated at both 25℃ and 50℃:

- o 2%PAC
- o 4%PAC
- o 2%PAC+1%XG
- o 2%PAC+2%XG

When the circulation loop was manufactured, it was a concern the circulation pump might not be able to run the more viscous samples containing XG. Upon circulating samples with 2%PAC+1%XG it was immediately clear that it was not possible. The flow through the loop was as good as zero and resulted in pump failure. Therefore tests with both 2%PAC+1%XG and 2%PAC+1%XG could not be done with the equipment at hand. The events leading up to the pump failure are further described in upcoming chapters.

3.10 Challenges discovered early on

From the start it was discovered that samples did not get the same values as the ones presented by Rye (2017). In general the new samples showed a tendency of lower shear stress. This might be because of small differences in mixing, although the mixing procedure was carried out as described by (Rye 2017).

After a few samples had been circulated in the flow loop, corrosion was observed from the container holding the fluid. This gave the fluid an orange color, and could in worst case have an effect on the rheological properties of the samples. It was considered to replace the container with one more withstanding to corrosion, but it would take weeks before testing could be resumed. Pictures of the corroded container and discolored sample are shown in Appendix D - Additional Photos.

4 Results and Analysis

All the results from sample testing with the Fann 35 viscometer are presented in this chapter. The results will be compared with Ryes and commented. Graphs from the measurements are shown, and a complete set of tables with values can be seen in Appendix B - Test Data.

4.1 Effect of Salt in Non-Circulated Samples

If the hypothesis is correct, we will be able to see a slower degrading tendency in the viscous fluid tested compared to the samples containing tap water without salt.

4.1.1 2%PAC+1%NaCl

The first sample mixed was 2% PAC + 1% NaCl. The sample was mixed at 24℃, same as comparative samples, to ensure that the results became as reliable as possible without temperature affecting the viscosity significantly.
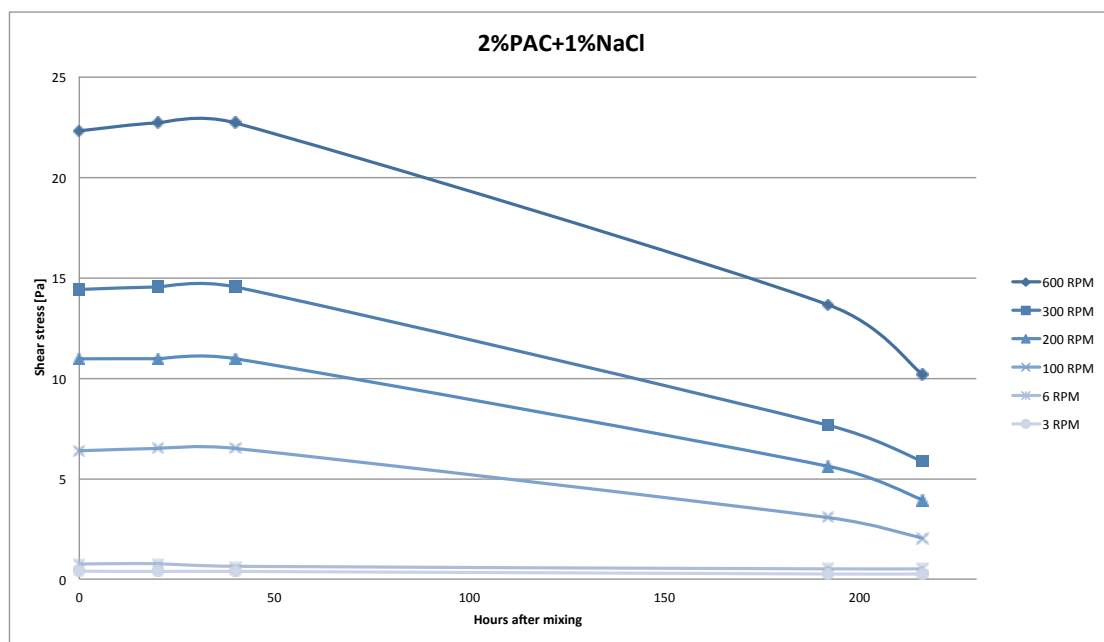
Figure 4: Shear Stress 2%PAC+1%NaCl

The shear stress, as shown in Figure 4, of the fluid had a slight tendency of increasing the first 40 hours or so before a turn and a decrease was observed. When 220 hours had passed the decrease became more severe.
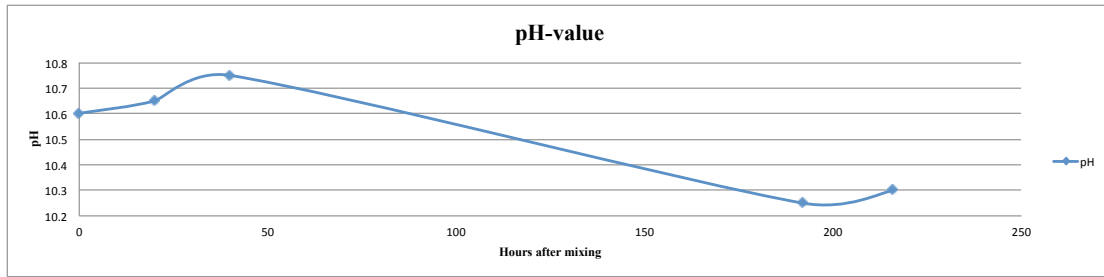
Figure 5: pH 2%PAC+1%NaCl

pH value for 2%PAC+1%NaCl had a slight incline up to 48 hours before turning and declining steadily. A small increase after 200 hours, but it only increased by 0,05.
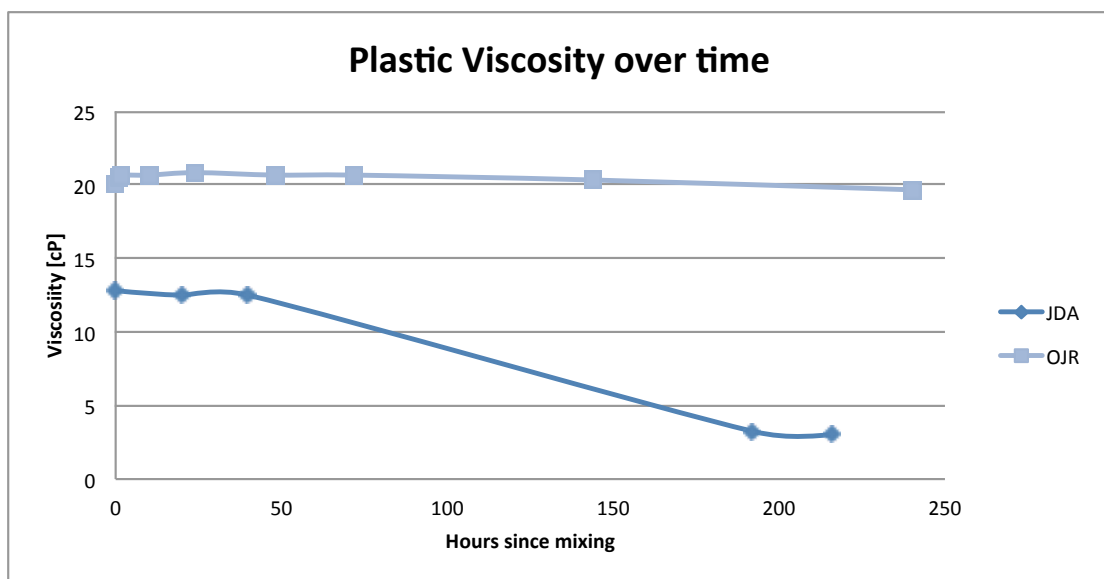
Figure 6: PV OJR vs JDA

Comparing the viscosity of the sample with OJR it shows a direct opposite of what we expected to see. The sample containing NaCl decreases only after 48 hours, while the one without NaCl seems to be stable.

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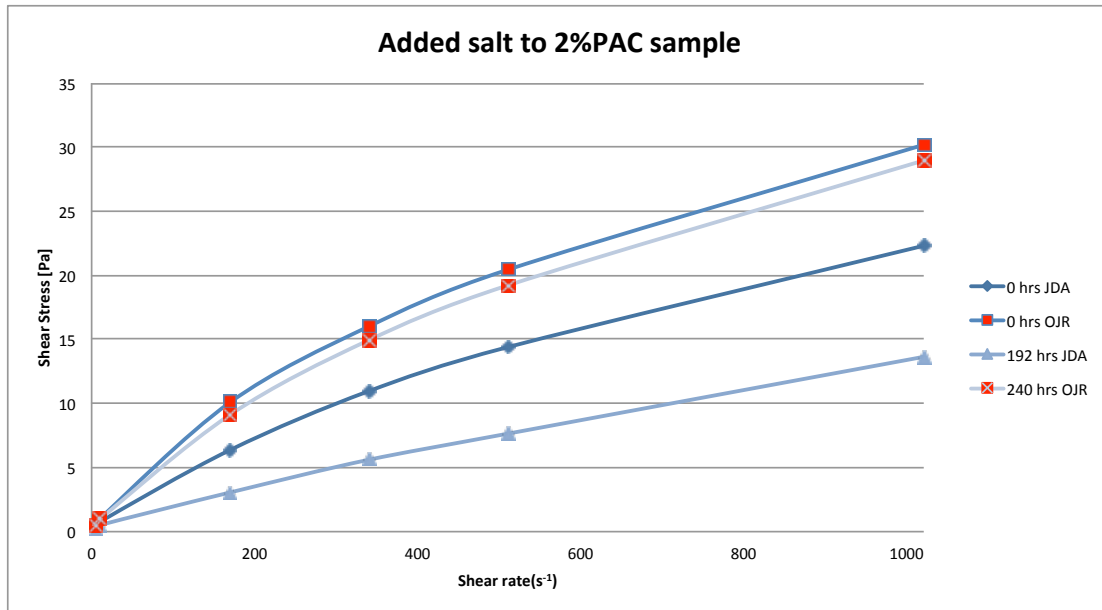
Figure 7: Bingham Plastic model showing changes in viscosity over time

Figure 7 shows the same tendency as in Figure 6, that the results from OJR are stable over time, but the sample containing NaCl has decreased over time.

Since the sample just after mixing had such a lower viscosity than previously mixed samples by OJR it could seem that the mixing procedure has been different. Because of this a new sample was made to see if it could give us a result more similar.

4.1.2 2%PAC+1%NaCl - Test Two
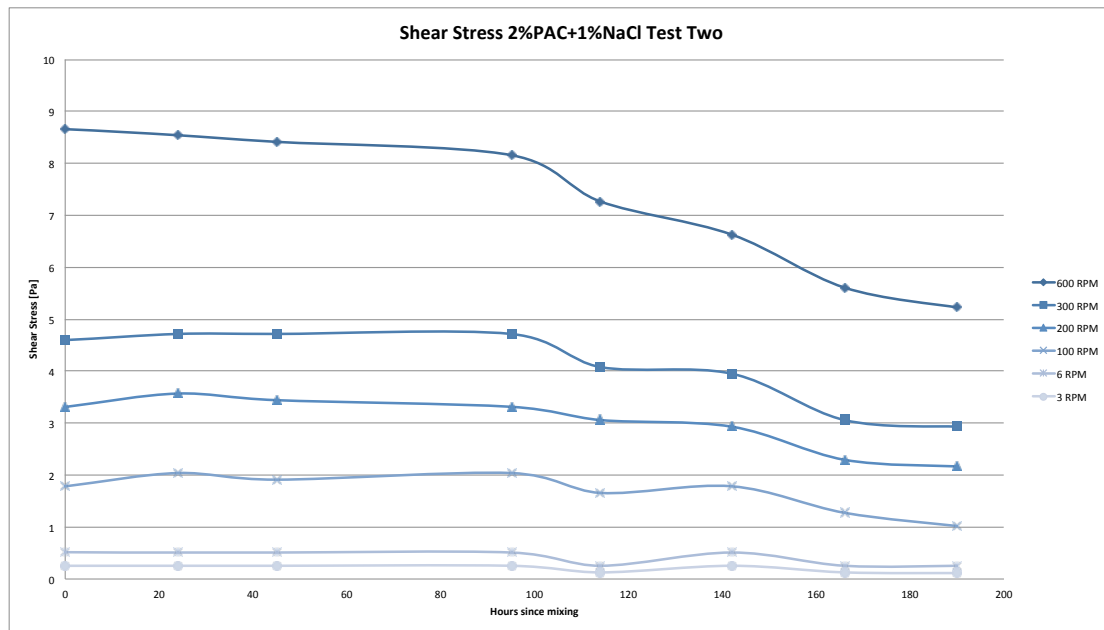
Figure 8: Shear Stress 2%PAC+1%NaCl - Test Two

The second test with 2%PAC+1%NaCl shows that the degradation begins to speed up after about 110 hours, as presented in Figure 8.
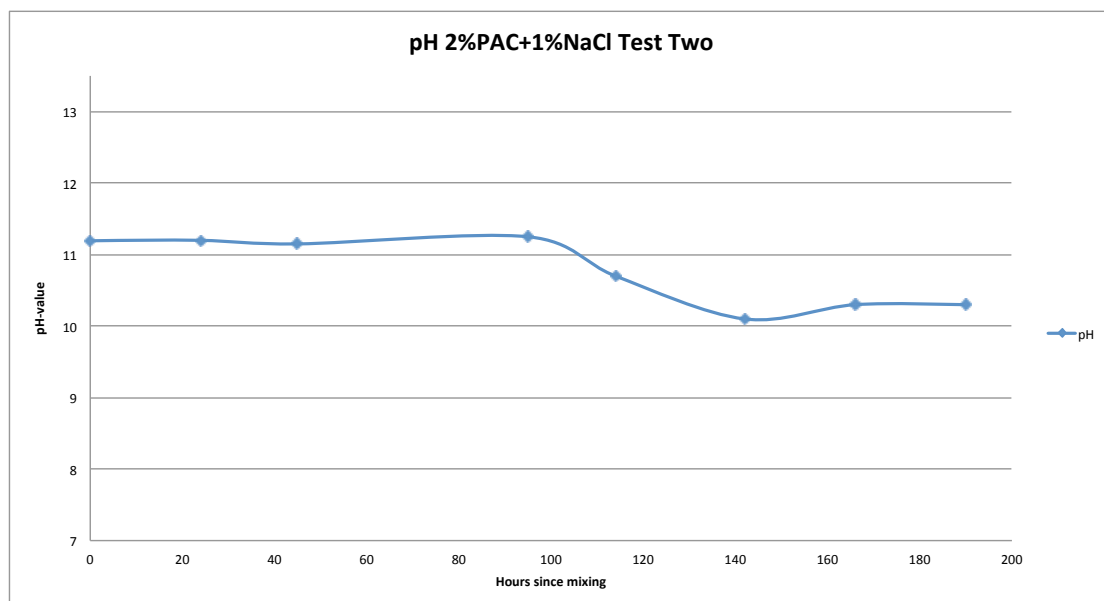
Figure 9: pH 2%PAC+1%NaCl - Test Two

Figure 9 shows pH for the second test with 2%PAC+1%NaCl that it is almost constant during the whole test period; a decrease of 1 is seen at the same time as degradation is sped up.
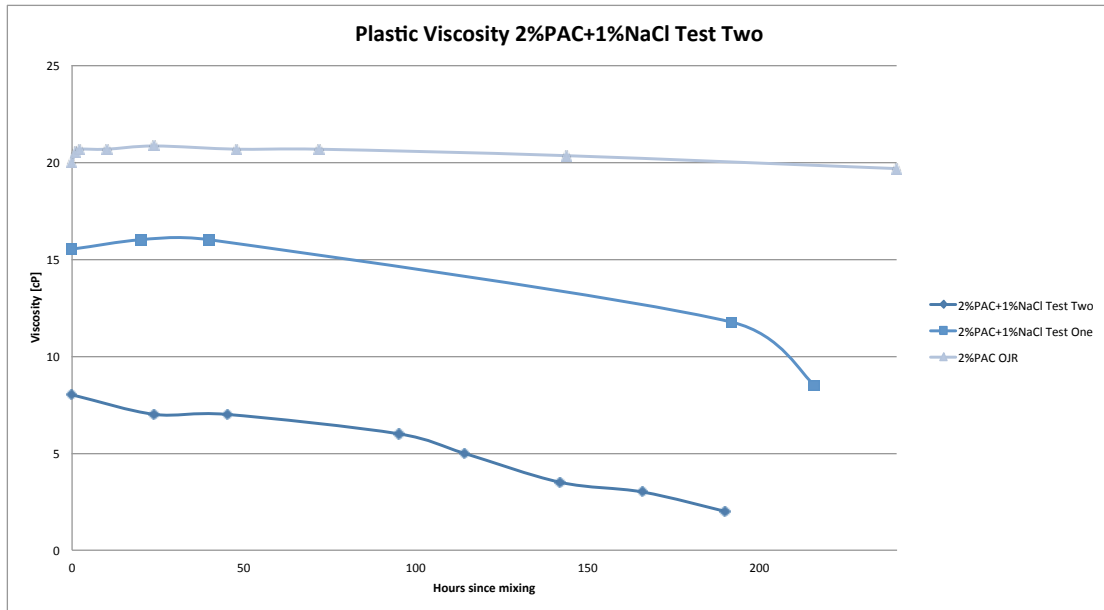
Figure 10: Plastic Viscosity Comparison Between 2%PAC Solution

The purpose of a second test with 2%PAC+1%NaCl was to get closer to the initial values of viscosity previously obtained by Rye. Figure 10 shows the opposite of the outcome wanted. The second test had a plastic viscosity of 8 cP after mixing, a decrease of 8 cP from the first test and 12 cP from Ryes results.

4.1.3 4%PAC+1%NaCl
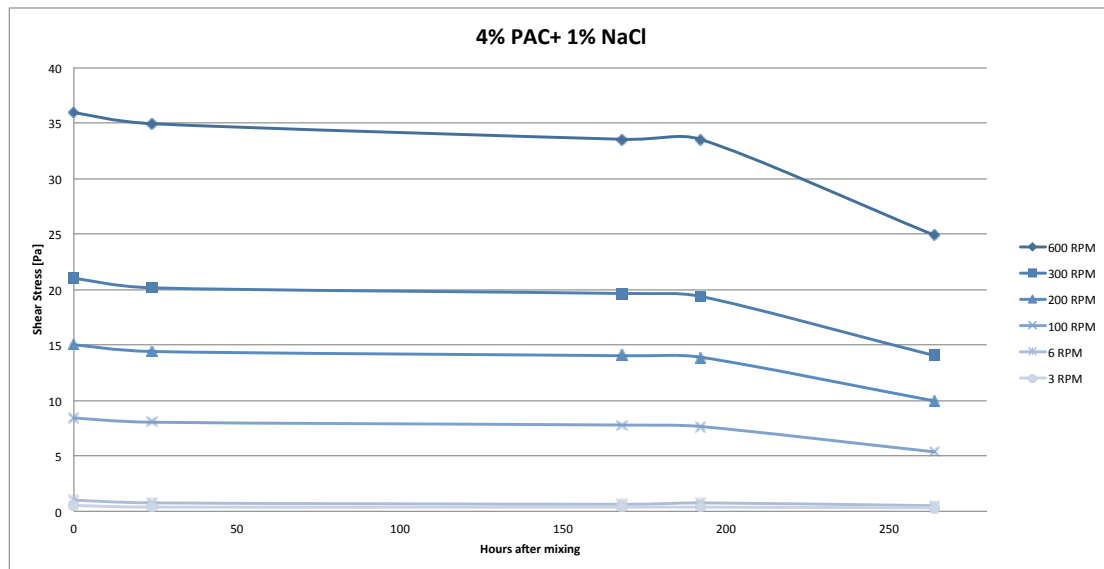
Figure 11: Shear Stress over time for 4%PAC+1%NaCl

Figure 11 shows how the shear stress for a 4%PAC+1%NaCl sample develops over time. The sample is stable for about 200 hours before starting to degrade.
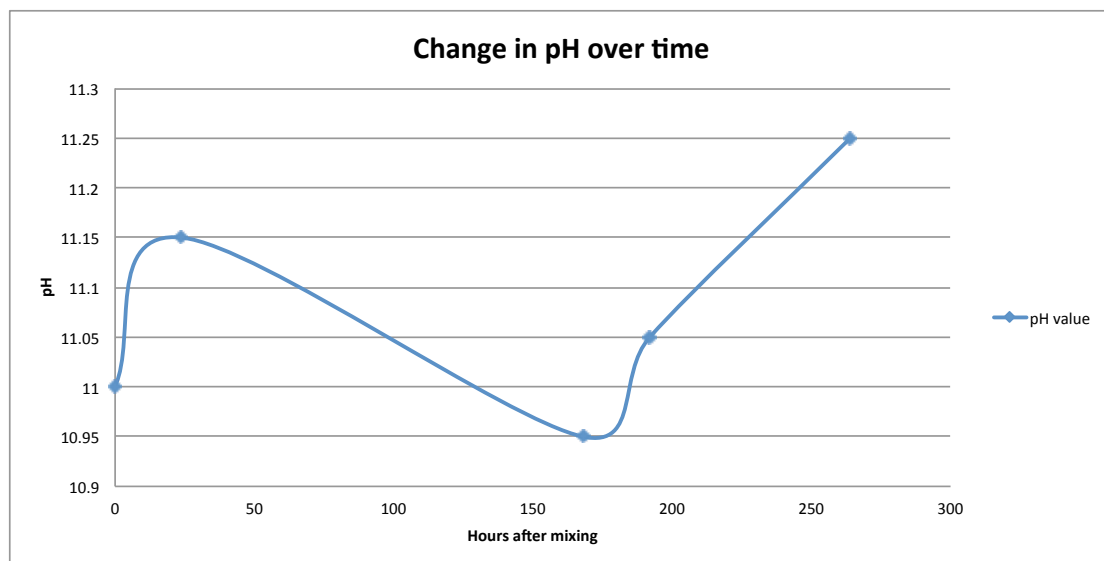
Figure 12: pH over time for 4%PAC+1%NaCl

Figure 12 presents the pH of the 4%PAC+1%NaCl, and it is quite stable ranging from about 11 to 11,25. The graph may give a false impression that it various a lot in time, but the variation is not enough to be significant.
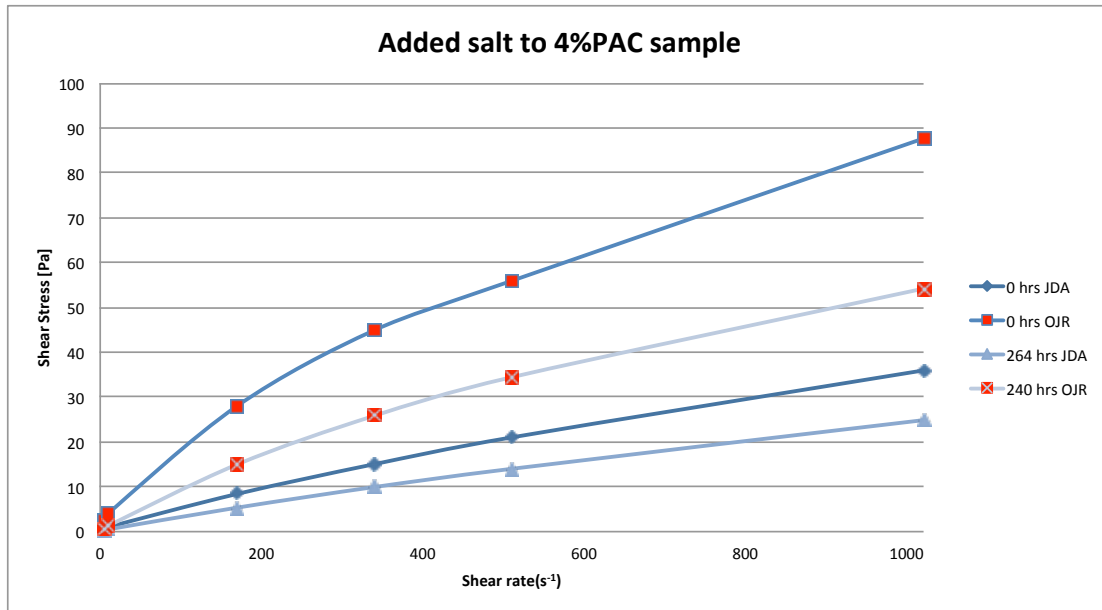
Figure 13: Bingham Plastic Viscosity comparisment 4%PAC with and without NaCl

The sample starts off with a significant lower viscosity than the previous sample without NaCl added as seen in Figure 13. From the graph we see that the sample with salt decreases shear stress for about 30 Pa at 1021 s^{-1} after 264 hours, while the one without salt decreases about 35 Pa at 1021 s^{-1} after 240 hours. Because of the difference in viscosity after mixing it is not possible to conclude with that the lesser degradation is a result of the NaCl added, or if it simply decrease less at lower viscosities.
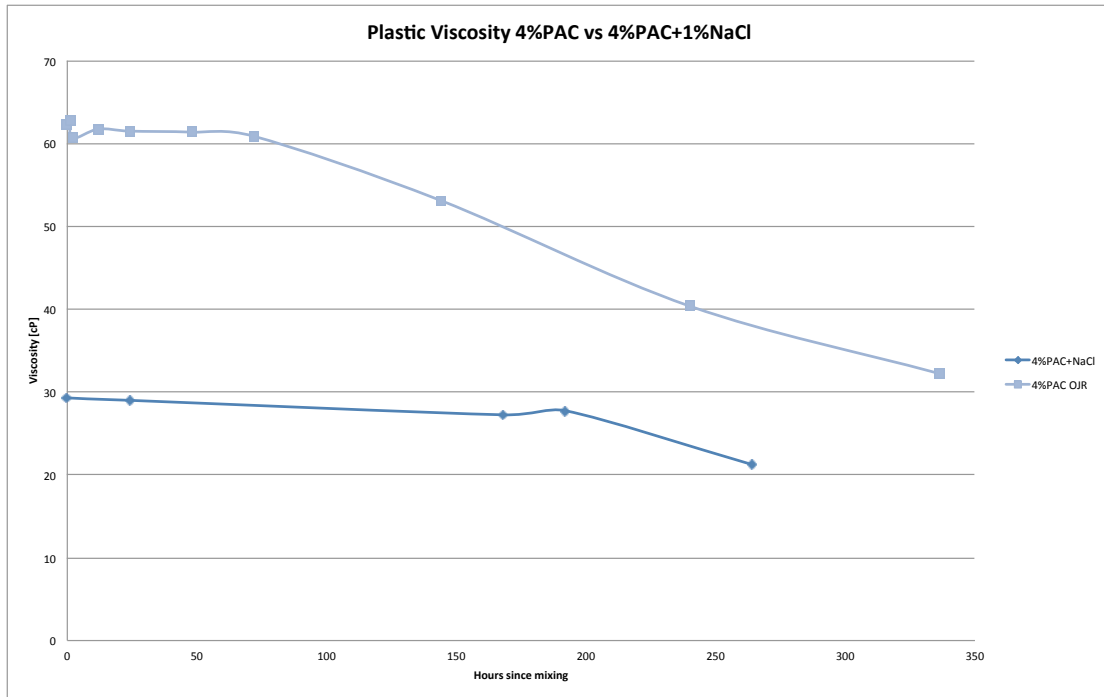
Figure 14: Plastic Viscosity 4%PAC vs 4%PAC+1%NaCl

As said before the previously mixed sample with 4%PAC has a higher initial viscosity than the 4%PAC+1%NaCl sample. In Figure 14 it is clear that the sample containing NaCl is able to maintain the initial viscosity, it starts to degrade after approximately 200 hours, while the sample without NaCl degrades after only 70 hours.

The difference in initial viscosities between the two samples was not expected and could be a result of improper mixing of sample. Another 4%PAC+1%NaCl sample was made in attempt to replicate the original properties obtained by OJR in his project.

4.1.4 4%PAC+1%NaCl - Test Two
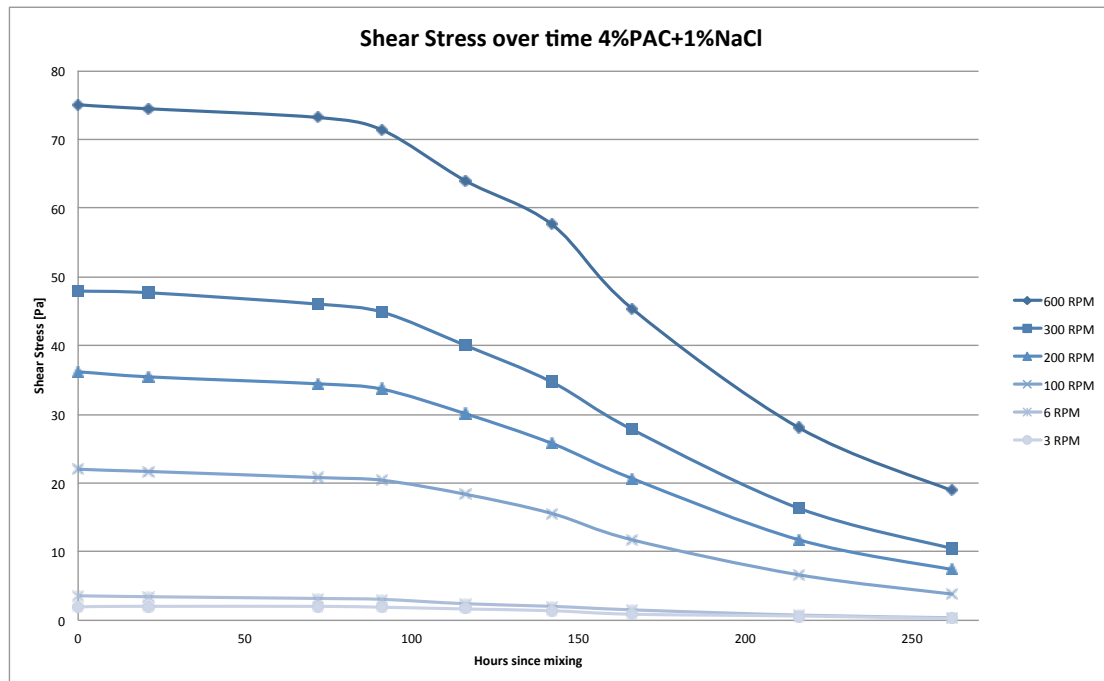
Figure 15: Shear Stress over time 4%PAC+1%NaCl - Test Two

Figure 15 displays how the shear stress decreases in the 4%PAC+1%NaCl sample. The degradation starts about 100 hours after mixing and decreases at a steady rate.
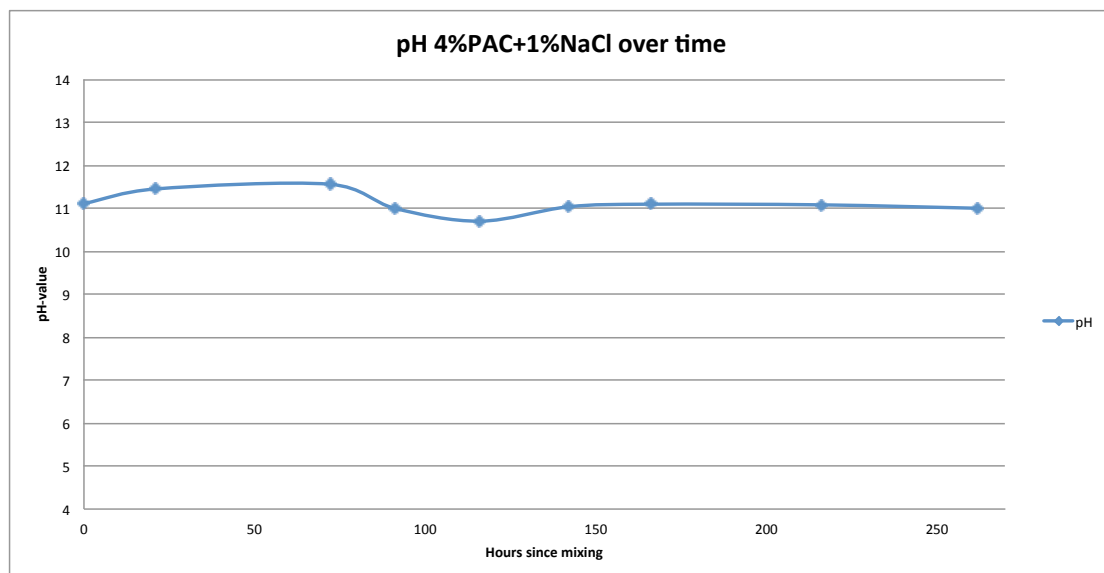
Figure 16: pH 4%PAC+1%NaCl over time - Test Two

pH value for the sample is stable throughout the test period with minor changes.
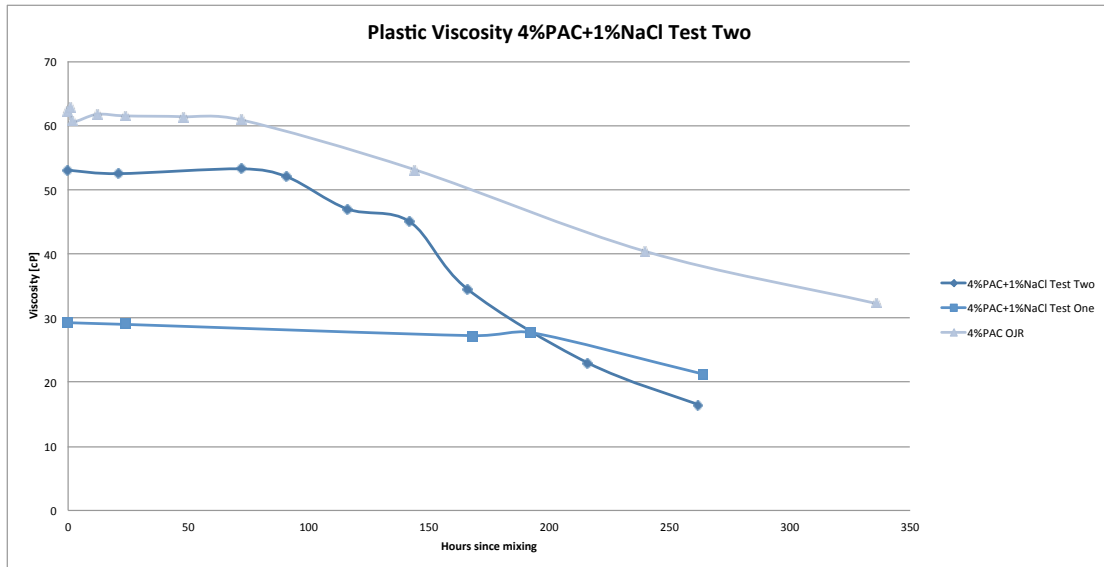
Figure 17: Plastic Viscosity 4%PAC+1NaCl - Test Two

The purpose of a second test with a 4%PAC+1%NaCl solution was to more accurately replicate previously tested 4%PAC solution. The results from the measurements are presented in Figure 17 and as seen the second test is significantly closer than test one. Test two starts to degrade earlier than test one, but slightly after the solution without salt.

4.1.5 2%PAC+1%XG+1%NaCl
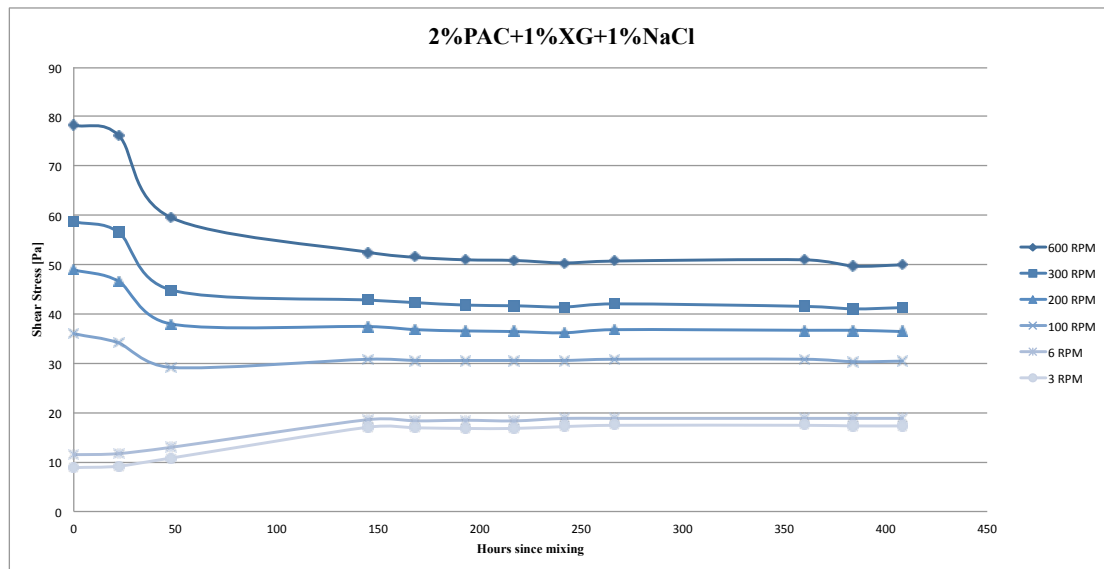
Figure 18: Shear Stress over time 2%PAC+1%XG+1%NaCl

The sample containing 2%PAC+1%XG+1%NaCl has a sharp decrease in shear stress after 48 hours before flattening out. It shows a stable viscosity over a long period of time and after 400 hours testing was discontinued.
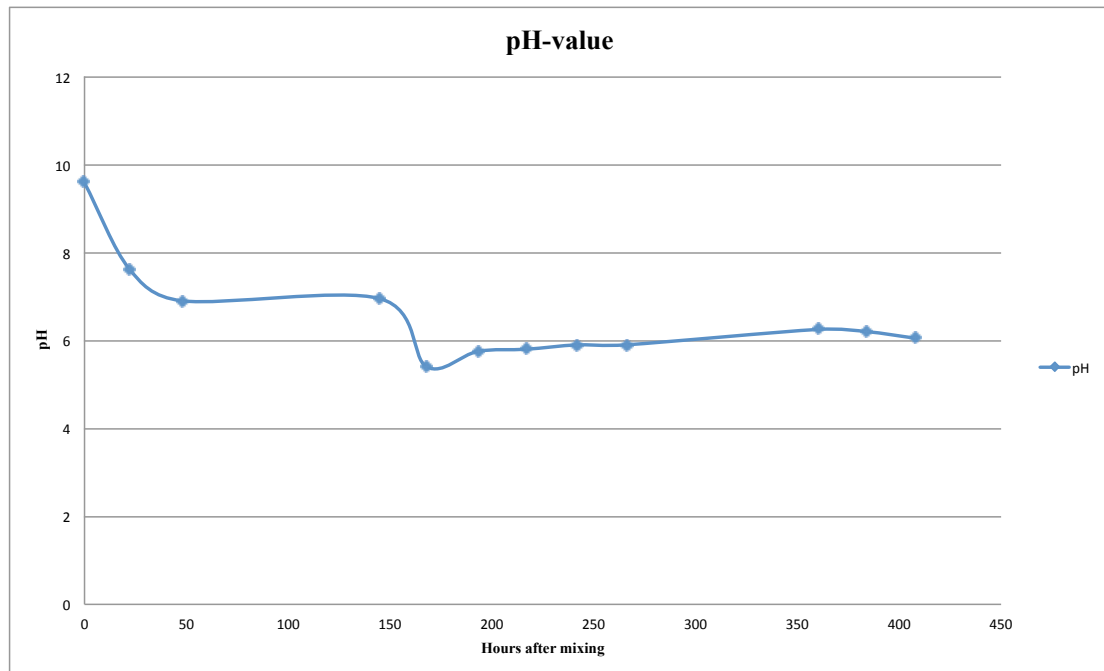
Figure 19: pH over time 2%PAC+1%XG+1%NaCl

Figure 19 displays the pH value for 2%PAC+1%XG+1%NaCl over time. It shows a steep decline before flattening out at around 50 hours. A sudden drop from 6,95 to 5,4

is seen 168 hours after mixing, which combined with the possibility of an error is not
that severe.
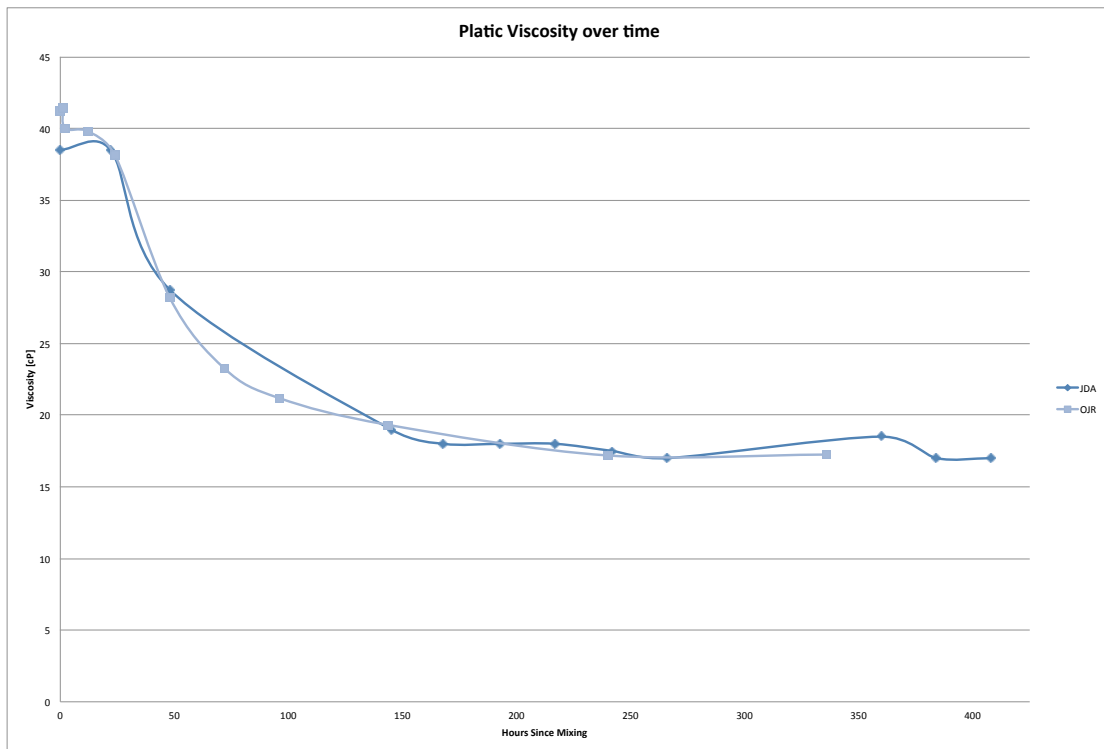
Figure 20: Difference in PV OJR vs JDA 2%PAC+1%XG+1%NaCl

In Figure 20 we see that there is a small to no difference between the sample
containing salt and the one without. They both seem to be stable after around 150
hours. The sample with salt have slightly higher values, but not of any significance.
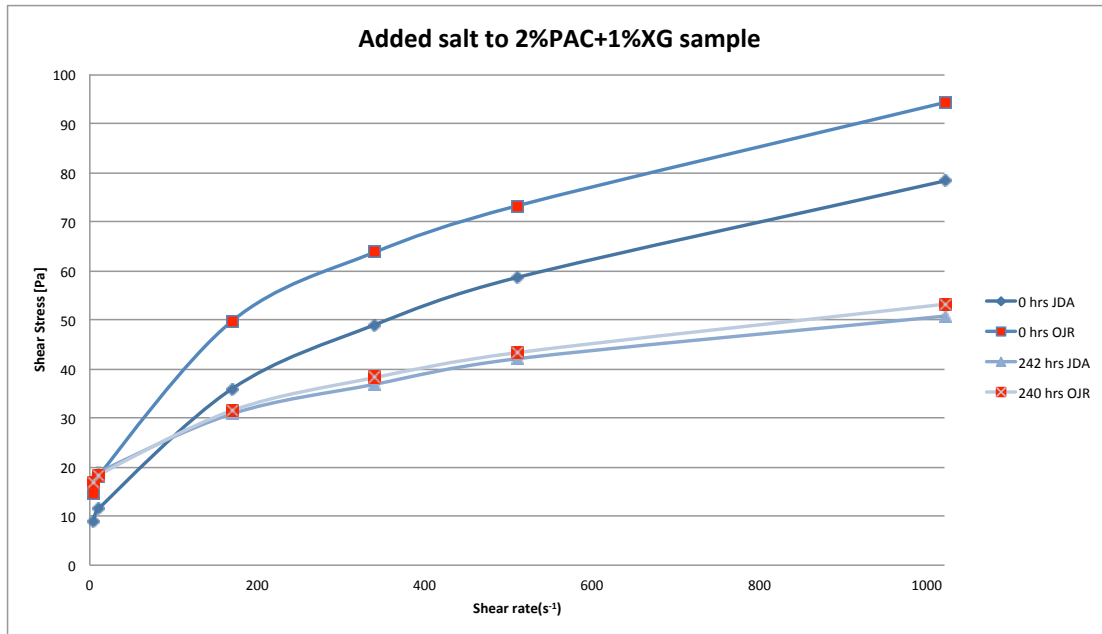
Figure 21: Bingham Plastic showing differences between OJR and JDA

Same in Figure 21 as in Figure 20, adding salt seem to have little effect on the life span of the fluid. Although the one containing salt has a decrease in shear stress of about 30 Pa while the one without has a decrease of 40 Pa since it started out with a slightly higher viscosity.

Salt Effect on Gel Strength 2%PAC+1%XG

Gel Strength is only considered in samples containing Xanthan Gum. Sample consisting of tap water and PAC does not have significant enough gel strength, in addition to the Fann 35 Viscometer that has a too high margin of error at such low values.
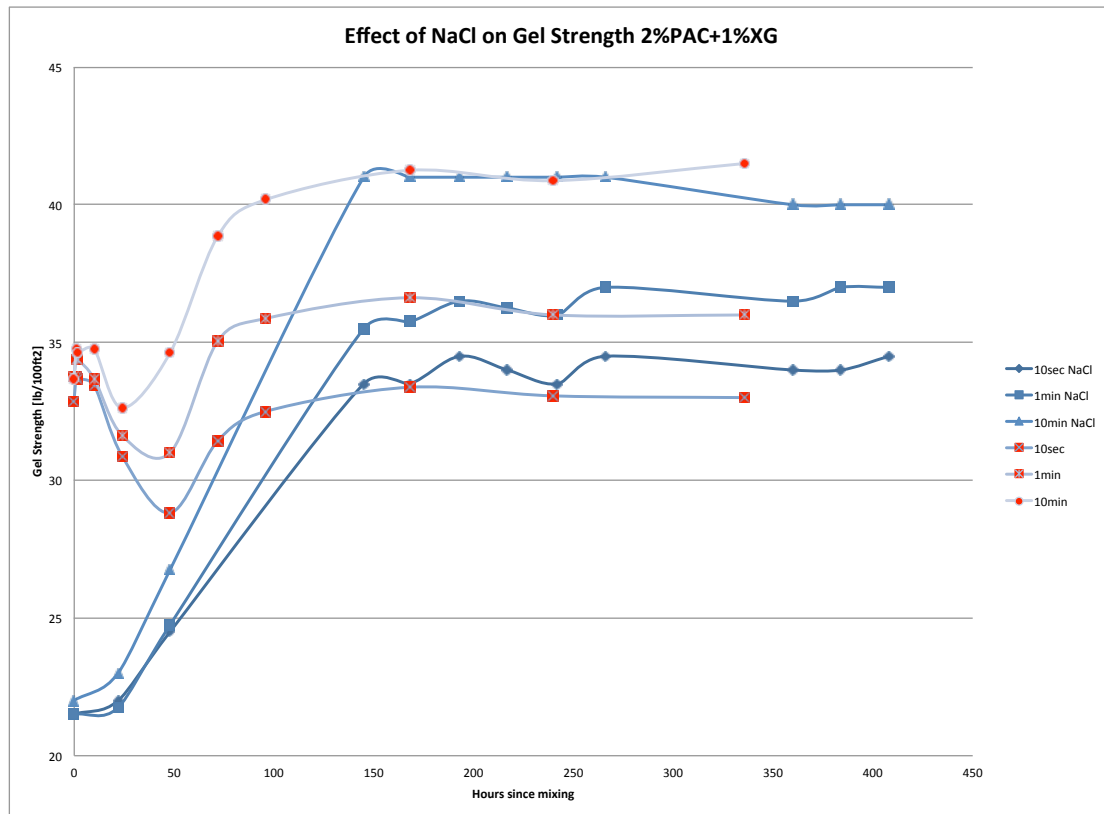
Figure 22: Effect of NaCl on Gel Strength 2%PAC+1%XG

Figure 22 displays both the gel strength over time for a 2%PAC+1%XG with and without 1%NaCl. Despite a difference of about 12 lb/100ft^2 they both stabilize after 150 hours at approximately the same values. The measurements taken just after mixing show an increasing viscosity. The forces applied during mixing are thinning out the fluid, and then it regenerates over time, which is characteristic for a viscoelastic fluid. After 17 days of testing it still had no tendency of degrading and further testing was discontinued.

4.1.6 2%PAC+2%XG+1%NaCl

When mixing was completed, the fluid seemed to be extraordinarily thick which was confirmed by the first measurements where dial reading at 600 RPM was 300+, out of range for scale. When using the Fann Viscometer it applies stress to the fluid, which will affect its rheological properties within short time. For it to be applicable for comparison two different people should not do it. The dial readings are not reliable for this thick sample. Despite this the testing was continued for the sample and the shear stress results are presented in Figure 23.
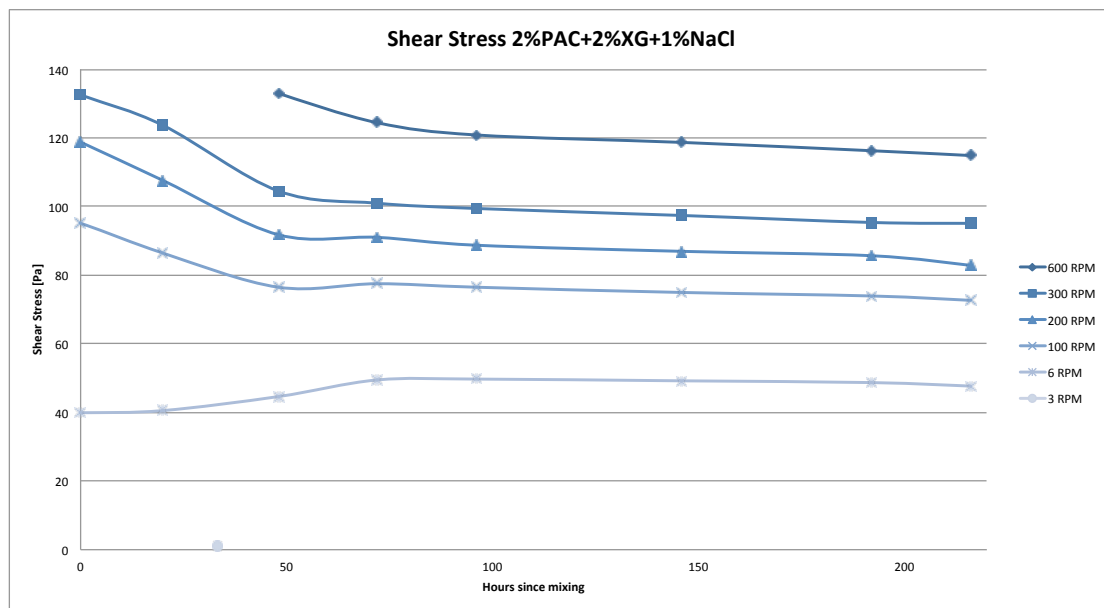
Figure 23: Shear Stress 2%PAC+2%XG+1%NaCl

The solution has a slight decrease in shear stress the first 75 hours before stabilizing.
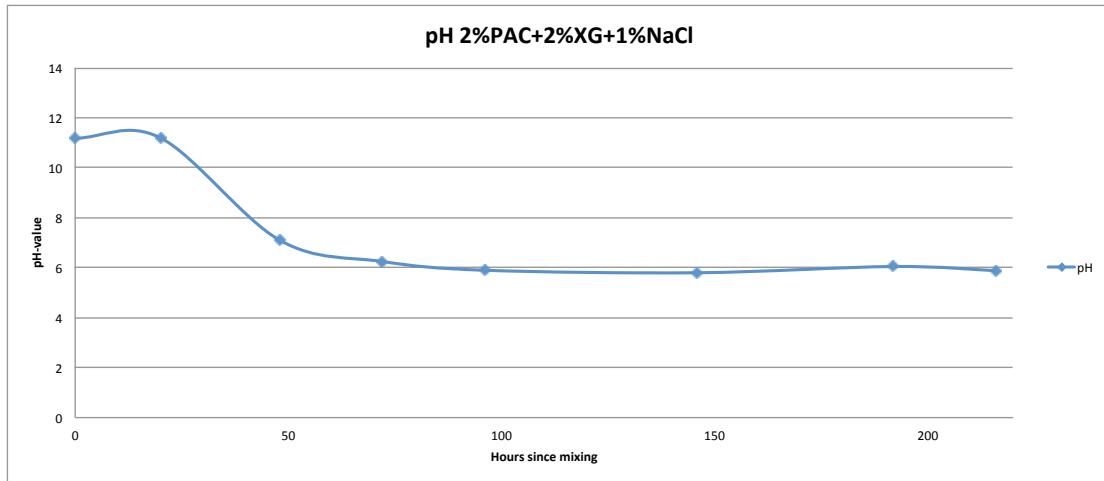
Figure 24: pH Value 2%PAC+2%XG

Figure 24 shows that the pH value follows the trend in Figure 23. It decreases when the viscosity decreases and stabilizes at the same time.
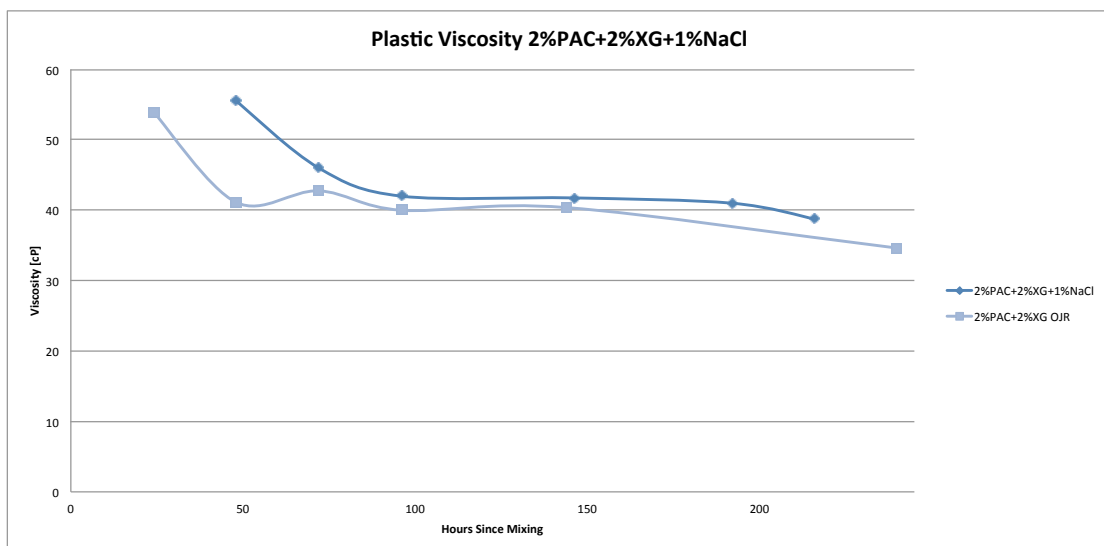
Figure 25: Plastic Viscosity 2%PAC+2%XG+1%NaCl

Comparing the two solutions with and without salt they seem to behave similar. In Figure 25 we can see that the solution with salt starts to decrease in viscosity slightly after the solution without. The effect of the salt could be efficient only in the early stage of decompositioning.

Salt Effect on Gel Strength 2%PAC+2%XG
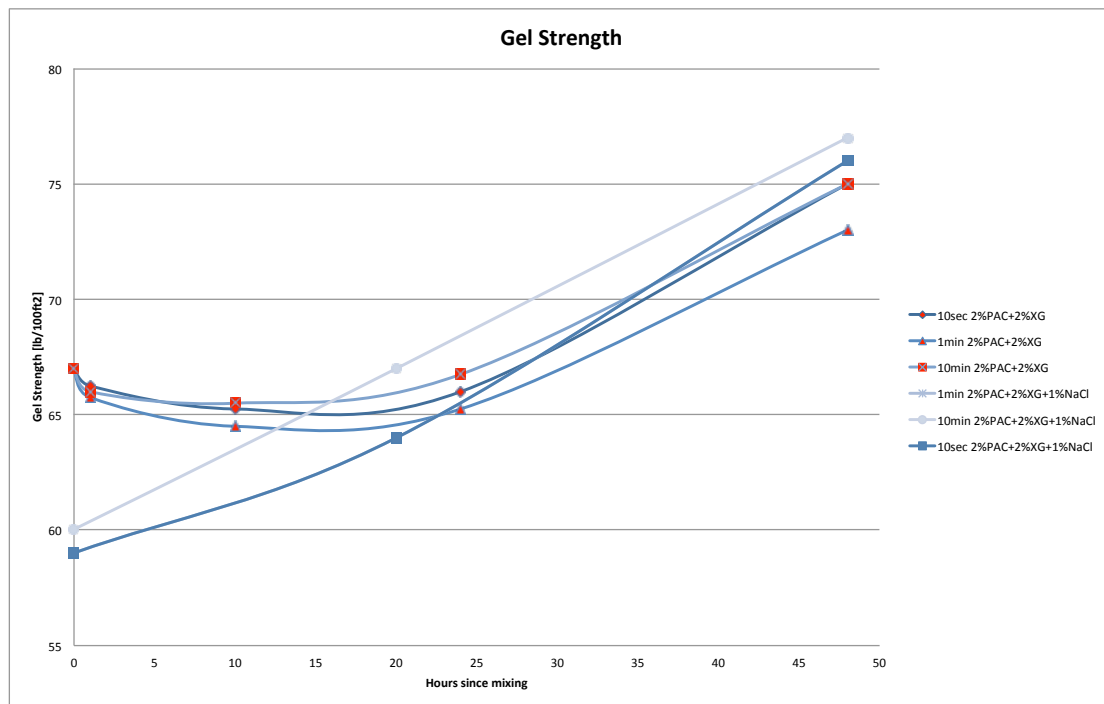
The gel strength for a 2%PAC+2%XG solution with and without 1%NaCl appears to be as good as the same. The lower values seen in Figure 26 just after mixing for the sample with salt is probably a result of longer mixing time than the sample without salt. The fluid is viscoelastic and is thinning when a force is applied, and it regenerates back to a thicker fluid, as seen after 24 hours.

4.1.7 4%PAC+2%NaCl

Samples with 4%PAC have proven to be the most reliable and comparable with previous samples measured by OJR. On account of this 2%NaCl is added to a 4%PAC solution for testing in addition to the 4%PAC+1%NaCl sample. This is to observe if increasing salt concentration is prolonging the fluids ability to retain its initial properties.
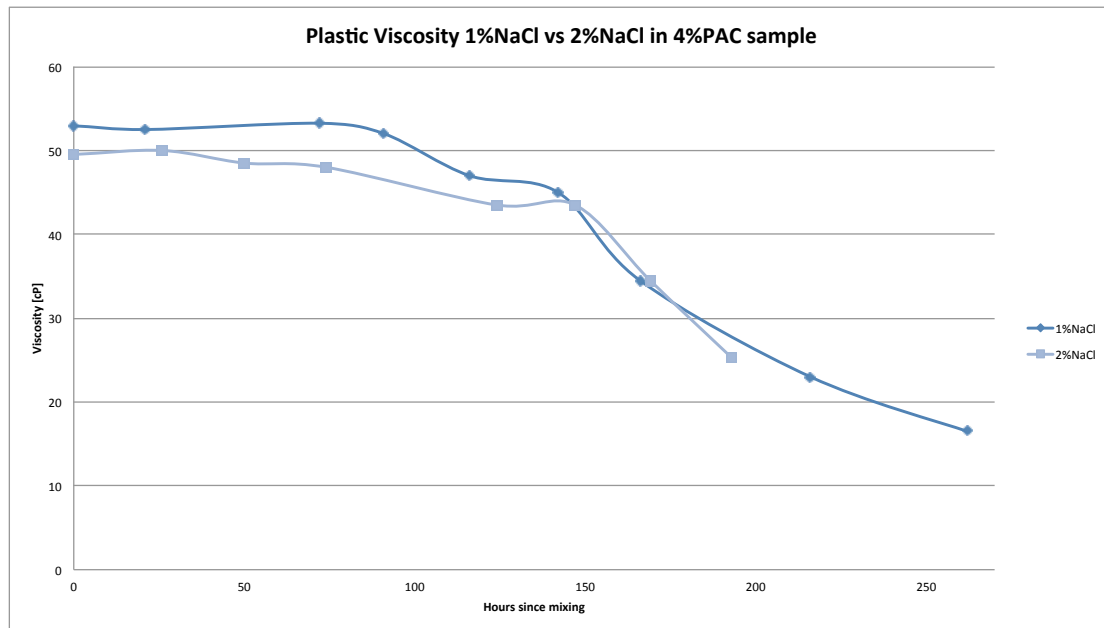
Figure 27: Plastic Viscosity 1%NaCl vs 2%NaCl in 4%PAC Sample

Adding an additional 1%NaCl to a 4%PAC+2%NaCl solution seems to have no effect in terms of enhancing the polymers ability to maintain its properties over time. As shown in Figure 27 they behave approximately the same throughout the whole experiment.
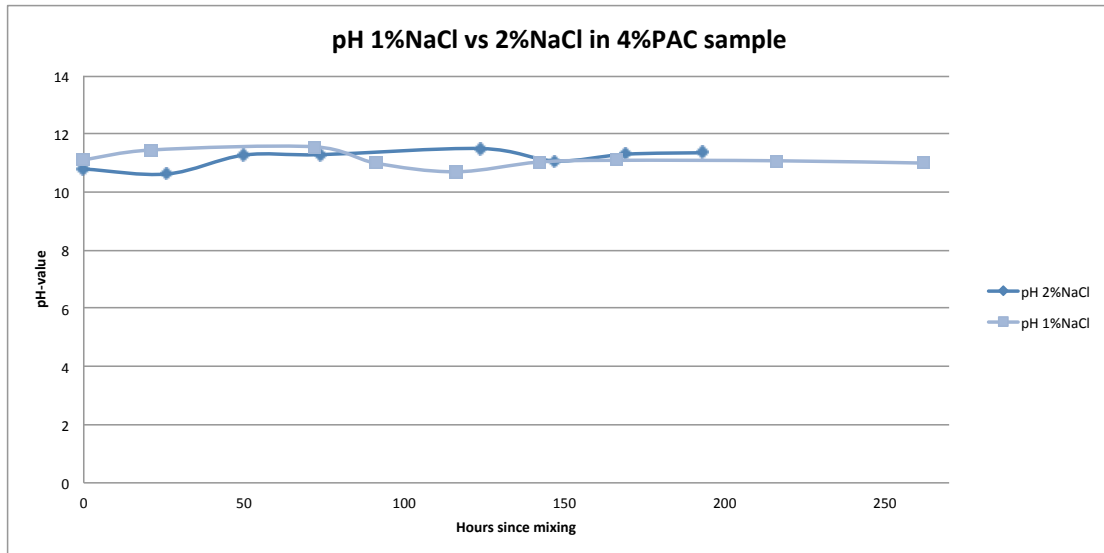
Figure 28: pH 1%NaCl vs 2%NaCl in 4%PAC Sample

Results from pH measurements are shown in Figure 28. The pH is stable between 10 and 12 and the difference between 1% and 2% NaCl are not of any significance.

4.2 Circulated Samples at 25℃

Samples are circulated instead of stored at glass flask to more likely simulate the in-situ effects of aging on a fluid. Samples are mixed identically as before. The non-circulated values are gathered from (Rye 2017).

4.2.1 2%PAC
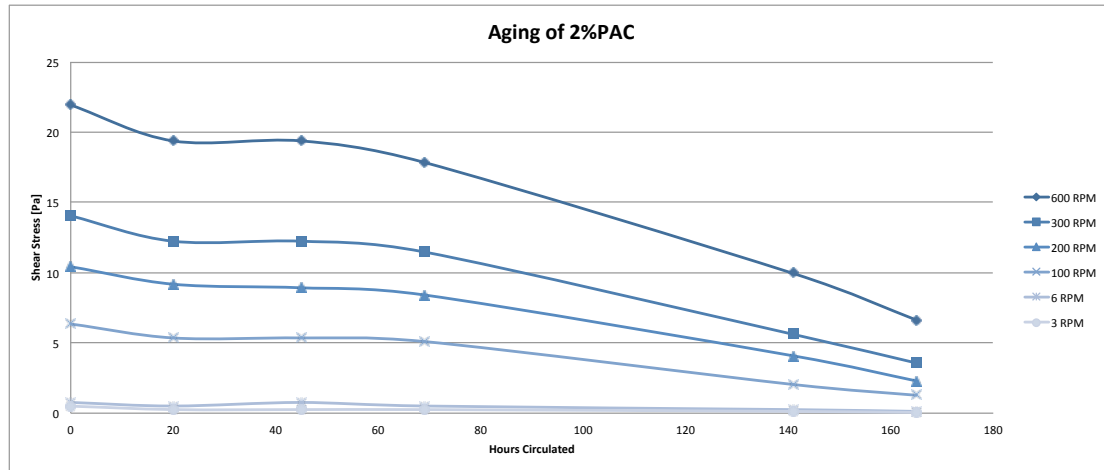
Figure 29: Shear Stress over time for 2%PAC circulated at 25℃

Despite the drop in shear stress the first 20 hours the sample is stable up to around 45 hours. After this point it decreases rapidly in correlations with a decreasing pH value as shown in Figure 30.
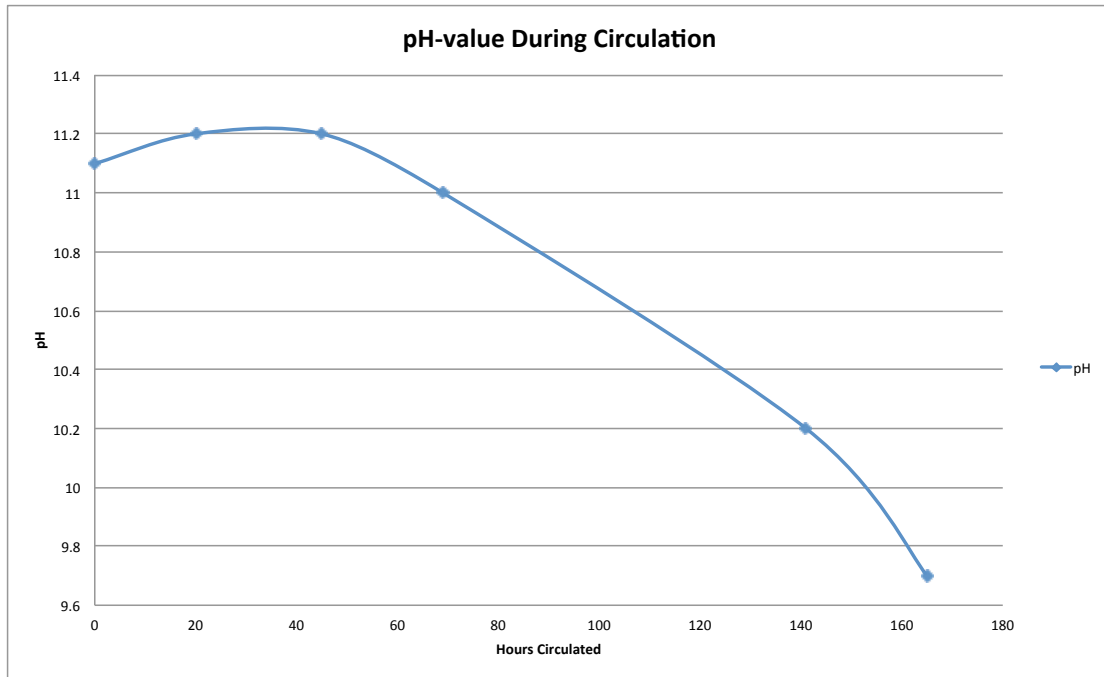
Figure 30: pH 2%PAC circulated over time

As seen in Figure 30 the pH value for the 2%PAC sample circulated is stable for about 50 hours before falling at a steady rate.
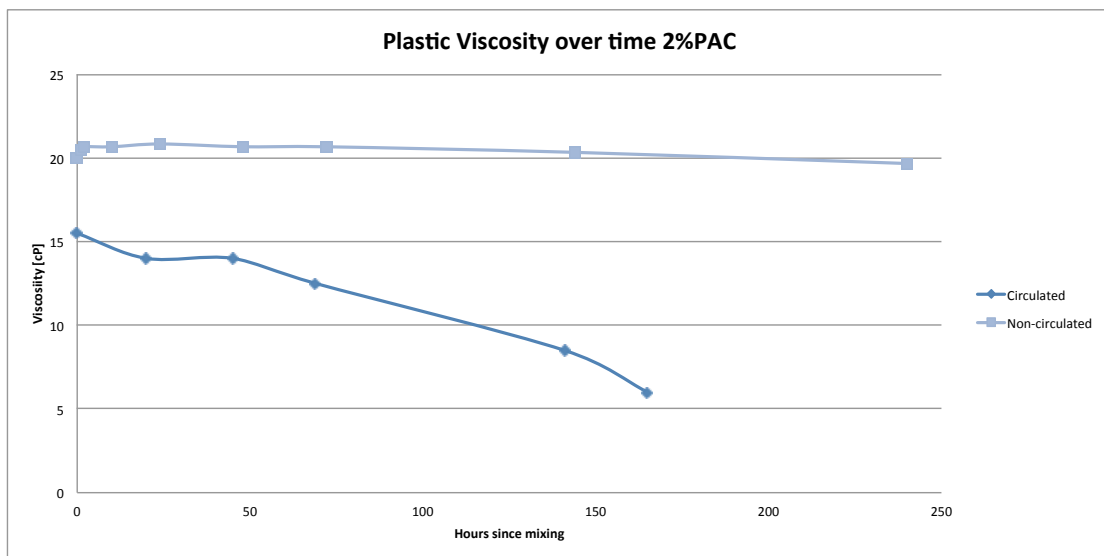
Figure 31: PV over time 2%PAC

The effects of circulation shown in Figure 31 are that the fluids viscosity, instead of being stable, is decreasing with time.

4.2.2 4%PAC
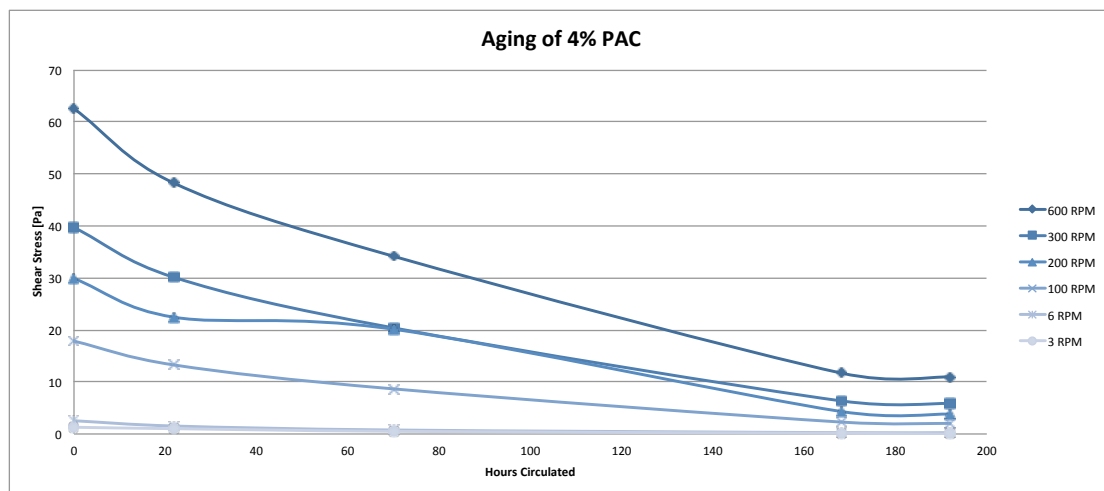
Figure 32: Shear Stress over time 4%PAC circulated

The figure above shows a continuously decrease in shear stress in time for the 4%PAC sample. At around 180 hours it has a tendency to be flattening out, but it is at such a low viscosity.
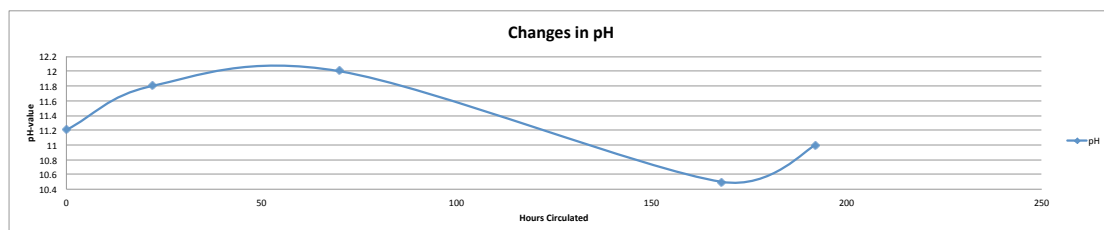
Figure 33: pH over time 4%PAC circulated

The changes in pH for the 4%PAC circulated sample are small and various. It is hard to say if there is some kind of correlation with the shear stress in Figure 32.
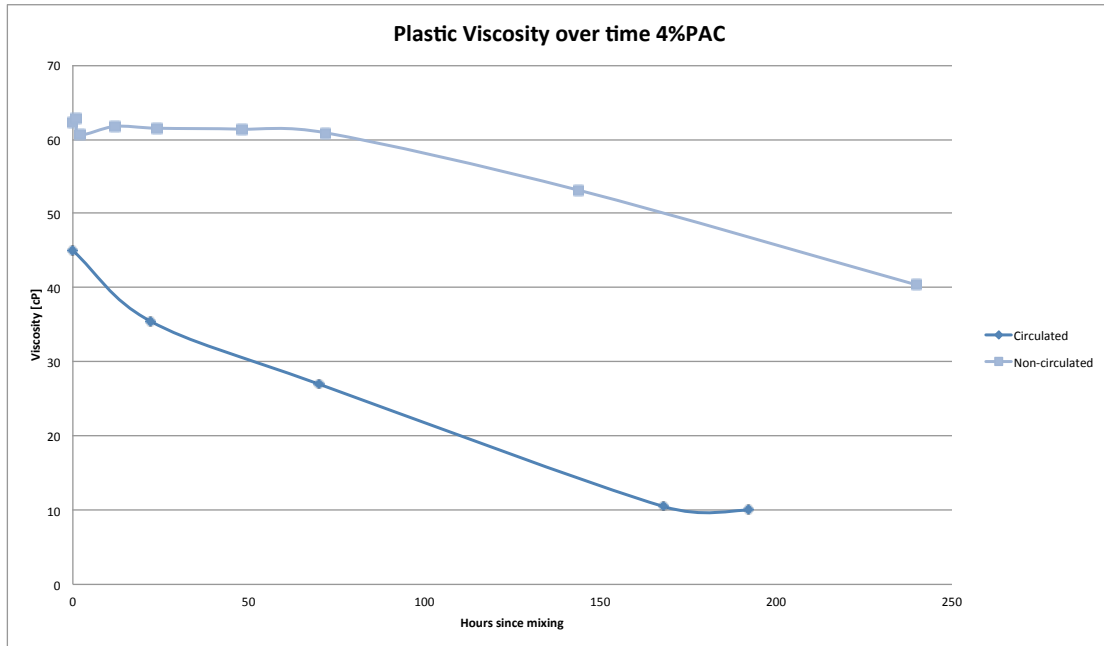
Figure 34: PV over time for 4%PAC circulated vs. non-circulated

In Figure 34 we see that the sample without circulation stays stable up to about 75 hours, while the sample circulated has a continuously decrease from the start. The decrease in viscosity in the circulated sample is a result of stress, and the tendencies of the results implies viscoelastic creep.

4.2.3 2%PAC+1%XG - Pump Failure

A sample of 2%PAC+1%XG was mixed and started circulated in the flow loop. The flow velocity seemed quite slow, but the pump was running. When the tests were supposed to resume 24 hours after start, the pump had stopped. It kept turning on and off and made irregular noise. When the sample was inspected it was clear that it had not been circulated. The loop was emptied and cleaned and pure tap water was attempted circulated without success. The pump kept making the irregular noise and would not circulate.

It was a concern early on that the pump may not be able to comprehend the most viscous samples. Since the pump broke down when circulating xanthan gum there is no point in repairing the existing pump, neither replacing it with an exact model. Trying to find a model that could comprehend such viscous fluids would take weeks, and due to the restricted time period during this thesis, further circulating will unfortunately not be possible.

The fluids properties that lead to pump malfunction were:
Shear Stress: 1021 s^{-1} - 94 Pa, 511 s^{-1} - 74 Pa, 340 s^{-1} - 64 Pa, 170 s^{-1} - 50 Pa, 10 s^{-1} - 18 Pa, 5,1 s^{-1} - 14 Pa.
Plastic Viscosity: 39 cP
Yield Point: 145 lb/100ft^2
pH: 10,6
Test temperature: 28℃

4.2.4 2%PAC+2%XG

As described in the previous chapter 4.2.3 2%PAC+1%XG - Pump Failure the circulation pump was not able to circulate samples containing xanthan gum. The sample containing 2%PAC+2%XG at 25℃ could not be tested.

4.3 Circulated Samples at 50℃

4.3.1 2%PAC
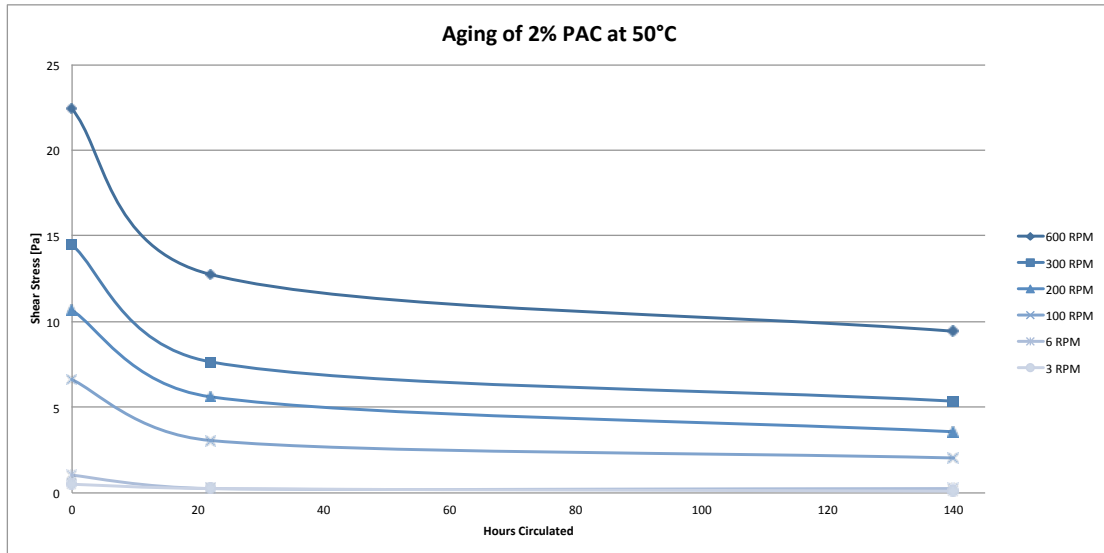
Figure 35: Shear Stress for 2%PAC sample circulated at 50℃

The 2%PAC sample circulated at 50℃ has a sharp drop in shear stress the first 24 hours. It seems to be stabilizing after this point, and has a small decrease over the next 120 hours. The polymer fails under stress and the most likely phenomenon in this case is viscoelastic creep.
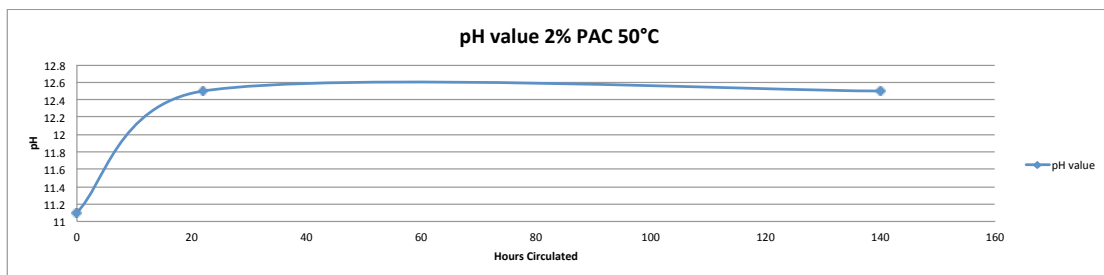
Figure 36: pH over time for 2%PAC sample circulated at 50℃

The pH value presented in Figure 36 shows an increase of about 1 the first 24 hours, the same time as a decrease in shear stress. Also correlating with the shear stress flattening out the pH value behaves similar.
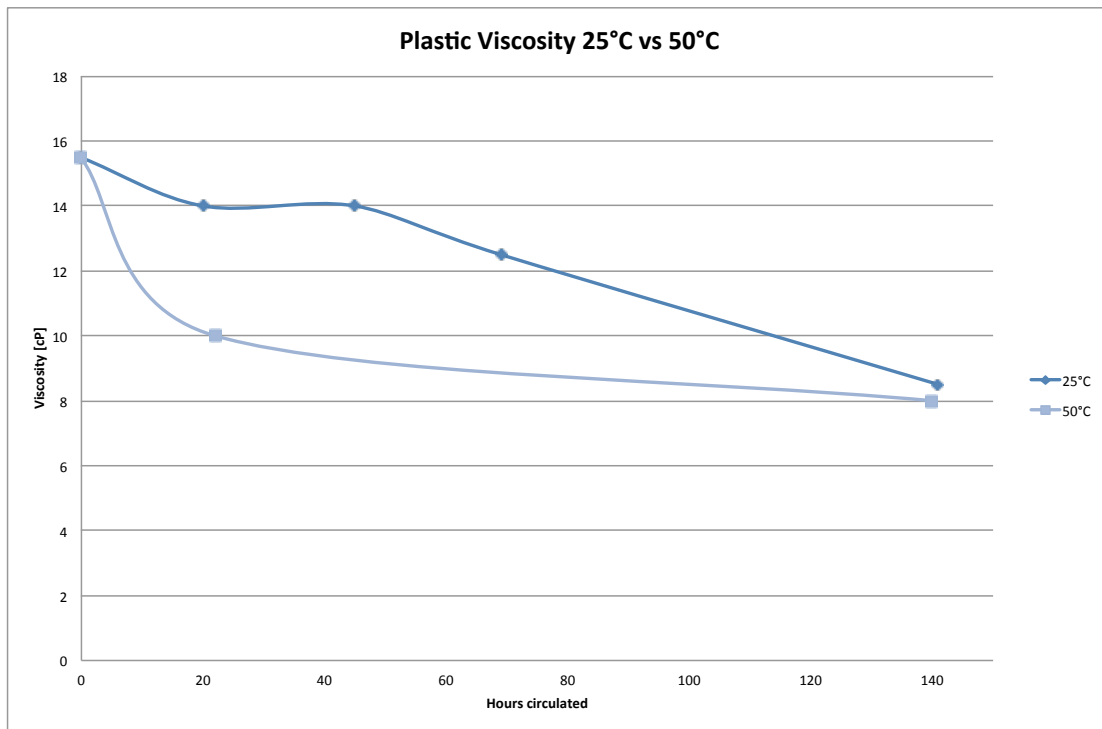
Figure 37: PV over time for 2%PAC 25℃ vs 50℃ circulated

In Figure 37 we see that the 2%PAC circulated at 50℃ has a sharper drop in viscosity the first 24 hours before flattening out. Where as the sample circulated at 25℃ appears more stable before decreasing after around 50 hours.

4.3.2 4%PAC
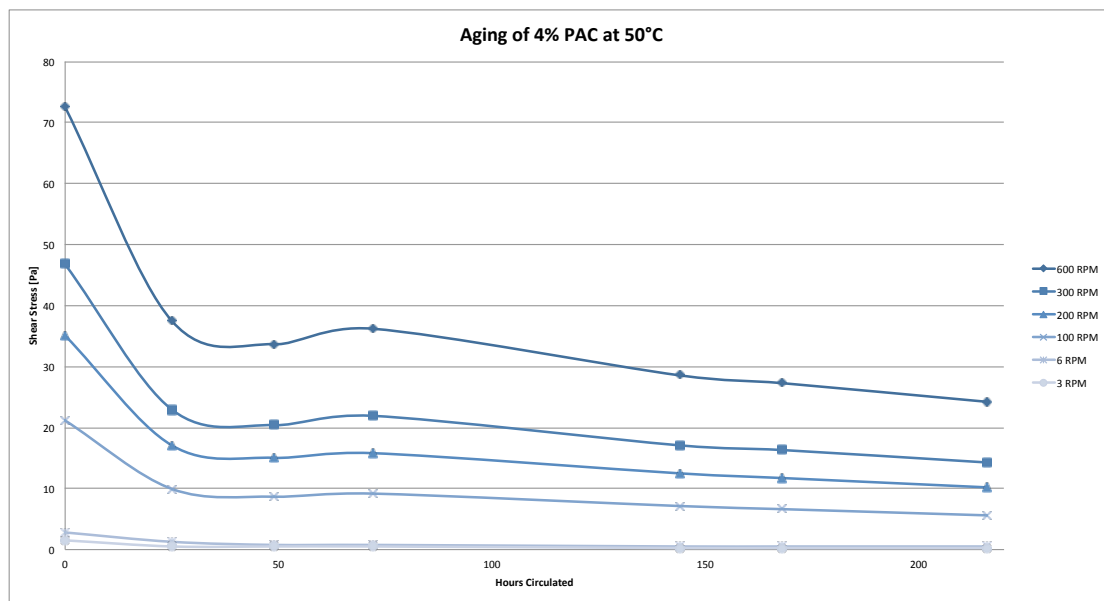
Figure 38: Shear Stress over time for 4%PAC circulated at 50℃

As seen in Figure 38 the shear stress for 4%PAC sample circulated at 50℃ has the sharp drop in shear stress the first 24 hours before it flattens out. The graph shows an increase in shear stress at 72 hours, but it could be an error. In no other samples has there been an increase after it started to show degradation. Looking at notes from testing the measurements taken at the sample at 72 hours were a bit delayed. This may have cooled the sample a bit, and gave the polymer time to regenerate, therefore altering the properties of the sample, which is expected from a viscoelastic fluid.
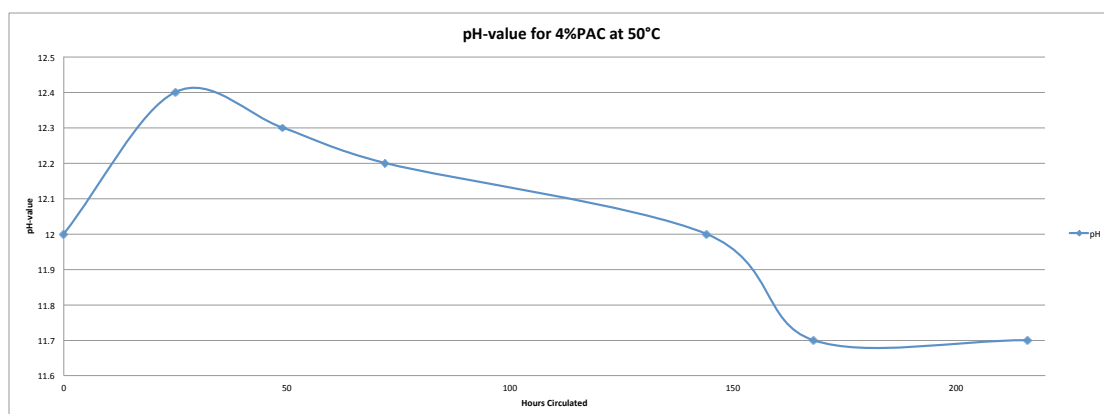
Figure 39: pH over time for 4%PAC circulated at 50℃

The pH value for the 4%PAC sample circulated at 50℃ has a steep inclination the first 24 hours before turning. It then decreases steady. It seems to drop fast after around 170 hours, but the difference in pH is only 0,3.

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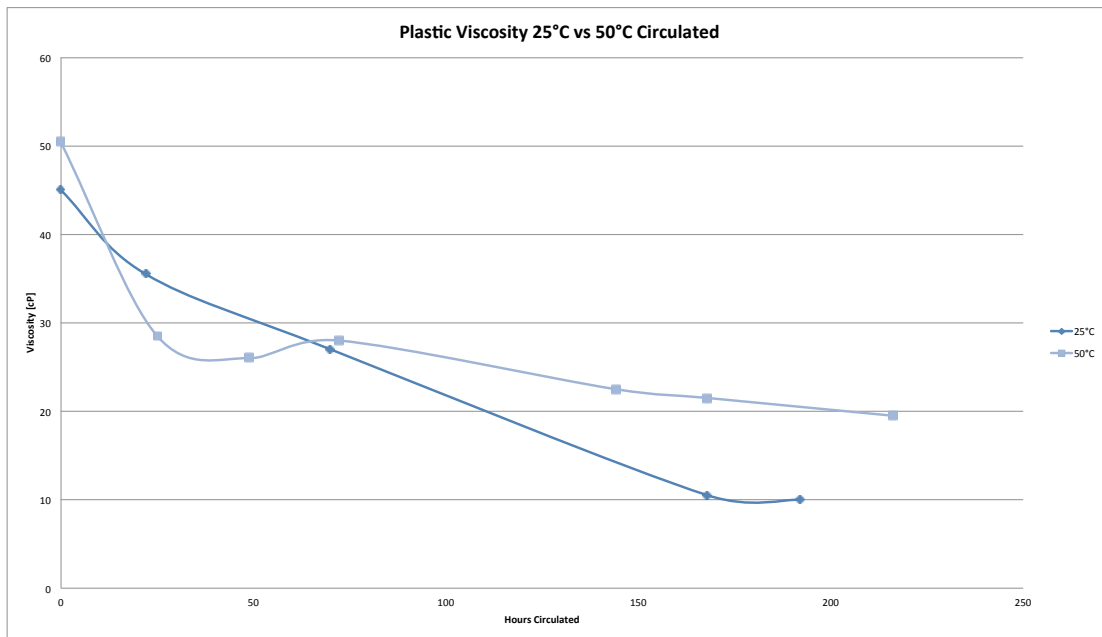
Figure 40: PV over time for 4%PAC 25℃ vs 50℃

Figure 40 illustrates actually that the 4%PAC sample circulated at 25℃ has a faster degradation than the sample circulated at 50℃. It has a steady decrease in shear stress. The 50℃ sample has the steep incline the first 24 hours before degrading at a slower rate.

4.3.3 2%PAC+1%XG

As described in chapter 4.2.3 2%PAC+1%XG - Pump Failure the circulation pump was not able to circulate samples containing xanthan gum. The sample containing 2%PAC+1%XG at 50℃ could not be tested.

4.3.4 2%PAC+2%XG

As described in chapter 4.2.3 2%PAC+1%XG - Pump Failure the circulation pump was not able to circulate samples containing xanthan gum. The sample containing 2%PAC+2%XG at 50℃ could not be tested.

4.4 Temperature-Viscosity

In OJRs thesis he heated some of the samples to 50℃ and observed if this affected the viscosity after mixing and over time. After mixing the samples was stored in airtight glass flasks in room temperature and not re-heated. It was suggested to investigate the influence on a sample that was exposed to heat in a short period of time compared to a sample that was circulated simultaneously with being exposed to heat.

4.4.1 2%PAC
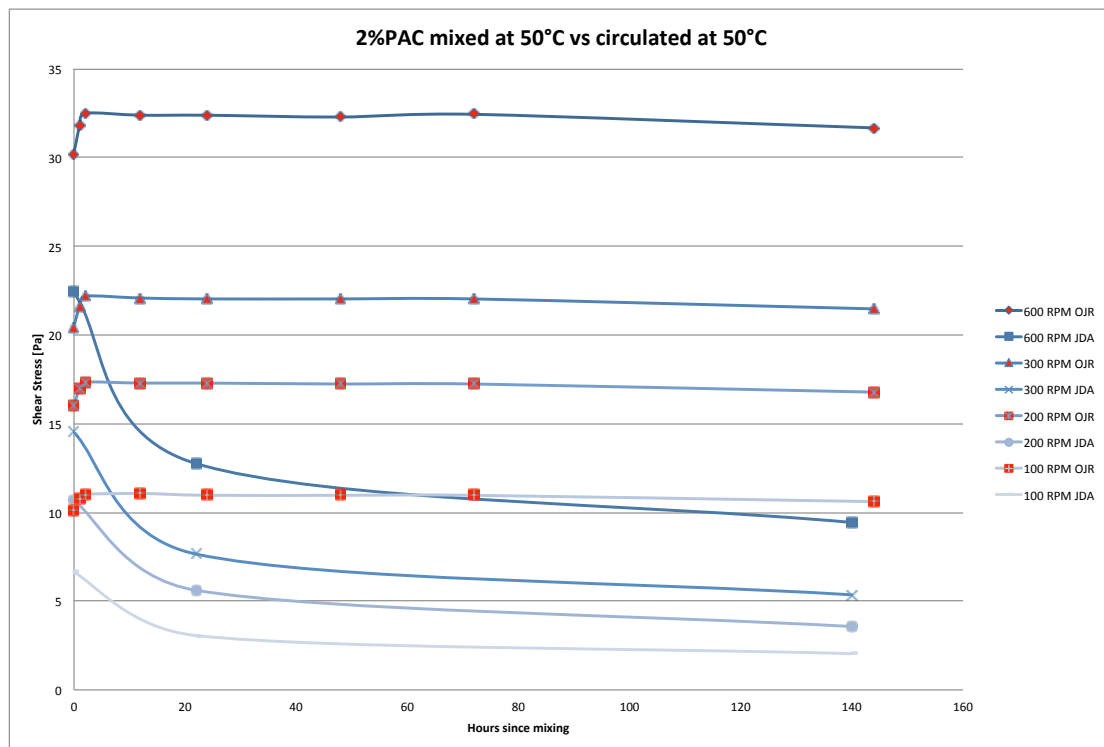
Figure 41: Shear Stress 2%PAC mixed at 50℃ vs circulated at 50℃

The data presented in Figure 41 shows first of all that in general that the samples mixed at 50℃ has a significantly higher value of shear stress then the sample mixed at 25℃ but constantly circulated at 50℃, which could be a result of higher solubility in higher temperature. Since the sample mixed by OJR are done months before the one in this project, we cannot say that because of the higher temperature when mixing gives you a higher viscosity. Along with a possible different mixing method it gives a high margin of error.

The sample constantly circulated at 50℃ has that sharp drop in shear stress the first 24 hours that have been observed in several of the other circulated samples. Where as the sample without circulation has a flat and steady curve. The circulated samples after about 24 hours have a slight higher decline then the non-circulated sample.
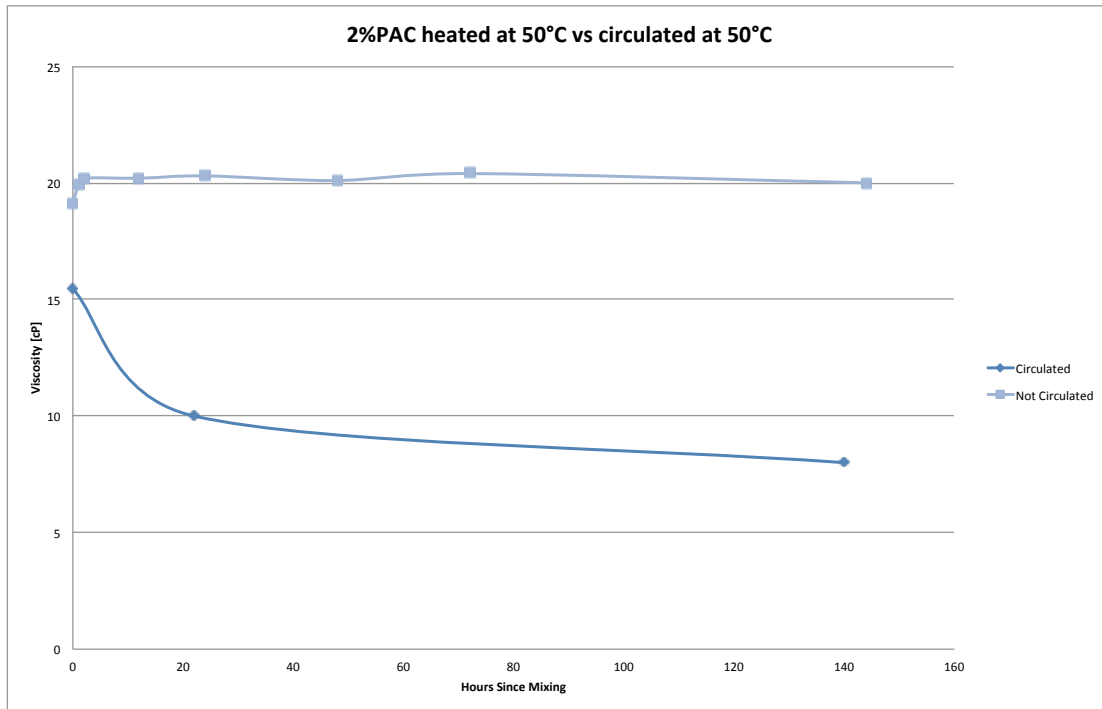
Figure 42: Plastic Viscosity 2%PAC heated at 50°C vs circulated at 50°C

Figure 42 shows that the PV has the same tendencies as shear stress in Figure 41. The sample circulated at 50℃ drops in viscosity immediately before incline become gentler.

4.4.2 4%PAC
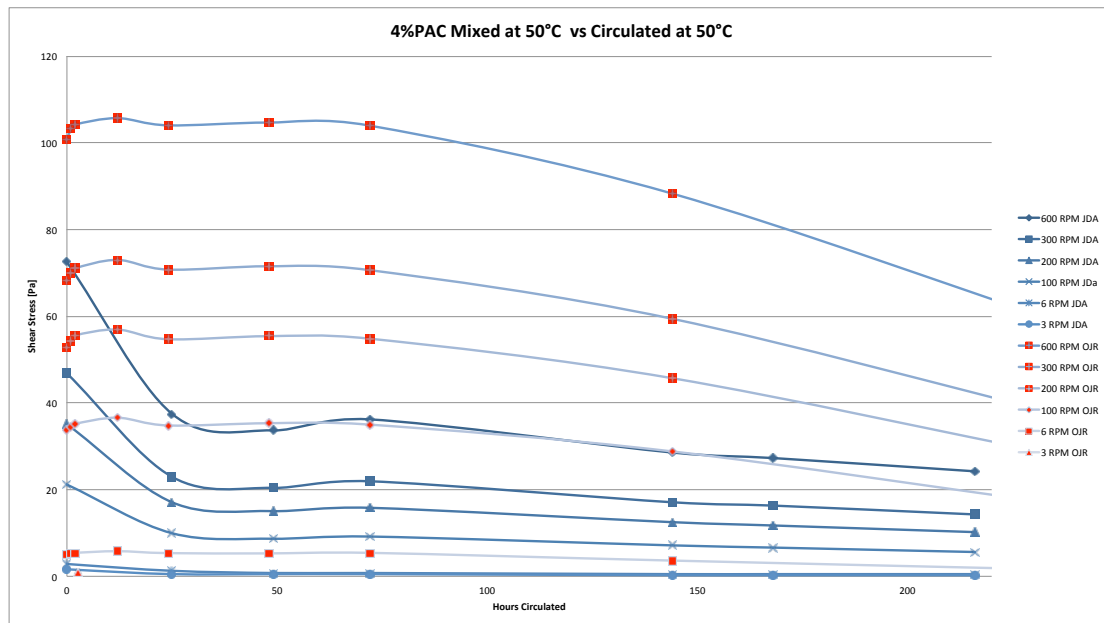
Figure 43: Shear Stress 4%PAC Mixed at 50℃ vs circulated at 50℃

From Figure 43 we can see that the 4%PAC sample mixed at 50℃ has an initially higher viscosity than the sample constantly circulated at 50℃. The circulated sample has the now characteristic drop in shear stress the first 24 hours or so, in contrast to the non-circulated sample that maintains its initial properties for about 75 hours. A sample mixed at 50℃ has a higher initial viscosity than an identical sample mixed at 25℃ (Rye 2017).
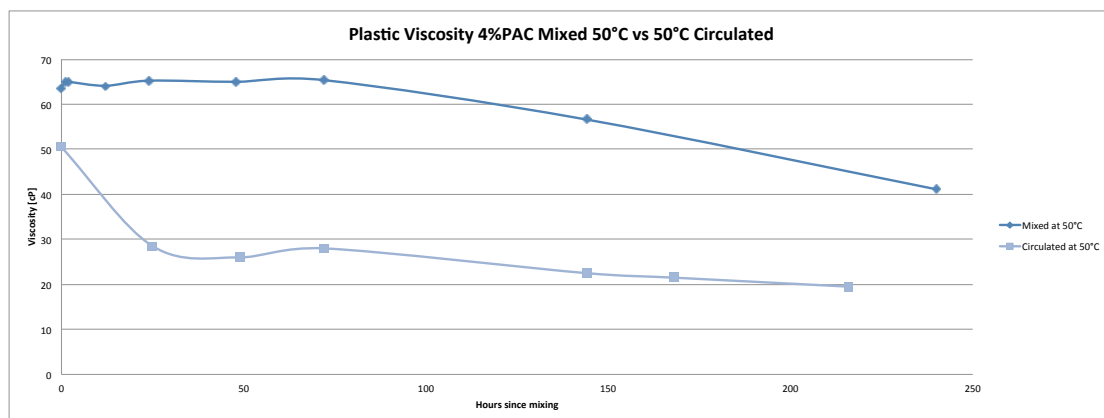
Figure 44: Plastic Viscosity 4%PAC Mixed 50°C vs 50°C Circulated

Figure 44 shows the same as seen in Figure 43 a higher initial viscosity and a large decrease the first 24 hours for the circulated sample. They both seem to have a similar degradation after 75 hours.

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5 Discussion

Observations made from the results of measurements and potential concerns regarding test methods and compositions are presented in this chapter.

Trying to duplicate the exact results that were presented in previous thesis have been a challenge all along, often the initial viscosity immediately after mixing has been lower than the viscosities obtained by Rye. Before testing was begun, the methods of measuring additives and mixing were demonstrated by Rye to ensure that the results would be as similar as possible. Fann 35 viscometer was calibrated, as well as there was a seamless transition between Ryes measurements and the measurements for this project as they were overlapping. Muds are complex, but it should been able to replicate the results obtained by Rye in such controlled environment as a laboratory. Small dissimilarities in mixing and in time spent mixing has probably influenced the properties of the samples made. Time spent on mixing should be logged; the shear stress exerted on the fluid will affect its properties. Temperatures will increase with longer mixing time, which could increase the polymers solubility and/or decrease as a result of thermal degradation.

All of the solutions with various concentrations of both PAC and xanthan gum show thixotropic behavior. In every sample the rheological properties have decreased with time.

pH measurements have shown that when the solutions start to degrade there is often a decrease in pH, but the decrease is small and to establish a correlation there would have to be a more detailed analysis.

By adding salt to the polymer solutions the expected outcome was to increase the time the solution were able to maintain its initial rheological characteristics. In a 2%PAC solution there has been little to no improvement, but in more viscous solutions, 4%PAC and solutions containing xanthan gum, the degradation is slower than in solutions without salt.

Comparing samples that are stored stationary against samples that are circulated both at 25°C we observe, what is most likely, shear stress affecting the fluid and accelerates the decomposing of polymers. Particularly the first 24 hours it is seen, in both fluids with 2%PAC and 4%PAC, a sharp decrease in viscosity before straightening out and the degeneration has a more moderate declining trend. These results correspond with the theory that a polymer under stress ultimately fails and loose its rheological characteristics rapidly before the decrease declines.

When samples with the same composition as samples circulated at 25°C were circulated at 50°C similar tendencies was observed but amplified. The steep decrease in viscosity the first 24 hours is greater with the elevated temperature. Increased temperature along with shear stress applied to polymers seems to decrease its lifespan. It was expected to have a greater decrease in viscosity due to thermal degradation.

The influence of a short heat exposure on a fluid compared to a fluid circulated while being exposed to heat were as predicted that the shear stress applied would decompose the polymers at a higher rate than without. The environment that it is in constantly affects the fluid, and it is not credible to make any assumptions that a fluid that was once exposed to heat would have the same changes in properties over a longer time period as a fluid that is constantly exposed to both heat and shear stress.

This project has used concentrations of both PAC and xanthan gum that are fairly high compared to the actual concentrations that would be used in an eventual drilling fluid. When samples with xanthan gum, and especially in the 2%PAC+2%XG+1%NaCl sample, were tested it was observed that the dial readings from the Fann 35 viscometer varied, and increased, within a short time period. This fluid is probably easily affected by the shear stress exerted from the Fann 35 viscometer and small differences in procedures will significantly affect the results. It was mentioned in 2.2 Xanthan Gum that temperature, when dissolving xanthan gum, could greatly affect the result, and neither the previous mixing by Rye and in this project are accurate enough in monitoring the temperature when mixing. Therefore test results from experiments containing xanthan gum cannot be considered credible.

6 Conclusion

The conclusion chapter will re-state the objectives and hypothesis presented in the introduction with corresponding results from experiments.

The first task of the project was to observe the effects of NaCl on samples containing PAC and PAC + Xanthan Gum. The effect of salt added in the samples was expected to result in a longer life span, and more continuity in its rheological characteristics. Salt should have nullified the bacteria effectiveness and therefore prevented degradation of mud properties. A 4%PAC solution with 1%NaCl had a decrease in shear stress of about 30 Pa at 1021 s^{-1} after 264 hours, while the one without salt decreased about 35 Pa at 1021 s^{-1} after 240 hours. The 2%PAC+1%XG solution with 1%NaCl decreased about 30 Pa at 1021 s^{-1} after 242 hours while the one without salt had a decrease of 40 Pa at 1021 s^{-1} after 240 hours. And by adding 1%NaCl in a 2%PAC+2%XG solution it started to degrade 24 hours after identical samples without salt. Increasing the salt concentration from 1% to 2% in a 4%PAC solution had no effect and they showed identical behavior.

The second stage of the experiments was to compare aging on flask with circulated aging at 25℃. By continuously circulating the fluid we expected to see a more significant and rapid decrease in viscosity in time due to the stresses applied. The polymers behave viscoelastic in both high and relatively low concentrations. The solutions show viscoelastic creep behavior where the polymer fails when exposed to stress.

Samples circulated at 25℃ and circulated at 50℃ were compared. We expected to observe that samples that were circulated when exposed to heat would have a greater factor of degradation. The statement that polymers are sensitive to temperatures and Figure 2 in chapter 2.4 Thermal Polymer Degradation is supported by the findings in this experiment. Plastic viscosity has decreased with increasing temperature in both solutions containing 2%PAC and 4%PAC. By increasing the temperature from 25℃ to 50℃ the plastic viscosity decreased by an additional 4 cP in a 2%PAC solution and 17 cP in a 4%PAC solution. The increased temperature seems to have enhanced the viscoelastic creep behavior.

At last previously heated, when mixed, samples were compared to new continuous heated and circulated samples at 50℃. It was said in the thesis by Rye that it could be a relation between samples once heated between samples hot rolled, but samples that were hot rolled were expected to decrease in viscosity with a higher rate. The findings from the experiments confirm that the viscosity changes are not similar over a period of time.

7 Self-Assessment and Further work

There are steps in this projects that should be questioned and considered improved if project is to be continued:

- o Log the time spent mixing a sample.
- o Use a container in the flow loop more resistant to corrosion.
- o Strict monitoring of temperature when dissolving xanthan gum

Possible topics for developing the project further on:

- o Consider revising the concentrations used in this project and use concentrations applicable to drilling fluids in use.
- o Investigate impact by various agitators on fluids.
- o Expose fluids to temperatures >50℃ and at least 80℃.
- o Compare fluids circulated and stationary when exposed to heat to isolate the effects of shear stress in heated environment.
- o Measurements done by Anton Parr rheometer for more accurate results at low shear rates.

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Appendices

Appendix A Equipment

Fann Viscometer Model 35SA(Fann)

Mixer

Janke & Kunkel

IKA-Labortechnik

RW 20 DZM

(IKA)

Heater and magnet mixer

Heidolph MR Hei-End

AC 230/240V 50/60Hz 825W

30-1400 1/min

(Scientific)

Scale

Sartorius Combics 1

(Scales)

Scale

Sartorius

CP 4202 S

Max 4200g

d= 0,01g

Circulation Pump

A-collection A3.2 25-40 180

Voltage: 230 V

Electric power: 4-23 W

Operational temperature: -10 - +110℃

Maximum pressure: 10 bar

(Ahlsell)

Flow Loop

A-collection circulation pump

Container: diameter = 18cm, height = 15cm

Outlet hose: diameter = 13mm, length = 90cm

Inlet hose: diameter = 19mm, length = 22cm

pH Meter

pHenomenal

pH 1000 L

pH-accuracy: $\pm 0{,}005 \pm 1$digit

(Lumitron)

Heated Cabinet

Termaks TS 9430

Capacity: 430 liter

Temperature range: up to 250℃

Temperature accuracy: ± 1℃

(Termaks)

Appendix B – Test Data

No circulation - 25℃

2%PAC+1%NaCl

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [°C]	pH	3	6	100	200	300	600
0	25	11,1	0,51	0,765	6,375	10,455	14,025	21,93
20	28	11,2	0,255	0,51	5,355	9,18	12,24	19,38
45	29	11,2	0,255	0,765	5,355	8,925	12,24	19,38
69	29	11	0,255	0,51	5,1	8,415	11,475	17,85
141	27	10,2	0,1275	0,255	2,04	4,08	5,61	9,945
165	27	9,7	0,051	0,1275	1,275	2,295	3,57	6,63

Sample Data			Gel strength			PV	YP
Time	Test temp	pH	10sec	1min	10min	[cP]	θ300-PV
0	24	10,6	2	2	1,5	15,5	12,75
20	23	10,65	2	2	2	16	12,5
40	23	10,75	2,5	2	2	16	12,5
192	25	10,25	1,5	2,5	1	11,75	3,25
216	25	10,3	0,5	1	1	8,5	3

2%PAC+1%NaCl - Test Two

Sample Data			Fann Viscometer RPM					
Time	Test temp	pH	3	6	100	200	300	600
0	25	11,2	0,255	0,51	1,785	3,315	4,59	8,67
24	25	11,2	0,255	0,51	2,04	3,57	4,7175	8,5425
45	25	11,15	0,255	0,51	1,9125	3,4425	4,7175	8,415
95	25	11,25	0,255	0,51	2,04	3,315	4,7175	8,16
114	26	10,685	0,1275	0,255	1,6575	3,06	4,08	7,2675
142	25	10,05	0,255	0,51	1,785	2,9325	3,9525	6,63
166	24	10,25	0,1275	0,255	1,275	2,295	3,06	5,61
190	26	10,28	0,11475	0,255	1,02	2,1675	2,9325	5,2275

Sample Data			PV	YP
Time	Test temp	pH	[cP]	θ300-PV
0	25	11,2	8	1
24	25	11,2	8	1,5
45	25	11,15	7,5	2
95	25	11,25	7,5	2
114	26	10,7	7,5	1,5
142	25	10,1	7	2
166	24	10,3	7	1
190	26	10,3	7	1

4%PAC+1%NaCl

Sample Data			Fann Viscometer RPM					
Time hrs	Test temp [°C]	pH	3	6	100	200	300	600
0	25	11	0,51	1,02	8,415	15,045	21,0375	35,955
24	25	11,15	0,3825	0,765	8,0325	14,4075	20,145	34,935
168	26	10,95	0,3825	0,6375	7,7775	14,025	19,635	33,5325
192	24	11,05	0,3825	0,765	7,65	13,8975	19,38	33,5325
264	25	11,25	0,31875	0,51	5,355	9,945	14,025	24,8625

Sample Data			Gel strength			PV	YP
Time hrs	Test temp	pH	10sec	1min	10min	[cP]	θ300-PV
0	25	11	2	2	2	29,25	12
24	25	11,15	2	2	2	29	10,5
168	26	10,95	1,75	2	2	27,25	11,25
192	24	11,05	2	1,25	1,25	27,75	10,25
264	25	11,25	1,25	1	1	21,25	6,25

4%PAC+1%NaCl - Test Two

Sample Data			Fann Viscometer RPM					
Time	Test temp	pH	3	6	100	200	300	600
0	25	11,1	2,04	3,57	21,93	36,21	47,94	74,97
21	25	11,45	2,04	3,4425	21,675	35,445	47,685	74,46
72	25	11,56	2,04	3,1875	20,7825	34,425	46,0275	73,185
91	25	11	1,9125	3,06	20,4	33,66	44,88	71,4
116	25	10,7	1,6575	2,4225	18,36	30,09	40,035	64,005
142	25	11,035	1,4025	2,04	15,555	25,755	34,68	57,63
166	26	11,095	0,8925	1,53	11,73	20,655	27,795	45,39
216	25	11,08	0,6375	0,765	6,63	11,73	16,32	28,05
262	25	11	0,255	0,3825	3,825	7,395	10,455	18,87

Sample Data			PV	YP
Time	Test temp [°C]	pH	[cP]	θ300-PV
0	25	11,1	53	41
21	25	11,45	52,5	41
72	25	11,56	53,25	37
91	25	11	52	36
116	25	10,7	47	31,5
142	25	11,035	45	23
166	26	11,095	34,5	20
216	25	11,08	23	9
262	25	11	16,5	4

2%PAC+1%XG+1%NaCl

Sample Data			Fann Viscometer RPM					
Time hrs	Test temp [°C]	pH	3	6	100	200	300	600
0	24	9,6	8,925	11,475	35,955	48,96	58,65	78,285
22	22	7,625	9,18	11,73	34,17	46,665	56,61	76,245
48	22	6,9	10,8375	13,005	29,1975	37,995	44,88	59,5425
145	24	6,95	17,085	18,615	30,855	37,485	42,84	52,53
168	23	5,4	16,9575	18,36	30,6	36,8475	42,33	51,51
193	23	5,75	16,83	18,4875	30,6	36,5925	41,82	51
217	23	5,8	16,83	18,36	30,6	36,465	41,6925	50,8725
242	22	5,9	17,2125	18,87	30,6	36,21	41,4375	50,3625
266	22	5,9	17,4675	18,87	30,855	36,8475	42,075	50,745
360	22	6,25	17,4675	18,87	30,855	36,72	41,565	51
384	22	6,2	17,34	18,87	30,345	36,72	41,055	49,725
408	24	6,05	17,34	18,87	30,4725	36,465	41,31	49,98

Sample Data			Gel strength			PV	YP
Time hrs	Test temp [°C]	pH	10sec	1min	10min	[cP]	θ300-PV
0	24	9,6	21,5	21,5	22	38,5	76,5
22	22	7,625	22	21,75	23	38,5	72,5
48	22	6,9	24,5	24,75	26,75	28,75	59,25
145	24	6,95	33,5	35,5	41	19	65
168	23	5,4	33,5	35,75	41	18	65
193	23	5,75	34,5	36,5	41	18	64
217	23	5,8	34	36,25	41	18	63,75
242	22	5,9	33,5	36	41	17,5	63,75
266	22	5,9	34,5	37	41	17	65,5
360	22	6,25	34	36,5	40	18,5	63
384	22	6,2	34	37	40	17	63,5
408	24	6,05	34,5	37	40	17	64

2%PAC+2%XG+1%NaCl

Sample Data			Fann Viscometer RPM					
Time hrs	Test temp	pH	3	6	100	200	300	600
0	26	11,2	33,15	39,78	95,37	118,83	132,6	
20	25	11,2	34,68	40,545	86,445	107,61	123,675	
48	25	7,1	40,29	44,625	76,5	91,8	104,55	132,855
72	24	6,25	45,39	49,47	77,52	91,035	100,98	124,44
96	26	5,9	45,645	49,725	76,5	88,74	99,45	120,87
146	25	5,8	45,2625	49,215	74,97	86,955	97,41	118,7025
192	26	6,05	44,88	48,705	73,95	85,68	95,37	116,28
216	25	5,88	43,86	47,685	72,675	82,875	95,115	114,8775

Sample Data			Gel strength		
Time hrs	Test temp	pH	10sec	1min	10min
0	26	11,2	59	59	60
20	25	11,2	64	64	67
48	25	7,1	76	76	77
72	24	6,25	83	82,75	89
96	26	5,9	84	82,5	90,5
146	25	5,8	82	82	89
192	26	6,05	82	80,5	89

4%PAC+2%NaCl

Sample Data			Fann Viscometer RPM					
Time hrs	Test temp	pH	3	6	100	200	300	600
0	26	10,8	2,04	3,06	17,85	30,6	41,565	66,81
26	25	10,625	1,785	2,805	17,2125	28,56	39,015	64,515
50	24	11,275	1,785	2,55	16,83	28,56	38,76	63,495
74	26	11,29	1,785	2,55	16,83	28,56	38,76	63,24
124	25	11,5	1,275	2,1675	15,3	25,8825	34,68	56,865
147	26	11,0725	1,21125	1,9125	13,77	23,205	31,62	53,805
169	26	11,305	0,765	1,53	10,965	18,7425	25,245	42,84
193	25	11,355	0,3825	0,765	7,65	13,515	18,4875	31,365

Sample Data			PV	YP
Time hrs	Test temp	pH	[cP]	θ300-PV
0	26	10,8	49,5	32
26	25	10,625	50	26,5
50	24	11,275	48,5	27,5
74	26	11,29	48	28
124	25	11,5	43,5	24,5
147	26	11,0725	43,5	18,5
169	26	11,305	34,5	15
193	25	11,355	25,25	11

Circulated - 25℃

2%PAC

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [°C]	pH	3	6	100	200	300	600
0	25	11,1	0,51	0,765	6,375	10,455	14,025	21,93
20	28	11,2	0,255	0,51	5,355	9,18	12,24	19,38
45	29	11,2	0,255	0,765	5,355	8,925	12,24	19,38
69	29	11	0,255	0,51	5,1	8,415	11,475	17,85
141	27	10,2	0,1275	0,255	2,04	4,08	5,61	9,945
165	27	9,7	0,051	0,1275	1,275	2,295	3,57	6,63

Sample Data			Gel strength			PV	YP
Circulated	Test temp [C]	pH	10sec	1min	10min	[cP]	θ300-PV
0	25	11,1	1	1,5	1,5	15,5	12
20	28	11,2	1	1,5	1	14	10
45	29	11,2	1	1,5	1	14	10
69	29	11	1	1,5	1	12,5	10
141	27	10,2	0,5	1	1	8,5	2,5
165	27	9,7	0,5	0,7	1	6	1

4%PAC

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [C]	pH	3	6	100	200	300	600
0	25	11,2	1,275	2,55	17,85	29,835	39,78	62,73
22	28	11,8	1,02	1,53	13,26	22,44	30,09	48,195
70	28	12	0,51	0,765	8,67	20,145	20,4	34,17
168	29	10,5	0,1275	0,255	2,295	4,335	6,375	11,73
192	27	11	0	0,255	2,04	3,825	5,865	10,965

Sample Data			Gel strength			PV	YP
Circulated	Test temp [C]	pH	10sec	1min	10min	[cP]	θ300-PV
0	25	11,2	4	4	4	45	33
22	28	11,8	3	3	3	35,5	23,5
70	28	12	2	2	1,5	27	13
168	29	10,5	0,5	0,5	1	10,5	2
192	27	11	0,5	0,5	0,5	10	1,5

2%PAC+1%XG

Pump Malfunction, no tests were possible to carry out.

2%PAC+2%XG

Pump Malfunction, no tests were possible to carry out.

Circulated - 50℃

2%PAC

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [°C]	pH	3	6	100	200	300	600
0	25	11,1	0,51	1,02	6,63	10,71	14,535	22,44
22	50	12,5	0,255	0,255	3,06	5,61	7,65	12,75
140	50	12,5	0,102	0,255	2,04	3,57	5,355	9,435

Sample Data			Gel strength			PV	YP
Circulated	Test temp [°C]	pH	10sec	1min	10min	[cP]	θ300-PV
0	25	11,1	1,5	1,5	1,5	15,5	13
22	50	12,5	1	1	1	10	5
140	50	12,5	0,5	1	0,5	8	2,5

4%PAC

Sample Data			Fann Viscometer RPM					
Circulated	Test temp [C]	pH	3	6	100	200	300	600
0	25	12	1,53	2,805	21,165	35,19	46,92	72,675
25	50	12,4	0,51	1,275	9,945	17,085	22,95	37,485
49	50	12,3	0,51	0,765	8,67	15,045	20,4	33,66
72	50	12,2	0,51	0,765	9,18	15,81	21,93	36,21
144	50	12	0,255	0,51	7,14	12,495	17,085	28,56
168	50	11,7	0,255	0,51	6,63	11,73	16,32	27,285
216	50		0,255	0,51	5,61	10,2	14,28	24,225

Sample Data			Gel strength			PV	YP
Circulated	Test temp [C]	pH	10sec	1min	10min	[cP]	θ300-PV
0	25	12	4,5	5	4	50,5	41,5
25	50	12,4	2	2	2	28,5	16,5
49	50	12,3	2	2	1,5	26	14
72	50	12,2	2	2	2	28	15
144	50	12	1,5	1,5	1,5	22,5	11
168	50	11,7	1	1,5	1,5	21,5	10,5
216	50	11,7	1	1	1	19,5	8,5

2%PAC+1%XG

Pump Malfunction, no tests were possible to carry out.

2%PAC+2%XG

Pump Malfunction, no tests were possible to carry out.

Appendix C - Notes During Experiments

Non-Circulated Samples

2%PAC+1%NaCl

1a has decreased in viscosity much faster than 1b. pH stable.

2%PAC+1%NaCl Test Two

All additive particles has dispersed and dissolved properly. Still the viscosity seems to be low, and even lower than test one.
Some particles seem to have flocculated after 24 hours.

2%PAC+1%NaCl

The time between testing has been far apart due to no access to the lab on weekends and sickness. Sample a and b are similar. pH stable.

4%PAC+1%NaCl

Both a and b are similar. They show slow or no decrease in viscosity after 192 hours. pH stable.
After waiting over 200 hours the sample has shown a decrease in viscosity.

4%PAC+1%NaCl Test Two

The second sample shows a higher viscosity than test two, and is closer to OJRs results.
Some particles seem to have flocculated after 24 hours.

All in all comparing with Ole Julius samples the viscosity is significantly lower, but the sample may seem to be stable for a longer time period.
The samples separate in glass flask after every test point.

2%PAC+1%XG+1%NaCl

Having trouble dissolving especially Xanthan Gum. Large lumps are created which are hard to break.

Thought that the lumps had dissolved, but when transferring the samples to jars, some lumps were seen.

This gives an additional uncertainty to the results.

Lumps of XG have dissolved over night. But gas bubbles are dispersed in the sample.

pH has decreased continuously for both 4 a and b after mixing.

The viscosity has been stable for over 380 hours and shows no signs of changing.

2%PAC+2%XG+1%NaCl

All additives seem to have dissolved. The fluid is apparently very thick, and dial reading at 600 RPM after mixing was 300+, out of scale. When using the Fann Viscometer it applies stress to the fluid, which will affect its rheological properties with time. For it to be applicable for comparison two different people shouldn't do it. The dial readings are not reliable for this thick sample.

4%PAC+2%NaCl

All particles are properly dispersed before testing. Some air trapped in the fluid.

Comments

All in all comparing with Ole Julius samples the viscosity is significantly lower, but the sample may seem to be stable for a longer time period.

The samples separate in glass flask after every test point.

Circulated Samples

2%PAC 25℃

After the sample had been circulated for 20 hours it had developed some foam. No lumps of PAC were visible.

The container in the flow loop has started to corrode which has resulted in discoloration of the sample. The sample can have been affected from this.

4%PAC 25℃

All of the particles seem to have been dispersed and dissolved properly. Some of the PAC sticks to the wall and has to be mixed in by hand.

Corrosion is also seen in this sample.

2%PAC 50℃

All particles have been dissolved into the fluid.

Pump seems to work optimal in heated conditions.

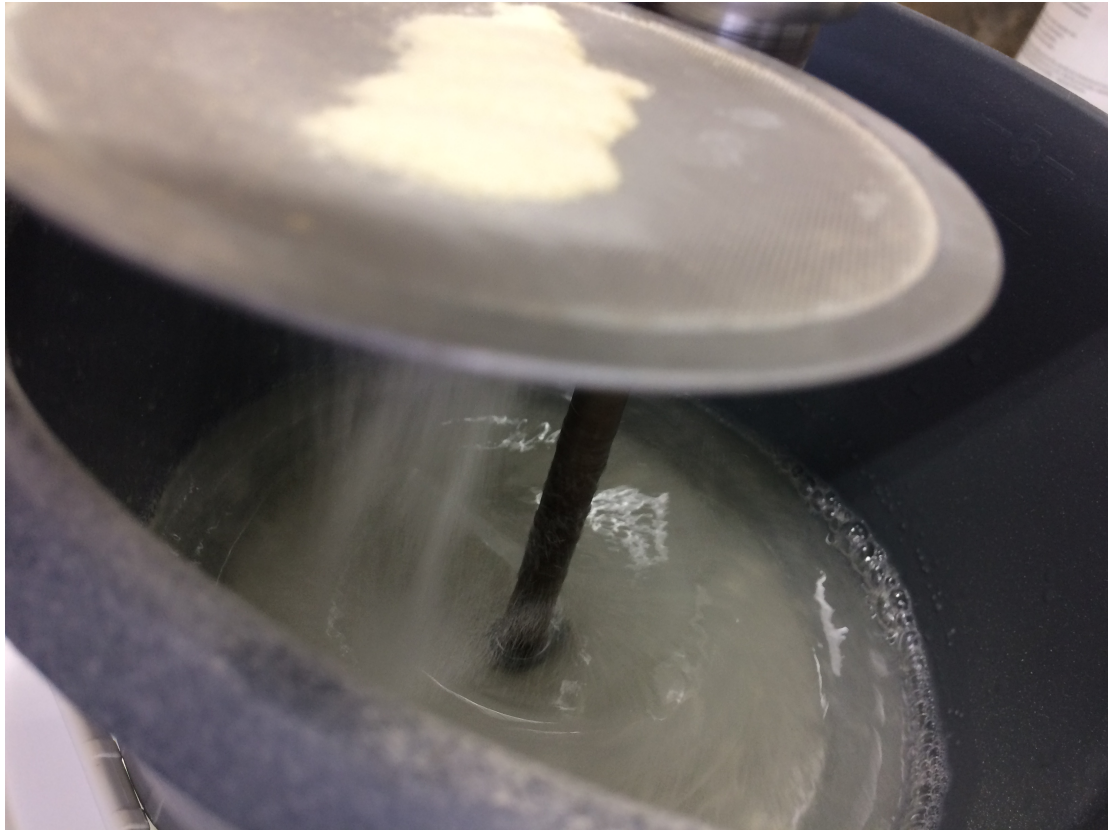**4%PAC 50℃**

All particles have been dissolved into the fluid.

Pump seems to work optimal in heated conditions.

2%PAC+1%XG

Pump malfunction. No tests were carried out after circulation started.

Appendix D - Additional Photos

Xanthan Gum mixing:

Picture above: Adding Xanthan Gum to a sample containing PAC through a fine mesh sieve while mixing.

Foam as a result from circulating sample:

Picture above: When samples were circulated foam was observed in the container of the circulation loop.

Discoloring from corrosion of circulation loop container:

Picture above: The container in the circulation loop started to corrode after a short
period of time and gave the sample an orange/rusty color.

Flow Loop container corrosion:

Pictures above: After 24 hours of circulation the container had corroded and particles had accumulated at the bottom.