UNIVERSITY OF ALBERTA

Effect of viscoelasticity and alkali on heavy oil EOR performance using HPAM, 'AA-NVP' co- and cross-linked polymers

by

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ABSTRACT

Polymer solutions are characterized based on their viscoelasticity to improve the displacement efficiency for enhanced oil recovery. Contribution of viscoelastic polymers solution's elasticity on oil recovery needs to be analyzed thoroughly for better screening of polymers for field operations. In this work, the individual effect of the elasticity of polymers (hydrolyzed polyacrylamide) on oil recovery, and residual resistance factor (RRF) was determined for secondary polymer flood oil recovery experiments with varying degree of water saturation. HPAM solutions, having identical shear viscosity but different elasticity, were analyzed. A series of flooding experiments were performed using a cylindrical core (simulating linear flow) sand pack saturated with heavy oil for different blends of HPAM. Results show that although polymer solutions with higher elasticity yield higher oil recovery, but they have high RRF values. Also, if the water saturation is high before polymer flooding, this elasticity behavior is prominent.

The injectivity and hydrolysis of HPAM in severe alkaline conditions is a major challenge for oil industry. It is of great importance that injected polymer or micro gels show higher injectivity and alkali resistance behavior without compromising with the amount of oil recovered. To overcome shortfall of conventional HPAM, new crosslinked (cP(AA-*st*-NVP)) and co (P(AA-co-NVP) polymer were synthesized using Acrylic Acid (AA) and N-vinyl-2-pyrrolidinone (NVP), and N,N'-methylenebisacrylamide as a crosslinking agent by free radical polymerization. These newly synthesized polymers were compared for rheology, heavy oil recovery, injectivity, RRF value with high molecular weight HPAM in alkaline and non-alkaline conditions. Crosslinked polymer and co-polymer showed stable viscoelastic properties in alkaline conditions than conventional HPAM due to intermolecular bonding, though the molecular weight for the later was high. The RF(resistance factor) and RRF for crosslinked polymer were much lower than HPAM, suggesting high injectivity and lower adsorption/retention of the crosslinked and co polymer. The overall recovery of heavy oil using cross linked polymer and copolymer was also ~7% higher than HPAM.

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CHAPTER 1

INTRODUCTION

1.1 Water and Polymer Flooding

During 1950s, waterflooding became a standard practice in order to maintain reservoir pressure and also to sweep out oil in reservoirs. Since then waterflooding has been studied and applied to numerous fields worldwide with variable degree of success. Secondary recovery is only capable of recovering small amount of oil leaving a significant portion of oil in the reservoir upon completion. EOR methods are then aimed at recovering this residual oil. Oil production strategies can follow the order of primary depletion (natural pressure production), secondary recovery and tertiary recovery processes. When the current method becomes uneconomical or the oil production rate drops to very low values , the next recovery method is applied. EOR aims at extracting as much recoverable oil from the reservoir as possible. Main categories of EOR methods include gas injection, chemical flooding and thermal processes.

Water flooding is the mostly used flooding method for secondary oil recovery. One of the major concerns associated with water flooding is its poor sweep efficiency. Unfavorable mobility ratio causes water to channel through oil regions leaving a considerable portion of recoverable oil in the reservoir resulting in lower oil recoveries. It thus decreases sweep efficiency and results in premature water production, which increases operating expenses (for additional water treatment). Efficiency of a water flood operation can be improved by lowering the water-oil mobility ratio in the system. This is achieved by adding a suitable water-soluble polymer to injected water, which increases the viscosity of the injecting fluid. Since the 1960s, polymers have been widely used to remedy these water flood problems for improved recovery of oil. The use of polymers has been attractive because only small quantities are necessary to effectively increase water viscosity. The increased viscosity of the injected water decreases mobility, thereby improving oil recovery. Polymer flooding is the simplest and most widely used chemical EOR technique. Early research work on polymer flood technology is well documented in detail by various authors[1-6] . Currently, more oil is produced by polymer flooding than all of the other chemical EOR processes combined[7].

In order to fully understand and appreciate the mechanism of polymer flooding, it is very essential to first gain knowledge about some of the key concepts associated with polymer flooding, such as, mobility ratio, injectivity, resistance factor and residual resistance factor.

i) Mobility Ratio

Mobility ratio, M, is the ratio of mobility of displacing fluid to the mobility of displaced fluid. It is defined for waterfloods as follows:

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_w/\mu_w}{k_o/\mu_o} \qquad (1)$$

where, λ_o and λ_w are the mobility of displaced fluid (oil) and the mobility of displacing fluid (water) respectively; μ_o and μ_w are the viscosities of oil and water respectively; k_o and k_w are the effective permeabilities of oil and water phases respectively.

If the mobility ratio is equal to or less than one, it is considered to be favorable for displacing oil. This is where polymer flooding comes into picture. As explained earlier, mobility ratio reduction is one of the main reasons why polymer flooding improves sweep efficiency and oil recovery over water-flooding.

ii) Injectivity

Injectivity represents the pressure gradient required to achieve a given injection flow rate[8]. For simple representation, injectivity is volume flux (u) of polymer solution or water injected for a single unit of pressure drop (ΔP). It is defined as:

$$I = u / \Delta P \tag{2}$$

Injectivity of a fluid depends on the viscosity of the fluid. If the viscosity of solution is low, it will be easier to inject certain volume of liquid solution. For polymer flooding operations, this injectivity can be described as well injectivity index. Polymer solution's viscosity is always higher than water, hence injectivity of polymer solution will be lower than normal water flooding case. A large part of flooding operations consists of surface facilities for the injection of water or polymer solution. Hence injectivity plays a important role in flooding operations economically.

iii) Resistance factor

The resistance factor is a term that is commonly used to indicate the resistance to flow encountered by a polymer solution as compared to the flow of plain water. Resistance factor gives a good measure of the apparent viscosity of the polymer solution. Resistance factor, F_R, can be defined as the ratio of mobility of water to the mobility of a polymer solution when there is no oil present in the system[1].

$$F_R = \frac{(\lambda_w)}{(\lambda_P)} = \frac{\left(k_w \middle/ \mu_w \right)}{\left(k_P \middle/ \mu_P \right)} \tag{3}$$

Under given flow rate in same core flooding system, assuming the flow in porous media follows Darcy's law, RF can be expressed as:

$$F_R = \frac{(\Delta P_P)}{(\Delta P_w)} \tag{4}$$

Resistance factor cannot be defined for the cases where oil is present.

iv) Residual resistance factor

It is defined as the ratio of the permeability to water before and after the injection of polymer solution[3]. The residual resistance factor is a measure of the tendency of a polymer to adsorb into the pores and thus partially block the porous medium. This indicates that residual resistance factor has a pronounced influence on the permeability of the porous medium. This can be defined for the scenarios where there is no change in saturation over the flooding of polymer.

$$F_{RR} = \frac{(k_w)_{before}}{(k_w)_{after}} \tag{5}$$

Under given flow rate in same core flooding system, using the assumption of Darcy's law, RRF is expressed in terms of pressure drops as:

$$F_{RR} = \frac{(\Delta P_w)_{after}}{(\Delta P_w)_{before}} \tag{6}$$

If residual resistance factor is high, it shows that adsorption and trapping of a polymer solution on porous media is on the higher side. Hence, for oil recovery operations, RRF value of polymer solution should be lower to avoid retention of polymer into the porous media.

1.2 Viscoelasticity

Viscosity can be defined a measure of its resistance to gradual deformation by shear stress or tensile stress. Viscosity is due to the friction between neighboring particles in a fluid that are moving at different velocities. For Newtonian fluids, shear stress (σ) is directly proportional to shear rate (γ) and the proportionality constant is called the viscosity (η) of the fluid. The relationship is:

$$\sigma = \eta\gamma \tag{7}$$

Elasticity is the tendency of solid materials to return to their original shape after being deformed. The elasticity of materials is described by a stress-strain curve, which shows the relation between stress (the average restorative internal force per unit area) and strain (the relative deformation). When an elastic material is stressed, there is an immediate and corresponding strain response. When the stress is removed the strain also returns to zero. The stress-strain relationship can adequately be described by Hooke's law. For Hooke's law, applied stress is directly proportional to the strain (ε). It can be denoted as:

$$\sigma = \mathrm{E}\varepsilon \tag{8}$$

where σ is the stress, E is the elastic modulus of the material, known as Young's modulus.

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. This results in time-dependent behavior, which means that a material's response to deformation or force may change over time. When such viscoelastic materials are subjected to sinusoidally oscillating stress, they behave in such a way that, they fall in between the categories of a perfectly elastic solid and a perfectly viscous liquid.[9] A good example is the flow of fluids in a natural reservoir where the pore channels are usually tortuous and converging/diverging. The viscoelastic property of a polymer is studied by dynamic mechanical analysis where a sinusoidal force (stress σ) is applied to a material and the resulting displacement (strain) is measured. For a perfectly elastic solid, the resulting strain and the stress will be perfectly in phase. For a purely viscous fluid, there will be a 90° phase lag of strain with respect to stress. Viscoelastic polymers have the characteristics in between where some phase lag will occur during DMA tests. Shear strain γ for these tests with angular frequency ω is expressed as:

$$\varepsilon = \varepsilon_0 \sin \omega t \tag{9}$$

After the application of the oscillatory shear strain due to the viscoelastic nature of the material the stress response (σ) is also a sinusoidal but out of phase relative to the strain can be represented as:

$$\sigma = \sigma_o \sin (\omega \mathrm{t} + \delta) \tag{10}$$

where δ is the lag in the phase angle and σ_o and ε_0 are the amplitudes of stress and strain. The complex modulus G^* can be used to represent the relations between the oscillating stress and strain is given by:

$$G^* = G' + i\, G'' \tag{11}$$

Here, elastic modulus G' is usually referred to as the storage modulus to describe the elastic storage of energy, because strain is recoverable in elastic materials. The viscous modulus G'' is referred to as loss modulus to describe the viscous dissipation or loss of energy due to permanent deformation in flow. It is the sum of the elastic component G' and the viscous component G''. The complex modulus is obtained from the ratio of the stress amplitude to the strain amplitude and parameter G' and G" are given as:[10]

$$\mathrm{G}^* = \sigma_o / \varepsilon_0 \tag{12}$$

$$\mathrm{G}' = \mathrm{G}^*(\cos\delta) \tag{13}$$

$$\mathrm{G}'' = \mathrm{G}^*(\sin\delta) \tag{14}$$

Oscillation tests provide important information related to the viscoelasticity of polymer solutions. Through these tests, one can determine whether viscous nature or the elastic nature of polymer is dominating over a given range of shear or angular frequency.

For the rheology measurements, C-VOR 150 Peltier Bohlin rheometer from Malvern Instruments, which has independent strain and stress controls, was used as shown in Figure 1.1. This rheometer consists of a cone and plate measuring system i.e. the equipment is based on rotational rheometery. It measures the torque generated by the sample in response to either an oscillatory or steady-shear strain deformation. Strain is applied by motor; torque is sensed by the transducer, and converted to time-varying or steady properties whose results are displayed in the rheometer software. The cone and plate rheometer provides the benefit of using relatively small sample volumes.

Figure 1.1: Bohlin Rheometer

Viscoelastic Models

Viscoelastic materials can be modeled in order to determine their stress or strain interactions. Two of these popular models are Maxwell Model and Kelvin-Voigt Model.

Viscoelastic behavior has elastic and viscous components modeled as linear combinations of springs and dashpots, respectively. These models can be equivalently modeled as electrical circuits. In an equivalent electrical circuit, stress is represented by current (Springs), and strain rate by voltage (dashpot). The elastic modulus of a spring is analogous to a circuit's *capacitance* (it stores energy) and the viscosity of a dashpot to a circuit's *resistance* (it dissipates energy). The elastic components, as previously mentioned, can be modeled as springs of elastic constant E, given the formula:

$$\sigma = E\varepsilon \tag{15}$$

where σ is the stress, E is the elastic modulus of the material, and ε is the strain that occurs under the given stress, similar to Hooke's Law.

The viscous components can be modeled as dashpots such that the stress–strain rate relationship can be given as,

$$\sigma = \eta \frac{d\varepsilon}{dt} \tag{16}$$

where σ is the stress, η is the viscosity of the material, and dε/dt is the time derivative of strain.

a. Maxwell Model : The Maxwell model can be represented by a purely viscous damper and a purely elastic spring connected in series, as shown in the diagram. The model can be represented by the following equation:

$$\frac{d\epsilon_{Total}}{dt} = \frac{d\epsilon_D}{dt} + \frac{d\epsilon_S}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}. \tag{17}$$

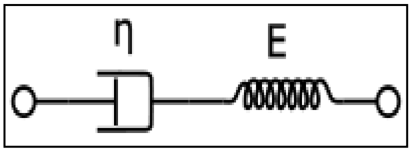

Figure 1.2 Schematic Representation of Maxwell Model using spring and dashpot

The model represents a liquid (able to have irreversible deformations) with some additional reversible (elastic) deformations. If put under a constant strain, the stresses gradually relax. When a material is put under a constant stress, the strain has two components as per the Maxwell Model. First, an elastic component occurs instantaneously, corresponding to the spring, and relaxes immediately upon release of the stress. The second is a viscous component that grows with time as long as the stress is applied. The Maxwell model predicts that stress decays exponentially with time, which is accurate for most polymers.

b. Kelvin-Voigt Model: The Kelvin-Voigt model, also known as the Voigt model, consists of a Newtonian damper and Hookean elastic spring connected in parallel, as shown in the picture. It is used to explain the stress relaxation behaviors of polymers. The constitutive relation is expressed as a linear first-order differential equation:

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt} \tag{18}$$

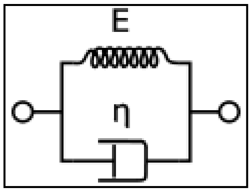

Figure 1.3 Schematic Representation of Kelvin-Voigt Model using spring and dashpot

This model represents a solid undergoing reversible, viscoelastic strain. Upon application of a constant stress, the material deforms at a decreasing rate, asymptotically approaching the steady-state strain. When the stress is released, the material gradually relaxes to its un-deformed state.

Polymer solutions used in polymer flooding can be closely represented with Maxwell model. Figure 1.4 shows the typical Maxwell type behavior of two moduli in oscillatory testing. The loss modulus dominates at very low frequencies, which shows polymer has liquid-like response at these frequencies. As the frequency increases, the storage modulus increases at a faster rate than the loss modulus, and the solid-like response governs after a certain frequency. This crossover frequency (CF) can be related to the relaxation time which can be approximated by taking the inverse of the numerical value of this CF in radians per second. Physically, the relaxation time indicates the time that it takes for the deformed material, e.g., a polymer chain, to regain its original configuration, and it is in direct relation to the degree of elasticity. If one sample shows higher relaxation time, then it has a higher degree of elastic property than the other. Hence, it will take longer for the deformed material to regain its original configuration.

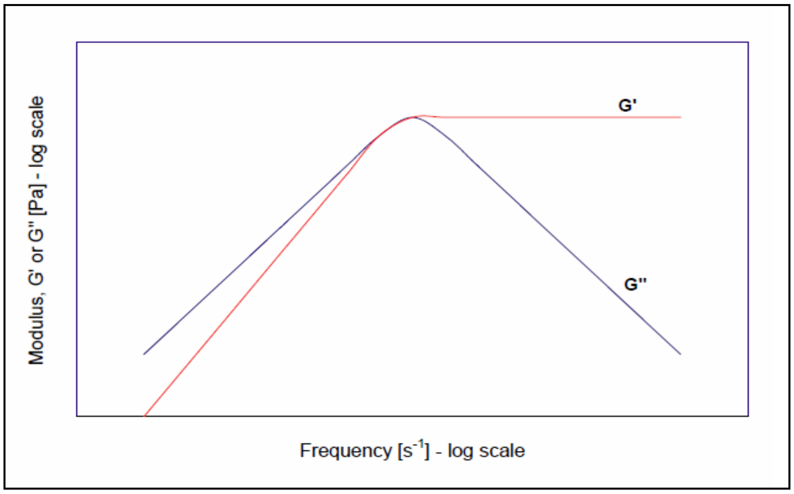

Figure 1.4: Typical Maxwell type behavior of elastic and viscous moduli in oscillatory testing[11]

Polyacrylamide is the most commonly used polymer for flooding operations. To achieve high viscosity, PAM's hydrolyzed form is used which is referred as hydrolyzed polyacrylamide (HPAM). Reason for higher solution viscosity for HPAM is its carboxylate groups, which cause chain expansion due to repulsion of the ionic groups. This work is divided into two separate studies for HPAM's characterization during polymer flooding.

1.3 Elasticity of HPAM Polymer

Understanding the rheological properties and behavior of viscoelastic polymers under different reservoir conditions is very important in order to get the best out of viscoelastic polymers, which would result in better recovery performance.

1.3.1 Problem Statement

There are various recent studies providing more information regarding the role of polymer solution rheology on sweep efficiency, suggested that selecting the type of polymer and understanding how its fluid rheology affects oil recovery are probably among the most critical factors that needs to be considered in designing a successful polymer flood operation. Laboratory and field experiments along with numerical simulations have shown that the viscoelastic characteristics of polymer solutions help improve polymer flood efficiency[12-18]. When the viscoelastic property of polymer solution is brought into full play, the displacement efficiency of a polymer would reach its maximum. Extensive literature is available aimed towards understanding the role played by viscoelasticity of polymers in improving polymer flood efficiency but analysis of individual effect of elasticity of viscoelastic polymers on improved oil recovery has recently come into picture for thorough understanding of rheological behaviour of viscoelastic polymers. Urbissionova et al.[19] and Veerbhadrappa et al.[20-21] studied the individual effect of elasticity of polymer solution on oil recovery for conventional oil and concluded that higher the elasticity of polymer solution, higher the oil recovery. In this work, the individual effect of elasticity of partially hydrolyzed polyacrylamide (HPAM) solutions on oil recovery is studied by comparing the results of oil displacement by polymer solutions having similar shear viscosity but different elastic properties for heavy oil. Also, the effect of different water saturations before the introduction of HPAM flooding on this elasticity behaviour is analyzed for better screening and implementation of polymer flooding.

1.3.2 Objectives of the Study

Objectives involved with this study were;

- To test a polymer screening criteria for selecting polymers, that have same average molecular weight, based on their elasticity values for heavy oil
- To study the individual effect of elasticity of viscoelastic polymers on EOR for heavy oil
- To analyze the implementation of polymer flooding based on elasticity behaviour at varying water saturations.

Literature Review, Methodology and results for this analysis are presented in Chapter 2.

1.4. Injectivity and adsorption of HPAM Polymer

Polymer flooding can be used in place of water flooding, or to augment an existing flood.

The use of polymer solution in flooding operations is mainly used for mobility ratio reduction. However, the effective use of polymers requires resolving several technical problems. For example, the high viscosity which enables mobility reduction, increases the injection pressure necessary to overcome the increased pressure-drop across the reservoir. Permeability reduction effect is sometimes added to the viscosity effect, requiring higher injection pressure. Other potential problems include the loss of viscosity, caused by mechanical degradation (due to high shear near the wellbore region) and the loss of polymer, caused by adsorption/retention.

In addition to the use of polymers for purposes of mobility control, the use of polymer gels was proposed for conformance control application. Conformance control is a technique to block the already well-swept layers of reservoir, in order to mobilize pockets of unswept oil and gas.[22] This concept is distinguished from the conventional EOR processes in that it is intended to block specific high permeability channels within a reservoir, rather than to improve sweep for broader reservoir volumes. For this process, the polymers should have the property of more retention in porous media which can be enhanced by more adsorption and trapping. The high retention of polymer in high permeable areas can then propagate the polymer to low permeable areas. The degree of hydrolysis is an important factor that affects adsorption and permeability reduction in case of polyelectrolytes such as HPAM[23-25]. Hydrolysis increases the hydrodynamic radius of polymer molecules because the negative charges on polymer molecules repel one another. The increased negative charge on polymer molecules decreases the adsorption level, due to the repulsion from negatively charged rock surfaces.

For mobility reduction operation, the polymer should have more concentrated on polymer backbone which will result in less adsorption while for conformance control polymer should have less negative charge on backbone to enhance the adsorption on rock surfaces.

Salinity and pH are two major factors that influence the viscosity and adsorption characteristics of HPAM solutions. Due to the shielding of negatives charges, the presence of electrolytes or protons drastically reduces viscosity. Divalent ions have considerably more effect on viscosity than do mono-valent ions. Temperature is another significant cause of viscosity reduction. As the designs of EOR processes are developed and improved, (i.e., the addition of alkali or acid, use of soft water, and high-temperature applications), it will be critical to understand the effects of the above variables on polymer viscosity. Polymer solutions with good injectivity and stability behavior in presence of other factors such as temperature, alkali, salinity are necessary for successful field use for EOR operations.

1.4.1 Problem Statement

Very often mobility and injectivity properties of the polymers or the corresponding solutions are poor especially for high molecular weight polymers due to very high value of viscosity for polymer solution. This results in plugging of well-bore as well as high cost for surface facilities. As HPAM is used with various other chemicals like alkali, surfactant, they can alter the chemical structure of polymer as it is prone to chemical and thermal degradation. HPAM in presence of divalent ions has a tendency of scale precipitation which can clog the wells. This can slow down the process as wells have to be cleaned and stimulated for an un-interrupted injection. To compensate the loss of viscosity, higher concentration or higher molecular weight HPAMs are used for EOR which can further reduce the injectivity and HPAM becomes an unsuccessful candidate for polymer flooding in severe alkaline or high temperature conditions. Thus, despite having benefits of injection fluid's increased viscosity, there is a major drawback of these polymers as it can lead to substantial reduction of injectivity, slow fluid throughput, and delayed oil production from flooded fields. There is need of polymer with better stability and improved injectivity without compromising with the oil recovered by polymer. The use of pH sensitive polymers could provide a way of reducing the injection pressures needed for the polymer solution. By injecting a pH buffered polymer solution at low pH, we can achieve significantly lower injection pressures since the polymer viscosity is low. The pH of the solution increases, due to reaction of polymer's acid content with the carbonate and other minerals in the reservoir rock the polymer viscosity increases by at least an order of magnitude which can allow lower injection pressures in polymer injection wells. Also increasing the pH of polymer solution can help in lowering the adsorption of polymer in the reservoir.

1.4.2 Objectives of the Study

Objectives involved with this study were;

- To test newly synthesized polymers using acrylic acid and N-vinyl-2-Pyrrolidinone for their solution's rheological stability during alkali-polymer flooding
- To compare AA-NVP based polymers for heavy oil recovery with HPAM
- To study the benefit of AA-NVP based polymers for improved injectivity as compared to HPAM for alkali-polymer flooding
- To analyze the adsorption benefits using AA-NVP based polymers for alkali-polymer flooding

Literature Review, Methodology and results for this analysis are presented in Chapter 3, 4 and 5.

1.5 Structure of the Thesis

Chapter 1 describes the polymer use for chemical flooding with some key definitions for enhanced oil recovery, significance of hydrolyzed polyacrylamide's (HPAM) viscoelastic properties and injectivity problems, and explains the objectives of the research.

Chapter 2 consists of the effect of elasticity of HPAM on secondary polymer flood oil recovery for heavy oil and also the effect of primary water flooding on polymer flood oil recovery trend based on elasticity .

Chapter 3 describes the synthesis of new co-polymer using Acrylic Acid (AA) and N-vinyl-2-pyrrolidinone (NVP) and compared it with HPAM for alkali-polymer flooding for oil recovery. It also highlights the importance of using acrylic acid as a mononmer for improving injectivity.

Chapter 4 discusses the injectivity study of copolymer and crosslinked polymer comparing with HPAM with no oil present in the core. It explains the advantages of new polymers for alkali-polymer flood and the mechanism behind it.

Chapter 5 analyzes the new crosslinked polymer for secondary flood oil recovery for alkali-polymer and polymer flooding. It also studies the crosslinked polymer's injecitvity as compared to HPAM.

Chapter 6 concludes the thesis with a summary of the experimental results and recommendations for further research.

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CHAPTER 2

Effect of Water Saturation on the Role of Polymer Elasticity during Heavy Oil Recovery

2.1. Introduction

Due to the rapid depletion of oil reserves, enhanced oil recovery (EOR) has become tremendously important in recent years. As early as the 1960s, polymer flooding as an displacement process in EOR, with the main functionality of increasing the viscosity of the displacing fluid, commonly water[1]. Polymers have been used extensively for EOR applications, and more oil is produced by polymer flooding than all of the other chemical EOR processes combined.[2] Polymer flooding has been applied under a wide range of reservoir properties, including reservoir temperature and pressure, permeability and geology, as well as varying oil viscosities, variable net pay thicknesses, brine chemistry, etc.[2] Continued improvements in technology and the knowledge baseline in the field of polymer-aided EOR operations have made the oil recovery process more and more economical.

In heavy oil reservoirs, polymer flooding could be carried out either as primary process (i.e. injection of polymer solution into reservoir containing oil and irreducible water saturation) or after primary water flooding for improvement of overall oil displacement. In the polymer flood stage, the polymer solution tends to flow along the current water channels because the injected polymer solution is aqueous phase and the flow resistance through the water channel is smaller than through the oil channels. Using water flood before polymer flood seems to be beneficial as resistance factor due to water flood help diverting the flow of polymer solution towards un-swept oil. But if the water flood is in large extent, viscous fingering during water flooding will be more. High viscous fingering will provide channels with minimal resistance for injected polymer solution and polymer solution could bypass the oil completely. This will leave a large amount of residual oil un-swept which can be difficult to recover. Therefore, in order to achieve the maximum oil recovery in a given reservoir, it is of fundamental and practical importance to determine an optimal timing and extent of water flood before polymer EOR.

Overall displacement efficiency during oil recovery (total oil recovered) consists of the macroscopic and microscopic displacement efficiency. Macroscopic efficiency is defined as a measure of the effectiveness of the displacing fluid in contacting the oil zone volumetrically while microscopic displacement efficiency refers to the effectiveness of displacing fluid in mobilizing the trapped oil at pore scale. It has been suggested for long time that polymer flooding can only improve the volumetric sweep efficiency (macroscopic) with no effect whatsoever on the microscopic displacement efficiency[3]. But the studies are still going on the concept that improved oil recovery due to polymer flooding consists of both volumetric sweep efficiency and microscopic displacement. These improvements of microscopic efficiency could be attributed to the distinctive flow properties of polymer solutions due to the viscoelastic properties. This proposition has generated controversial arguments[4-8].

The viscoelasticity of EOR polymers is the key property that makes polymer flooding one of the most widely used chemical EOR techniques. When viscoelastic materials encounter repetitive stress, their behaviour corresponds to a perfectly elastic solid and a perfectly viscous liquid.[9] This can be attributed to the flow of fluids in a natural reservoir where the pore channels are tortuous and converging/diverging. Polymer solutions flowing through these sections come across shear as well as elongation in the direction of flow. Figure 2.1 describes the flow path of the polymer in a porous media. This flow is distinctively different from the Newtonian flow. Here, polymer molecules continuously stretch and recoil. Laboratory and field experiments along with numerical simulations have shown that the viscoelastic characteristics of polymer solutions help improve polymer flood efficiency.[10−17] Viscoelastic polymers can partly displace oil trapped in pore throats, sudden expansion pore paths and dead ends, thereby increasing overall oil recovery.[18] Han et al.[12] studied the displacement efficiency of a polymer flood operation and, using core flooding experiments and numerical simulations, concluded that the viscoelastic property of polymers maximizes the displacement efficiency. Masuda et al.[11] concluded that the viscoelastic effect of the polymer solution improves oil recovery significantly, using experiment results combined with 1D simulations of polymer flooding. Many authors such as Wang et al.,[19] Xia et al.,[20] Jiang et al.[21] and most recently Zhang et al.[10] suggest that the rheological properties of polymers have a large influence on oil recovery operations.

However, the individual effect of viscoelastic polymer elasticity on EOR remains largely unexplored. There are various mechanism described by Wei et al.[1] which enhances microscopic displacement efficiency. Some of these are: pulling effect, stripping, oil thread or column flow, shear thickening. Wang et al.[13] pointed out that the relationship between capillary number and oil recovery for Newtonian fluids do not apply to fluids with elastic properties. The velocity distribution in porous media is quite different from Newtonian fluids because of the elastic nature of polymers. Polymers can also exert a strong “pulling effect” on different types of residual oil. Experiments have shown that as the elastic properties of polymer fluids increased, there was an increase in microscopic oil recovery. Jiang et al.[22] and Wang et al.[23] conducted a field-scale polymer flooding operation using viscoelastic polymers, which resulted in higher oil recovery compared to water flooding. They concluded that high elasticity led to improved displacement efficiency and high viscosity resulted in better volumetric sweep, resulting in improved oil recovery. Interfacial tension between oil and polymer could destabilize the long oil column and break it into droplets. Elasticity of polymer could resist this interfacial deformation. Thereby, oil column could be either drained to a thinner cross section causing it to break it up into smaller ganglia, which results in lower residual oil saturation or the thinned oil column could be broken into longer-length oil ganglia which is more mobilizable[23]. Hou et al.[24] described the increase in microscopic efficiency in polymer flooding and argued that polymer diverts the flow profile of displacing fluid that cause the redistribution of oil saturation.

Therefore, in addition to viscosity, elasticity must also be considered when selecting a polymer operation for EOR. Therefore, it is of utmost importance to understand and conceptualize the individual effect of elasticity on improved oil recovery to develop a better screening model for any polymer flood operation. Urbissinova et al.[25] compared the two polyethylene oxide (PEO) blends with identical viscosity behaviour and different elastic characteristics and concluded that the one with higher elasticity results in higher oil recovery. During the flow of the PEO blends in porous media, a pronounced “expanding piston” behaviour induced by the elastic properties of the polymer solutions was observed. It was suggested that this piston-like movement resulted in higher sweep efficiency and lower residual oil saturation. They repeated the experiments using hydrolyzed acrylamide and achieved similar results. Veerbhadrappa et al.[26] analyzed the viscous fingering mechanisms for viscoelastic polymers with similar viscosity, but different elastic behaviour in two-phase horizontal immiscible flow systems. Their study concluded that elasticity is one of the most important screening criterions for selecting polymer solutions and that higher sweep efficiency could be achieved with stable displacement fronts for higher elasticity polymers.[27]

Elastic properties of polymers play an important role in EOR, and must be considered before choosing a polymer solution for flooding. Polymers with similar average molecular weight, but different MWD will have similar viscosity, but different elasticity[28]. Thus, MWD is used as a measure of the polymer solution's elasticity. In this study, the effect of elasticity was isolated from the shear viscosity effect. Four hydrolyzed polyacrylamide (HPAM) samples with similar shear viscosity, but different degrees of elasticity were used in the flooding experiments. The study represents the effect of polymer solution elasticity on secondary polymer flood oil recovery. The introduction of polymer flood timing was also varied by changing the pore volume of water flooded during primary water flood recovery to analyze the effect of elasticity on reservoirs.

2.2. EXPERIMENTAL PROCEDURE

2.2.1. Materials

2.2.1.1. Polymers

Four different grades of FLOPAAM polymers (AB005 V, 3130 S, 3330 S and 3630 S, supplied by SNF SAS in dry powder form, were used in the preparation of the four HPAM solutions. These polymers are anionic and water-soluble with a degree of hydrolysis of 25-30 mol %. Table 2.1 shows the four HPAM polymer grades with their average molecular weights as reported by SNF SAS.

Dehghanpour[29] described in his work that zero shear rate viscosity can be represented in terms of molecular weight and suggested that zero shear rate viscosity of the mixture can be estimated by multiplying the viscosity of mixture component powered by their mass fractions as:

$$\mu_{0,B} = \prod_{i=1}^{n} \mu_{0,i}^{\omega_i} \qquad (1)$$

He concluded both the theories can be combined to obtain the average molecular weight of the polymer blend which is given by the following equation[26,27,29,30]

$$M_{w,B} = \prod_{i=1}^{n} M_{w,i}^{\omega_i} \qquad (2)$$

where $M_{w,B}$ is the average molecular weight of the blend, ω_i is the weight fraction of polymer grade i, and $M_{w,i}$ is the average molecular weight of polymer grade i. By keeping the same average molecular weight but different MWD, it was possible to prepare polymer solutions with similar shear viscosity and variable elastic characteristics.

By adjusting the weight fraction of the polymer grades by trial-and-error, it was possible to create four HPAM samples with a similar average molecular weight of approximately 2,000,000 Da. Table 2.2 shows the weight fractions of the pure grade polymers used to prepare the four different HPAM samples (denoted as HPAM-1 to HPAM-4) and their average molecular weight. The polymer solutions of 0.1 wt % were prepared by adding calculated quantities of polymer grades (shown in Table 2.2) directly to deionized water. Polymer grades were added in decreasing order of their molecular weights. Powders were added in three lots with constant stirring maintained at 300 rpm using a magnetic stirrer in ~15 s intervals. Proper care was taken to ensure that polymers were not added too rapidly to avoid lumping of the powder. The solution was stirred for approximately 24 hours until it became completely transparent and no filtration was needed.

2.2.1.2 Oil

Crude oil used in the study was collected from a heavy oil reservoir in north-central Alberta. Basic sediment and water from the crude oil was removed by high-speed centrifugation. The oil viscosity was ~1200 cP at 25 °C. Oil viscosity was checked using a rheometer (described in Section 2.3) each time prior to the experiment to maintain consistency.

2.2.1.3. Porous Media

Potters Industries Inc. supplied SPHERIGLASS A-GLASS 3000 grade glass beads that were used as the porous media in all of the flooding experiments. They were 325-mesh size with a particle size distribution of 30-50 microns. Perforated screens at either end of the core were used. The absolute permeability of the porous medium was found to be 450 mD ± 2%. The core was packed dry using a mallet as well as a pneumatic vibrator, ensuring a tight pack.

2.3. Rheological Characterization

Two types of rheology tests were conducted in order to characterize HPAM solutions: the viscometry test and oscillation test. A C-VOR 150 Peltier Bohlin rheometer with a cone and plate measuring system was used for these tests. Polymer solution samples were placed in between a 60-mm diameter stationary plate and a rotating 40-mm diameter upper cone at a 4° angle, which were separated by a gap of 150 μm. All measurements were carried out at room temperature.

2.3.1. Viscometry Test

Viscometry tests were carried out under a range of shear rates from 1 to 100 s^{-1}. Figures 2.1 and 2.2 show shear stress versus shear rate and shear viscosity versus the shear rate behaviour of the HPAM solutions, respectively.

2.3.2. Oscillation Test

Oscillation tests (or frequency sweep tests) measure viscoelastic properties such as viscous modulus and elastic modulus as a function of frequency at constant stress. A constant shear stress of 0.04775 Pa was maintained throughout, and tests were carried out at a frequency range of 0.01-1 Hz (0.06283-6.283 rad/s).

2.4. Secondary Polymer Flood

To study the role of elasticity on secondary polymer flood recovery, four sets of experiments were performed during linear core flooding in a secondary polymer flood mode (Figure 2.2). Secondary polymer flood recovery experiments were conducted in a cylindrical core holder mounted horizontally to represent linear flow. The core holder had an internal diameter of 28.57 mm and a height of 152.4 mm. Pressure readings were recorded throughout the experiment using a pressure transducer.

a. Sandpack preparation: Initially, the core holder was tightly packed with dry spherical glass beads, and water was injected into the core holder to measure the pore volume and permeability of the core. Pore volume was calculated using material balance between the injected water and water collected on the producer side. Permeability was calculated by varying the flow rates until a stable pressure was obtained on each flow rate.

b. Oil saturation: The core holder was then saturated with heavy oil with a viscosity of 1200 cP at 25 °C. The volume of oil required to saturate the sandpack core was recorded. Oil was injected using a piston-based accumulator using an ISCO syringe pump 500D at constant pressure to avoid leakage during oil injection. Water ejected by the oil was also collected to calculate irreducible water saturation in the core.

c. Primary Water flooding: For secondary flooding experiments, three sets of experiments were performed. The time of polymer flood introduction was varied by injecting 0 PV, 0.5 PV and 1 PV of water into the core holder at a constant flow rate of 0.5 mL/min.

d. Secondary Polymer Flooding: For secondary flooding, the polymer solution injection into the linear sand pack core holder was maintained at a constant flow rate of 0.25 mL/min. The produced effluents (i.e. oil and polymer solution) were collected at regular intervals, and the volume of oil and polymer solution collected were measured separately. The pressure needed to inject the polymer solution was recorded throughout the experiment. Flooding continued until the water cut was greater than 95 %. Typically, the volume of polymer solution injected was around 2 PV.

e. Extended water flooding: After polymer flooding, extensive water flooding (up to 20 PV) was conducted to produce the remaining oil as well as to measure the permeability.

2.5. Residual Resistance Factor

It is defined as the ratio of the permeability to water before and after the injection of polymer solution[31]. Residual resistance factor has a pronounced influence on the permeability of the porous medium. This can be defined for the scenarios where there is no change in saturation over the flooding of polymer.

$$F_{RR} = \frac{(k_w)_{before}}{(k_w)_{after}} \tag{3}$$

Under given flow rate in same core flooding system, using the assumption of Darcy's law, RRF is expressed in terms of pressure drops as:

$$F_{RR} = \frac{(\Delta P_w)_{after}}{(\Delta P_w)_{before}} \tag{4}$$

If the residual resistance factor is high, it shows that adsorption and trapping of a polymer solution on porous media is on the higher side. Hence, for oil recovery operations, RRF value of polymer solution should be lower to avoid retention of polymer into the porous media.

2.6. Results and Discussion

2.6.1 Rheological behaviors of polymer solutions

A comparison of the steady shear rheological results for 0.1 wt % HPAM-1 to HPAM-4 aqueous solutions at 25 °C is presented in Figure 2.3 (after 24 hours of mixing). The shear viscosity values of the HPAM solutions with the same average molecular weight were found to be very close to each other. Thus, the four blended polymers used for this study showed a similar viscosity profile. Figure 2.4 compares the viscous modulus for all four polymer solutions. The viscous moduli of HPAM-2, HPAM-3 and HPAM-4 were very close to each other in the frequency range of 1-10 rad/s. The viscous modulus of HPAM-1 was slightly lower than the other HPAM samples in the low angular frequency region. However, at an angular frequency between 0.5 and 5 rad/s, they all have similar viscous moduli. Results from Figures 2.2 and 2.3 confirm that HPAM samples with higher average molecular weight will have higher shear viscosity or viscous moduli.

2.6.2 Dynamic viscoelastic behaviors

To analyze the elasticity difference, elastic modulus values obtained from oscillation tests were compared for all of the HPAM samples with an average molecular weight of 2,000,000 Da. In Figure 2.5, the elastic modulus versus angular frequency graph shows that, among polymers having the average molecular weight 2,000,000 Da, HPAM-4 has the highest elasticity followed by HPAM-3, HPAM-2 and HPAM-1. This can be directly correlated with the high MWD value for HPAM-4. Due to the high MWD, polymer chains tend to elongate more when shear is applied. This increases the stretching of the polymer in pore throats, and the polymer is able to reach the oil deep in the pores. To confirm that higher elasticity is beneficial in EOR, linear core flooding experiments were performed to assess oil recovery performance.

2.6.3 Oil Recovery Performance

The four HPAM samples with an average molecular weight of 2,000,000 Da were used in linear core flooding experiments, which was conducted in three stages as described earlier: primary water flooding (0 PV, 0.5 PV and 1 PV), followed by 2 PV of secondary polymer flooding (HPAM-1 to HPAM-4) and finally extensive water flooding for up to 20 PV. The results of the secondary flood recovery linear core flooding experiments 1 PV of water flooding are shown in Figure 2.6. Secondary polymer flood recovery for HPAM-4 was 63 % calculated based on the remaining oil after water flooding, which was highest among the four HPAM polymers tested. This higher recovery can be attributed to the high elasticity of HPAM-4. HPAM-1 had the lowest elasticity and had the lowest secondary polymer flood recovery (57 %). The recovery performance of these four polymer solution samples is in the ascending order of HPAM-1 < HPAM-2 < HPAM-3 < HPAM-4, which correlates well with the ascending order of elasticity in the HPAM samples as represented by the elastic modulus (see Figure 2.5). A similar trend was observed when polymer flooding was introduced after 0.5 PV of water flooding and with no water flooding. Figure 2.7 compares the polymer flooding performance for HPAM-1 and HPAM-4 after different pore volume levels of water flooding. In the case with no primary water flooding (i.e. 0 PV of water flooding), the oil recovery for the more elastic HPAM-4 polymer solution was higher by ~5 % than the lower elastic HPAM-1 polymer solution, whereas the difference was ~7 % after 0.5 PV of primary water flooding. The difference between HPAM-1 and HPAM-4's oil recovery increases with an increase of water saturation in the reservoir, suggesting that the effect of elasticity is more profound in the secondary polymer flood mode as the elastic nature of the polymer solution may help divert the flow to unswept regions, thus increasing recovery. It is important to note that, oil recovery results (figure 2.7) do no suggest that recovery is higher for secondary polymer flood, as the total volume of injected fluid in different in all three cases. However, the purpose is to show the effect of polymer solution elasticity during secondary flooding, therefore the amount of polymer solution injected in all three cases was kept same for both polymers HPAM-1 and HPAM-4, i.e., 2 PV. The different of oil recovery percentage increased between HPAM-1 and HPAM-4 polymer solution as the amount of water present in the reservoir increased (i.e. amount of primary water injected). At microscopic level, for high water saturation, the pulling effect of high elastic polymer solution is more than the lower one. As injected could act as a barrier to polymer flow and thus, reducing the effective pore radius for polymer solution flow, therefore requiring more pulling force to remove the trapped oil from dead ends. In some literatures this effect has been characterized by normal force or Weissenberg number. HPAM-4 with higher elastic tendency could provide this effect higher than HPAM-1.

One of the advantages of polymer flooding is that pore plugging results in polymer solution reaching "inaccessible pore volume" and redirects the injected polymer solution to unswept areas.[32] The higher RRF value for HPAM-4 as compared to the other polymer solutions after 1 PV of water flooding also indicates that polymer solution elasticity can contribute significantly towards the blockage of porous media and reduce water phase permeability. When injected, a polymer solution with high elasticity has a greater tendency to form polymer agglomerates or associations within the porous media as it sticks between two pore throats, thus plugging the small pores and reducing permeability. This phenomenon together with adsorption resulted in a RRF value ~4 times higher for the most elastic HPAM polymer solution, which could have decreased the required viscosity enhancement and resulted in more stable viscous front propagation, as compared to the least elastic polymer solution. The higher RRF values, in turn, direct the polymer solution to the areas which are still unswept. Therefore, the polymer solution is able to push the oil towards the producer, and hence oil recovery increases.

Figure 2.8 shows the pressure drop profile during polymer flooding after 1 PV of water flooding for all four polymers. It is evident that the pressure drop during HPAM-4 polymer flooding was the highest among the four polymers. The order of the least to greatest pressure drop is as follows: HPAM-1 < HPAM-2 < HPAM-3 < HPAM-4. This order can be ascertained by the elastic behaviour of the HPAM polymers and the observed RRF values. Figure 2.9 compares the pressure profile for HPAM-1 and HPAM-4 during polymer flooding after different pore volume levels of water flooding. The pressure drop for the more elastic HPAM-4 was always greater than the less elastic HPAM-1. The process of expansion and contraction when entering and exiting a pore causes a greater pressure drop across a core of viscoelastic fluid than for pure viscous fluids.[19,33] Pressure drop for polymer flood after 1 PV WF was highest followed by 0.5 PV WF and no WF cases. It is difficult to measure the breakthrough of polymer in secondary flooding; however the pressure drop or production profile may suggest this behavior. Comparing HPAM-1 and HPAM-4 pressure drop profiles, least elastic HPAM-1 might have early breakthrough than HPAM-4 for all cases studied (figure 2.9) as the pick of the pressure drop during HPAM-1 polymer flooding appears earlier than that for the later polymer solution flooding. HPAM-4 polymer flood seems to have created stable oil bank while displacement. Previous studies have shown that polymer solution elasticity helps in creating stable front propagation, lesser fingering and delayed breakthough[26]. The observations from pressure drop profile confirm this phenomenon. Moreover, it is evident from the figure that the amount of injected water during primary water flooding aids in pressure build up during secondary polymer flooding. This could be as a result of polymer adsorption or entrapment in earlier water flooding zones and polymer diversion into un-swept zones of the porous media. The pressure drop of highest elastic polymer solution, HPAM-4, was higher whereas the least elastic HPAM-1 had lower pressure drop. Thus, elasticity has aided the flow diversion more for HPAM-4 yielding higher sweep efficiency. High elasticity polymer solution will result in higher injection pressure and more polymer solution is forced to invade into larger pores, mobilising more trapped oil.

2.7 Conclusion

- The effect of water saturation on the role of elasticity during heavy oil recovery was successfully studied using polymers with different elastic properties. Four polymer solutions (HPAM-1 to HPAM-4) with similar average molecular weights, but different MWD were prepared.
- Difference in heavy oil recovery during polymer flooding between the various polymer solutions was found which can be attributed to differences in their elasticity.
- A large difference in heavy oil recovery between HPAM-1 and HPAM-4 was observed after 1 PV of primary water flooding, compared to cases with 0.5 PV of water flooding and no water flooding. These results illustrate that the effect of elasticity is more profound on oil recovery and pressure drop when there is more water saturation.
- The required injection pressure for the more elastic polymer solution (HPAM-4) is higher than that of the least elastic polymer solution (HPAM-1). Higher RRF values and higher pressure drop values for HPAM-4 compared to the other polymer solutions indicate that polymer solution elasticity can contribute significantly to pore plugging and reduce water

phase permeability.

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NOMENCLATURE

F_{RR} = Residual Resistance Factor
k_w = Permeability of water, *mD*
k_p = Permeability of Polymer solution, *mD*
$M_{w,B}$ = Average Molecular Weight of Polymer Blend
ω_i = Weight Fraction of polymer grade i
$M_{w,i}$ = Average Molecular Weight of Polymer Grade i
λ_w = Mobility of water
λ_p = Mobility of Polymer solution
μ_w = Viscosity of water, *cP*
μ_p = Viscosity of polymer solution, *cP*
ΔP_w = Pressure Drop during Water Injection, *kPa*
ΔP_P = Pressure Drop during Polymer Injection, *kPa*

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Table 2.1: HPAM grades and their average molecular weights

HPAM Grade	Average Molecular Weight (Da)
3630 S	20,000,000
3330 S	8,000,000
3130 S	2,000,000
AB 005V	500,000

Table 2.2: Composition and weight average molecular weights of HPAM samples

HPAM Sample	Mass Fraction of HPAM Grades				Avg. Molecular Weight
	3630	3330	3130	AB005	
HPAM 1	0	0	1.0	0	2.000E+06
HPAM 2	0.11	0.15	0.41	0.33	2.008E+06
HPAM 3	0.25	0.00	0.35	0.40	2.043E+06
HPAM 4	0.20	0.16	0.15	0.49	2.006E+06

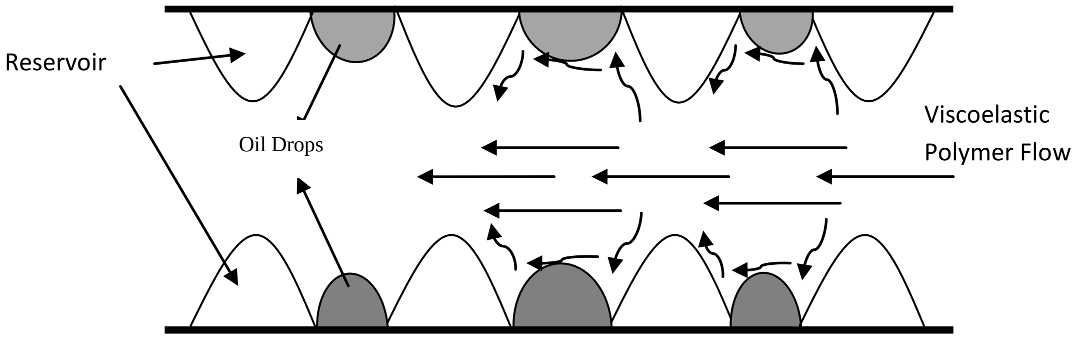


Figure 2.1: Flow Path of Polymer in porous media

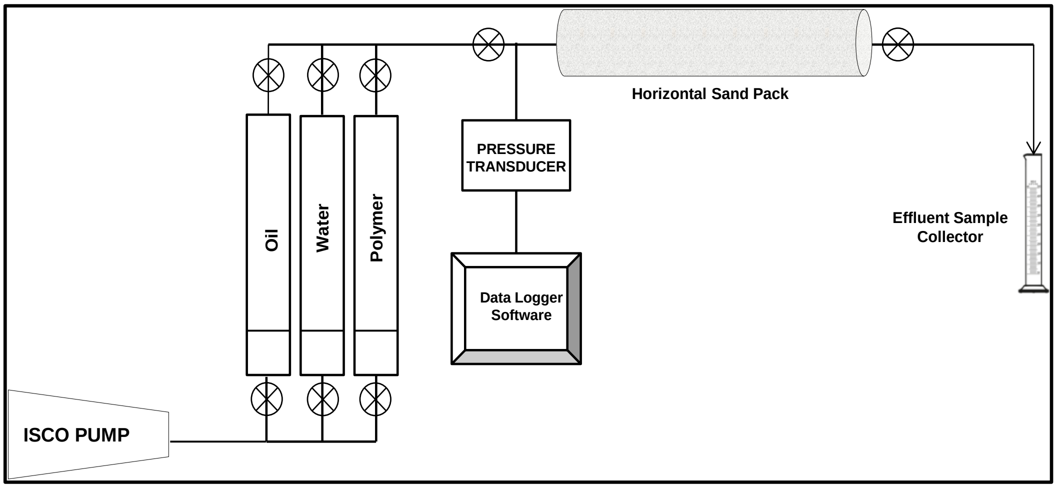


Figure 2.2: Experimental Setup for Linear Core Flooding

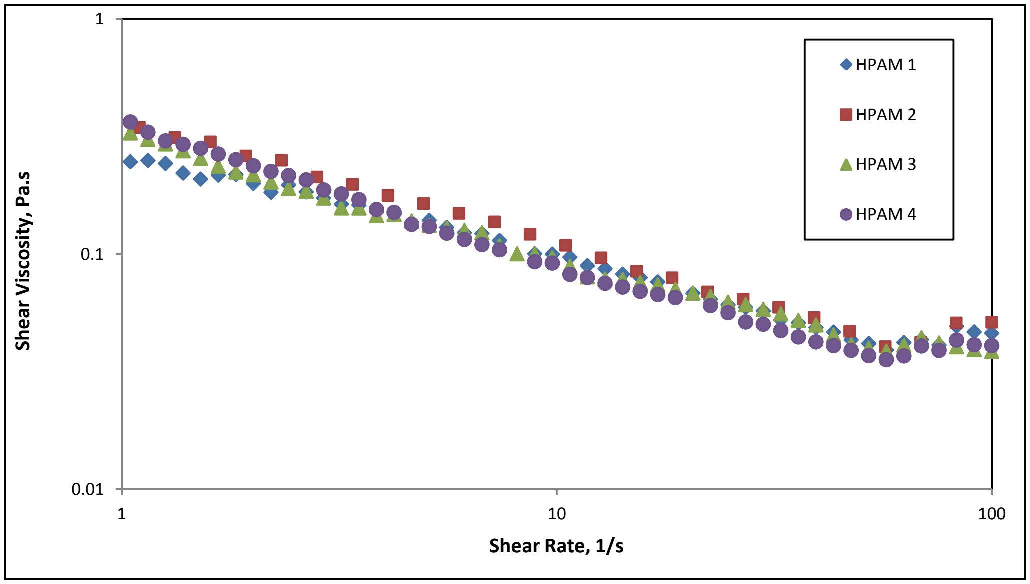


Figure 2.3: Shear viscosity vs. Shear rate plot

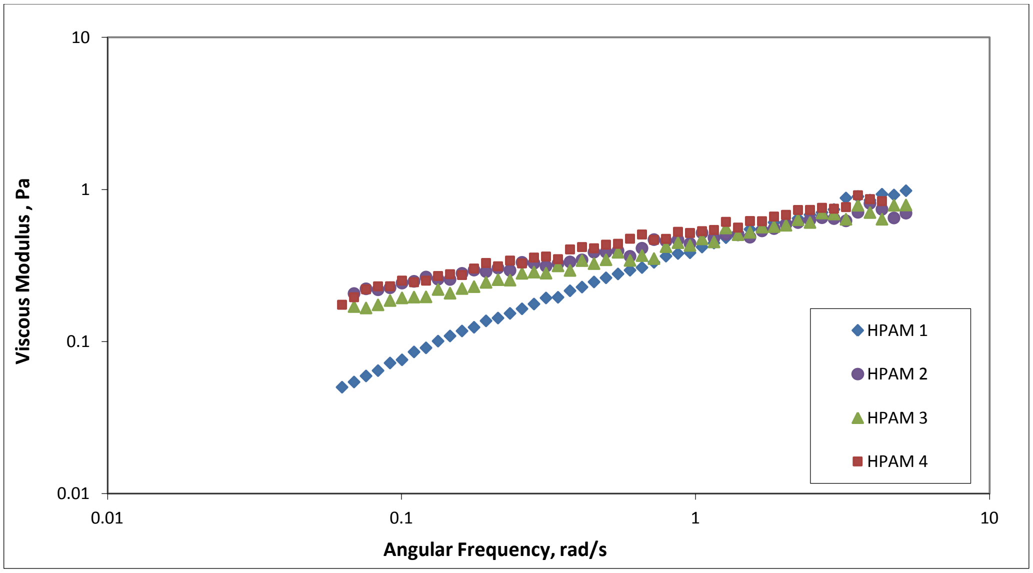


Figure 2.4: Viscous modulus vs. Angular frequency plot

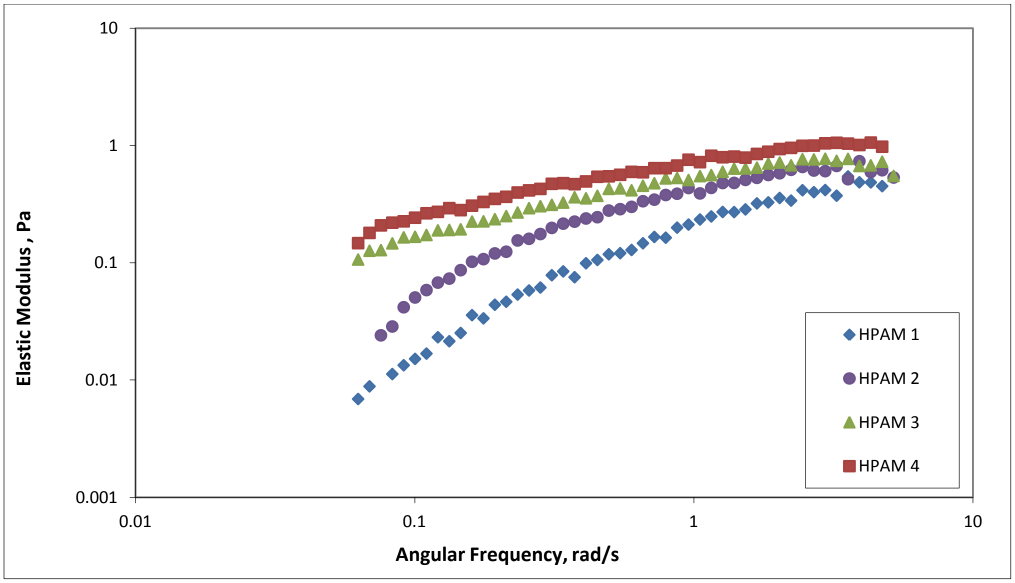


Figure 2.5: Elastic modulus vs. Angular frequency plot

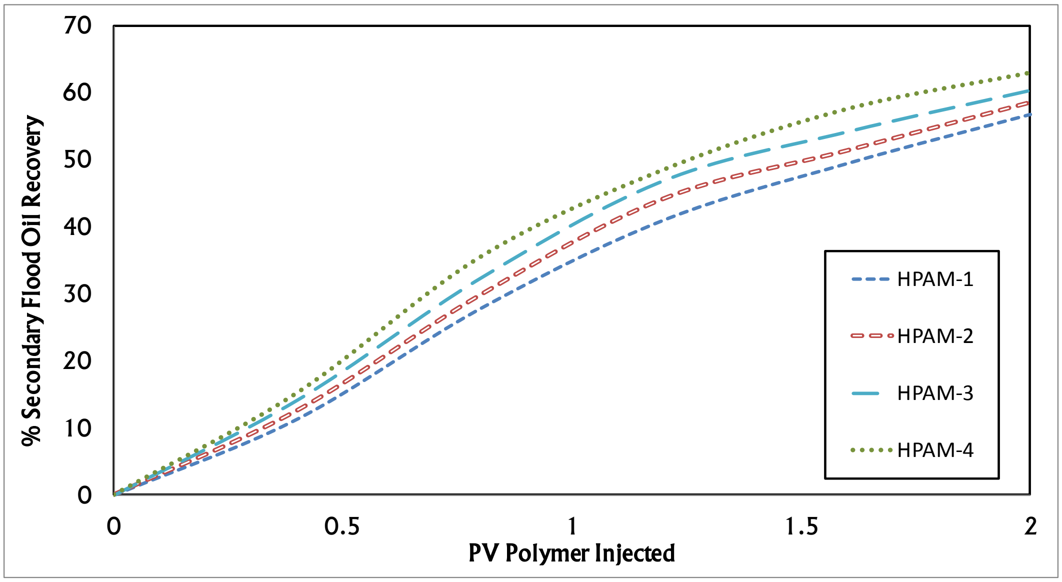
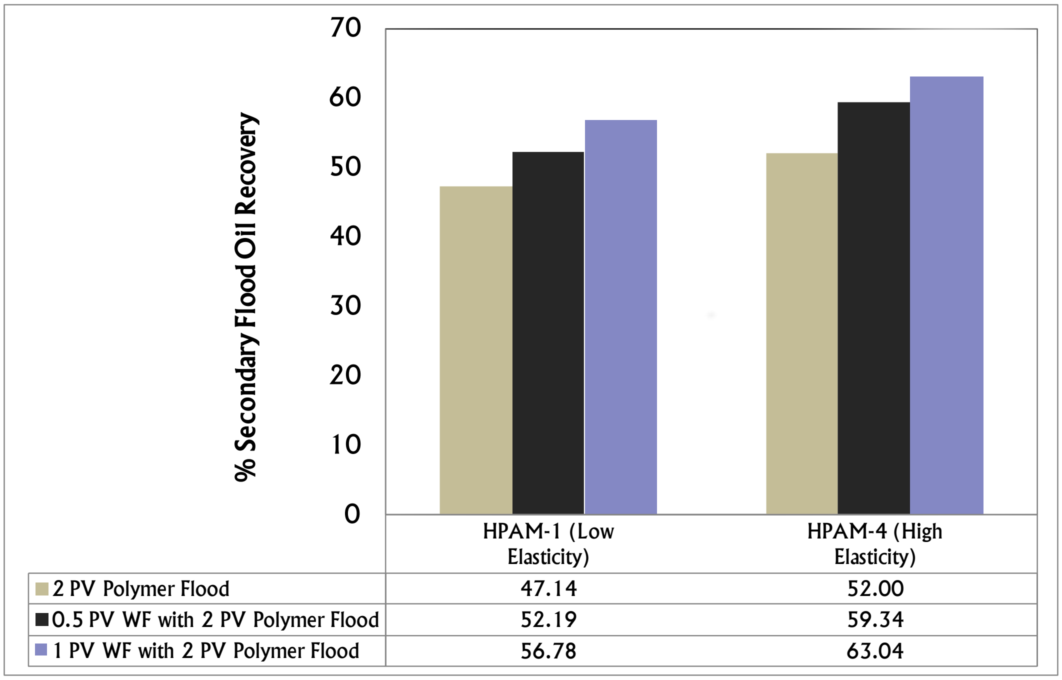


Figure 2.6: Secondary polymer flood oil recovery for HPAM-1 to HPAM-4 for 1 PV water flooding case



	HPAM-1 (Low Elasticity)	HPAM-4 (High Elasticity)
■ 2 PV Polymer Flood	47.14	52.00
■ 0.5 PV WF with 2 PV Polymer Flood	52.19	59.34
■ 1 PV WF with 2 PV Polymer Flood	56.78	63.04

Figure 2.7: Comparison of different water flooding cases for secondary polymer flood oil recovery by Polymers used

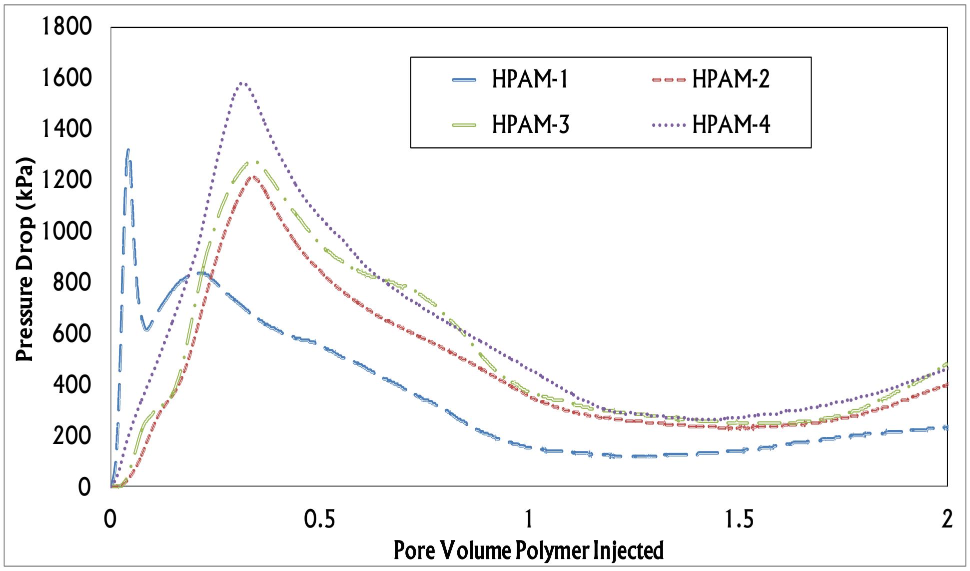


Figure 2.8: Pressure drop profile during polymer flooding after 1 PV of primary water flooding

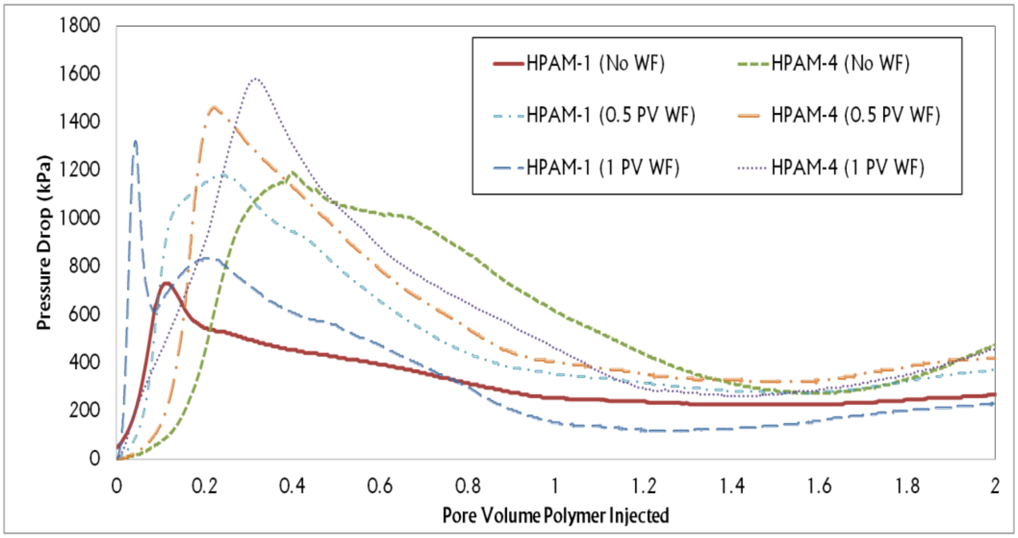


Figure 2.9: Pressure drop profile for polymer flooding after different PV of water flooding

CHAPTER 3

Investigation of Alkali Resistant Copolymer of Acrylic Acid (AA) and N-vinyl-2-pyrrolidinone (NVP) for Improved Heavy Oil Recovery

3.1 INTRODUCTION

Hydrolyzed Polyacrylamide (HPAM) is one of the most commonly used polymers for flooding field operations in heavy oil reservoirs. This traditional polymer relies on chain extension and physical enlargement of solvated chains for viscosity enhancement. Reason for higher solution viscosity for HPAM is its carboxylate groups, which cause chain expansion due to repulsion of the ionic groups.[1]

HPAM is a polyelectrolyte, with negative charges on the carboxylate groups. Because of this negative charge, there are strong interactions between the polymer and any cations present in the solvent, especially at higher degree of hydrolysis. Depending on the EOR process, polymers can encounter various chemical species, including: salts, alkalis and surfactants. The presence of these chemicals may significantly alter the chemical and physical nature of the polymer molecule and consequently, the viscosity and elasticity of the polymer solution. HPAM undergoes hydrolysis reaction of the acrylamide groups in the presence of alkali. It is characterized by a high initial rate of reaction which slows down significantly as the reaction proceeds. The high initial reaction rate is due to the adjacent amide group's catalytic effect. On the other hand, the slowness in rate of reaction is due to the columbic repulsion between the negative charges of the carboxylate groups on the polymer chain and the hydroxide ions. This reaction rate depends on pH and temperature[2]**.** The viscosity of HPAM decreases rapidly as salinity and hardness increases. This is due to shielding of ionic groups, which reduces repulsion and causes chain contraction. The complexing ability of the carboxylate groups of HPAM can lead to polymer precipitation in the presence of high concentrations of ions[3-4].

Alkali used for chemical EOR creates a high pH environment and can increase the charge density on the rock surface to more negative charge. Alkali also reacts with naphthenic acids in the crude oil to create in-situ soap (i.e., saponification)[5-6]. In-situ saponification provides free chemicals to reduce interfacial tension between flooding agent and oil, which in turn reduces the residual oil saturation. Therefore, alkali-polymer flood offers a great potential for increasing oil recovery in various field projects at low economical cost without the need of surfactant. David Pool (now called Black Creek) in Alberta was successfully exploited by alkali-polymer flood with 21.1% incremental recovery[7-8]. Alkali can also reduce the adsorption of anionic surfactant on the rock surfaces ensuring surfactant slug propagation through porous media without much loss during ASP chemical EOR[9-10].

Despite the benefits of alkali and polymers for oil recovery, incompatibility of alkali and HPAM polymer has been well documented in recent studies that lead to reduction of chemical solution viscosity. In general, chains of some polymer molecules readily spread in the solution without alkali, but they curl in presence of alkali[11-13]. At high concentrations of alkali (~1%), some polymer chains curl tightly and the molecules do not fully spread resulting lower viscoelastic properties and hence lower recovery**.** Previous studies showed that for HPAM polymer, higher alkali concentration does not guarantee higher oil production, as the reduction of polymer viscosity due to alkali may reduce the sweep efficiency. Therefore, it requires higher concentration of polymer to compensate the loss of viscosity. In Daqing oilfield it is reported that to offset the negative effect of NaOH on viscosity, the polymer concentration was increased from 0.12% to 0.16% and 0.23% in some cases[14]. Many researchers have reported loss of viscoelastic properties of HPAM polymers due to alkali[1,14-19]. The decrease of loss and storage modulus is believed due to increase of ionic strength.

Chen et al. observed similar recovery performance for three different alkalis NaOH, Na_2CO_3 and Sodium metaborate when their concentration was low[19]. However, at higher concentration (> 1wt %), NaOH being strong alkali resulted into lowest recovery compared to other two weaker alkalis, Na_2CO_3 and sodium metaborate.

High concentration of alkali could also cause problems such as pump sticking due to deposition of alkali, formation erosion and productivity reduction. Scale precipitation can occur by reactions between alkali and hard ions such as Ca^{2+} and Mg^{2+} present in the formation brine. Also, at high pH there will be interaction between formation rock (additional source of carbonate or silicate ions) and alkali, which also results in loss of injectivity[20]. At the producing wells, precipitation of scale may restrict production and foul well equipment. With the current higher concentrations of alkali being used in the field, it is important to control well scaling[21].

Hence, to overcome these limitations of HPAM as well as to achieve better stability and viscoelastic properties for the polymers in chemical EOR, there is a great need of polymers that resist loss of viscoelasticity, which in turn will reduce the need of makeup polymers. Our study discusses the potential application of copolymer of N-Vinyl Pyrrolidinone (NVP) and acrylic acid (AA) as an alternate to HPAM, its effectiveness in maintaining viscoelastic properties in presence of strong alkali (NaOH) and oil recovery performance in alkali-polymer flood.

3.2 Effect of pH on polyacrylic acid, polyacrylamide and their copolymer with NVP

HPAM polymer can be obtained when polyacrylamide (PAM) is hydrolyzed in presence of alkali. The fraction of the backbone amide units, which have been hydrolyzed i.e. the fraction of existing carboxyl groups, is called the degree of hydrolysis. When hydrolysis is complete, or when the amide groups have been replaced totally by the carboxyl groups, it is called poly-(acrylic acid) (PAA).

There are two kinds of pH sensitive materials: one that carries acidic group like carboxylic (-COOH) and sulfonic (-SO_3H) and swell in basic pH, and others with basic groups like amide (-NH_2) and swell in acidic pH. PAA is an example of the acidic ones and Chitosan is an example of the basic ones. Their response to pH is similar in nature, but opposite. This response is due to the presence of ionisable functional groups (like -COOH, -NH_2), which get ionized and acquire a charge (+/-) in a certain pH based on the stimuli. As a result, polymer chains now have similarly charged groups; hence electrostatic repulsion occurs which expands the polymer chain. The opposite happens when pH changes and the functional groups lose their charge hence the repulsion, and the polymer coils back. The factors, which could affect the charge distribution or the electrostatic interaction, can have influence on the polyelectrolyte configuration and its global size or structure. For most polyelectrolytes, these factors include the degree of hydrolysis, the ionic strength, the solvent quality, the solution pH value, the polyelectrolyte concentration, and the solution temperature.

However, hydrogel networks formed by PAA have the ability to absorb many times their weight in water and are the basis of a class of materials called super absorbents. Shamsudeen et al.[22] studied the swelling of non-hydrolyzed (no acrylic acid moieties) and hydrolyzed PAM gels at different pH. They stated that the swelling ratios of the hydrolyzed gels are exceptionally higher at all pH values compared to the non-hydrolysed systems. The carboxyl groups (-COOH) will be dissociated based on the pH environment. High dissociation of ions increases the ion pressure inside the gel, which in turn increases osmotic pressure. Dissociation of ions will be low in the acid region and high in the alkaline region. This phenomenon eventually results in an enhanced swelling of the gel system in the alkaline region. Although at very high pH, when osmotic pressure equilibrium is achieved, high number of movable counterions in solutions decreases the osmotic pressure in the hydrogel and hence swelling decreases at very high pH values. Thakur et al.[23] also studied the pH effect on swelling of PAA and stated that electrostatic repulsion is the main reason for the swelling.

Wang et al.[24] analyzed copolymer made of AA and AMPS (2-acrylamido-2-methylpropanesulfonic acid) using crosslinking agent N, N'-methylenebisacrylamide and concluded that in acidic medium (pH <5), the carboxylate (COO^-) and sulfonate (SO_3^-) groups on the polymeric chain can turn into carboxylic acid and sulfonic acid groups. As a result, the main anion-anion repulsive forces were diminished, and the association among -COOH and $-SO_3H$ groups was increased due to the hydrogen-bonding interaction. This increased the physical crosslinking degree and reduced the swelling ratio. When the pH values are in the range of 5-10, ionization of carboxylate and sulfonate groups occurs and the electrostatic repulsion between carboxylate and sulfonate groups causes an enhancement of the swelling ratio. For higher pH value (>10), a charge screening effect of the counter ions (Na^+) limits the repulsion of corboxylate and sulfonate and hence, swelling and leads to a decrease of the swelling ratio. Similarly, Pandey et al.[25] analysed the swelling behavior of the hydrogels consisting of PAM at different NaCl concentrations and concluded the swelling ratio was inversely proportional to ionic strength. This may be attributed to a change in osmotic pressure and a reduction in the repulsive forces at a higher ionic strength. The lower swelling at a higher ionic strength could also be explained due to the neutralization of the carboxylate anions in the presence of Na^+, resulting in decreased electrostatic repulsive forces, which was a controlling factor for swelling.

Huh et al.[26] proposed to utilize pH change as the trigger for hydrogels to increase their size in-situ, This could be essential in improving injectivity as PAA solution exhibits a low viscosity at low pH, but at pH values higher than a critical value, the viscosity will increase drastically due to electrostatic repulsion. By injecting a polyelectrolyte at low-pH, low viscosity and good injectivity is achievable. Once deep in the reservoir, the pH of water can increase due to reaction of injected acid with the carbonate and other minerals in the reservoir rock. Also, PAA as injectant will help in preventing the problem of chemical loss as the adsorption of PAA is small on rock surface as compared to other EOR polymers.

NVP and its copolymers can be used for wide applications as hydrogels and membranes used in drug-delivery systems. Beside of its low chemical toxicity and high solubility in water/organic solvents, NVP based polymers have the ability to react with different kind of substrates like dyes, surfactants and polymers. Because of this property, it is an important component for many pharmaceutical and cosmetics products also.[27]

AM being the most commonly used monomer for EOR polymers, various studies have be conducted to synthesize new polymers with AM and NVP in order to achieve better stability as well as rheological and swelling properties. Doe[28] studied the effect of incorporation of NVP to AM chains. He stated that adding NVP group could increase the stability of acrylamide. The new monomer can protect the acrylamide chain in the polymer by steric hindrance as well as intra-molecular hydrogen bonding in AM-NVP polymer. This stability concerns both thermal and chemical degradation. Radical reaction is prevented by hindrance while intra-molecular hydrogen bonding can decrease chemical hydrolysis. Also the stability increases with NVP concentration.[29] As there will be more active sites available for hydrogen bonding as well as higher number of large VP group.

When hydrogel samples of AM-NVP were tested with different pH conditions, there is no influence of pH on swelling behaviour for these hydrogels. The reason behind this can be attributed to two constituents of hydrogels as (N-vinyl-2pyrrolidinone) and AM, which are non-polyelectrolytes. Hence, there is an absence of ionisable groups to produce electric charges along the polymeric chains. Thus there will be no electrostatic interaction inside the gel to repel the polymer chains and increase the osmotic pressure. Here it is worth mentioning that the swelling behaviour of cross-linked polyacrylamide hydrogels cannot be affected greatly by the pH of the external solution because the possible hydrolysis of amide groups of polyacrylamide into carboxylic group is not feasible. The polymer will be stable due to steric hindrance of NVP but will not have ideal swelling and viscous properties. However, as it has been discussed above, copolymer containing PAA has negative charged ions in high pH due to conversion of carboxylic group to carboxylate ion, hence there is a electrostatic repulsion between polymer chains. NVP being a non-ionic moiety does not participate in the repulsion. Thus AA-NVP polymer has better swelling characteristics as compared to copolymer containing AM. Figure 3.1 shows the chemistry related to AM, AA and NVP.

3.3. Materials Used & Method of Solution Preparation

Crude oil used in the study was collected from a heavy oil reservoir in north-central Alberta. Basic sediment and water from the crude oil was removed by high-speed centrifugation. The oil viscosity was ~700 CP @ 22 deg C. FLOPAAM polymer 3130S supplied by SNF SAS in dry powder form was used in the preparation of HPAM solutions. FLOPAAM 3130S is anionic and water-soluble with a degree of hydrolysis of 25-30 mole % and average molecular weight of 2×10^6.

3.3.1. ***Synthesis of Poly (acrylic acid-st-1-vinyl-2-pyrrolidinone) (P(AA-co-NVP))***

Acrylic acid (AA) was purchased from Sigma-Aldrich (Canada) and purified by passing through a basic alumina column. 1-vinyl-2-pyrrolidinone (VP) was obtained from Sigma-Aldrich (Canada) and purified by distillation. Water used in this study was purified with a Millipore Milli-Q system. Other chemicals were used as received.

The P(AA-*co*-NVP) copolymers were polymerized by free radical polymerization. A typical synthesis protocol is as follows. AAc (2.89 g, 40.1 mmol), VP (0.495 g, 4.45 mmol), and 4, 4'-azobis (4-cyanovaleric acid) (ACVA) (1.0 mg, 3.56×10^{-3} mmol) were dissolved in 5 mL of *N*, *N*-dimethylformamide (DMF). After degassing with nitrogen gas for 30 min, the mixture was allowed to polymerize for 24 h at 60 °C under inert atmosphere. The resulting highly viscous P(AA-*co*-NVP)copolymer was diluted with DMF (10 mL) and subsequently purified by dialysis against ethanol and water. Finally, the P(AA-*co*-NVP) copolymer was collected as a powder after freeze-drying.

As different concentrations of monomers/initiator (see Table 3.1) were tried for synthesis of P(AA-*co*-NVP), their shear viscosity behaviour under alkali conditions were compared in Figure 3.2 to select the one (No. 4) with comparable rheology as FLOPAAM 3130S.

The polymer solutions of 0.1% concentration (wt %) were prepared by adding them to deionized water. Powders were added with constant stirring maintained at 350 rpm using a magnetic stirrer in the interval of ~15 seconds. Proper care was taken to ensure that polymers are not added too rapidly in order to avoid lumping of the powder. The solution was stirred for approximately 24 hours until it became completely transparent and no filtration was needed.

3.4. Viscoelasticity Characterization of Polymer Solutions

Viscoelasticity measurements were carried out by a C-VOR 150 Peltier Bohlin rheometer (Malvern Instruments, USA) with cone and plate measuring system and strain model measurements at 22^0C +/- 0.5^0C. Polymer samples were placed in between a stationary plate with a diameter of 60 mm and a rotating upper cone with a 4º angle and a diameter of 40 mm, separated by a gap of 150 µm. Following rheological tests were conducted for the polymers.

3.4.1. *Viscometry Tests*

Viscometry tests were carried out at shear rates varying from 1 to 100 s^{-1}. Shear viscosity was plotted as a function of shear rate for polymer samples in both alkaline and non-alkaline conditions (Figure 3.3).

3.4.2. *Oscillation Tests*

Frequency tests were carried out on polymer samples at a frequency range of 0.01 to 1 Hz, keeping the stress value constant at 0.04775 Pa. Oscillatory measurements provide the absolute values of the complex modulus |G*|, the storage modulus or elastic modulus G', the loss modulus or viscous modulus G", at a constant frequency and constant strain. These magnitudes of frequency and strain were chosen so as to provide a stress of reasonable magnitude for the purpose of sensitivity. Figure 3.4 shows elastic modulus and viscous modulus as a function of angular frequency.

HPAM polymer FLOPAAM 3130S and synthesized P(AA-*co*-NVP) polymer were further tested for oil recovery performance during core-flooding experiments in straight polymer flood mode and in alkali-polymer flood for comparison.

3.5. Core Flooding Experiments

3.5.1. *Experimental Set-up*

A cylindrical horizontal core holder (diameter 1 1/4", length 6”) was used for flooding experiments. Perforated screen at either ends of the core were used. Glass beads used in core flooding experiments were of 325 mesh size with a particle size distribution of 30-50 microns, supplied by Potters Industries LLC. For each test, fresh glass beads were packed to ensure the same wettability. The core was packed dry, using a mallet as well as a pneumatic vibrator ensuring a tight pack. Pore volume (PV) of the porous medium was measured by direct method. Volume of glass beads in the visual cell was subtracted from the bulk volume of the cell. A specific gravity of 2.5 was used for calculating the volume of glass beads in the model for each experiment using the known mass that was required for packing. The porosity values are reported in Table 3.2 for each experiment.

The ISCO syringe pump 500D was used for saturating the core with heavy oil. The volume required for saturation was also measured and reported in Table 3.2 which was in agreement with the volume calculation from glass bead volume, thus showing the quality packing was similar for each experiment.

Graduated cylinders were used for collecting and measuring effluent samples during the flooding process at regular time steps. A schematic of experimental set-up is shown in Figure 3.5. Core and fluid properties are listed in Table 3.3.

All the experiments were performed with model in horizontal position therefore; the gravity was assumed to have no influence in the observations of the experiments.

3.5.2. *Effective Shear Rate in Porous Media*

Christopher and Middleman suggested the following equation to estimate shear rates in cores[30]

$$\gamma = \frac{3n+1}{4n} \frac{4Q}{A(8k\phi)^{0.5}} \tag{1}$$

Where γ is shear rate, 1/s; (3n + 1)/4n is a non-Newtonian correction factor for power-law fluids; Q is flow rate, cm^3/s; A is cross sectional area of the core, cm^2; k is permeability, cm^2 and $\emptyset$ is porosity.

For the type of fluids we have used n values changed between 0.45 and 0.56. Substituting n values of 0.45 and 0.56, k = 350-380 md; φ = 42-45%; A= 6.413 cm^2; and a flow rate of 0.25ml/min would yield to shear rate of ~ 27-30 s^{-1} in porous media.

3.5.3. *Flooding Procedure*

Flooding experiments were conducted via following method:

- Initially core was prepared as described in aforementioned section and the effective porosity of the core was measured.
- The core was flooded with water to establish connate water saturation and permeability was measured by varying the flow rate between 0.25 ml/min to 6 ml/min and recording the pressure drop along the core.
- The core was then flooded with the crude oil; the effluents were collected to obtain initial water and oil saturations in the core through material balance.
- After saturation, core was flooded with 1 PV of water, displacing oil to establish residual oil saturation and stable pressure drop.
- For secondary flood recovery polymer or alkaline-polymer solution was injected for 4 PV until a stabilized pressure is achieved at a given flow rate.
- At the end, permeability of the core was measured by subjecting the core to 15-20 PV of water flood at different flow rates and stabilized pressures as a function of injection rate was recorded.

Flow rates for waterflood and chemical flood were held constant at 0.25 ml/min (1.84

ft/day and shear rate 27-29s^{-1}).

Volumes of effluent from producer were collected at regular intervals. Pressure drop across the core was recorded using OMEGADYNE Inc. pressure transducer that had a full-scale limit of 2500 psig.

P(AA-*co*-NVP) polymer was used for heavy oil recovery in both alkali and non-alkali conditions. Oil recoveries for both cases were then compared with FLOPAAM 3130S to analyze the change in oil recovery.

3.5.4. Residual Resistance Factor

It is defined as the ratio of the permeability to water before and after the injection of polymer solution[32]. The residual resistance factor is a measure of the tendency of a polymer to adsorb into the pores and thus partially block the porous medium. This indicates that residual resistance factor has a pronounced influence on the permeability of the porous medium. This can be defined for the scenarios where there is no change in saturation over the flooding of polymer.

$$F_{RR} = \frac{(k_w)_{before}}{(k_w)_{after}} \tag{4}$$

Under given flow rate in same core flooding system, using the assumption of Darcy's law, RRF is expressed in terms of pressure drops as:

$$F_{RR} = \frac{(\Delta P_w)_{after}}{(\Delta P_w)_{before}} \tag{5}$$

Table 3.3 shows residual resistance factor of FLOPAAM 3130S and P(AA-*co*-NVP) with and without 1% NaOH.

3.5.5. *Discussion of Shear thinning in porous media*

At low velocities in porous media, FLOPAAM 3130S solution generally shows mild shear thinning behavior[33-38].

Chauveteau et al. observed that the permeability reduction remained constant at lower shear rates and then increases as the shear rate increases[366]. The onset of the shear thickening was observed at effective shear rate ~ 100 s^{-1}.

The effective shear rate in porous media for the experiments conducted here, ~27-29 s^{-1}, is well below the effective shear rate for onset of shear thickening as observed by Chauveteau et al[36]. Note that the permeability and polymer type could influence the onset of shear thickening however; it is safe to assume that the experiments performed in this study are in the effective shear rate of shear thinning.

Recently, Seright et al. reported resistance factor vs. flux rate using porous media with 3000 to 5000 md permeability and HPAM polymers with molecular weight (M.W) ~ 18-20 millions[38]. They have reported that shear thickening was observed when they used flux rate above 10 ft/day.

The Flux rate for the model used in our experimental study ($A = 6.413\ cm^2$) with injection rate of 0.25 ml/min was equal to 1.84 ft/day, which is well below that critical flux value of 10 ft/day reported by Seright et al.[39]

Comparing our experimental results with the previously published data, we have concluded that flow rates used in our experiments might not be high enough to induce shear thickening effect.

3.6. Results and Discussion

3.6.1. Rheological behaviors of polymer solutions

The comparative steady-shear rheological results of 0.1 wt % P(AA-*co*-NVP) and FLOPAAM 3130S aqueous solutions at 22 degC are presented in Figure 3.3 with no alkali and 1% NaOH addition (for 24 hours of mixing).

For FLOPAAM 3130S (with no alkali and 1% NaOH), the shear viscosity decreased with increasing the shear rate (Figure 3.3(a)). This is ascribed to uncoiling and aligning of polymer chains when exposed to shear flow. At shear rates > $0.1s^{-1}$ the shear viscosity-shear rate relationship was fitted with the power law model. The apparent viscosity of FLOPAAM 3130S polymer decreased significantly in 1% NaOH solution. While for P(AA-*co*-NVP) from Figure 3.3(b), it is clear that polymer sample showed slight improvement in apparent viscosity in presence of 1% NaOH. The apparent viscosity FLOWPAM and P(AA-*co*-NVP) polymer is compared in Figure 3.3(c). This comparison shows that P(AA-*co*-NVP) has good shear-thinning behaviour, similar to FLOPAAM 3130S, under alkali environment, which is favourable for the AP solution to penetrate into the near wellbore. Moreover, the apparent viscosity of the P(AA-*co*-NVP) and FLOPAAM 3130S in presence of 1% NaOH is very similar within the whole shear rate range examined (Figure 3.3(c)). This result is quite attractive, as one must bear in mind that the molecular weight of P(AA-*co*-NVP) is almost half than that of HPAM.

3.6.2. Dynamic viscoelastic behaviors

In the past, elasticity of polymer solutions hasn’t been considered as an important parameter for macroscopic sweep efficiency. However, in recent years it has gained a significant focus for mobilization of residual oil. Recent studies show that elasticity of a polymer influences the micro-scale displacement recovery. Generally, higher the elasticity of a polymer, i.e., elastic or storage modulus (G’) higher the incremental recovery, when viscosities are same[37, 39-45].

Figure 3.4(a) and 3.4(b) show the comparative variation of viscoelastic properties for P(AA-*co*-NVP) and FLOPAAM 3130S solution as a function of NaOH. In Figure

3.4(c), the storage moduli (G') and loss moduli (G") of FLOPAAM 3130S and P(AA-*co*-NVP) solution, with NaOH, as a function of frequency are presented. It is evident from the figures that in presence of NaOH, the loss modulus (G") and elastic modulus (G') of the P(AA-*co*-NVP) solution remains nearly unchanged. However, G' and G'' of FLOPAAM 3130S polymer solution decreased after addition of NaOH. G' of P(AA-*co*-NVP) rapidly surpasses G'' in the course of addition of alkali, indicating that the elastic behavior predominates at high alkali concentration.

It is important to note that P(AA-*co*-NVP) showed improvement in rheological and dynamic viscoelastic properties in presence of alkali. This is because of an increase in electrostatic repulsion in polymer chains due to conversion of carboxylic group to carboxylate ion, resulting in polymer swelling and increased rheological and viscoelastic properties. For HPAM, Na^+ ions shield the charge on hydrolyzed carboxylic group; hence there is no significant change in polymer swelling and its rheological as well as viscoelastic behaviour. Higher elastic properties of copolymer as a result of stretching of polymer chains in alkaline solution could possibly allow the polymer to elongate more in porous media. While in case of HPAM, elongation of HPAM chains may not be significant due to shielding of hydrolyzed carboxylate group in presence of alkali.

In past, NVP monomer has been used with AM to form copolymers as it protects the AM group from harsh conditions like high temperature and presence of divalent ions[47]. The copolymer (Superpusher SAV505 from SNF Floeger) is known to be more resistant to hydrolysis as the number of NVP units surrounding acrylamide group increases**.** The mechanism suggested for this stability could be steric hindrance or intramolecular hydrogen bonding.[28-29]

Compared with FLOPAAM 3130S, the unique rheological responses furnish P(AA-*co*-NVP) polymer with a great alternate potential to enhance oil recovery in heavy oil reservoirs. To further understand this potential, core flooding experiments were performed.

3.6.3. Oil Recovery Performance

After comparing the rheological data for both polymers, core flooding experiments were conducted to analyze their performance for oil recovery. The experiments were performed as per the procedure described earlier.

Increase in percentage oil recovery because of the polymer flooding is shown in Figure 3.6 with respect to pore volume of polymer injected. Oil recovery with P(AA-*co*-NVP) + 1% NaOH (AP flood) increased significantly as compared to straight polymer flood of P(AA-*co*-NVP) without alkali (Table 3.2). This oil recovery increase is mainly because of alkali reducing the interfacial tension, considering the sweep efficiency was similar for polymer and alkali-polymer flood as the rheology of P(AA-*co*-NVP) remained nearly unchanged after addition of 1% NaOH. On the other hand, there is only a slight change in increased oil production in case of FLOPAAM 3130S polymer + 1% NaOH compared to straight FLOPAAM 3130S polymer. From these results it is evident that in case of FLOPAAM 3130S, the benefit of IFT reduction by addition of 1% NaOH on overall recovery was minimum due to loss of viscosity in presence of alkali and consequently lower sweep efficiency.

The overall recovery of P(AA-*co*-NVP) + 1%NaOH and FLOPAAM 3130S + 1% NaOH are comparable. This is due to the reason that both these AP solutions have similar rheological profile as shown earlier. However, it is important to note that molecular weight of P(AA-*co*-NVP) is almost half than the FLOPAAM 3130S and increasing the molecular weight of P(AA-*co*-NVP) could have the additional positive effect on oil recovery.

3.6.4. Pressure Drop

The results of pressure change during polymer flooding and alkali-polymer flooding for both polymers, FLOPAAM 3130S and P(AA-*co*-NVP) are shown in Figure 3.7 to compare the movement of flooding agent through porous media. The maximum pressure during all four flooding experiments and the stable end pressure values are reported in Table 3.4. A typical profile shows an increase in pressure drop at early stage of flood due to mobilization of viscous fluids. After sometime, favorable relative permeability effects dominate and consequently decrease in pressure drop to a stable end pressure. The highest-pressure drop was observed during FLOPAAM 3130s polymer flood, which also has the highest shear viscosity. Generally, it is believed that alkali decreases the polymer viscosity and improves injectivity. The pressure drop during AP flood depends on the solution viscosity and oil mobilization. Recently, Kazempour et al.[18] reported reduction of viscosity of polymer solution with addition of alkali and consequently they observed lower pressure drop for AP flood compared to respective polymer flood. In our experiments, both AP floods, FLOPAAM 3130S +1%NaOH and P(AA-*co*-NVP) +1%NaOH, showed lower pressure drop compared to respective polymer floods. Addition of 1% NaOH decreased the maximum pressure drop across the core to ~372 kPa from ~585 kPa for FLOPAAM 3130S polymer, and to ~ 235 kPa (lowest of all four coreflood) from ~605 kPa for P(AA-*co*-NVP). One could have expected this for FLOPAAM 3130S as addition of 1% NaOH has reduced the shear viscosity of solution. However, in the case of P(AA-*co*-NVP), the shear viscosity showed very negligible change after addition of 1% NaOH, but the pressure drop reduced significantly. This could be due to the fact that addition of alkali has reduced the copolymer P(AA-*co*-NVP) adsorption and retention in the core.

The values of residual resistance factor are reported in Table 3.3. The residual resistance factor for FLOPAAM 3130S increased from ~ 3 in polymer flood to ~ 10

during AP flood. While in case of P(AA-*co*-NVP), the residual resistance factor remained same for both the cases. This suggests that the addition of 1% NaOH has increased the adsorption/retention of FLOPAAM 3130S polymer, but for P(AA-*co*-NVP), adsorption/retention of polymer decreased with addition of 1% NaOH. This can also be confirmed by the change in polymer adsorbed layer thickness.

3.7. Conclusion

1. P(AA-*co*-NVP) copolymer was synthesized using acrylic acid (AA) and N-vinyl-2-pyrrolidinone (NVP) and studied as an alternate to HPAM for chemical flooding of heavy oil recovery.
2. P(AA-*co*-NVP) has shown improved rheological and dynamic viscoelastic properties under strong alkali conditions because of an increase in electrostatic repulsion in polymer chains due to conversion of carboxylic group to carboxylate ion, resulting in polymer swelling. For HPAM, Na^+ ions shield the charge on hydrolyzed carboxylic group; hence there is no significant change in polymer swelling and its rheological as well as viscoelastic behaviour.
3. The oil recovery for high molecular weight HPAM polymer did not show significant improvement during AP flood over polymer flood, as lower sweep efficiency due to viscosity reduction under strong alkali influence negates the recovery improvement by lower IFT. However, for P(AA-*co*-NVP) copolymer, the addition of strong alkali increased the oil recovery during AP flood as sweep efficiency increased due to improved rheological and dynamic viscoelastic properties in presence of alkali. The final recovery during AP flood for P(AA-*co*-NVP) is comparable to that for higher molecular weight HPAM. Potentially, higher molecular weight P(AA-*co*-NVP) copolymer can increase oil recovery

higher than conventional HPAM during chemical flood.

4. Experimental results show that the injectivity of P(AA-*co*-NVP) is significantly higher than HPAM in both flooding modes, polymer and alkali-polymer, and the observed residual resistance factor is lower. During AP flood, polymer retention and adsorption is also lower for P(AA-*co*-NVP) than HPAM. Higher injectivity for P(AA-*co*-NVP) is because of the steric hindrance provided by NVP group present in the copolymer. This also assisted in lower adsorption of polymer on porous media. For HPAM, adsorption is lower in absence of alkali, i.e. during polymer flood, due to lesser amount of charge density. While in alkali environment, number of carboxylate ions increased (high charge density), hence resulted into higher adsorption of polymer during AP flood.

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Nomenclature

A = Cross sectional area of the core, cm^2

e = Adsorbed Polymer Layer Thickness, μm

F_R = Resistance Factor

F_{RR} = Residual Resistance Factor

G' = Elastic modulus

G'' = Loss modulus

k = Permeability, cm^2

k_w = Permeabilty of water, mD

k_p = Permeabilty of Polymer solution, mD

n = Flow Behaviour Index

f = Porosity, fraction

λ_w = Mobility of water

λ_p = Mobility of Polymer solution

μ_w = Viscosity of water, cP

μ_p = Viscosity of polymer solution, cP

ΔP_w = Pressure Drop during Water Injection, kPa

ΔP_P = Pressure Drop during Polymer Injection, kPa

r_P = Average Pore Diameter, μm

g = Shear rate in porous media, $1/s$

Q = Flow rate, cm^3/s

3.8 References

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Table 3.1. Monomer/Initiator Variation for desired polymer

S.No.	Monomer/Initiator Ratio	VP content in feed (mol %)	AAc content in feed (mol %)	Solvent DMF (ml)
1	6260	20	80	5
2	12520	20	80	5
3	12520	20	80	10
4*	12520	10	90	5

* Selected for the comparison with FLOPAAM 3130S

Table 3.2. Core properties and Oil recovery

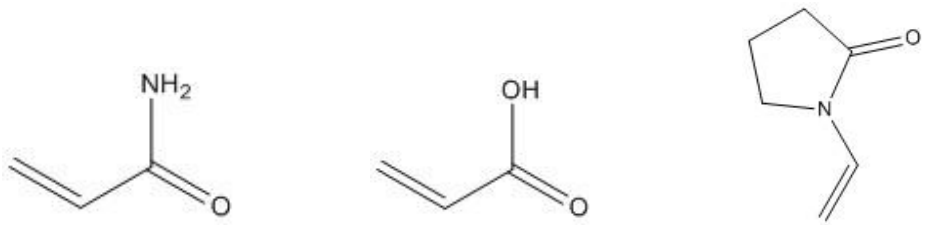
Flooding Agent	Porosity (%)	Water Permeability (mD)	Initial oil saturation (S_{oi} %)	Waterflood recovery (%OOIP)	Polymer Flood Recovery (%OOIP)	Final Oil Recovery (%OOIP)	pH
Flopaam 3130S	44.1	388.13	88.7	12.7	41.4	54.1	7.5
Flopaam 3130S + 1% NaOH	42.9	355.28	89.1	11.9	45.9	57.8	12.2
P(AA-*co*-NVP)	43.6	357.54	88.5	13.2	37.7	50.9	3.6
P(AA-*co*-NVP) + 1% NaOH	44.1	372.66	89.3	12.6	47.3	59.9	12.2

Table 3.3. Residual Resistance Factor Value

Flooding Agent	Residual Resistance Factor
Flopaam 3130S	3.04
Flopaam 3130S +1% NaOH	10.02
P(AA-*co*-NVP)	3.53
P(AA-*co*-NVP) +1% NaOH	3.72

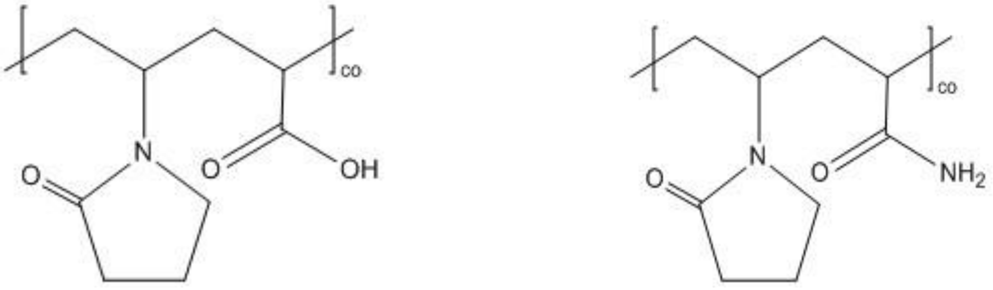
Table 3.4. Maximum and Final pressure drops during polymer flooding

RUN	Flooding Agent	Maximum Pressure (kPa)	End Pressure (kPa)
1	FLOPAAM 3130S	584.5	206.8
2	FLOPAAM 3130S + 1% Alkali	372.1	260.6
3	P(AA-*co*-NVP)	606.7	179.3
4	P(AA-*co*-NVP) + 1% Alkali	234.4	144.8



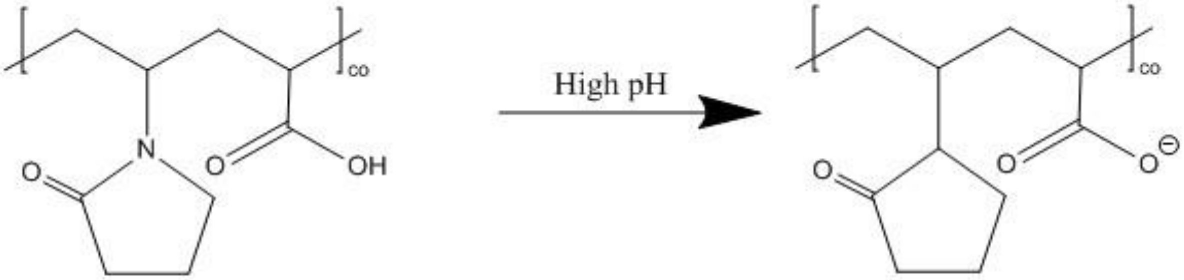
Acrylamide Acrylic Acid N-Vinyl-2-Pyrrolidinone

(a)



AA-NVP copolymer AM-NVP copolymer

(b)



(c)

Figure 3.1: Chemical structures (a) Monomers (b) Copolymers, and (c) Negative charge generation at high pH increasing electrostatic repulsion

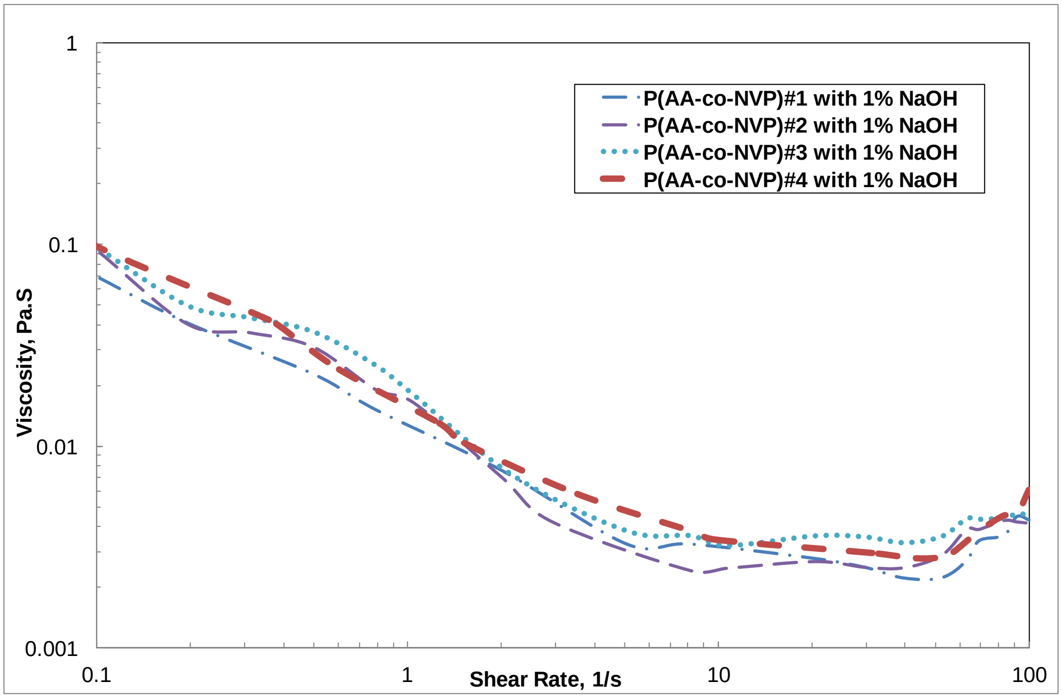


Figure 3.2: Viscosity of various compositions (Table-3.1) of P(AA-*co*-NVP) in presence of 1% NaOH (25°C)

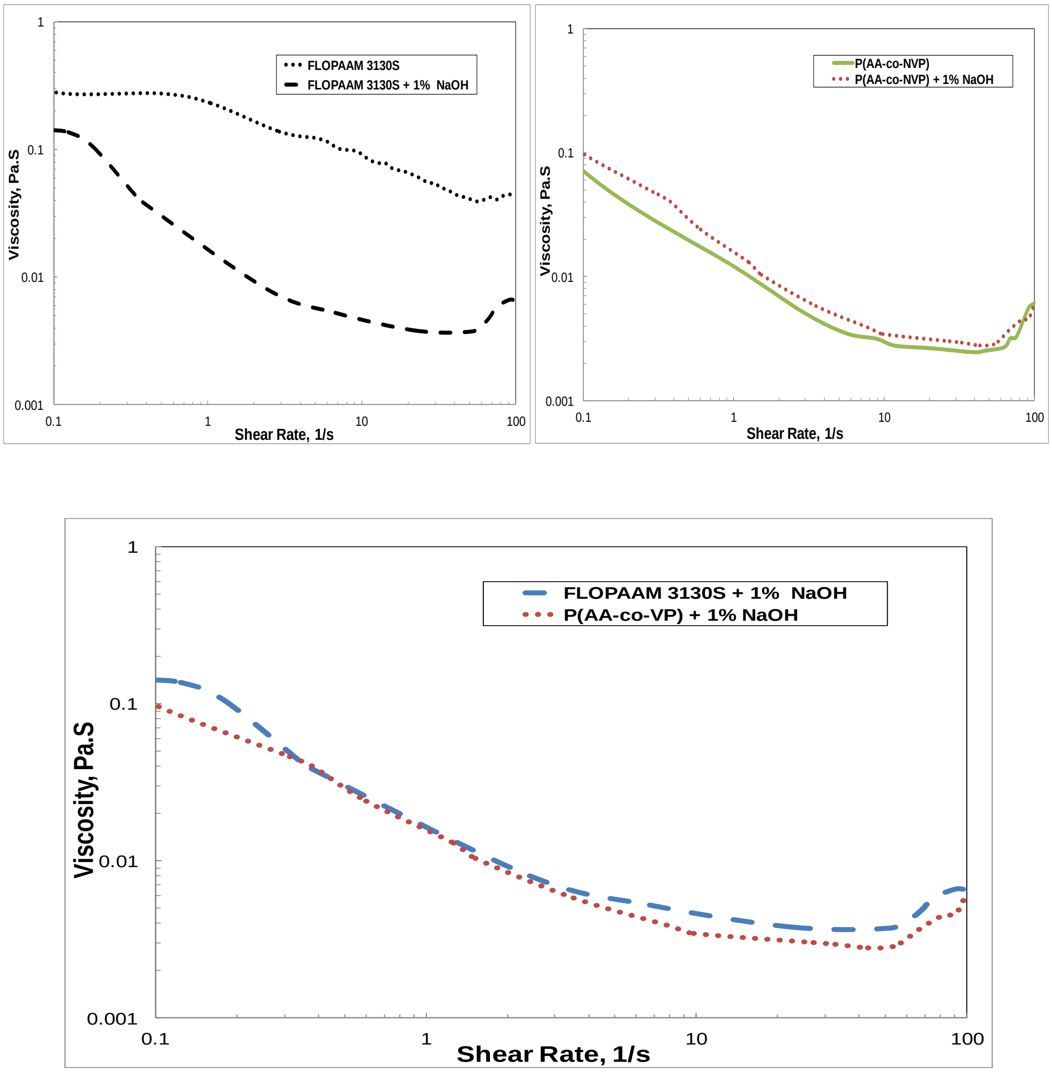


Figure 3.3: Shear rate vs viscosity Plot (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-NVP)+ 1% NaOH, and (c) FLOPAAM 3130S + 1% NaOH vs P(AA-*co*-NVP)+ 1% NaOH

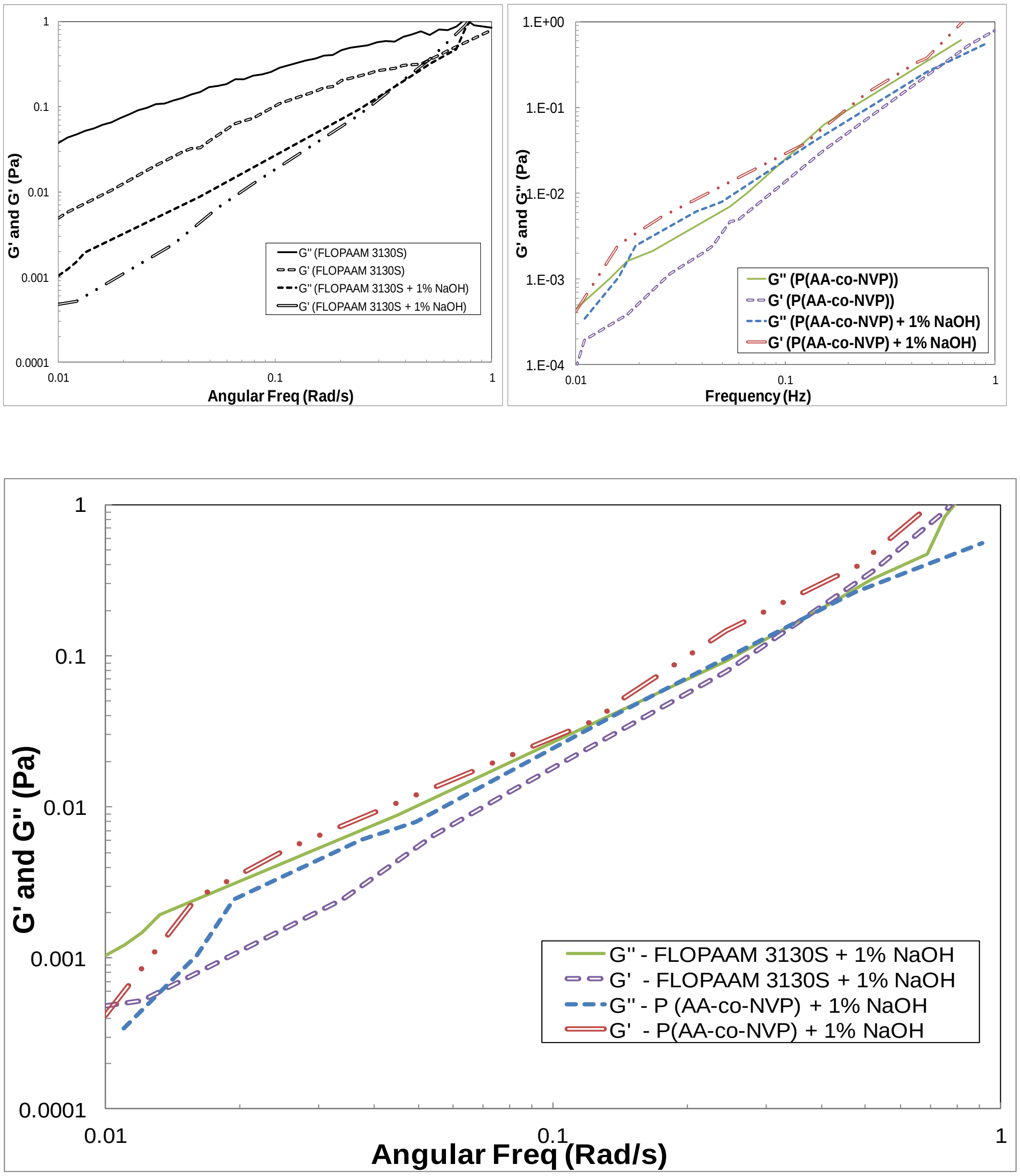


Figure 3.4: Viscous and elastic modulus vs angular frequency (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-NVP) + 1% NaOH, and (c) FLOPAAM 3130S + 1% NaOH vs P(AA-*co*-NVP)+ 1% NaOH

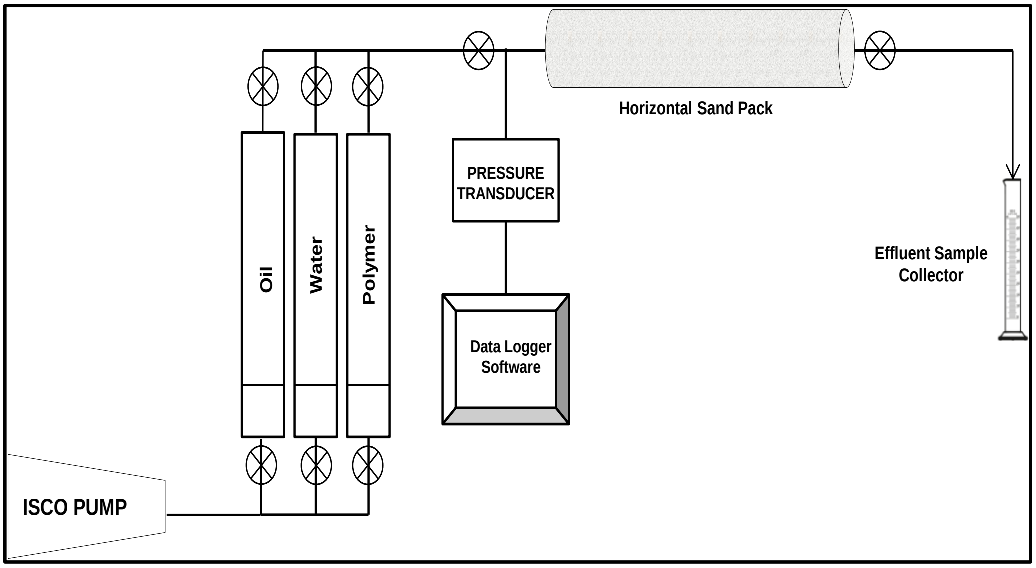


Figure 3.5: Experimental setup for core flooding: linear core with a injector and producer on opposite sides

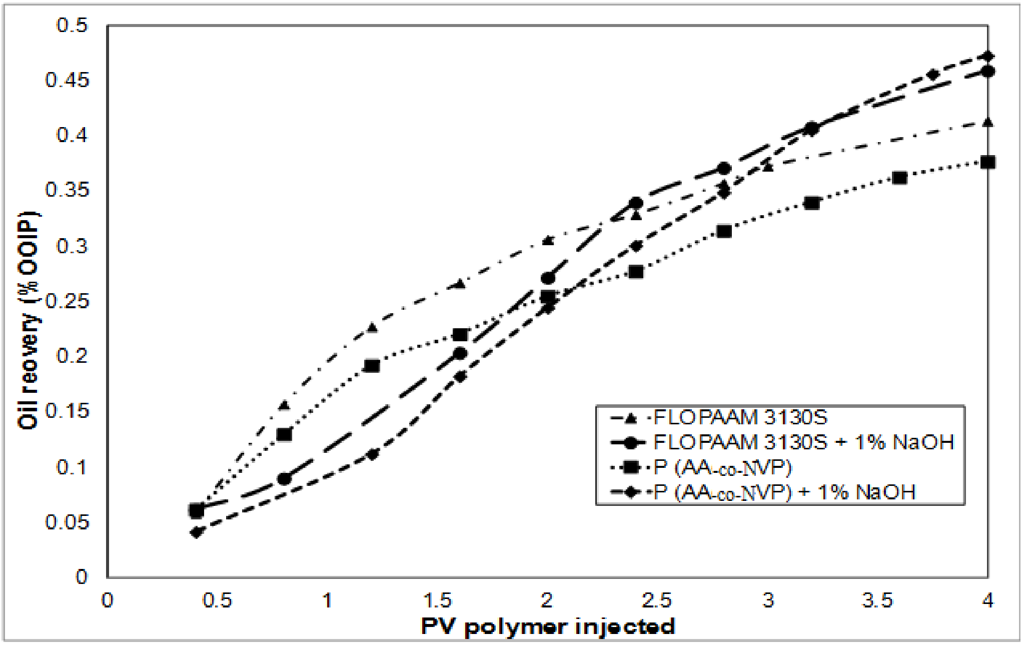


Figure 3.6: Percentage oil recovery based on OOIP for polymer and alkaline-polymer flooding

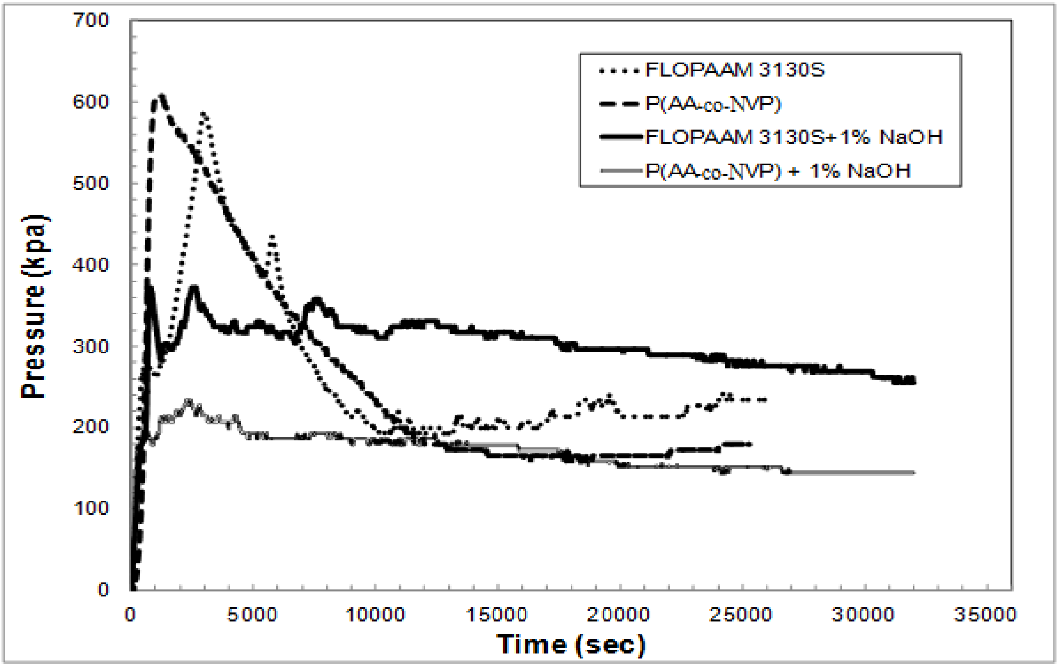


Figure 3.7: Pressure drop during polymer and alkaline-polymer flooding

CHAPTER 4

Improving injectivity of chemical EOR for heavy oil recovery using acrylic acid and N-vinyl-2-pyrrolidinone copolymers and crosslinked polymers

4.1. Introduction

During chemical enhanced oil recovery (EOR), polymer flooding can be used in place of water flooding or to augment an existing flood. In mobility control processes, the polymer is used to alter the fractional flow characteristics of the water phase, which displaces the oil. In profile control processes, however, polymer gels are used to block water channels and divert flow to portions of the reservoir which have not been properly swept.

There are a number of water-soluble polymers that are being widely used in chemical EOR processes for mobility control. The most common polymer currently used in industry is polyacrylamide with varying degrees of hydrolysis (charge densities) and molecular weights[1]. Their main purpose is to increase the viscosity of injection water that slows down the water phase in porous media. As shown in Eq. 1, the mobility ratio is inversely proportional to the water viscosity. Increased viscosity then reduces the mobility ratio.

$$\mathrm{M} = \frac{\lambda_w}{\lambda_o} = \frac{k_w/\mu_w}{k_o/\mu_o} \qquad (1)$$

With a reduced mobility ratio, the sweep efficiency increases and consequently, oil recovery improves.

In some cases, a favorable mobility ratio alone is not sufficient for oil recovery improvement. For example, if the reservoir is heterogeneous, polymer-assisted water flooding can be carried out to reduce water mobility in the high-permeability layers to recover oil from the low-permeability layers. These types of water-diverting techniques (also called profile correction, conformation improvement, etc.) have been performed for many years. An important function of these polymers is the improvement of vertical sweep efficiency around the vicinity of injection wellbores. Therefore, mobility control is considered an attempt to improve the *volumetric* sweep efficiency of a reservoir, while conformance control is an attempt to improve only the *vertical* sweep efficiency[2]. Conventional polymer floods (mobility reduction) are very effective in controlling mobility as they are used in very high concentrations so that the polymer is able to sweep as much of the reservoir as possible. However, in profile control treatments (for conformance control/water shutoff), polymer gel/polymer microgel floods are much more suitable as gelant is able to propagate through high permeability channels. Typically, these solutions contain lower concentrations of polymer than those designed for mobility control. The difference between conventional polymer floods and polymer gel floods is the presence of a crosslinker. Crosslinking agents yield a polymer network that enables a more significant, longer lasting and optimal permeability reduction which results in increased resistance to flow in high permeability areas and hence, assists in fluid diversion[3-6].

A specific application of polymer in the oil and gas industry may warrant different characteristics of flow and adsorption as well as design. For example, polymers used in EOR should have high injectivity and low adsorption. On the other hand, high adsorption and thick residual polymer layers are key in the successful use of polymers in water shut-off. For mobility control applications, the injectivity behavior of a polymer solution is one of its most important characteristics. Polymer solutions with good injectivity behavior are necessary for successful field use. Very often the injectivity and mobility properties of the polymers or the corresponding solutions are poor and may cause undesired plugging (in pores and throats of a rock or subterranean formation), especially for high molecular weight polymers (Mw > 8 million Da). This is mainly because micro gel formation arises from partially soluble traces of branched or crosslinked chain species due to the manufacturing process[7]. These micro gels can damage the formation due to the plugging of pores and therefore, lead to an undesired significant increase in the injection pressure, a reduction of injectivity as well as the blocking of sweep-targeted areas of the reservoir. Thus, despite beneficially increasing the injection fluid's viscosity, there are major drawbacks to these high molecular weight polymers since they can lead to a substantial reduction in injectivity, slow fluid throughput and delayed oil production from flooded fields. Moreover, the most typically used high molecular weight polymer (i.e. hydrolyzed polyacrylamide (HPAM) polymer) could undergo chemical or thermal degradation and cause severe loss of injectivity even at the near wellbore condition.

In western Canada, chemical flooding is used for heavy oil recovery from shallow and thin pay reservoirs, requiring the use of polymers for mobility control. The injectivity of chemical solutions is a major challenge for many operators in western Canada and in China where they often require well stimulation and wellbore cleaning for improved injectivity. In 2009, Cenovus reported an increase in operating pressure in their two horizontal wells with injected ASP solution that caused a decrease in the injection rate of the flood from a design of 150 m^3/d to well below 120 m^3/d at times at their Pelican Lake site.[8] Increasing the injection rate into the pool and thereby increasing the production rate while maintaining a voidage replacement ratio (VRR) of 1.0 could optimize the operations. The Taber South ASP Pilot in southern Alberta, a tertiary ASP flood application in a mature water flood in a medium gravity oil pool, also reported severe equipment scaling problems and injectivity loss.[9] About 12% of polymer injection wells at Daqing, China, had poor injectivity or decreasing injectivity. The reservoirs with poor injectivity behavior typically require physical or chemical treatment that can be very expensive and severely affect the overall economics of a polymer flooding operation. Therefore, it is important that the injected polymer or micro gels show higher injectivity (i.e. lower injection pressure) to ensure that these micro gels propagate into the reservoir and not damage the formation by plugging the pores of the rock. With the development of many new types of water-soluble polymers, it is crucial to investigate whether these can be successfully injected in core samples if these are to be applied in EOR.

The use of hydrophobically modified polymers has been suggested as a replacement due to HPAM's unfavorable degradation in presence of alkali or salt (divalent ions in general). Hydrophobic groups will aggregate in semi-dilute water solutions, thus increasing the solution viscosity. This increase in solution viscosity can be higher than HPAM depending on the concentrations. Studies have demonstrated that the resistance factor (RF) and residual resistance factor (RFF) can also be higher for hydrophobically modified polymers due to the significantly higher adsorption of hydrophobically modified polyacrylamides as compared to HPAMs (i.e. through the development of a thicker polymeric layer on the rock surface). [10-17] A high amount of adsorption (and thus a thicker layer) can cause issues with injectivity (i.e. plugging, where an exponential increase in the pressure of the reservoir is observed). However, the issue of injectivity is debatable as no injectivity problems have been reported for hydrophobically modified PAMs in dilute and semi-dilute regimes. The formation of a gel layer, on the injection side, was observed only below a critical threshold permeability and pore throat radius.[18]

The use of pH-sensitive polymers could provide a way of reducing the injection pressures needed for the polymer solution. By injecting a pH-buffered polymer solution at low pH, we can achieve significantly lower injection pressures since the polymer viscosity is low. The pH of the solution increases, due to a reaction of the polymer's acid content with the carbonate and other minerals in the reservoir rock, and the polymer viscosity increases by at least an order of magnitude.[19] This allows lower injection pressures in polymer injection wells. Kazempour et al.[20] mentioned that increasing the pH could reduce this adsorption of polymer onto rock surfaces, which will result in lower RF values, hence increasing the injectivity. They showed that alkali increases the ionic strength and alters the surface charge. Thus, the addition of alkali to the polymer, which decreases the viscosity of the polymer and reduces water saturation, could lead to a decrease in pressure drop.

Huh et al.[2] proposed to utilize pH change as the trigger for hydrogels to increase their size in situ. This is essential in improving injectivity since a polyacrylic acid (PAA) solution exhibits a low viscosity at low pH, but at pH values higher than a critical value, the viscosity will increase drastically due to electrostatic repulsion. By injecting a polyelectrolyte at low pH, low viscosity and good injectivity is achievable. Once deep in the reservoir, the pH of water can increase due to a reaction of the injected acid with the carbonate and other minerals in the reservoir rock. Also, using PAA as an injectant will help in preventing chemical loss because the adsorption of PAA is small on rock surfaces as compared to other EOR polymers.

The objective of this work is to study AA-NVP copolymers and crosslinked polymers as alternatives to conventional HPAMs with similar viscoelastic properties, but improved injectivity for AP flooding. The injectivity characteristics of the HPAM and the acrylic acid and N-vinyl-2-pyrrolidinone (AA-NVP) copolymer and crosslinked polymer were evaluated by core flow experiments.

4.2. Materials

4.2.1 Polymers

The polymer selected for the experiments was Flopaam 3130S supplied by SNF SAS in dry powder form. Flopaam 3130S is a polyacrylamide and water soluble with a degree of hydrolysis of 25-30 mol % with an average molecular weight of 2×10^6. Other polymers in the study include a copolymer [P(AA-*co*-NVP)] and two crosslinked polymers [cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$]. AA was purchased from Sigma-Aldrich (Canada) and purified by passing it through a basic alumina column. NVP was obtained from Sigma-Aldrich (Canada) and purified by distillation. The Milli-Q system was used in this study to purify water with a Millipore. Other chemicals were used as received. Fig. 4.1 shows the monomers (Fig. 4.1(a)) used, probable co-polymer structure (Fig. 4.1(b)), the crosslinker used for polymerization (Fig. 4.1(c)) and the probable crosslinked polymer structure (Fig. 4.1(d)).

4.2.1.1 Synthesis of co-polymer [P(AA-*co*-NVP)]

The copolymer was polymerized by free radical polymerization. The following is a typical synthesis protocol: AA (2.89 g, 40.1 mmol), NVP (0.495 g, 4.45 mmol) and 4,4'-azobis (4-cyanovaleric acid) (ACVA) (1.0 mg, 3.56×10^{-3} mmol) were dissolved in 5 mL of N,N-dimethylformamide (DMF). The mixture was allowed to polymerize for 24 h at 60 °C under inert atmospheric conditions after degassing with nitrogen gas for 30 min. The resulting highly viscous copolymer was diluted with DMF (10 mL) and subsequently purified by dialysis against ethanol and water. Finally, after freeze-drying, the copolymer was collected as a powder.

4.2.1.2 Synthesis of Crosslinked Polymers [cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$]

AA (2.89 g, 40.1 mmol), NVP (0.495 g, 4.45 mmol), 4,4'-azobis(4-cyanovaleric acid) (ACVA) (1.0 mg, 3.56×10^{-3} mmol) and N,N'-methylenebisacrylamide (6.8 mg, 4.46

$\times 10^{-2}$ mmol) (crosslinker: 0.1 mol%) were dissolved in 10 mL of N,N-dimethylformamide (DMF). After degassing with nitrogen gas for 30 min, the mixture was allowed to polymerize for 12 h at 60 °C under inert atmospheric conditions. The resulting highly viscous crosslinked polymer [cP(AA-*st*-NVP)$_1$] was diluted with DMF (10 mL) and subsequently purified by dialysis against ethanol and water. Crosslinked polymer [cP(AA-*st*-NVP)$_1$] was collected after freeze drying as a powder. By changing the crosslinker concentration to 0.05 mol % (3.4 mg, 2.23 $\times 10^{-2}$ mmol), crosslinked polymer [cP(AA-*st*-NVP)$_2$] was prepared.

4.2.2 Alkali

The alkali used in this study was pellet-sized NaOH (more than 97 % purity) ordered from Sigma-Aldrich. The alkali concentration used for the experiments was 1 wt %.

4.3. Viscoelasticity Characterization of Polymer Solutions

Viscoelasticity measurements were performed by a C-VOR 150 Peltier Bohlin rheometer (Malvern Instruments, USA) with a cone-and-plate measuring system and strain model measurements at 25 ºC +/- 0.5 ºC. The cone and plate specifications for the rheometer are 60 mm for the plate diameter and for the rotating upper cone a 4º angle and diameter of 40 mm, separated by a gap of 150 µm. Polymer samples were placed in between the stationary plate and the upper cone so that the volume of the sample covered the area below the rotating cone. The following sections detail the rheological tests that were conducted for the polymers.

4.3.1 Viscometry Tests

Viscometry tests were carried out at shear rates varying from 1 to 100 s^{-1}. Shear viscosity was plotted as a function of shear rate for polymer samples in both alkaline and non-alkaline conditions.

4.3.2 Oscillation Tests

Frequency tests were carried out on polymer samples at a frequency range from 0.01 to 1 Hz, keeping the stress value constant at 0.04775 Pa. Oscillatory measurements provide the absolute values of the complex modulus |G*|, the storage modulus (elastic modulus) G' and the loss modulus (viscous modulus) G" at constant frequency and constant strain. These magnitudes of frequency and strain were selected based on the stress needed for sensitivity check.

4.4. Core Flooding Experiments

4.4.1 Experimental Setup and Petro physical Properties of Core

The diameter and length of the core used for packing sand were 1 1/4" and 6", respectively. Perforated screen at either ends of the core were used as the injector and producer. The glass beads used in the core flooding experiments were 325-mesh size with a particle size distribution of 30-50 microns and were supplied by Potters Industries LLC. To ensure the same wettability, fresh glass beads were packed for each experiment. To ensure a tight and dry pack, a mallet as well as a pneumatic vibrator was used. Permeability and porosity were measured by injecting water in the core. Porosity was measured using a specific gravity of 2.5 for the glass beads and measuring the mass of glass beads used. The pore volume (PV) of the porous medium was measured by direct method. The volume of the glass beads in the visual cell was subtracted from the bulk volume of the cell. Injection pressure and flow rate were recorded using an Omega-Dyne pressure transducer. An ISCO syringe pump 500D was used for the injection of water and polymer. Permeability for the cores lies between 340 and 370 mD.

4.4.2. Core flood Procedure

Figure 4.2 shows the schematic of the apparatus used for experiments. Experimental procedure for the injection is as follows:

1) **Primary water injection (Permeability Calculation):** Water was injected into the core at constant flow rates of 0.5, 1.0, 2.0, 3.0 and 4.0 ml/min, and the differential pressure was recorded. Water was flushed until the differential pressure stabilized.

2) **Polymer Solution Injection (Resistance Factor Calculation):** Then, the water was displaced with a polymer/polymer-alkali solution. The flow rates used for the polymer/polymer-alkali solution were same as that for water injection. Here, differential pressure was also recorded. Stable differential pressures were achieved for each flow rate.

3) **Post water injection (Residual Resistance Factor Calculation):** water was injected using the same flow rates as the primary water injection, and the differential pressure was noted. Until a constant differential pressure was attained, water was injected at each flow rate.

4.5. Important Definitions

4.5.1 Resistance Factor

The resistance factor is a term that is commonly used to indicate the resistance to flow encountered by a polymer solution as compared to the flow of plain water[21]. Resistance factor gives a good measure of the apparent viscosity of the polymer solution. Resistance factor, F_R, can be defined as the ratio of mobility of water to the mobility of a polymer solution when there is no oil present in the system.

$$F_R = \frac{(\lambda_w)}{(\lambda_P)} = \frac{\left(k_w \middle/ \mu_w \right)}{\left(k_P \middle/ \mu_P \right)} \tag{2}$$

Under given flow rate in same core flooding system, assuming the flow in porous media follows Darcy's law, RF can be expressed as:

$$F_{RR} = \frac{(\Delta P_P)}{(\Delta P_w)} \tag{3}$$

Resistance factor cannot be defined for the cases where oil is present. Table 4.1 shows resistance factor of Flopaam 3130S, P(AA-*co*-NVP), cP (AA-*st*-NVP)$_1$ and cP (AA-*st*-NVP)$_1$ with and without 1% NaOH.

4.5.2 Residual Resistance Factor

It is defined as the ratio of the permeability to water before and after the injection of polymer solution[22]. The residual resistance factor is a measure of the tendency of a polymer to adsorb into the pores and thus partially block the porous medium. This indicates that residual resistance factor has a pronounced influence on the permeability of the porous medium. This can be defined for the scenarios where there is no change in saturation over the flooding of polymer.

$$F_{RR} = \frac{(k_w)_{before}}{(k_w)_{after}} \tag{4}$$

Under given flow rate in same core flooding system, using the assumption of Darcy's law, RRF is expressed in terms of pressure drops as:

$$F_{RR} = \frac{(\Delta P_w)_{after}}{(\Delta P_w)_{before}} \tag{5}$$

If the residual resistance factor is high, it shows that adsorption and trapping of a polymer solution on porous media is on the higher side. Table 4.2 shows residual resistance factor of Flopaam 3130S, P(AA-*co*-NVP), cP (AA-*st*-NVP)$_1$ and cP (AA-*st*-NVP)$_1$ with and without 1% NaOH.

4.5.3 Injectivity

Injectivity represents the pressure gradient required to achieve a given injection flow rate[23]. For simple representation, injectivity is amount of polymer/water injected for a single unit of pressure. It is defined as:

$$I = u / \Delta P \tag{6}$$

Where ΔP is the pressure gradient and u is the injection flow rate (superficial velocity, ft/d).

Injectivity of a fluid depends on the viscosity of the fluid. If the viscosity of solution is low, it will be easier to inject certain volume of liquid solution. For polymer flooding operations, this injectivity can be describe as well injectivity index. Polymer solution's viscosity is always higher than water, hence injectivity of polymer solution will be lower than normal water flooding case. A large part of flooding operations consists of surface facilities for the injection of water or polymer solution. Hence injectivity plays a important role in flooding operations economically.

The injectivity loss I_r due to the polymer injection can be calculated as:

$$I_r = 1 - {}^{I_P}\!\big/_{I_w} \tag{7}$$

Where I_r represents polymer injectivity and I_w represents water injectivity. A loss of 0.5 to 0.9 is acceptable in fields. If it is greater than 0.9, the polymer concentration or injection rate should be modified for an economical operation. Injectivity reduction value for each run is shown in Table 4.3.

4.6. Results and Discussion

4.6.1 Effect of Alkali on Polymer Viscosity

Fig. 4.3 shows the plot of shear viscosity with respect to shear rate for all four polymers used under alkaline and non-alkaline conditions at room temperature. For each of the polymers, shear viscosity decreases as shear rate is increased, which means each of them follows a shear-thinning behaviour. This can be related to the breakage of polymer chains when exposed to high shear flow. At shear rates > 0.1 s^{-1}, the viscosity-shear rate relationship was fitted with the power law model.

The viscosity of Flopaam 3130S is higher than the other three polymers. The crosslinked polymers' viscosity is higher than that of the copolymer (Fig. 4.4(a)), which could be due to the better swelling properties of the crosslink structure as compared to the general copolymer structure. In Fig. 4.3(b), there is only a minimal change in the viscosity of the copolymer. In Figs. 4.3(c) and 4.3(d), both crosslinked polymers display similar behaviour (i.e. minimal change) when encountered with alkaline conditions. In Fig. 4.3(a), Flopaam 3130S has a significant drop in shear viscosity in presence of NaOH.

Viscosity results for all four polymers in the presence of 1% NaOH are shown in Fig. 4.3(b). It is important to note that the viscosity of Flopaam 3130S and the copolymer in the presence of 1% NaOH is very similar within the whole shear rate range examined. However, for the crosslinked polymers, there is no change in viscosity under alkaline conditions, and their viscosity values are higher than those of Flopaam 3130S and the copolymer. Thus, the behaviour of the crosslinked polymers can be beneficial for application in the oil field.

4.6.2 Effect of Alkali on Elastic Properties

Figures 4.5(a) to 4.5(d) compare the variation of viscoelastic properties for Flopaam 3130S, the copolymer and crosslinked polymers in alkaline and non-alkaline conditions. It is evident from these figures that the presence of NaOH had little impact on the elastic modulus (G') and viscous modulus (G") of the NVP-based polymer solutions. However, G' and G'' of the Flopaam 3130S polymer solution decreased after the addition of NaOH. The G' of all four polymers in 1% NaOH are presented in Fig. 4.6 as a function of frequency.

The new polymers, copolymer and crosslinked polymers showed more improvement in their rheological and dynamic viscoelastic properties in alkaline conditions compared to non-alkaline conditions. For the copolymer and crosslinked polymers, there is an increase in electrostatic repulsion in their polymer chains due to the conversion of their carboxylic groups to carboxylate ions, resulting in polymer swelling and increased rheological and viscoelastic properties. For HPAM, Na^+ ions shield the charge on the hydrolyzed carboxylic group; hence, there is either no significant change in polymer swelling and its rheological and viscoelastic behaviour or there is a decrease in these properties due to the hydrolysis of the polyacrylamide chain. The higher elastic properties of the copolymer and crosslinked polymers, as a result of the stretching of polymer chains in the alkaline solution, could possibly allow the polymer to elongate more in porous media. For HPAM, due to the shielding of the hydrolyzed carboxylate group in the presence of 1% NaOH, the elongation of HPAM chains may not be significant.

4.6.3 Injectivity loss during Polymer Injection (Resistance Factor Analysis)

The differential pressure increases across the core as the polymer is injected due to the higher viscosity of the polymer (see Fig. 4.7). If the pressure drop during one polymer injection is much higher than the second core, it indicates that most of the polymer molecules are adsorbed near the front of the core. If the RF value is the same or nearly the same for two cores in a series, the polymers could be considered as uniformly distributed throughout the core.

RF can be used to measure the efficiency of a polymer solution to sweep the reservoir and is determined by the ratio of the differential pressure during polymer injection and the differential pressure during primary injection. The differential pressure during the injection of Flopaam 3130S is much higher than that of the copolymer and crosslinked polymer, which can be directly attributed to the higher viscosity of Flopaam 3130S (compared to the copolymer and crosslinked polymer). In alkaline conditions, the viscosity values almost fall in the same range or have higher values than in non-alkaline conditions. Still, as shown in Fig. 4.3(b), the differential pressure for Flopaam 3130S + 1% NaOH is still higher than the copolymers and crosslinked polymers in 1% NaOH solution. This can further be ascertained to the RF (ratio of differential pressure during polymer injection and water injection). Table 4.1 shows the RF values for all eight cases, which include both alkaline and non-alkaline conditions. Initially, RF increases as a function of shear rate for Flopaam 3130s, but for the copolymer and crosslinked polymers, the RF almost remains as constant as the pressure gradient during the injection. This trend was similar for all four polymers in the 1% NaOH solution (Fig. 4.8). In the 1% NaOH solution, the RF for HPAM was nearly three to four times higher than the copolymer and crosslinked polymers.

The injectivity determines the pressure gradient required to achieve a given injection flow rate. Significant viscosity augmentation may result in injectivity reduction. Table 4.2 shows the injectivity loss (I_r) for each run. It is evident that for Flopaam 3130S, the I_r values are significantly larger compared to those of the copolymer and crosslinked polymers for both alkaline and non-alkaline conditions. Lower injectivity can adversely affect oil production rate in the early stages of the polymer flood.

When the I_r value for each polymer in alkaline conditions (1% NaOH) was compared to that for non-alkaline conditions, the injectivity of HPAM improved marginally whereas both of the crosslinked polymers had no significant change in I_r in the presence of NaOH. For the copolymer, although I_r increased in alkaline conditions compared to non-alkaline conditions, its I_r values were still lower than the corresponding HPAM I_r values. The improvement in HPAM injectivity in the 1% NaOH solution can be described by the viscosity loss, which is the result of polymer chain breakage in the presence of 1% NaOH.

The low RF and higher injectivity of the crosslinked polymers in all of the shear ranges studied, especially at high values of shear (flow), make crosslinked polymers strong candidates to replace HPAM polymers in the oil fields. These results also show that a polymer that has similar viscosity as high molecular weight HPAM, but higher injectivity could be better for mobility control because a greater volume of polymer can be injected with a lower pressure drop and near wellbore damage will be less.

4.6.4 Effect of polymer retention during extensive water flooding (Residual Resistance Factor Analysis)

RRF can be calculated using the ratio of the pressure gradient of water into the core after polymer injection to the pressure gradient of water before the polymer injection (i.e. primary water injection). When the pressure differential for post-water injection was compared with primary water injection, post-water injection ΔP was always higher. This higher pressure differential represents the permeability reduction due to polymer retention (adsorption and entrapment). For the effective persistence displacement of injected polymer solution, it is important that RRF be reduced to increase the effective polymer viscosity in the porous media. The lower RRF suggests less retention and in depth propagation of the polymer solution in the porous media.

Table 4.3 shows the RRF for all four polymers. In the experiments, the RRF values for HPAM as well as the copolymer and crosslinked polymers were higher in the 1% NaOH solution compared to the non-alkaline RRF values. The increase of RRF in alkaline conditions could be attributed to the retention of some polymer due to its interaction with NaOH, which results in plugging the pores and hence, pressure drop increases when final water flooding was introduced. This results in high RRF values during AP flooding compared to only P flooding. The copolymer and crosslinked polymers showed significantly lower RRF values than HPAM in both P and AP flooding (with 1% NaOH), signifying that polymer retention is extremely low in porous media, which is a very beneficial. RRF values for all four polymers in 1% NaOH solution as a function of flow rate or flux are presented in Fig. 4.9. The RRF value for HPAM increases with flow rate while the copolymer and crosslinked polymers have almost a constant value over the range of flux. Among all of the polymers, cP (AA-*st*-NVP)$_2$ has the lowest RRF in the flux range studied, suggesting the lowest adsorption near wellbore plugging.

4.7. Conclusion

- Acylic acid (AA) and N-vinyl-2-pyrrolidinone were used to synthesize new polymers (copolymer [P(AA-*co*-NVP)] and crosslinked polymer [cP(AA-*st*-NVP)]) due to their better swelling properties as well as stability in alkaline conditions.
- The laboratory experiments were conducted to evaluate AA-NVP copolymer and crosslinked polymers for near-wellbore injection improvement and mobility

control. Flopaam 3130s (HPAM) was compared with the new polymers in terms of rheology, injectivity and residual resistance factor.

- In alkaline conditions (1% NaOH), Flopaam 3130s had a similar viscosity profile as the copolymer; however, the crosslinked polymer had the highest viscosity.
- In alkaline conditions, the elasticity (elastic modulus) of Flopaam 3130s was almost the same as the copolymer.
- Injectivity loss value (represented by RF) for Flopaam 3130 was significantly higher than the copolymer and crosslinked polymers for both alkaline and non-alkaline conditions. The AA-NVP-based polymers' improved injectivity, despite having viscosity in the same range of the polyacrylamide, resulted in lower pressure drop, which can directly be related to the pumping costs for flooding operations during oil recovery. Improved oil recovery can be attributed to higher viscosity behaviour.
- Considering viscosity stability, the injectivity and residual resistance factor, the crosslinked polymers performed better than the conventional high molecular weight HPAM for AP flooding.
- The high injectivity of these polymers enable the effective injection of AP solution through the near wellbore region and ensures the long distance transport of the polymer solutions for mobility control.
- The adsorption of the copolymer and crosslinked polymers on rock is small compared to HPAM.

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Nomenclature

F_R = Resistance Factor

F_{RR} = Residual Resistance Factor

G' = Elastic modulus, Pa

G'' = Loss modulus, Pa

I = Injectivity, ml/min/kPa

I_P = Polymer Injectivity, ml/min/kPa

I_w = Water Injectivity, ml/min/kPa

I_r = Injectivity Loss

k_w = Permeabilty of water, *mD*

k_p = Permeabilty of Polymer Solution, *mD*

M = Mobility Ratio

λ_w = Mobility of water

λ_p = Mobility of Polymer Solution

μ_w = Viscosity of water, *cP*

μ_p = Viscosity of polymer solution, *cP*

ΔP_w = Pressure Drop during Water Injection, *kPa*

ΔP_P = Pressure Drop during Polymer Injection, *kPa*

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Table 4.1: Resistance Factor for four polymers in alkaline and non-alkaline conditions

Flooding Agent	Flowrate (ml/min)				
	0.5	1	2	3	4
Flopaam 3130s	4.00	6.99	15.22	14.99	12.16
Flopaam 3130s + 1% NaOH	1.50	3.33	5.50	6.11	7.12
P (AA-*co*-NVP)	2.00	1.33	1.17	1.25	1.60
P (AA-*co*-NVP)+ 1% NaOH	4.00	3.00	2.43	2.62	2.45
cP (AA-*st*-NVP)$_1$	1.50	1.33	1.25	1.17	1.42
cP (AA-*st*-NVP)$_1$+ 1% NaOH	2.00	1.50	2.00	1.60	2.00
cP (AA-*st*-NVP)$_2$	2.00	1.50	1.67	1.50	1.60
cP (AA-*st*-NVP)$_2$+ 1% NaOH	3.00	2.00	2.00	1.60	1.66

Table 4.2: Injectivity loss for four polymers in alkaline and non-alkaline conditions

Flooding Agent	Flowrate (ml/min)				
	0.5	1	2	3	4
Flopaam 3130s	0.75	0.86	0.93	0.93	0.92
Flopaam 3130s + 1% NaOH	0.33	0.70	0.82	0.84	0.86
P (AA-co-NVP)	0.50	0.25	0.14	0.20	0.37
P (AA-co-NVP)+ 1% NaOH	0.75	0.67	0.59	0.62	0.59
cP (AA-st-NVP)1	0.33	0.25	0.20	0.14	0.30
cP (AA-st-NVP)1+ 1% NaOH	0.50	0.33	0.50	0.38	0.50
cP (AA-st-NVP)2	0.50	0.33	0.40	0.33	0.38
cP (AA-st-NVP)2+ 1% NaOH	3.00	2.00	2.00	1.60	1.66

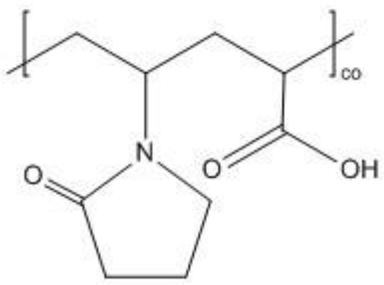
Table 4.3: Residual Resistance Factor for four polymers in alkaline and non-alkaline conditions

Flooding Agent	Flowrate (ml/min)				
	0.5	1	2	3	4
Flopaam 3130s	5.00	4.00	3.66	3.75	3.33
Flopaam 3130s + 1% NaOH	4.99	4.00	5.25	6.77	8.26
P (AA-co-NVP)	2.00	1.00	0.83	0.88	0.80
P (AA-co-NVP)+ 1% NaOH	4.00	3.66	2.96	3.86	3.80
cP (AA-st-NVP)1	1.50	1.33	1.50	1.17	1.14
cP (AA-st-NVP)1+ 1% NaOH	3.00	3.00	3.00	2.40	2.33
cP (AA-st-NVP)2	2.00	1.50	1.67	1.50	1.80
cP (AA-st-NVP)2+ 1% NaOH	3.00	2.00	2.34	2.00	1.83

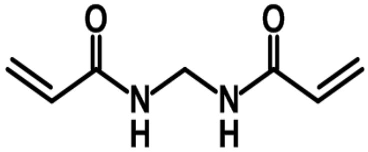
Acrylic Acid

N-Vinyl-2-Pyrrolidinone

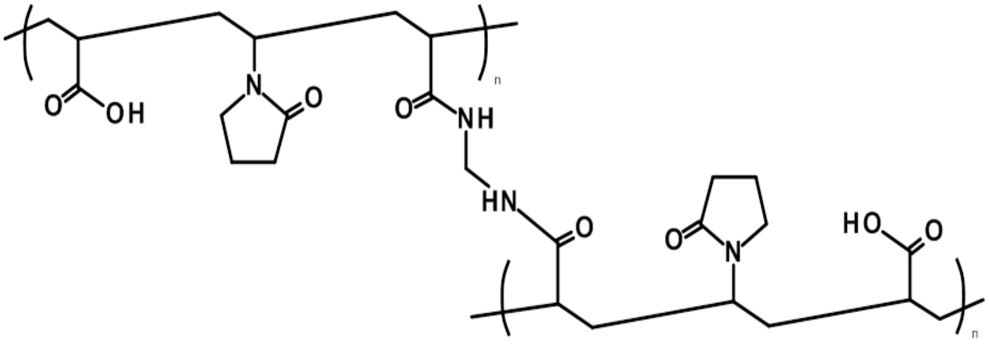
(a)



(b)



(c)



(d)

Figure 4.1: Chemical structures (a) Monomers (b) Copolymer (c) Crosslinker (d) Probable AA-NVP Crosslinked Polymer Structure

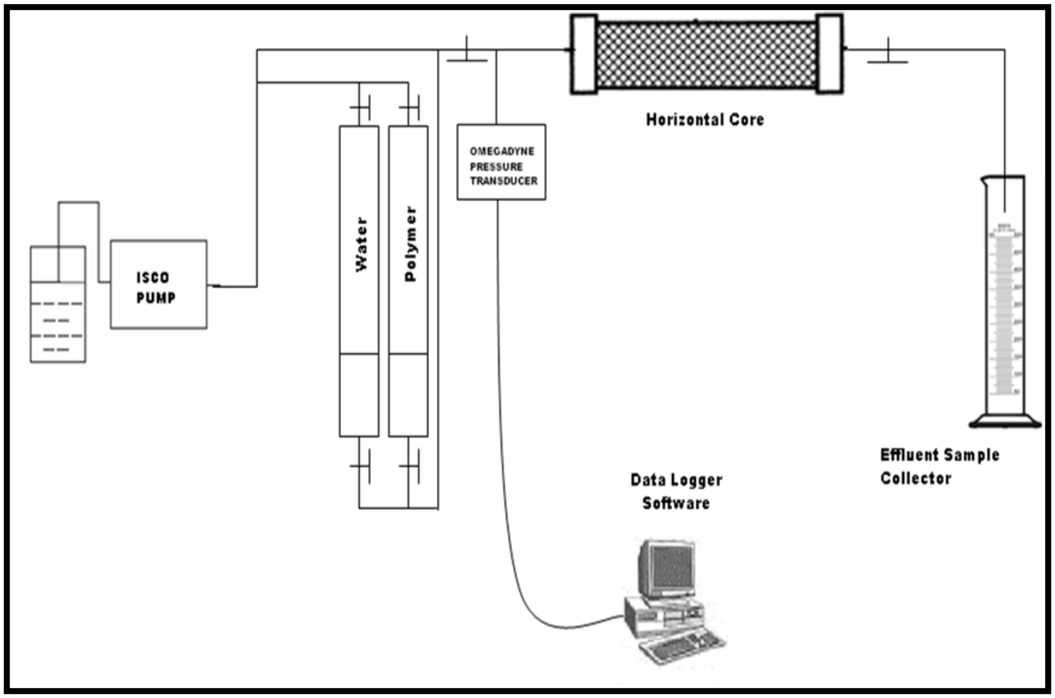
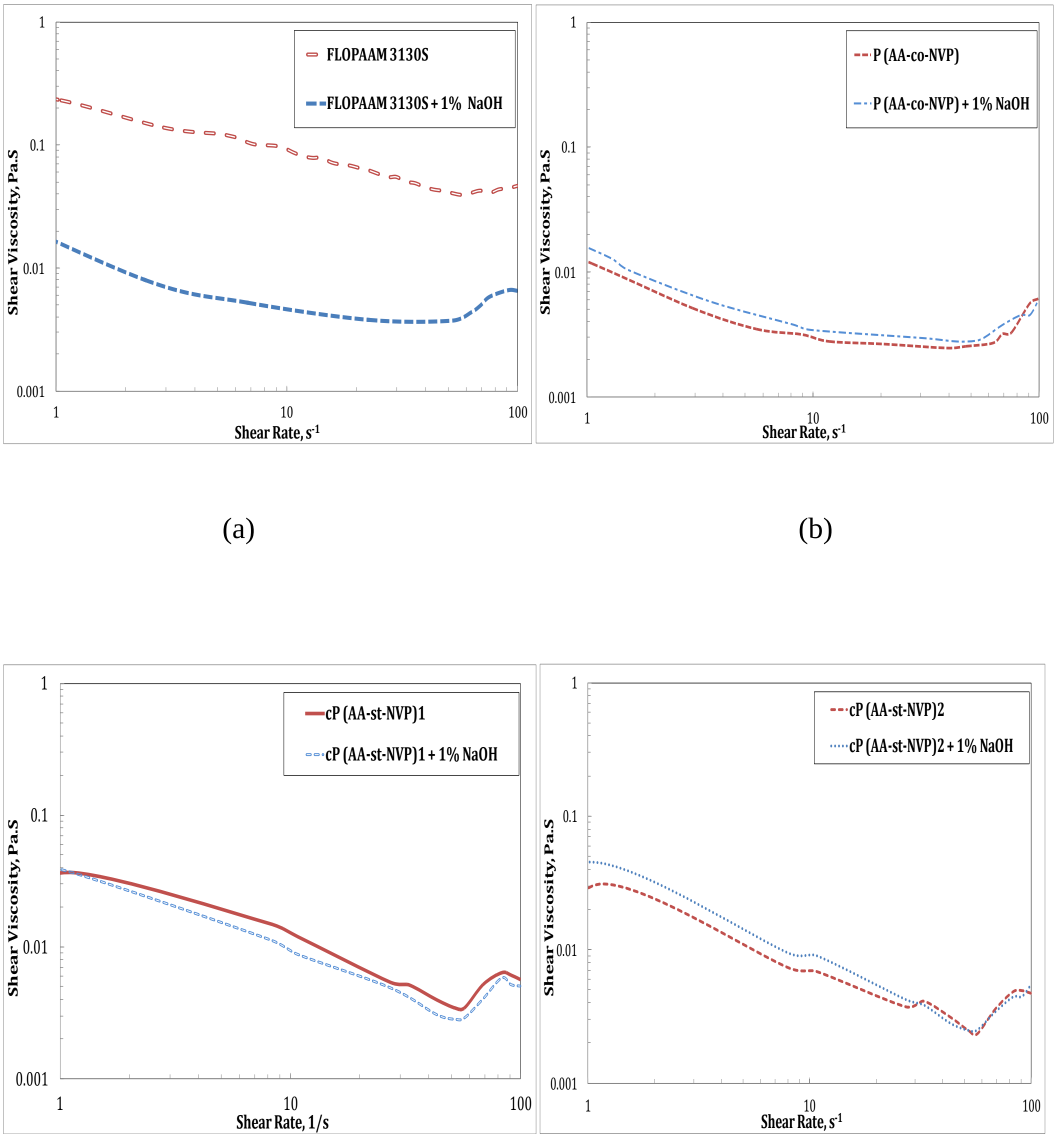


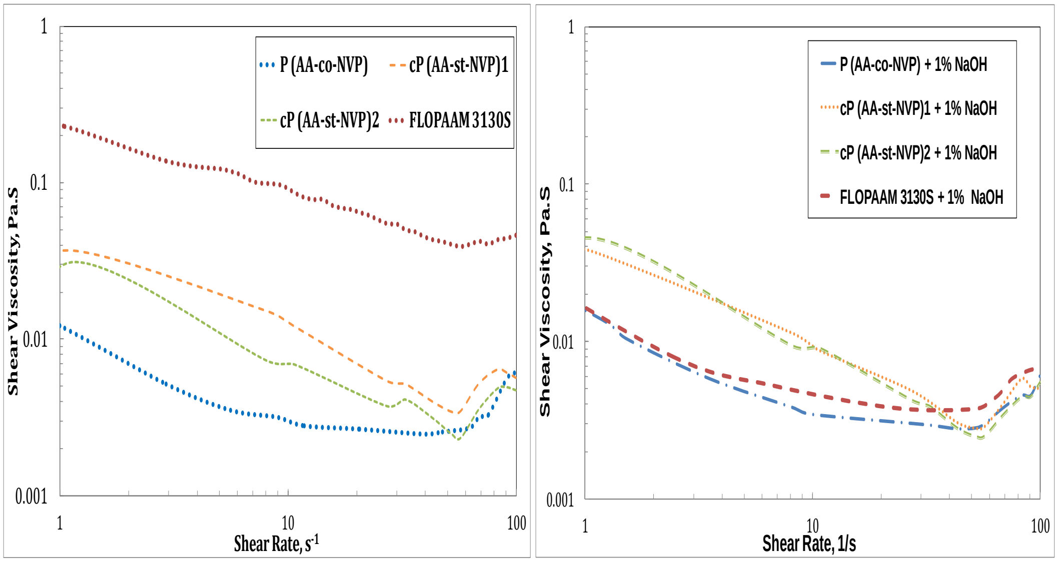
Figure 4.2: Experimental Schematic



(a) (b)

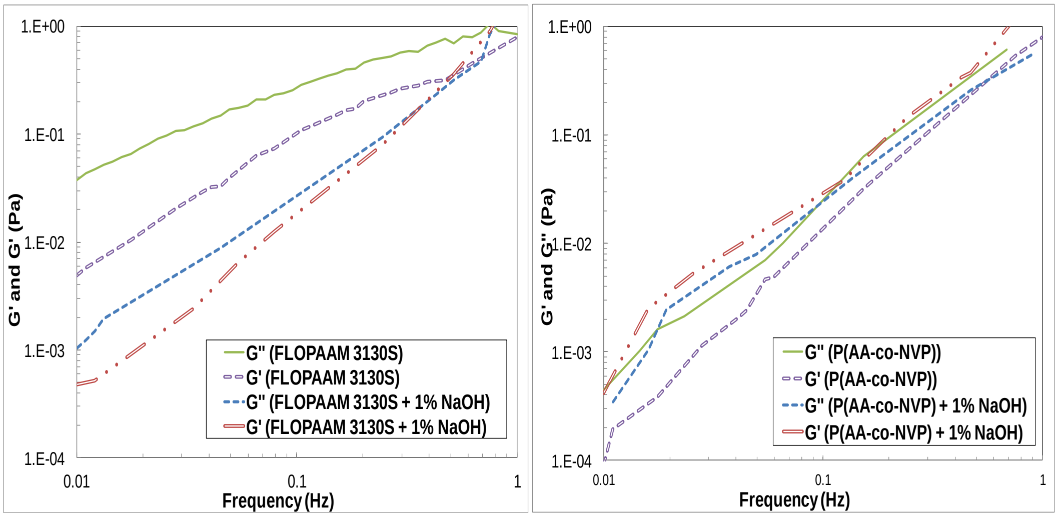
(c) (d)

Figure 4.3: Shear Rate vs Shear Viscosity Plot (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-VP) + 1% NaOH, (c) cP(AA-*st*-NVP)$_1$ vs cP(AA-*st*-VP)$_1$ + 1% NaOH, and (d) , cP(AA-*st*-NVP)$_2$ vs cP(AA-*st*-VP)$_2$ + 1% NaOH

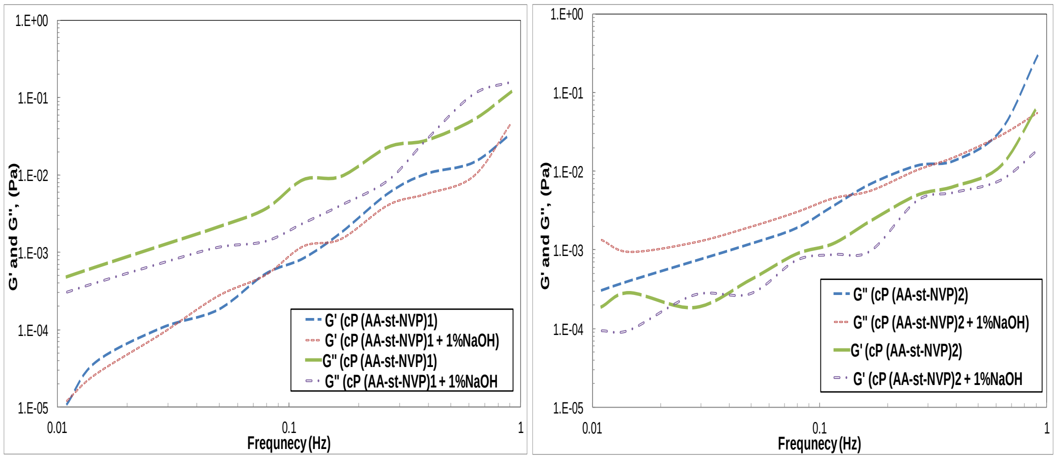


(a) (b)

Figure 4.4: Shear Rate vs Viscosity Plot (25°C) (a) All four polymers, (b) All four polymers + 1% NaOH



(a) (b)



(c) (d)

Figure 4.5: Viscous and Elastic Modulus vs Angular Frequency (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-VP) + 1% NaOH, (c) cP(AA-*st*-NVP)$_1$ vs cP(AA-*st*-VP)$_1$ + 1% NaOH, and (d) , cP(AA-*st*-NVP)$_2$ vs cP(AA-*st*-VP)$_2$ + 1% NaOH

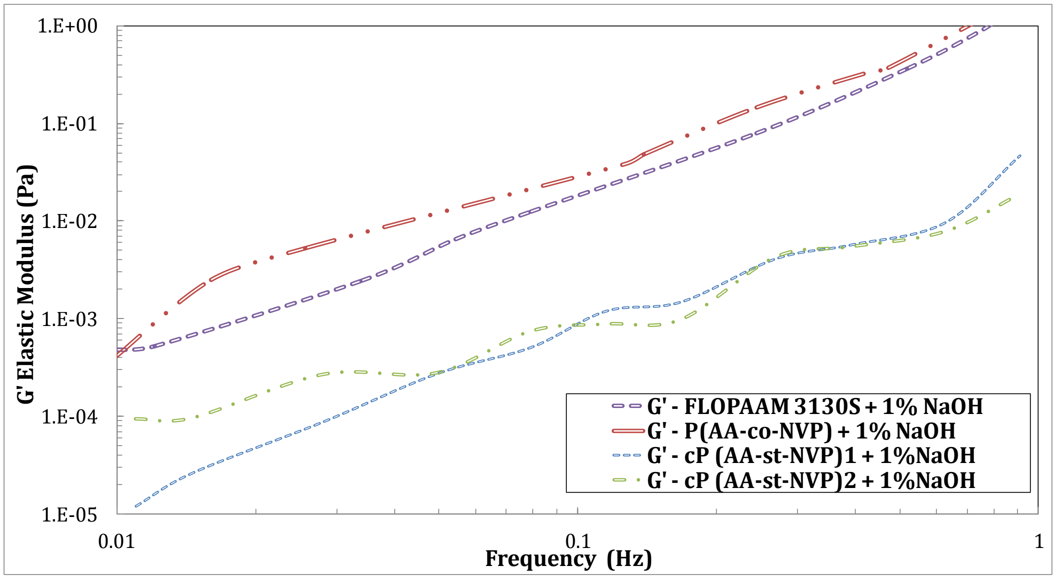


Figure 4.6: Elastic Modulus vs Angular Frequency (25°C) for all four polymers in alkaline conditions

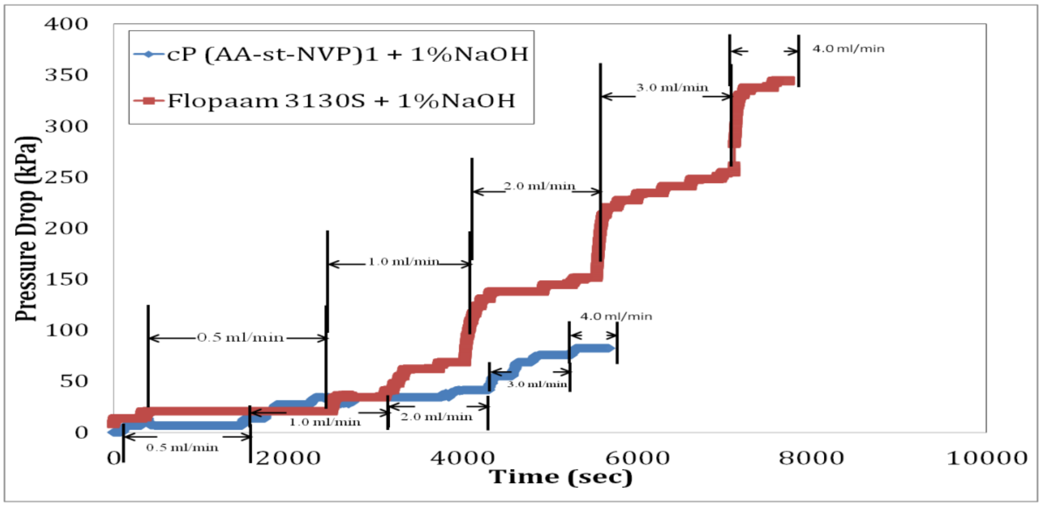


Figure 4.7: Pressure drop comparsion for alkaline conditions for Crosslinked Polymers and HPAM

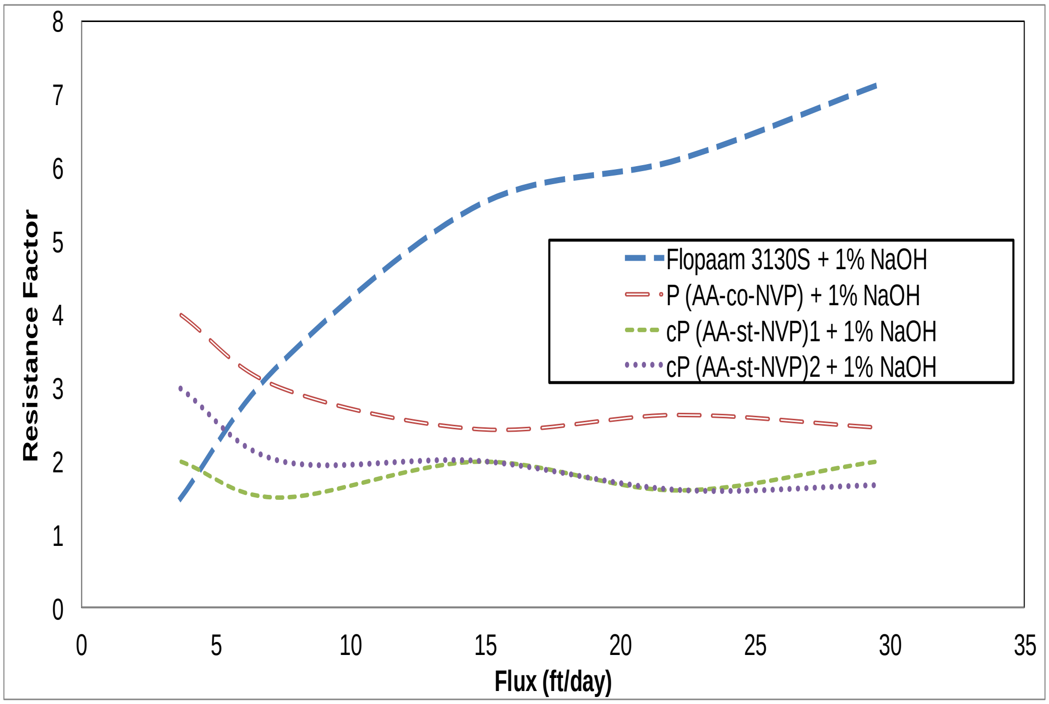


Figure 4.8: Resistance Factor with respect to flux for all four polymers in alkaline conditions

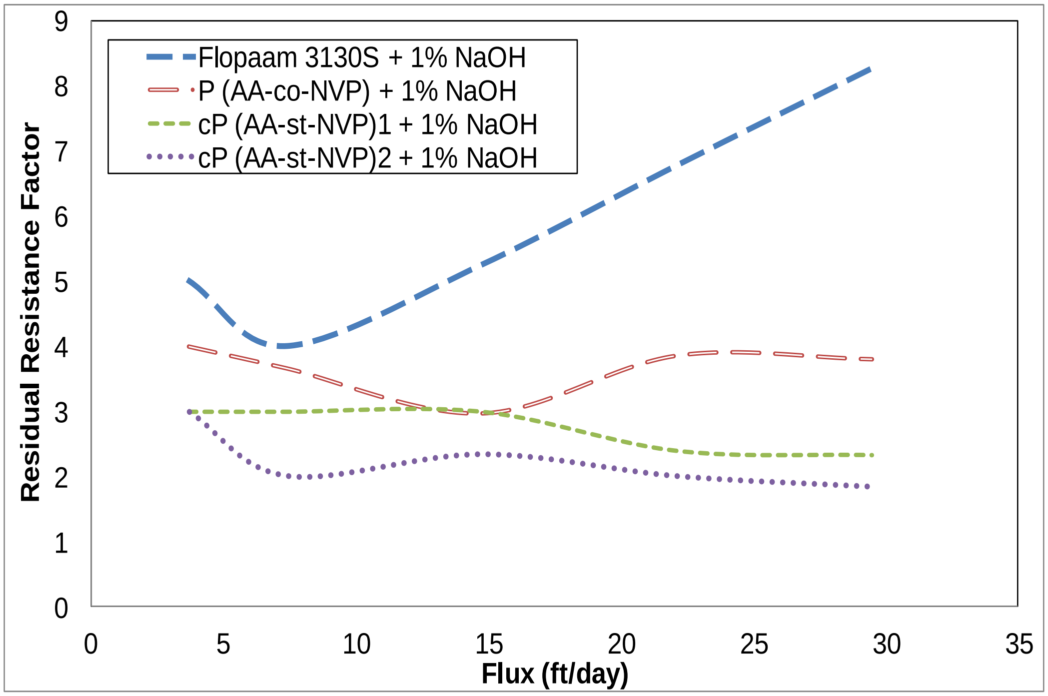


Figure 4.9: Residual Resistance Factor with respect to flux for all four polymers in alkaline conditions

CHAPTER 5

Improving AP Flood Injectivity and Heavy Oil Recovery Performance using Crosslinked Polymer of Acrylic Acid (AA) and N-vinyl-2-pyrrolidinone (NVP) compared to High Molecular Weight Hydrolyzed Polyacrylamide

5.1 Introduction

There are wide varieties of way; polymers can be used to enhance the production of oil or gas from reservoirs. Function of these polymers is mainly to control the viscosity of the aqueous fluids, which are injected into the reservoir for oil recovery. It is well known that efficiency can be improved by decreasing the mobility difference between the injected water and the oil in place, which is easily done by adding a water soluble polymer to the aqueous phase.

Another problem, which occurs in different flooding processes, is the reservoir heterogeneity which means different zones have different permeability. For this polymer flooding is carried out to reduce the mobility ratio for high permeability areas as well as plugging these areas. Thus, polymer moves to low permeability areas and is able to recover the oil from the reservoir. This increases polymer's ability to increase vertical sweep efficiency near well bores. Several attempts have been made to counter this reservoir heterogeneity problem with the use of water diverting techniques (also called profile correction, conformation improvement).

A specific application of polymer in oil and gas industry may warrant different characteristics of flow and adsorption as well as design. For example, polymers used in enhanced oil recovery should have high injectivity and low adsorption. On the other hand, high adsorption and thick residual polymer layers are the key for a successful use of polymers in water shut-off. Similarly, design criteria for mobility control projects differ from wellbore profile control projects. If the project is a mobility control project, then a rather large slug of polymer is injected, beginning early in the life of the water flood. However, wellbore profile control (treatment to correct vertical conformance problems) treatments use small slugs of cross-linked polymer.

Injectivity is one of the main characteristics for polymer used for mobility improvement operations. Polymer solutions with good injectivity behavior are necessary for successful field use. As high molecular weight polymers used for mobility improvement, they can be harder to inject due to their extremely high viscosity. The polymer should be easier to inject into well bore and also, should be able to push oil towards the production well.

Blocking higher-permeability layers with chemical reagents along the flow direction of water can efficiently increase the water-swept volume and maintain the productive section of reservoir. Thus by the help of profile modification technology, water cut can be decreased as well as oil production can be increased. Previously water shut technology with gel treatment was tried for the unsuccessful improvement of permeability heterogeneity near well bore (normally 5-10 m)[1]. One of the reason for its failure can be the high viscosity of polymer flooding solution which decreases the injectivity at a given injection pressure. A solution to overcome the problem of profile modification as well as mobility reduction is required which does not interfere with injectivity and still is a good candidate for polymer flooding. One of the solutions is the cross-linked polymer. They have better swelling in porous media which will increase the oil recovery and their injectivity doesn’t compromise with the economics of flooding operation.

Mobility control is an attempt to improve the '*volumetric*' sweep efficiency of a reservoir (e.g. through the use of polymers and/or foam), while conformance control is an attempt to improve only the '*vertical*' sweep efficiency (e.g. through the use of gels, microgels, packers, and/or surfactant foams)[2].

Difference between conventional polymer floods and polymer gel floods is the presence of a crosslinker. Crosslinking agents yield a polymer network which enables a more significant, longer lasting, and more optimizable permeability reduction (RRF) which results in increased resistance to flow in high permeability areas and hence, assists in fluid diversion effects[3-5].

For mobility control effects, conventional polymer floods (mobility reduction) are very effective as they are used in very high concentrations so that polymer is able to sweep as much of the reservoir as possible. However, polymer gel/polymer microgel floods are much more suitable for conformance control/water shutoff as gelant is able to propagate through high permeability channels. They have these enhanced permeability reduction capabilities brought about by the presence of crosslinker[3,6].

Wang et al.[7] studied the expansive granular crosslinked polymer (EGCP) to correct in-depth permeability for severe heterogeneous reservoir pay zones. This polymer had some particular performance characteristics like easy swelling, easy injection operation.

The method to make crosslinked polymer is based on cross-linked reactions involving σ-band between macromolecular chains. σ-band can keep the structure of micro-gel as it can withstand high temperature and salinity.

HPAM (Hydrolyzed Polyacrylamide) polymer is obtained when polyacrylamide (PAM) is hydrolyzed in presence of sodium hydroxide. The fraction of the backbone amide units, which have been hydrolyzed i.e. the fraction of existing carboxyl groups, is called the degree of hydrolysis. When hydrolysis is complete, or when the amide groups have been replaced totally by the carboxyl groups, it is called poly-(acrylic acid) (PAA).

NVP and its copolymers can be used for wide applications as hydrogels and membranes used in drug-delivery systems. Beside of its low chemical toxicity and high solubility in water/organic solvents, NVP based polymers have the ability to react with different kind of substrates like dyes, surfactants and polymers. Because of this property, it is an important component for many pharmaceutical and cosmetics products also.[27]

Wang et al.[8] analyzed copolymer made of AA and AMPS (2-acrylamido-2-methylpropanesulfonic acid) and concluded that in acidic medium (pH <5), the carboxylate (COO^-) and sulfonate (SO_3^-) groups on the polymeric chain can turn into carboxylic acid and sulfonic acid groups. As a result, the main anion-anion repulsive forces were diminished, and the association among -COOH and -SO_3H groups was increased due to the hydrogen-bonding interaction. This increased the physical crosslinking degree and reduced the swelling ratio. When the pH values are in the range of 5-10, ionization of carboxylate and sulfonate groups occurs and the electrostatic repulsion between carboxylate and sulfonate groups causes an enhancement of the swelling ratio. For higher pH value (>10), a charge screening effect of the counter ions (Na^+) limits the repulsion of carboxylate and sulfonate and hence, swelling and leads to a decrease of the swelling ratio. Similarly, Pandey et al.[9] analysed the swelling behavior of the hydrogels consisting PAM at different NaCl concentrations and concluded the swelling ratio was inversely proportional to ionic strength. This may be attributed to a change in osmotic pressure and a reduction in the repulsive forces at a higher ionic strength. The lower swelling at a higher ionic strength could also be explained due to the neutralization of the carboxylate anions in the presence of Na^+, resulting in decreased electrostatic repulsive forces, which was a controlling factor for swelling.

Acrylamide being the is the most commonly used monomer for EOR polymers, various studies have be conducted to synthesize new polymers with AM and NVP in order to achieve better stability as well as rheological and swelling properties. Doe[10] studied the effect of incorporation of NVP to AM chains. He stated that adding NVP group could increase the stability of acrylamide. The new monomer can protect the acrylamide chain in the polymer by steric hindrance as well as intra-molecular hydrogen bonding in AM-NVP polymer. This stability is against both thermal and chemical degradation. Radical reaction is prevented by hindrance while intra-molecular hydrogen bonding decreases chemical hydrolysis. Also the stability increases as the NVP concentration goes higher.[11] As there will be more active sites available for hydrogen bonding as well as higher number of large VP group.

When hydrogel samples of AM-NVP were tested with different pH conditions, there is no influence of pH on swelling behaviour for these hydrogels. The reason behind this can be attributed to two constituents of hydrogels as (N-vinyl-2-pyrrolidinone) and AM, which are non-polyelectrolytes. Hence, there is an absence of ionisable groups to produce electric charges along the polymeric chains. Thus there will be no electrostatic interaction inside the gel to repel the polymer chains and increase the osmotic pressure. Here it is worth mentioning that the swelling behaviour of cross-linked polyacrylamide hydrogels cannot be affected greatly by the pH of the external solution because the possible hydrolysis of amide groups of polyacrylamide into carboxylic group is not feasible. The polymer will be stable due to steric hindrance of NVP but will not have ideal swelling and viscous properties. However, as it has been discussed above, copolymer containing PAA has negative charged ions in high pH due to conversion of carboxylic group to carboxylate ion, hence there is a electrostatic repulsion between polymer chains. NVP being a non-ionic moiety does not participate in the repulsion. Thus

AA-NVP polymer has better swelling characteristics as compared to copolymer containing AM.

Therefore, it is of great importance that injected polymer or micro gels show higher injectivity, i.e., lower injection pressure, making sure that these micro gels propagate into the reservoir and not damage the formation by plugging the pores of the rock. Also, the oil recovery achieved in flooding operation (P or AP flooding) should not be compensated. Thus, it is an objective of the this work to study alternative polymers to conventional HPAM which allow for the preparation of solutions showing improved injectivity in polymer flood or enhanced oil recovery techniques. The injectivity characteristics of the HPAM and different crosslinked PAA were evaluated by core flow experiments. The combination of a higher injectivity, high thickening capability and the low molecular weight of the cross linked PAAs makes them suitable for application in chemical enhanced oil recovery, i.e. either AP or ASP flood (EOR, especially for low permeable reservoirs). The polymers used in the study avoid or reduce microgel formation and, thus, reduce the plugging problems observed for prior art polymers used for chemical injection techniques.

5.2 Materials Used & Method of Solution Preparation

5.2.1 Materials

Polymers

FLOPAAM polymer 3130s supplied by SNF SAS in dry powder form was used in the preparation of HPAM solutions. FLOPAAM 3130s is anionic and water-soluble with a degree of hydrolysis of 25-30 mole % and average molecular weight of 2 000 000 Da.

Acrylic acid (AA) was purchased from Sigma-Aldrich (Canada) and purified by passing through a basic alumina column. 1-vinyl-2-pyrrolidinone (VP) was obtained from Sigma-Aldrich (Canada) and purified by distillation. Crosslinked agent used was N,N'-

methylene-bisacrylamide. Water used in this study was purified with a Millipore Milli-Q system. Other chemicals were used as received. Monomers, Crosslinking agent and probable cross-linked poly structure are shown in Figure 5.1.

5.2.2 Synthesis of Poly(acrylic acid-st-1-vinyl-2-pyrrolidinone) (cP(AA-st-NVP) with small amount of cross-linker.

The AA-NVP polymers were polymerized by free radical polymerization with small amount of cross-linker to increase the viscosity. Four runs were tried by changing concentration or method to get the maximum yield and viscosity. Amount of Acrylic Acid and NVP used were 2.89g (40.1 mmol) and 0.495 g (4.45 mmol). The initiator used was 4'-azobis (4-cyanovaleric acid) (ACVA) and amount used was 1.0 mg, 3.56×10^{-3} mmol). Solvent used was 10 ml of N,N-dimethylformamide (DMF). After degassing with nitrogen gas for 30 min, the mixture was allowed to polymerize for 12 h at 60 °C under inert atmosphere. The four runs used were as follows:

- ***a)*** ***Run1:*** Crosslinker (N,N'-methylene-bisacrylamide) used in run 1 was 0.5 mol% (34.3 mg, 2.23×10^{-1} mmol). After the polymerization, bulk gel was observed in the polymerization tube and could not dissolve to large amount of good solvent for the copolymer.
- ***b)*** ***Run2:*** Crosslinker (N,N'-methylene-bisacrylamide) used in run 1 was 0.1 mol% (6.8 mg, 4.46×10^{-2} mmol). The resulting highly viscous polymer was diluted with DMF (10 mL) and subsequently purified by dialysis against ethanol and water. Finally polymer was collected as a powder after freeze-drying. This was named as cP $(AA\text{-st-}NVP)_1$ for further reference.
- ***c)*** ***Run3:*** Crosslinker (N,N'-methylene-bisacrylamide) used in run 1 was 0.05 mol% (3.4 mg, 2.23×10^{-2} mmol). The resulting highly viscous polymer was diluted with DMF (10 mL) and subsequently purified by dialysis against ethanol and

water. Finally polymer was collected as a powder after freeze-drying. This was named as cP $(AA\text{-}st\text{-}NVP)_2$ for further reference.

Crude oil used in the study was collected from a heavy oil reservoir in north-central Alberta. Basic sediment and water from the crude oil was removed by high-speed centrifugation as well as gravity segregation. The oil viscosity was ~1200 cP @ 22^{o} C. Oil viscosity was checked using rheometer (described later) each time before the experiment to maintain the consistency for mobility ratio.

The polymer solutions of 0.1% concentration (wt %) were prepared by adding them to deionized water. Powders were added with constant stirring maintained at 350 rpm using a magnetic stirrer in the interval of ~15 seconds. Concentration of Alkali (NaOH) used was 1 wt%. Proper care was taken to ensure that polymers are not added too rapidly in order to avoid lumping of the powder. The solution was stirred for approximately 20 minutes until it became completely transparent and no filtration was needed.

5.3. Viscoelasticity Characterization of Polymer Solutions

Viscoelasticity measurements were carried out by a C-VOR 150 Peltier Bohlin rheometer (Malvern Instruments, USA) with cone and plate measuring system and strain model measurements at 22^{0}C +/- 0.5^{0}C. Polymer samples were placed in between a stationary plate with a diameter of 60 mm and a rotating upper cone with a 4º angle and a diameter of 40 mm, separated by a gap of 150 µm. Following rheological tests were conducted for the polymers.

5.3.1. *Viscometry Tests*

Viscometry tests were carried out at shear rates varying from 1 to 100 s^{-1}. Shear viscosity was plotted as a function of shear rate for polymer samples in both alkaline and non-alkaline conditions (Figure 5.2 and 5.3).

5.3.2. *Oscillation Tests*

Frequency tests were carried out on polymer samples at a frequency range of 0.01 to 1 Hz, keeping the stress value constant at 0.04775 Pa. Oscillatory measurements provide the absolute values of the complex modulus |G*|, the storage modulus or elastic modulus G’, the loss modulus or viscous modulus G”, at a constant frequency and constant strain. These magnitudes of frequency and strain were chosen so as to provide a stress of reasonable magnitude for the purpose of sensitivity. Figure 5.4 and 5.5 and shows elastic modulus and viscous modulus as a function of angular frequency.

HPAM polymer FLOPAAM 3130S and synthesized crosslinked polymers were further tested for oil recovery performance during core-flooding experiments in straight polymer flood mode and in alkali-polymer flood for comparison.

5.4 Core Flooding Experiments

5.4.1. *Experimental Set-up*

A cylindrical horizontal core holder (diameter 1 1/4", length 6”) was used for flooding experiments. Perforated screen at either ends of the core were used. Glass beads used in core flooding experiments were of 325 mesh size with a particle size distribution of 30-50 microns, supplied by Potters Industries LLC. For each test, fresh glass beads were packed to ensure the same wettability. The core was packed dry, using a mallet as well as a pneumatic vibrator ensuring a tight pack. Pore volume (PV) of the porous medium was measured by direct method. Volume of glass beads in the cylindrical core was subtracted from the bulk volume of the core. A specific gravity of 2.5 was used for calculating the volume of glass beads in the model for each experiment using the known mass that was required for packing. Experimental Schematic is shown in Figure 5.6.

The ISCO syringe pump 500D was used for saturating the core with heavy oil. Oil was injected using a piston based accumulator at constant pressure to avoid leakage during oil injection. The volume required for saturation was also measured which was in agreement with the volume calculation from glass bead volume, thus showing the quality packing was similar for each experiment.

Graduated cylinders were used for collecting and measuring effluent samples during the flooding process at regular time steps. All the experiments were performed with model in horizontal position. Therefore, the gravity was assumed to have no influence in the observations of the experiments.

5.4.2. *Effective Shear Rate in Porous Media*

Christopher and Middleman suggested the following equation to estimate shear rates in cores[12]

$$\gamma = \frac{3n+1}{4n} \frac{4Q}{A(8k\phi)^{0.5}} \qquad (1)$$

Where γ is shear rate, 1/s; (3n + 1)/4n is a non-Newtonian correction factor for power-law fluids; Q is flow rate, cm^3/s; A is cross sectional area of the core, cm^2; k is permeability, cm^2 and $\emptyset$ is porosity.

For the type of fluids we have used n values changed between 0.45 and 0.56. Substituting n values of 0.45 and 0.56, k = 350-380 md; φ = 42-45%; A= 6.413 cm^2; and a flow rate of 0.25ml/min would yield to shear rate of ~ 27-30 s^{-1} in porous media.

5.4.3. *Flooding Procedure*

Initially core was prepared as described in aforementioned section and the effective porosity of the core was calculated. Procedure for flooding experiments conducted is as follows:

- The core was flooded with water to establish connate water saturation and permeability was measured by varying the flow rate between 0.25 ml/min to 6 ml/min and recording the pressure drop along the core.
- The core was then flooded with the crude oil at constant pressure; the effluents were collected to obtain initial water and oil saturations in the core through material balance.
- After saturation, core was flooded with 1 PV of water, displacing oil to establish residual oil saturation and stable pressure drop.
- For secondary polymer flood recovery polymer or alkaline-polymer solution was injected for 4 PV until a stabilized pressure is achieved at a given flow rate.
- At the end, permeability of the core was measured by subjecting the core to 15-20 PV of water flood at different flow rates and stabilized pressures as a function of injection rate was recorded.

Flow rates for waterflood and chemical flood were held constant at 0.25 ml/min (1.84 ft/day and shear rate 27-29s^{-1}) based on eq. 1. Volumes of effluent from producer were collected at regular intervals. Pressure drop across the core was recorded using OMEGADYNE Inc. pressure transducer having a full-scale limit of 2500 psig.

The new crosslinked polymers were compared for oil recovery in alkaline and non-alkaline conditions and then compared to HPAM to compare the advantage of using NVP as a monomer.

5.4.4. *Residual Resistance Factor*

It is defined as the ratio of the permeability to water before and after the injection of polymer solution[13]. The residual resistance factor is a measure of the tendency of a polymer to adsorb into the pores and thus partially block the porous medium. This indicates that residual resistance factor has a pronounced influence on the permeability of the porous medium. This can be defined for the scenarios where there is no change in saturation over the flooding of polymer.

$$F_{RR} = \frac{(k_w)_{before}}{(k_w)_{after}} \tag{3}$$

Under given flow rate in same core flooding system, using the assumption of Darcy's law, RRF is expressed in terms of pressure drops as:

$$F_{RR} = \frac{(\Delta P_w)_{after}}{(\Delta P_w)_{before}} \tag{4}$$

If residual resistance factor is high, it shows that adsorption and trapping of a polymer solution on porous media is on the higher side. Hence, for oil recovery operations, RRF value of polymer solution should be lower to avoid retention of polymer into the porous media.

Table 5.1 shows residual resistance factor of FLOPAAM 3130S, P(AA-co-NVP) as well as crosslinked polymers cP(AA-st-VP)$_1$ and cP(AA-st-VP)$_2$ with and without 1% NaOH.

5.5. Results and Discussion

5.5.1. Rheological behaviors of polymer solutions

Figure 5.2 shows the comparative steady-shear rheological results of 0.1 wt % P(AA-*co*-NVP), cP(AA-*st*-NVP)$_1$, cP(AA-*st*-NVP)$_2$ and FLOPAAM 3130S aqueous solutions at 25 degC are presented with no alkali and 1% NaOH addition. For each of the polymers, shear viscosity decreases as shear rate is increased which means each of them follows a shear-thinning behaviour. This can be related to the breakage of polymer chains when exposed to high shear flow. At shear rates > $0.1s^{-1}$ the shear viscosity-shear rate relationship was fitted with the power law model.

For non-alkaline conditions, the shear viscosity Flopaam 3130S is much more than other three polymers as molecular weight of HPAM is twice of copolymer and crosslinked polymers. Crosslinked polymer's shear viscosity is higher than co-polymer, which is due to better swelling properties of crosslink structure as compared to general co-polymer structure.

From figure 5.2(b), it can be seen that there is no change in the shear viscosity of copolymer P(AA-*co*-NVP) in presence of 1% NaOH. Both the crosslinked polymers cP (AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$, in figure 5.2(c) and 5.2(d), show the similar behaviour as they only show a minimal change when encountered with alkaline conditions. While, for Flopaam 3130S (in figure 5.2(a)), there is a significant drop in shear viscosity in presence of NaOH.

Shear viscosity results for all four polymers in presence of Alkali are shown in figure 5.3. Shear viscosity of co-polymer P(AA-*co*-NVP) and FLOPAAM 3130S in presence of 1% NaOH is very similar within the whole shear rate range examined. For cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$, in alkaline conditions, shear viscosity values are higher than HPAM and co-polymer P(AA-*co*-NVP) which can be attributed to the empty space between the polymer chains due the repulsion of carboxylate ions when encountered with alkaline conditions. This behaviour of AA and NVP based polymers can be beneficial in field application as the molecular weight of P(AA-*co*-NVP), cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$ is almost half than that of HPAM.

This comparison clearly shows similar to Flopaam 3130S, under alkali environment, other three polymers, their shear-thinning characteristics will be favourable for the AP solution to penetrate into the near wellbore as during the time of injection the viscosity value will be lower for copolymer and crosslinked polymers due to high shear rate. Once it reaches into the reservoir, polymer doesn't face shear rate as high as injection pipeline. Hence, the viscous nature of polymer recovers which fulfils polymer's primary objective mobility reduction.

5.5.2 Dynamic viscoelastic behaviors

Figure 5.4(a) to 5.4(d) show the comparative variation of viscoelastic properties for P(AA-*co*-NVP), cP(AA-*st*-NVP)$_1$, cP(AA-*st*-NVP)$_2$ and FLOPAAM 3130S solution in alkaline and non-alkaline conditions. It is evident from the figures that in presence of NaOH, elastic modulus (G') and viscous modulus (G") of NVP based polymers' solution shows very small difference. However, G' and G'' of FLOPAAM 3130S polymer solution decreased after addition of NaOH. In Figure 5.5 the elastic moduli (G') of all four polymer solution, with NaOH, as a function of frequency are presented.

The new polymers showed improvement in alkaline conditions as compared to non-alkaline conditions in terms of rheological and dynamic viscoelastic properties. For co-polymer and crosslinked polymers, there is an increase in electrostatic repulsion in polymer chains due to conversion of carboxylic group to carboxylate ion, resulting in polymer swelling and increased rheological and viscoelastic properties. For HPAM, Na^+ ions shield the charge on hydrolyzed carboxylic group; hence there is no significant change in polymer swelling and its rheological as well as viscoelastic behaviour or rather there is decrease due to hydrolysis of polyacrylamide chain. Higher elastic properties of P (AA-*co*-NVP), cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$ as a result of stretching of polymer chains in alkaline solution could possibly allow the polymer to elongate more in porous media. For HPAM, due to shielding of hydrolyzed carboxylate group in presence of alkali, elongation of HPAM chains may not be significant.

In past, NVP monomer has been used with AM to form copolymers as it protects the AM group from harsh conditions like high temperature and presence of divalent ions[47]. The copolymer (Superpusher SAV505 from SNF Floeger) is known to be more resistant to hydrolysis as the number of NVP units surrounding acrylamide group increases**.** The mechanism suggested for this stability could be steric hindrance or intramolecular hydrogen bonding.[10-11]

Stable and unchanged viscoelastic behviour of P(AA-*co*-NVP), cP (AA-*st*-NVP)$_1$ and cP (AA-s*t*-NVP)$_2$ polymer compared to HPAM suggests a great alternate potential for enhance oil recovery in heavy oil reservoirs. To further understand their behavior as a flooding agent, core flooding experiments were performed.

5.5.3. Oil Recovery Performance

After comparing the rheological data for the both the polymers, core flooding experiments were conducted to analyze their performance for oil recovery.

Increase in percentage oil recovery because of the polymer flooding is shown in Figure 5.7 with respect to pore volume of polymer injected for HPAM and new cross-linked polymer. Oil recovery increases when the condition changes from non--alkali to alkali. This oil recovery increase is mainly because of alkali reducing the interfacial tension, as the mobility improvement ability for copolymer P (AA-co-NVP) in alkaline conditions is almost similar to non-alkaline environment as visible from their rheological behaviour which showed no significant change with and without 1% NaOH. While for cross-linked polymers cP (AA-st-NVP)$_1$ and cP (AA-st-NVP)$_2$ as rheological behaviour doesn’t change much in absence and presence of 1% NaOH, oil recovery for both conditions differ by at least 6-7%. This is again due to the IFT reduction effect of alkali with polymer, hence the oil recovery increases. On the other hand, there is only a slight change in increased oil production in case of FLOPAAM 3130s polymer + 1% NaOH compared to only FLOPAAM 3130s polymer flooding. From these results it can be said that in case of FLOPAAM 3130s, the benefit of IFT reduction by addition of 1% NaOH on overall recovery was minimum due to loss of viscosity in presence of alkali and consequently lower sweep efficiency and lower mobility ratio improvement.

The overall recovery of P(AA-*co*-NVP), cP (AA-*st*-NVP)$_1$, cP(AA-st-NVP)$_2$ and FLOPAAM 3130S has a difference of approximately 5% when compared among each other in alkaline conditions (Figure 5.8). This is due to the reason that polyacrylamide loses its structure in presence of alkali and not able to provide the mobility reduction ability in porous media. While for co-polymer and crosslinked polymer viscosity loss is minimal. This is combined with alkali's IFT reduction capability which decreases the residual oil saturation. Hence oil recovery for alkali-polymer flooding for NVP based polymer is higher than polyacrylamide. Also, it is important to note that molecular weight of P(AA-*co*-NVP)is almost half than the FLOPAAM 3130S and increasing the molecular weight of P(AA-*co*-NVP) could have the additional positive effect on oil recovery.

5.5.4. Injectivity Analysis

Differential pressure increases across the core as the polymer is injected into the core due to higher shear viscosity of polymer. Differential pressure during the injection Flopaam 3130S is much higher than co-polymer and crosslinked polymer which can be directly attributed to high molecular weight (hence, high viscosity) of Flopaam 3130S as compared to P(AA-*co*-NVP), cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$. In alkaline conditions, although, shear viscosity values almost lies in the same range or else have higher values (in case of crosslinked polymers; figure 3(b), the differential pressure for Flopaam 3130S + 1% NaOH is still higher than NVP based polymers in 1% NaOH solution (Figure 5.9). This can be ascertained by the fact that polyacrylamide's retention is more on the porous starting from the early stages of polymer flooding which makes it tough for the incoming polymer to propagate into the reservoir. The reason behind the high retention of HPAM is that there are more active sites for adsorption on grains in porous media as compared to co-polymer and crosslinked polymer. Also, the scale precipitation with 1% NaOH for polyacrylamide is more as there is no protection for polymer backbone, this scale precipitate on porous media and plugs the pore. As pore starts getting plugged, it increases the injection pressure for incoming polymer. Thus, injectivity for HPAM with 1% NaOH decreases. For, P(AA-*co*-NVP), cP(AA-*st*-NVP)$_1$ and cP(AA-*st*-NVP)$_2$ the polymer backbone is shielded by steric hindrance of large NVP functional group which not only prevents alkali hydrolysis, it doesn't allow the carboxylate groups to attach to reservoir grains. Also, precipitation of NVP based polymer is lower compared to HPAM in presence of 1% NaOH. Thus, injectivity for co-polymer and crosslinked polymer is much better as compared to polyacrylamide i.e. injectivity loss for new polymers is lower. Lower injectivity can adversely affect oil production rate in the early stages of the polymer flood.This can be verified further by high residual resistance factor for HPAM and low RRF for co-polymer and crosslinked polymers (Table 5.1).

Low resistance factor and higher injectivity of crosslinked polymers for all shear ranges studied here, especially at high values of shear (flow), makes them a strong candidate to replace HPAM polymers in the fields. These results also show that a polymer that has similar viscosity as high molecular weight HPAM but higher injectivity could be better for mobility control because more volume of polymer can be injected with low pressure drop and near wellbore damage as would be preferable.

Shear stability of P (AA-*co*-NVP), cP(AA-*st*-NVP)$_1$ and cP (AA-*st*-NVP)$_2$ is better than HPAM. This can be described as not only the molecular weight, but also hydrophobic interactions between the polymers chains contribute to the viscosifying power of polymer. Hence, formation of networks in a polymer is an important factor.

When polymer is injected into the porous media i.e. high shear rates are applied, HPAM chains are tore apart and molecular weight of polymer decreases. But for NVP based crosslinked polymers, comparatively weak intermolecular network is broken but polymer backbone remains intact. When the solution reaches the porous media, shear rates cease and polymer crosslinker network is reformed which restores the viscosity. Similarly for NVP based co-polymer, NVP group provides shear hindrance to the polymer backbone chain.

5.6 Conclusion

- Cross-linked polymer [cP (AA-*st*-NVP)] was prepared by Acylic Acid (AA) and N-vinyl-2-pyrrolidinone using N,N'-methylenebisacrylamide as crosslinking agent for mobility reduction operations with improved injectivity due to their better swelling properties as well as stability in alkaline conditions new polymers Oil recovery experiments were conducted to evaluate AA and NVP crosslinked polymers for secondary polymer flood oil recovery as well as improved injectivity near well bore as compared to polyacrylamide.
- Cross-Linked polyumer in presence of NaOH shows higher shear viscosity profile as compared to HPAM when analyzed for rheology. Elasticity of cross-linked polymer is lower than polyacrylamide as well as AA-NVP copolymer.
- Oil recovery for crosslinked polymer is 6% higher when compared with HPAM in presence of 1% NaOH.
- RRF value for polyacrylamide was significantly higher than P (AA-*co*-NVP), cP (AA-*st*-NVP)$_1$ and cP (AA-*st*-NVP)$_2$ for alkaline conditions which shows that polyacrylamide's adsorption on porous media is much higher than NVP based polymers.

- High RRF value can be attributed to low injectivity as polymer adsoprtion blocks the pore which can increase the pressure drop for polymer propagation.
- One of the main advantage of new cross-linked polymer was its low molecular weight. The alkali-polymer flood recovery was improved for cP (AA-st-NVP) as compared to HPAM, despite having molecular weight half that of HPAM.

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5.7 References

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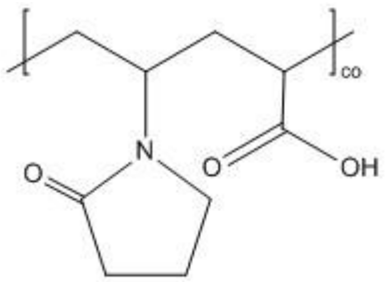
Table 5.1: Average Pressure and RRF Comparison for polymers in alkali conditions

Injected Solution	Average Pressure (kPa)	Residual Resistance Factor
Flopaam 3130S + 1% NaOH	173.5	10.02
P(AA-co-NVP) + 1% NaOH	168.5	3.72
cP (AA-st-NVP)$_1$ + 1% NaOH	150.5	2.15
cP (AA-st-NVP)$_2$ + 1% NaOH	138.0	1.71

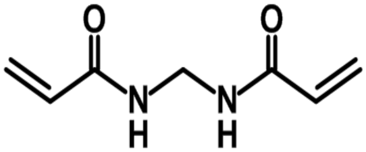
Acrylic Acid

N-Vinyl-2-Pyrrolidinone

(a)



(b)



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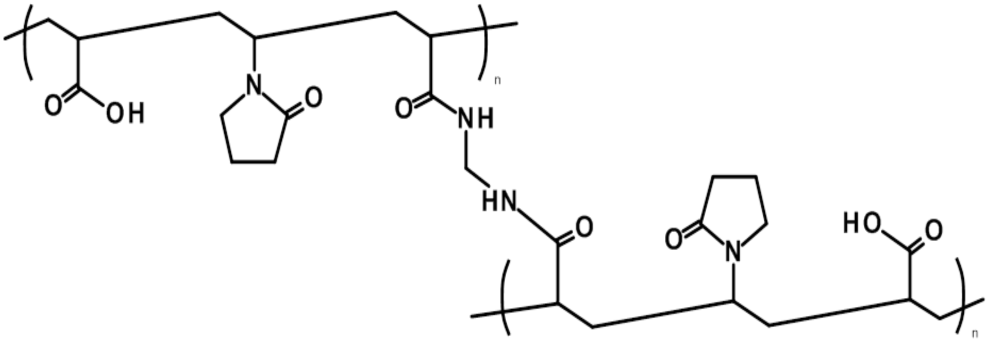
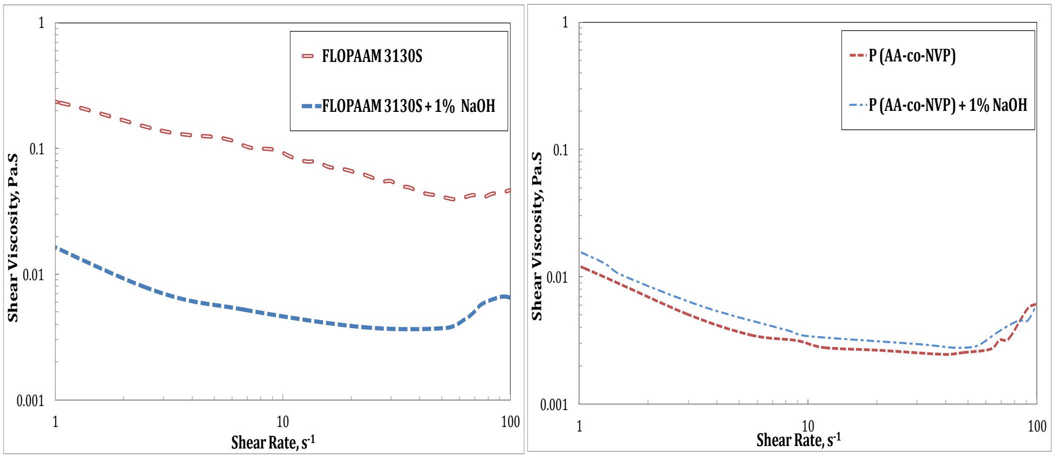
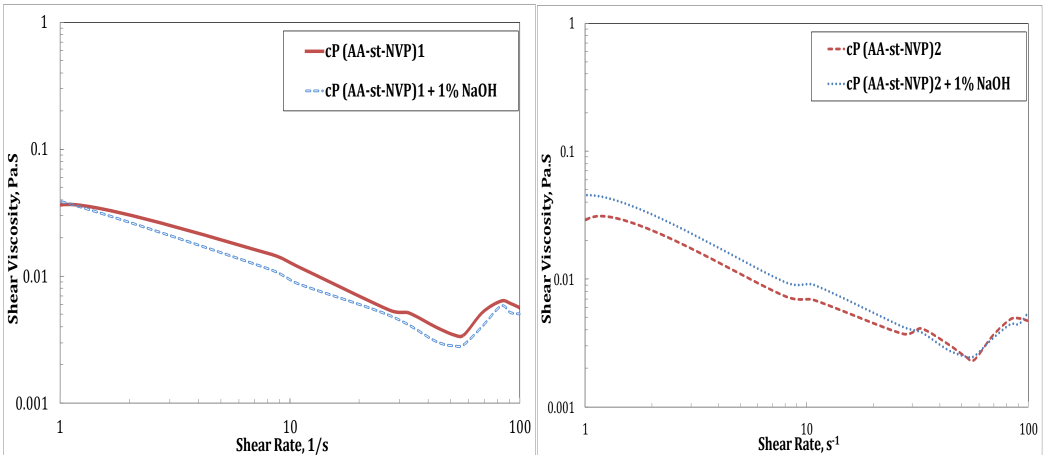


(d)

Figure 5.1: Chemical structures (a) Monomers (b) Copolymer (c) Crosslinker (d) Probable AA-NVP Crosslinked Polymer Structure

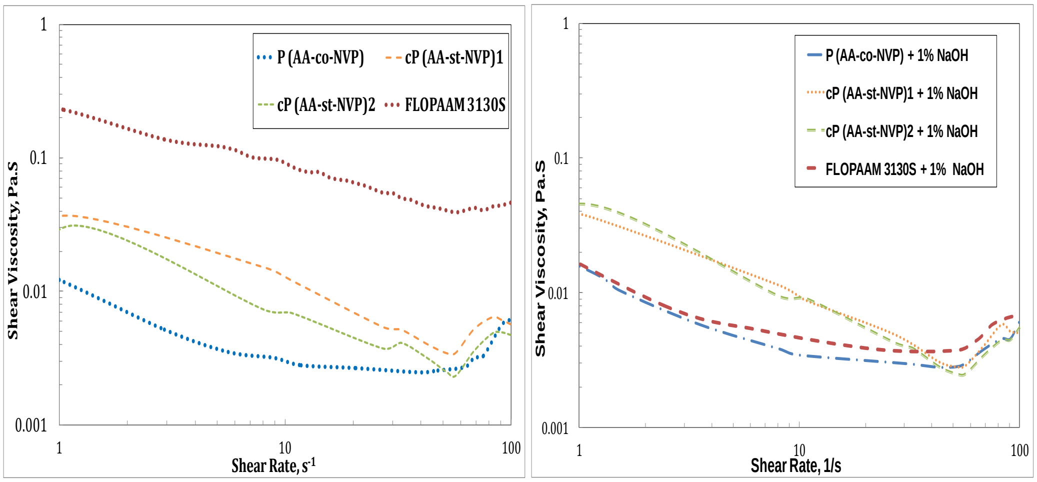


(a) (b)



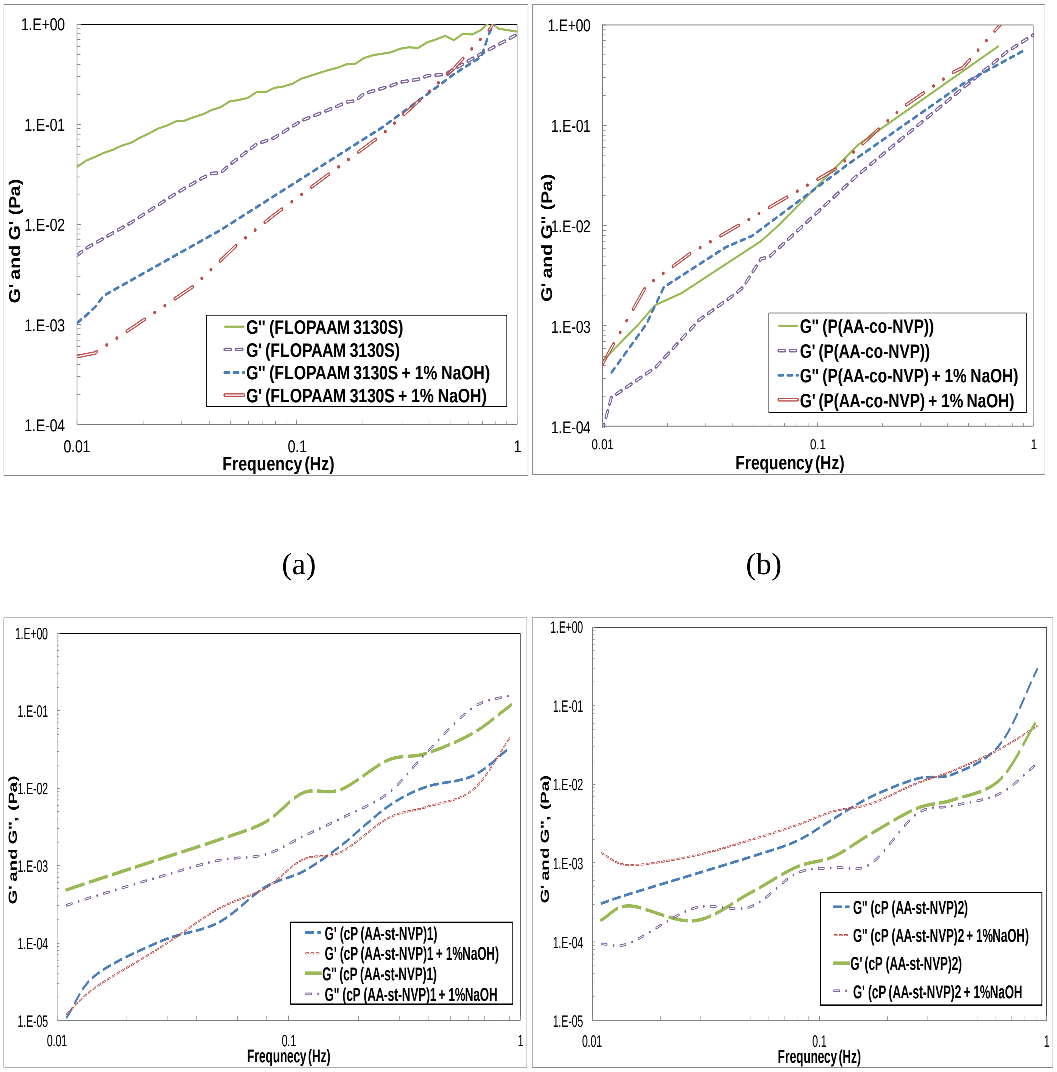
(c) (d)

Figure 5.2: Shear Rate vs Shear Viscosity Plot (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-VP) + 1% NaOH, (c) cP(AA-*st*-NVP)$_1$ vs cP(AA-*st*-VP)$_1$ + 1% NaOH, and (d) , cP(AA-*st*-NVP)$_2$ vs cP(AA-*st*-VP)$_2$ + 1% NaOH



(a) (b)

Figure 5.3: Shear Rate vs Viscosity Plot (25°C) (a) All four polymers without 1% NaOH, (b) All four polymers with 1% NaOH



(a) (b)

(c) (d)

Figure 5.4: Viscous and Elastic Modulus vs Angular Frequency (25°C) (a) FLOPAAM 3130S vs FLOPAAM 3130S+1% NaOH, (b) P(AA-*co*-NVP) vs P(AA-*co*-VP) + 1% NaOH, (c) cP(AA-*st*-NVP)$_1$ vs cP(AA-*st*-VP)$_1$ + 1% NaOH, and (d) , cP(AA-*st*-NVP)$_2$ vs cP(AA-*st*-VP)$_2$ + 1% NaOH

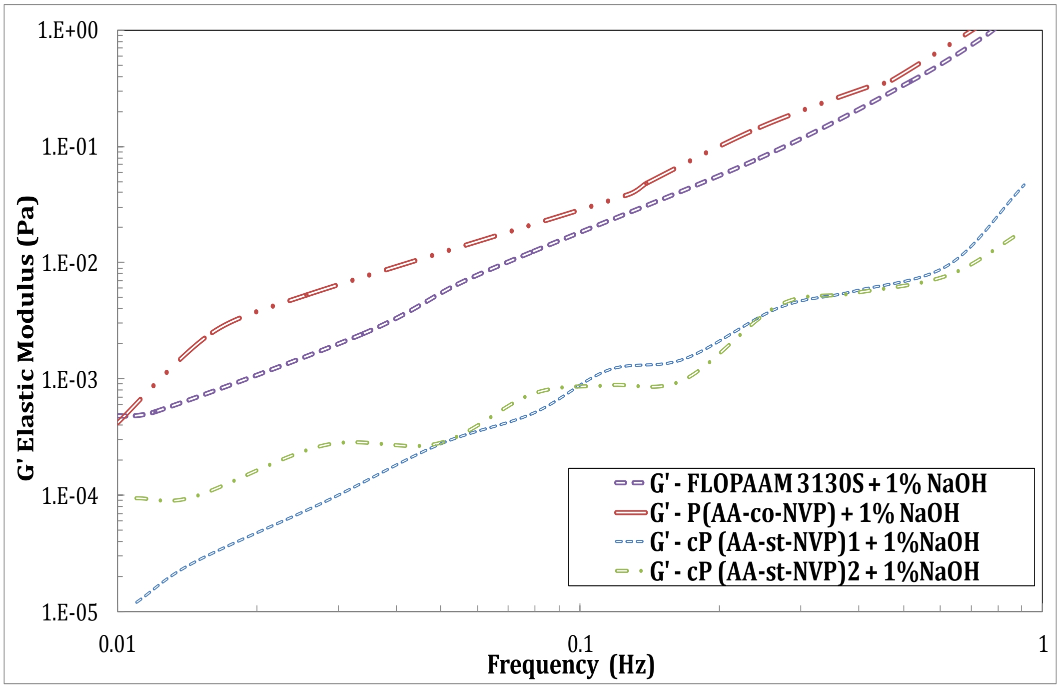


Figure 5.5: Elastic Modulus vs Angular Frequency (25°C) for all four polymers in alkaline conditions

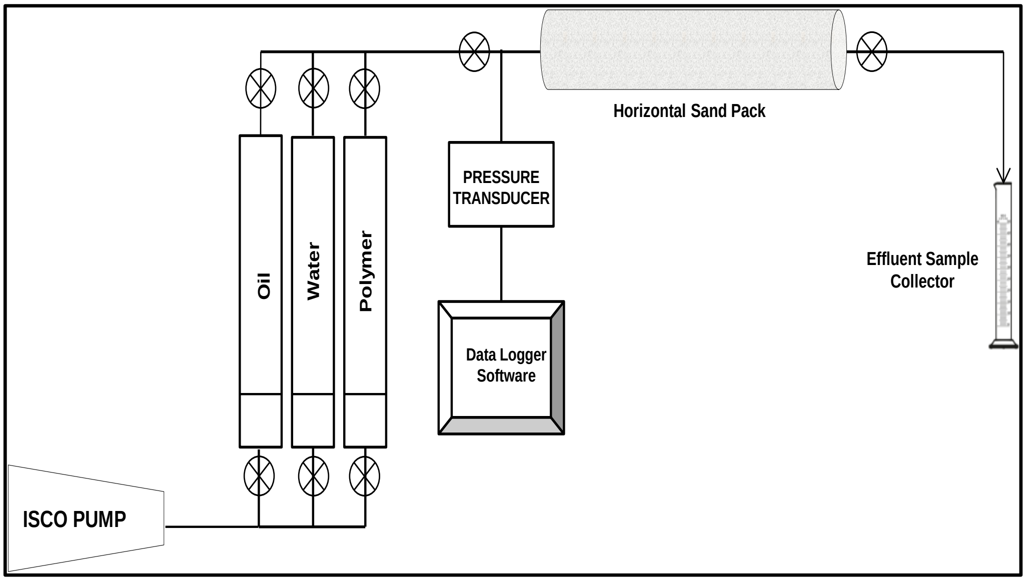


Figure 5.6: Experimental Schematic

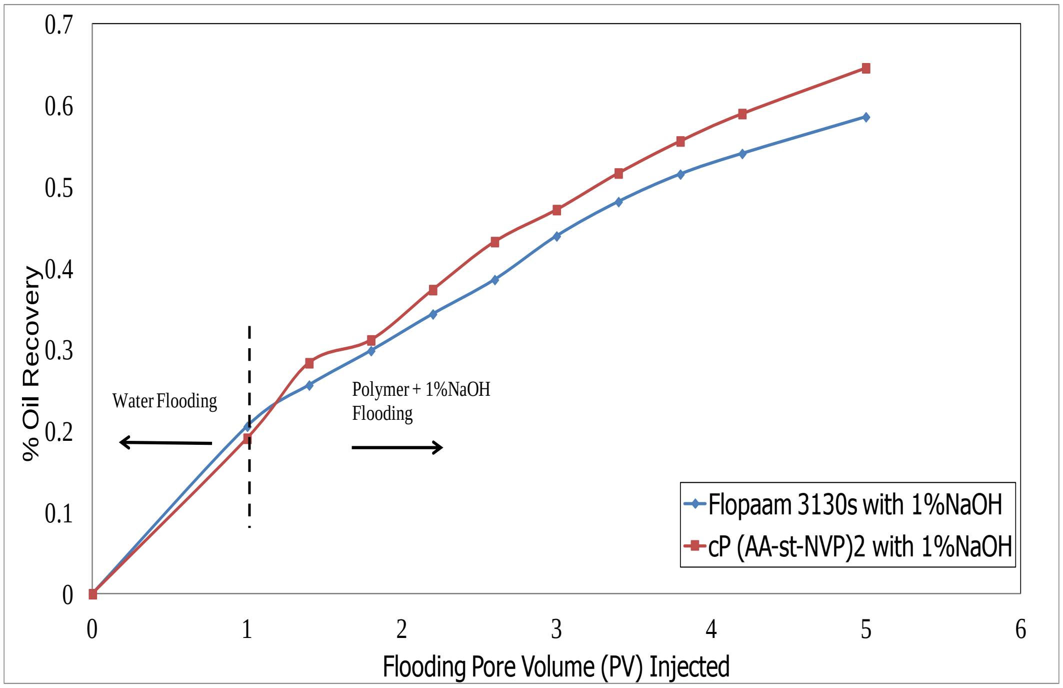
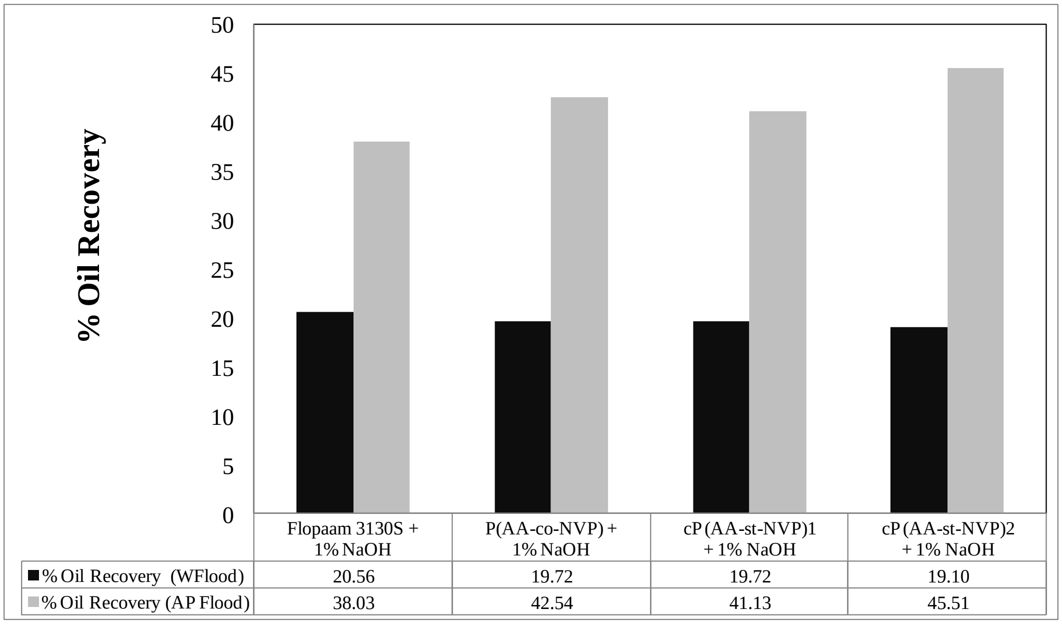


Figure 5.7: Comparison of Oil Recovery for Polyacrylamide and Crosslinker with 1% NaOH with Pore volume injected



	Flopaam 3130S + 1% NaOH	P(AA-co-NVP) + 1% NaOH	cP (AA-st-NVP)1 + 1% NaOH	cP (AA-st-NVP)2 + 1% NaOH
■ % Oil Recovery (WFlood)	20.56	19.72	19.72	19.10
▨ % Oil Recovery (AP Flood)	38.03	42.54	41.13	45.51

Figure 5.8: Comparison of Oil Recovery all four polymers with 1% NaOH

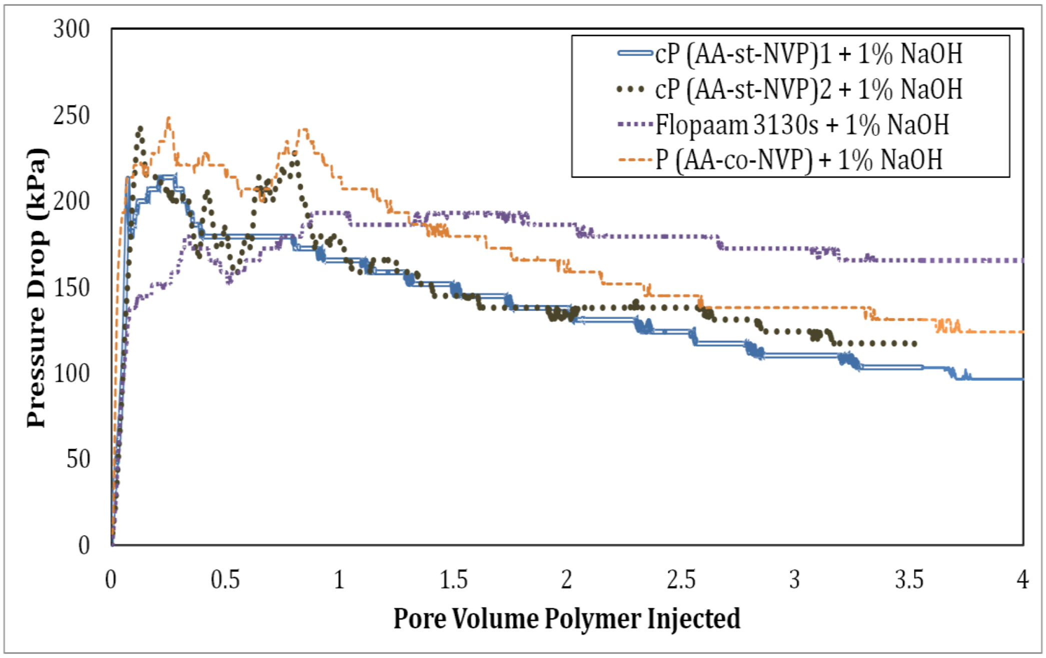


Figure 5.9: Comparison of pressure drop all four polymers with 1% NaOH

CONCLUSIONS

- Polyacrylamide was studied for effect of elasticity behavior with changing water flood. Polymer having similar viscosity and different elasticity were compared.
- Difference in heavy oil recovery during polymer flooding between the various polymer solutions was found which can be attributed to differences in their elasticity.
- A large difference in heavy oil recovery between HPAM-1 and HPAM-4 was observed after 1 PV of primary water flooding, compared to cases with 0.5 PV of water flooding and no water flooding. These results illustrate that the effect of elasticity is more profound on oil recovery and pressure drop when there is more water saturation.
- The required injection pressure for the more elastic polymer solution (HPAM-4) is higher than that of the least elastic polymer solution (HPAM-1). Higher RRF values and higher pressure drop values for HPAM-4 compared to the other polymer solutions indicate that polymer solution elasticity can contribute significantly to pore plugging and reduce water phase permeability.
- Higher elasticity polymer shows more increase in recovery as water saturation was increased. This shows that elasticity's effect is more significant on heavy oil recovery if reservoir has already been water flooded.
- Higher values of RRF and higher pressure drop for HPAM-4 compared to other polymer solutions indicates polymer elasticity can contribute significantly in the pore plugging and reduce water phase permeability.

- Polyacrylamide was compared with N-Vinyl-2-Pyrrolidinone and acrylic acid based polymers for injectivity improvement and mobility reduction properties .
- HPAM was compared with P (AA-co-NVP) (copolymer) , cP (AA-st-NVP)$_1$ and cP (AA-st-NVP)$_2$ (Cross-Linked polymers) for both alkaline and non-alkaline conditions for rheology.
- Viscosity of HPAM is almost similar to copolymer and lower than cross-linked polymer in presence of 1% NaOH.
- Viscosity of HPAM changed significantly when alkaline and non-alkaline conditions were compared. However, NVP-AA based polymers has minimal or almost no change for these conditions.
- Polymers were compared for Alkali-Polymer flooding of heavy oil for oil recovery analysis. Secondary polymer flood recovery for HPAM with alkali lower by 6% as compared to new co- and cross-linked polymers.
- Alkali's IFT reduction ability improves oil recovery by generating in-situ surfactants with acid present in heavy oil. For polyacrylamide viscosity loss was compensated by IFT reduction property of alkali which results in lower oil recovery.
- HPAM was compared for pure injectivity analysis for AP flooding in porous media without any oil with copolymer and crosslinked polymer.
- Copolymer and crosslinked polymer in alkali conditions showed high values of Resistance Factor as compared to HPAM which can be attributed to better injectivity of AA-NVP polymer solutions.
- High RRF value represents high amount of polymer adsorption on porous media. High amount of adsorbed polymer increases injection pressure due to pore-plugging.

Recommendations

After studying HPAM for elasticity behaviour under various water flooding conditions and newly synthesized polymer for injectivity and oil recovery, there is still scope for further research and are recommended here:

- AA-NVP based polymers must be studied with Alkali-polymer-surfactant flooding to analyze their compatibility and behavior with surfactants
- AP flood, ASP floods can be tried on heavy oil displacement experiments to understand the effect of elasticity under those conditions.
- The core-flooding experiments with and without oil were carried out in stainless steel core. These experiments must be carried out in Borofloat glass models to visually analyze the elasticity behaviour and alkali-polymer interactions with oil.
- Alkali used in our experiments was lab scale NaOH. The experiments needs to be carried out using a organic alkali.
- Polymer concentration must be measured before and after the flooding experiments and compared for a better understanding of the mechanism of degradation/adsorption of polymers.