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Investigation of Polymer stability at high temperature and high salinity

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CERTIFICATION OF APPROVAL

Investigation of Polymer Stability at High Temperature and High Salinity

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Nikita Mazurenko

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ABSTRACT

With growing global energy demand and depleting reserves, EOR (Enhanced Oil Recovery) from existing and brown fields has become more and more important. Among EOR (Enhanced Oil Recovery) methods polymers play an important role and are being applied all over the world. The list of diversified Enhanced Oil Recovery methods highlights chemical EOR as an expensive method. Due to that fact field applications of that method have almost been stopped within past two decades around the world, except for China, North Sea, Malaysia and Middle East.

Usage of polymers belongs to chemical enhanced recovery. Polymers are being mixed with water in order to form a solution that is to be injected inside the reservoir for the purposes of increase in ultimate recovery of hydrocarbons. However before injecting the solution into the formation it is crucial to know the behavior of the polymer within the reservoir conditions. This is the key step that has to be done before implementation can actually get started, as some factors of reservoir can influence the structure of polymers and herby can affect the overall predicted performance of injected solution.

This project is aimed to investigate the impact of temperature as well as salinity on stability on polymeric solution, which is being used as Enhanced Oil Recovery (EOR) method with the purpose in improving sweep and displacement efficiency. During this work the author has identified the type of polymer that is to be used and investigated on stability.

Simulation is to be conducted using Eclipse software. Analysis of the simulation results is to be conducted later on in order to verify which method is providing more effective and efficient outcomes.

Actually there is a list of factors that might affect the polymeric solution, which includes such factors as temperature and also salinity. Temperature refers to the thermal conditions inside the reservoir as well as the salinity. Hereby both salinity and temperature can have influence on polymer stability. Stability of polymers due to high temperature and salinity is to be investigated in this study in order to come up with optimum decision for polymer solution.

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Today fossil fuels represent more than 85% of the world's energy. With the growing rate of production (approx. 87 million barrels per day – 32 billion barrels per year) it becomes obvious that the industry has to find sufficient volume of oil around the world just to replace the depleted reserves and sustain the industry development and performance at the desired level.

Conventional oil and heavy oil remain in reservoirs worldwide after conventional recovery methods have been exhausted in quite large amounts. Hereby it is of high importance for the Oil and Gas industry to recover as many hydrocarbons as possible in order to supply the increasing world energy market demand.

Likewise, in order to maximize the ultimate recovery of hydrocarbons from a particular reservoir, several methods can be implemented after the natural depletion stage is totally over. There are secondary methods, which comprise water or gas injection. These methods assist in maintaining the reservoir pressure in order to ensure hydrocarbon flow to the production wells continues. Usually the recovery factor at the end of this particular stage remains below 40% of the OOIP (Oil Originally in Place). Especially for such cases tertiary methods are being developed in order to overcome this kind of issues, so that recovery factors reach above 60%.

Polymer flooding belongs to chemical enhanced recovery. This method is well-known around the world leading oil companies and has more than 40 years of successful commercial application with relatively low risk and constant application over a wide range of diversified reservoir conditions. The main procedure includes dissolving polymer in the injected water in order to increase its viscosity and to improve the sweep efficiency inside the hydrocarbon reservoir.

A typical polymer flooding project involves standard procedure of mixing and injecting polymer for extended period of time until the least percentage 30% of the reservoir pore volume has been successfully injected. This stage is later on being followed by continued waterflooding for a long period of time. It will drive the polymer slug and the oil bank in front of it toward the production wells.

Surfactants can also be combined with polymer (SP for Surfactant Polymer) to mobilize the trapped oil through changing the interfacial tension between Oil and Water and making the oil more mobile and hereby easy to produce.

There exists also an addition of Alkali to the Surfactant Polymer System (ASP). It generates in-situ surfactants and can alter the wettability of the rock, hereby mobilizing more oil.

1.2 Problem Statement

Hydrolyzed polyacrylamide (HPAM) is an important additive used to enhance the sweep efficiency during chemical enhanced oil recovery. Although HPAM is widely used in oil industry, there is an uncertainty whether the properties will change due to high salinity and high temperature operating condition, thus this project is being carried out to investigate the rheological behavior of HPAM under high temperature and high salinity conditions.

1.3 Objective

The main objective of this research is to investigate the effect of high temperature and salinity on the stability of polymers (i.e. HPAM) and polymeric solution using Eclipse software.

1.4 Scope of Study

Five different parameters have been chosen to conduct the study. Pressure and master solution concentration will be fixed throughout the simulation to compare the results of each study that will be carried out. The scope of the study will be on the viscosity trend of HPAM at fixed high pressure, fixed master concentration, different high temperatures, different dilute concentrations and different hydration periods.

1.4.1 The relevancy of the Project

In this project we will be focusing on rheological properties at high salinity and high temperature conditions. It will be highly beneficial for companies around the world dealing with Enhanced Oil Recovery, which are still investigating until which extend does HPAM can operate as viscosifier. Furthermore, the result of this project will allow companies to operate with certainty and confidence with polymeric solutions, which are stable under various reservoir conditions.

1.4.2 Feasibility of the project within the scope and time frame.

The project is being divided into two sections. The first section will basically include finding, reading and collection relevant information from journals, technical papers, and books for the research topic. In this section one, the author will provide parameters to be tested during the simulation. The main factor that is being affected during polymer flooding process is to be properly selected and appointed accordingly for investigation and analysis during further simulation.

The second section of the project will be mainly be concentrated on carrying out simulation itself in order to test the behavior of HPAM (Hydrolyzed Polyacrylamide) under various conditions as stated before. The relevant data that has been obtained during the literature review is to be used accordingly in order to ensure the reliability and feasibility of the project.

After that on the basis of results of simulation it will become possible to come up with clear and detailed conclusion and propose recommendations related to the entire project study and investigation.

CHAPTER 2: LITERATURE REVIEW

Nowadays partially hydrolyzed polyacrylamide is gaining more scientific interest from the researchers around the world due to its wide usage in various industries and commercial application, especially in oil industry. “The viscosity of hydrogel, which is produced by a dilute or semidilute HPAM solution cross-linked with cross linker, is higher than that of non-crosslinked HPAM solution of same concentration”. (Zhang et al. 2008) Thus it means that HPAM acts as the most suitable substance to be used as the sweeping fluid to further recover the oil in the reservoir after the first stage of production.

Hereby, it is said that the viscosity varies significantly depending on certain parameters such as temperature, pressure, concentration and etc. A lot of studies have been carried out to determine the behavior of HPAM under these circumstances. “The effects of solvent, salt type and concentration, degree of hydrolysis, and polymer concentration on viscosity have been investigated. It was shown that the reduced viscosity of salt-free solution of partially hydrolyzed polyacrylamide as a result of polymer chain expansion increases with decreasing polymer concentration”.(Zeynali et al. 2004)

The mobility control process is basically based on maintaining effective mobility ratio to improve sweep efficiency. Likewise, Figure 1.2 provides an obvious example of how microscopic displacement efficiency improves with help of polymer flowing comparing to waterflooding (James J.Sheng 2011).

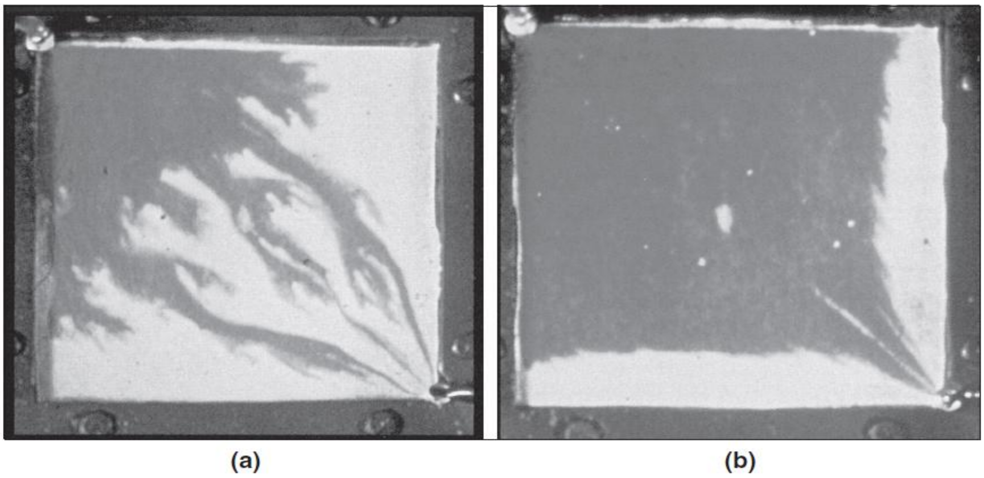

(a) (b)

FIGURE 1.2 Schematic of macroscopic displacement efficiency improvement by polymer flooding (b) over waterflooding (a). *Source: Courtesy of Surtek, a chemical EOR service company in Golden, Colorado.*

Further models and correlations have been invented to prove the behavior of HPAM in order to extend its usage purposes. “By devising the mathematical model for the rheological behavior of PAAM solution, which relates yield stress at various temperatures and concentration, it can be proven that, at higher concentrations of PAAM solution leads to increment in the shear stress. When the concentration is fixed and the temperature is varied, the shear stress decreases with increasing temperature. Furthermore it has been concluded that PAAM solution has a non-Newtonian fluid characteristic and its yield stress decreases with increasing temperature”. (Yang and Yen, 2001) Thus, it proves that rheological studies are very important in determining the exact behavior of HPAM under various conditions.

Basically there are two main types of polymers, which are:

- synthetic polymers such as hydrolyzed polyacrylamide (HPAM)
- biopolymers, such as xanthan gum

The natural polymers and their derivatives (i.e. sodium carboxymethyl cellulose, guar gum and hydroxyl ethyl cellulose (HEC)) are less commonly used.

The key parameters and characteristics of various polymers play an important role when it comes to selection the most appropriate type for polymer flooding.

Likewise “–O–“ in the backbone of polymers result in low thermal stability and thermal degradation at high temperatures (T) (only suitable at temperatures less than 80˚C). Examples of such polymers include sodium alginate, HEC, polyoxyethylene, carboxymethyl cellulose, xantham gum and others.

On the other hand carbon chain in the backbone will result in not severe degradation at temperatures less than 110˚C and good thermal stability. Polyvinyl, polyacrylate and HPAM belong to this group of polymer structures.

In comparison, good visosifiers require $-COO^{-}$in hydrophilic group. That will result in less adsorption on sandstones, which is being caused by repulsion between the chain links. However there is precipitation of Ca^{2+} as well as Mg^{2}. This group includes such polymers as: sodium carboxymethyl cellulose, sodium alginate, HPAM and also xantham gum.

In addition –OH or –CONH in hydrophilic group will not result in any precipitation of Ca^{2+} or Mg^{2} and will have good chemical stability without any repulsion between chain links. Absence of repulsion will result in less viscosifying powder. For this type there will be high adsorption due to hydrogen bond being formed on the sandstone rocks. This group includes: polyvinyl, HEC, HPAM, polyacrylamide (Zhao, 1991).

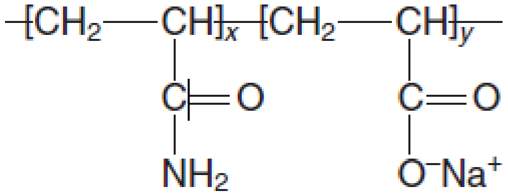
Hereby from the discussed characteristics now it becomes possible to state what kind of properties a reliable polymer should have:

- Negative ionic hydrophilic group – in order to reduce adsorption on rock surfaces;
- Good viscosifying powder;
- No “–O–“ in the backbone (carbon chain) in order to ensure thermal stability;
- Nonionic hydrophilic group in order to provide strong chemical stability

Based on these criteria discussed it becomes obvious that HPAM is an acceptable polymer and that has been approved by many years of application in industry.

HYDROLYZED POLYACRYLAMIDE

Wide specter of EOR applications includes HPAM as the one, which is widely used (Manrique et al.,2007). The reason for selection this type of polymers for improved recovery is that HPAM solutions have better viscoelasticity, comparing to xanthan solutions (Wang et al., 2006a). Polyacrylamide is able to adsorb strongly on mineral surfaces. Hereby, the polymer is being partially hydrolyzed in order to reduce adsorption through the reaction of polyacrylamide with a base, like sodium or potassium hydroxide as well as sodium carbonate. Hydrolysis process converts some of amide groups (CONH2) into carboxyl groups (COO−). Figure 1.3 demonstrates this process:



$$-[CH_2-\underset{\underset{\underset{NH_2}{|}}{C=O}}{\underset{|}{CH}}]_x-[CH_2-\underset{\underset{\underset{O^-Na^+}{|}}{C=O}}{\underset{|}{CH}}]_y-$$

Figure 1.3 Hydrolysis process of HPAM.

The degree of hydrolysis represents the mole fraction of amide groups, which have been converted by hydrolysis. Its value usually ranges from 15 up to 35% for commercial products.

The process of polyacrylamide hydrolysis introduces negative charges on the backbones of polymer chains. This results in a significant effect on the rheological properties of the polymer solution itself. At low values of salinities, the negative charges on the polymer backbones tend to repel each other and, as result, polymer chains stretch. In case of addition of an electrolyte, such as NaCl, the repulsive forces are being shielded by a double layer of electrolyte and that reduces the chain stretch.

When the values of hydrolysis go above 40%, the flexible chains are being significantly compressed as well as distorted, and that results in viscosity reduction. For example, in hard waters (with high contents of Ca2+ and Mg2+), as hydrolysis goes beyond 40%, flocculation may occur. Flocculation represents the process where colloids leave the suspension in the form of floc or flake. This may happen both spontaneously and as a result of clarifying agent addition. This action is different from precipitation, because before the flocculation occurs, colloids are simply being suspended in a liquid and not dissolved in a solution.

Since EOR process is time-consuming, hereby polymer stability is an important factor. Basically, hydrolysis level is required not to go more than 40% after three months. However, in case of polyacrylamide, hydrolysis goes very fast under acidic and basic conditions. At high temperature levels, the hydrolysis occurs fast under neutral conditions as well. Hereby it becomes obvious that HPAM is not being tolerant to high temperature or high salinity (Wang et al., 2003a).

2.1 Polymer Stability

Polymer degradation refers to any process that breaks down the molecular structure of macromolecules. The main degradation pathways of concern in oil recovery applications are chemical, mechanical, and biological. The research work on polymer stability from the mid-1970s to late-1980s is summarized in Sorbie (1991).

2.1.1 Chemical Stability

Chemical degradation refers to the breakdown of polymer molecules, either through short-term attack by contaminants, such as oxygen and iron, or through longer-term attack to the molecular backbone by processes such as hydrolysis. The latter is caused by the intrinsic instability of molecules even in the absence of oxygen or other attacking species. In other words, polymer chemical stability is mainly controlled by oxidation-reduction reactions and hydrolysis.

2.1.2 Oxidation Reduction

The presence of oxygen virtually always leads to oxidative degradation of the polyacrylamide polymer. However, at a low temperature, the effect of dissolved oxygen on HPAM solution viscosity is not significant, and the polymer solution could be stable for a long time. As the temperature increases, even if a small amount of oxygen exists, HPAM solution viscosity quickly decreases with time. For example, the half-lives for a polymer at 50°C, 70°C, and 90°C are 117, 20, and 2.6 hours, respectively. As the oxygen concentration increases, the viscosity decreases faster (Luo et al., 2006).

Yang and Treiber (1985) studied the chemical stability of polyacrylamide solution under simulated field conditions. They identified the main variables encountered by a polymer solution in the field as oxygen, temperature, oxygen scavengers, metal/metal ions, hydrogen sulfide, pH, salinity/hardness, chemical additives, and biocide. Their main finding was that the rate and extent of polymer degradation were governed mainly by the oxygen content of the solution and temperature, although they remarked that limited levels of oxygen produced only limited polymer degradation. At low oxygen levels (1 part per billion, ppb), they found that their polyacrylamides were stable over 500 days up to 93.3°C and indeed showed an increase in viscosity over this time. This increase had been reported previously by Ryles (1983), later by Luo et al. (2006) and by Han et al. (2006a). (See Figure 5.21.) This behavior is thought to be the result of the increasing degree of hydrolysis that occurs at elevated temperatures. When the oxygen was completely consumed, the degradation reaction stopped; this behavior is contrary to the general suspicion that after the reaction is initiated by oxygen, it will proceed without further oxygen supply.

2.1.3. Hydrolysis

This section reviews the effects of temperature and divalent on hydrolysis. Effect of Temperature In the absence of oxidative degradation, the backbone chain of vinyl polymers, such as polyacrylamide, is quite thermally stable to temperatures as high as 120°C (Ryles, 1983). Indeed, Ryles (1988) found that polyacrylamide was stable at 90°C for at least 20 months under controlled conditions. At elevated temperatures, however, the pendant amide groups tend to hydrolyze, therefore increasing the total carboxylate content of the polymer. This increase results in significant changes in solution properties, rheology, and phase behavior because the primary mechanism of polyacrylamide degradation is found to be amide group hydrolysis. Thermal stability tests performed by Ryles (1988) showed that the dissolved salts had just a minor effect on the hydrolysis rate and that the temperature was the main determining factor. From his data, we can see the following:

- The higher the temperature, the faster the rate of hydrolysis.
- The higher the temperature, the higher the degree of hydrolysis.
- Hydrolysis was significantly affected by temperature.
- The divalent concentration strongly affected viscosity reduction.
- The highest viscosity retention occurred at 40 to 50% hydrolysis.

This observation is consistent with the observation by Kong (1996). The preceding observations are consistent with those by Moradi-Araghi and Doe (1984). In alkaline conditions, initially hydrolysis is fast. As the hydrolysis reaches a certain level, the electrostatic repulsion between carboxyl group and OH− limits further hydrolysis at pH > 13. Finally, hydrolysis is stopped. Therefore, pH has been found to have a minimum effect. At a high temperature, acrylamide is progressively hydrolyzed into acrylic acid; thus, hydrolysis is increased, as shown in Figure 5.24. In the beginning, hydrolysis increased almost linearly with aging time. After hydrolysis of 44%, the rate of increase slowed down. One of the HPAM characteristics is that hydrolysis quickly increases at high temperatures. Consequently, hydrolysis directly affects HPAM stability. The preceding observations can be supported by data from Han et al. (2006a). They investigated the effect of initial hydrolysis and found that the rate of hydrolysis was higher at a higher initial hydrolysis. Therefore, a higher initial hydrolysis is needed in a low-temperature (e.g., 55°C) reservoir so that high viscosity can be quickly reached. In a high-temperature reservoir, the HPAM viscosity near the wellbore will be lower if a polymer with a lower initial hydrolysis is used. This technique will improve polymer injectivity. As the polymer moves deep into the reservoir, hydrolysis increases and viscosity also increases.

Tan (1998) investigated the effect of temperature gradient near wellbore on HPAM polymer thermal stability. For the reservoir he studied, there was a temperature gradient from 40°C near the injection wellbore to 75°C deep in the reservoir. He observed that when the polymer was under thermal degradation gradually from 40°C to 75°C, the polymer had higher viscosity retention than when the polymer was under 75°C thermal degradation right from the beginning. During the early stages of thermal degradation, oxygen is consumed, and no oxygen is available during the later stages. Tan's experiments showed that the polymer would be more stable if it is under thermal degradation when the temperature is gradually increased so that the oxygen is consumed at low temperatures. However, the initial polymer viscosities were different in his experiments (57.8 mPa·s at 75°C constant temperature compared with 77.5 mPa·s under the temperature gradient). The water TDS was 362.6 mg/L, and sand was used in the tests. Tan tried to imitate the actual thermal degradation conditions. He also observed that oil did not affect the polymer thermal stability.

2.1.4 Polymer Rheology

In a discussion of rheology, one important parameter is viscosity. First, we should be aware of the different terminologies related to viscosity. Bulk viscosity is the viscosity measured in a viscometer, which was discussed previously. In situ viscosity in porous media is not directly measured. Instead, it is calculated according to the Darcy equation using core flood experimental data. This calculated viscosity is called apparent viscosity. Sorbie (1991) used the terms apparent viscosity (the symbol ηapp) to describe polymer solution viscosity in porous media and effective viscosity (the symbol ηeff) to describe polymer viscosity in a single capillary tube. For bulk viscosity, he used the symbol μ to describe Newtonian viscosity, η to describe non-Newtonian viscosity, and η to describe elongational viscosity.

2.1.5 Equation to Define Polymer Adsorption

The Langmuir-type isotherm can be used (Lakatos et al., 1979) in order to describe polymer adsorption. The Langmuir-type isotherm is given by

$$\hat{C}_p = \min\left(C_p, \frac{a_p\left(C_p - \hat{C}_p\right)}{1 + b_p\left(C_p - \hat{C}_p\right)} \right),$$

where Cp is the injected polymer concentration, or in general, the polymer concentration before adsorption. Cp – $\hat{C}_p$ is actually the equilibrium concentration in the rock-polymer solution system. ap and bp are empirical constants. The unit of bp must be the reciprocal of the unit of Cp. ap is dimensionless. Note that Cp and $\hat{C}_p$ must be in the same unit. Because the Cp unit is usually in wt.%, using the unit for $\hat{C}_p$ in wt.% has some advantages. ap is defined as

$$a_p = \left(a_{p1} + a_{p2} C_{sep}\right)\left(\frac{k_{ref}}{k}\right)^{0.5},$$

where ap1 and ap2 are input or fitting parameters, Csep is the effective salinity, k is the permeability, and kref is the reference permeability of the rock used in the laboratory measurement.

The reference permeability (kref) is the permeability at which the input adsorption parameters are specified. and take into account the salinity, polymer concentration, and permeability.

Note that the Langmuir model is an equilibrium relationship, and its application assumes adsorption is instantaneous and reversible in terms of polymer concentration. When polymer adsorption is considered to be irreversible, the Langmuir model cannot be used directly when the polymer concentration is declining. An additional parameter, $\hat{C}_p$ max, must be used to track the adsorption history.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

Different findings, observations and methodologies are gathered from the research works of other researchers, who were dealing with topics related to the present study. These findings are to be studied in details and incorporated in this project.

The relevancy of findings should be verified in order to ensure that the entire project has been accomplished according to anticipated plan.

☑ Initially, various journals as well as technical papers have to be read through to get the general understanding of the project and obtain the major factors that influence polymeric solution during polymer flooding.

☑ Afterwards it is needed to identify the objective of this project and to come up with a proven method to run the simulation next semester.

☑ The main part of the simulation will include the simulation using Eclipse software. The input data is to be selected accordingly to proposed topic and the polymeric solution is to be selected in order to visualize the entire polymer flooding process and ensure that study is feasible and project can be successfully implemented.

☑ After that the polymeric solution is to be tested in the software on stability at increase in temperature. The main objective of this part of simulation is to verify the ultimate temperature that the solution is able to withstand without changing its properties (i.e. viscosity).

- ☑ Another part of the simulation will include the investigation of polymeric solution stability at variation in salinity. The aim is to investigate what is the ultimate salinity that certain type of polymer can withstand without changing its properties or composition.

- ☑ Next stage includes verification of obtained results and relation to the project study.

- ☑ After that simulation work using Eclipse for waterflooding is required to be performed in order to visualize the alternative recovery process.

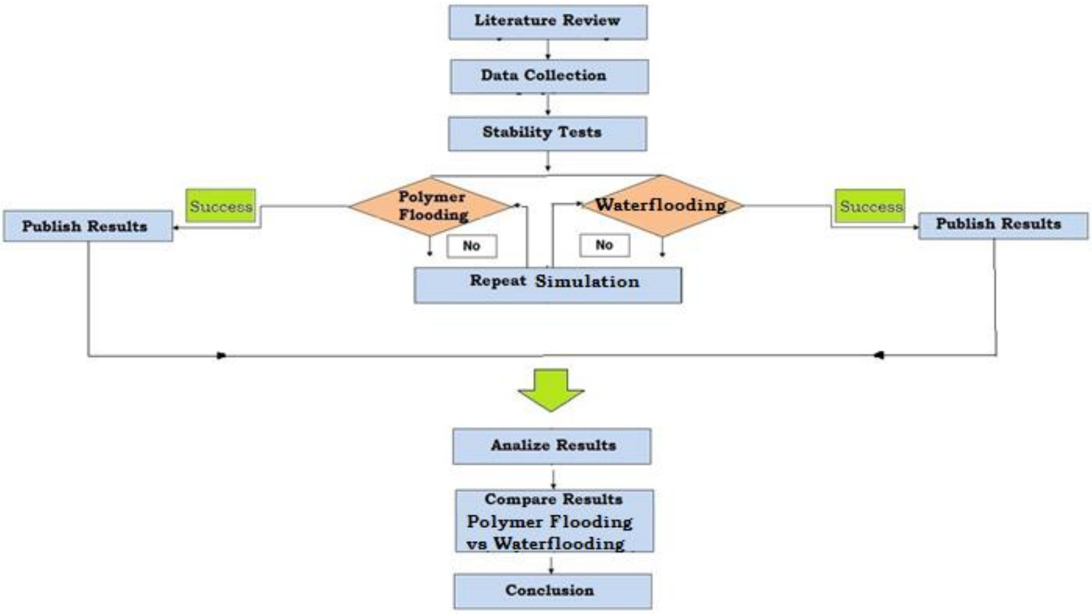
- ☑ The results from both simulations of polymer flooding and waterflooding are to be compared between each other in order to verify the best method to be implemented for EOR.

- ☑ All results have to be collected and combined accordingly in order to have enough data for project conclusion.

- ☑ After all the results have been obtained the entire project should be concluded and project feasibility should be verified and related to real-life application.

- ☑ The last part includes presentation of the project and submission of prepared study.

3.2 Methodology Flow Chart



CHAPTER 4: VALIDATIONS

In this project there are two parameters which will be tested during the simulation namely, temperature and salinity. With these parameters being tested, a better study can be conducted on the behavior of HPAM under various conditions.

For the simulation part, it is decided that two of the parameters which are pressure and master concentration will remain constant throughout the simulation. Whereas, the other parameters will vary in order to understand the viscosity behavior of HPAM under high pressure and high temperature condition. The parameter that will reveal the change of polymeric solution is wettability. It is to be analyzed throughout the project.

On the basis of data accumulated from literature review where similar experiments have been conducted previously, it will become possible to perform a reliable and feasible simulation. According to simulations' results it will become possible to conclude what are the key parameters (temperature, salinity) that influence change in viscosity of polymeric solution and hereby what are the ultimate values of these key parameters and what is the optimum composition the solution should have in order to withstand the reservoir conditions and successfully, as well as effectively achieve the goal of enhanced oil recovery.

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Properties of polymer solutions

Viscosity is the most important parameter for polymer solution. As mentioned earlier, hydrolyzed PAM, or HPAM, is the most used polymer in enhanced oil recovery. Some of factors which affect polymer viscosity are discussed next.

5.1.1. Salinity and Concentration Effects

The dependence of polymer solution viscosity at zero shear rate (μ_p^0) on the polymer concentration and on salinity may be described by the Flory–Huggins equation (Flory, 1953),

$$\mu_p^0 = \mu_w\left(1 + \left(A_{p1}C_p + A_{p2}C_p^2 + A_{p3}C_p^3\right)C_{sep}^{S_p}\right), \tag{1.1}$$

where μ_w is the water viscosity with its unit being the same as μ_p^0; Cp is the polymer concentration in water; Ap1, Ap2, Ap3, and Sp are fitting constants; and Csep is the effective salinity for polymer. The items in the parentheses must be dimensionless.

The factor $C_{sep}^{S_p}$ allows for dependence of polymer viscosity on salinity and hardness. The effective salinity for polymer, C_{sep}, is given by:

$$C_{sep} = \frac{C_{51} + (\beta_p - 1)C_{61}}{C_{11}}, \tag{1.2}$$

where C51, C61, and C11 are the anion, divalent, and water concentrations in the aqueous phase; and βp, whose typical value is about 10, is measured in the laboratory.

The unit for C51 and C61 is meq/mL, and the unit for C11 is water volume fraction in the aqueous phase. The commonly used laboratory units for salinity are wt.% and ppm (mg/L). In principle, any units could be used, as long as they are used consistently in a study. It is suggested that one unit be used throughout a study. The unit meq/mL is a good scientific unit of salinity because it considers the effects of different ions with different electrolyte strength. In most cases, the unit is chosen based on convenience, not science.

Most often, the total amount of chloride is used because NaCl is the most common salt. The justification of using it is that the current technology really cannot describe the effect of every single ion on chemical EOR. For example, when HPAM reacts with multivalent metal ions, such as Al3+, Cr3+, and Ti3+, in a solution, a weak gel is formed. In this case, we cannot simply use Eq. 1.2 to calculate effective salinity. Equation 1.2 shows that divalents have a larger effect on the effective salinity than monovalents at the same concentration. In general, the order of effect is Mg2+ > Ca2+ > Na+ > K+. The activity of these ions is 10 to 20 kJ/mol, which is much less than the value for chemical reactions (about 200 kJ/mol). Therefore, the salt effect on polymer solution is a reversible electrostatic effect (Niu et al., 2006). Note that electrolyte concentrations in the laboratory are commonly expressed in terms of the aqueous phase volume, which includes the volume of surfactant and cosolvent in addition to water. C11 in Eq. 1.2 is used to correct the aqueous volume.

5.1.2 Temperature Effect

At a low shear rate, the polymer solution apparent viscosity decreases with temperature according to the Arrhenius equation,

$$\mu_p = A_p \exp\left[\frac{E_a}{RT}\right], \tag{1.3}$$

where Ap is the frequency factor, Ea is the activity energy of the polymer solution, R is the universal gas constant, and T is the absolute temperature. Eq. 1.3 shows that the viscosity decreases rapidly as the temperature increases. As the temperature increases, the activity of polymer chains and molecules is enhanced, and the friction between the molecules is reduced; thus, the flow resistance is reduced and the viscosity decreases. Different polymers have different Ea. With a higher Ea, the viscosity is more sensitive to temperature. HPAM has two Eas. When the temperature is less than 35°C, Ea is low, and the viscosity does not change too much as the temperature increases. When the temperature is higher than 35°C, Ea is high, and the viscosity is more sensitive to the variations in temperature.

Equation 1.3 can be rewritten as

$$\mu_p = \mu_{p,ref} \exp\left[E_a\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right], \qquad (1.4)$$

where $\mu_{p,ref}$ is the viscosity at the reference temperature T_{ref}. When measurements are made at different temperatures, the preceding equation may be used to fit the measurement data by adjusting Ea if Ea does not change at different temperatures.

5.2 Simulation of Polymer Flooding

All the above stated processes and equations are to be interpreted and simulated using the Schlumberger Eclipse Software. In order to simulate the process Eclipse manual is to be used to ensure proper flow of the simulation and compliance with goals and objectives.

There are two versions of Eclipse – Eclipse 100 and Eclipse 300. Each of them is encompasses different sets of activities and simulation options. For this project it has been decided to select Eclipse 100, as it is able to simulate the correlation between the salinity and viscosity of polymer solution.

For temperature influence on stability of polymer solution the newer version of the software – Eclipse 2012 and above is required as relevant correlations are included there.

However before proceeding to the simulation process itself it is important to understand all the keywords involved in creation of the simulation model.

5.2.1 Overview of Eclipse Software

An ECLIPSE data input file is split into sections, each of which is introduced by a keyword. A list of all section-header keywords is given below, together with a brief description of the contents of each section. A more detailed breakdown of the section contents may be found in the section overviews which follow immediately after this general overview.

After the section overviews, this manual contains a detailed description of the data for each keyword, in alphabetical keyword order. Some keywords are recognized by both ECLIPSE 100 and ECLIPSE 300, while others are valid in only one of the simulators. A flag table under each keyword heading indicates which simulator(s) the keyword may be used with, and the section(s) in which the keyword is entered. The flag table also indicates whether the keyword is specific to one of the ‘special extensions’ which are licensed separately. In keywords that are recognized by both simulators, some data items may apply only to one simulator. These items are distinguished in this manual by margin notes, such as ECLIPSE 100 only. Furthermore, in data items requiring an option to be selected from a list of available options, some of the options may be valid in only one of the simulators; these options are similarly distinguished by a margin note. Margin notes such as ECLIPSE 300 are also employed to indicate that a paragraph of text applies to just one of the simulators.

5.2.2 Data file sections

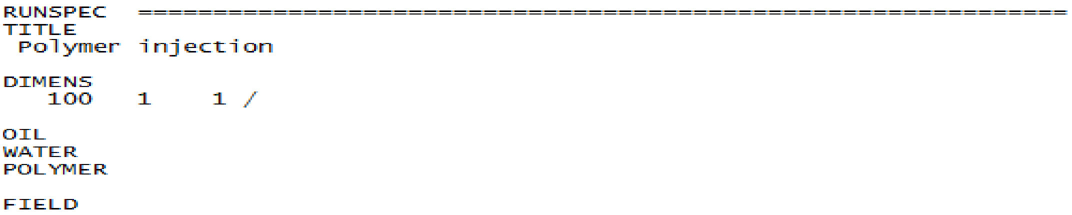
- The RUNSPEC section is the first section of an ECLIPSE data input file. It contains the run title, start date, units, various problem dimensions (numbers of blocks, wells, tables etc.), flags for phases or components present and option switches. The RUNSPEC section consists of a series of keywords, which turn on the various modeling options, or contain data (for example problem dimensions).
- The GRID section determines the basic geometry of the simulation grid and various rock properties (porosity, absolute permeability, net-to-gross ratios) in each grid cell. From this information, the program calculates the grid block pore volumes, mid-point depths and interblock transmissibilities.
- The EDIT section contains instructions for modifying the pore volumes, block center depths, transmissibilities, diffusivities (for the Molecular Diffusion option), and non-neighbor connections (NNCs) computed by the program from the data entered in the GRID section.
- The PROPS section of the input data contains pressure and saturation dependent properties of the reservoir fluids and rocks.
- The REGIONS section divides the computational grid into regions for:
    - Calculation of saturation functions (relative permeability and capillary pressure)
    - Calculation of PVT properties (fluid densities, FVFs, viscosities)

- Equilibration (setting initial pressures and saturations)
- Reporting of fluids in place and inter-region flows
- Calculation of directional relative permeabilities
- Calculation of saturation functions for imbibition (Hysteresis option)
- Calculation of ROCKTAB properties for the Rock Compaction option
- Calculation of initial tracer concentrations (Tracer Tracking option)
- Calculation of the saturation table end points from depth tables (for the saturation table End Point Scaling option)
- Calculation of mixture properties (Miscible Flood option)\
- Specifying pressure maintenance regions.

- The SCHEDULE section specifies the operations to be simulated (production and injection controls and constraints) and the times at which output reports are required. Vertical flow performance curves and simulator tuning parameters may also be specified in the SCHEDULE section.
- The SOLUTION section contains sufficient data to define the initial state (pressure, saturations, compositions) of every grid block in the reservoir. This data may take the form of equilibration, restart and enumeration.
- The SUMMARY section specifies a number of variables that are to be written to Summary files after each time step of the simulation. The graphics post-processor may be used to display the variation of variables in the Summary files with time and with each other.

5.2.3 Simulation Process

According to the flow described in the manual the following processes were included in Eclipse Data File, which is to be run upon completion in the simulator in order to provide results.

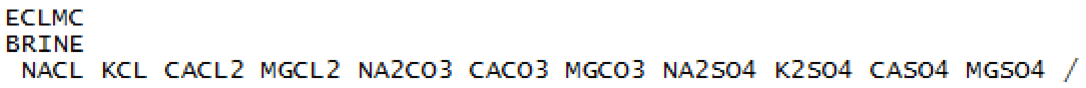


```
RUNSPEC  ===============================================================
TITLE
 Polymer injection

DIMENS
   100   1    1 /

OIL
WATER
POLYMER

FIELD
```

Figure 1.4 Eclipse Data File

As can be clearly seen from the Figure 1.4, the main three components that are included in this simulation are oil, water and polymer. Keyword FIELD designates that all dimensions are in field units.

FIELD keyword is followed by dimensions of region, table (with multipliers and properties values, which are used for calculations described further on) and well dimensions.

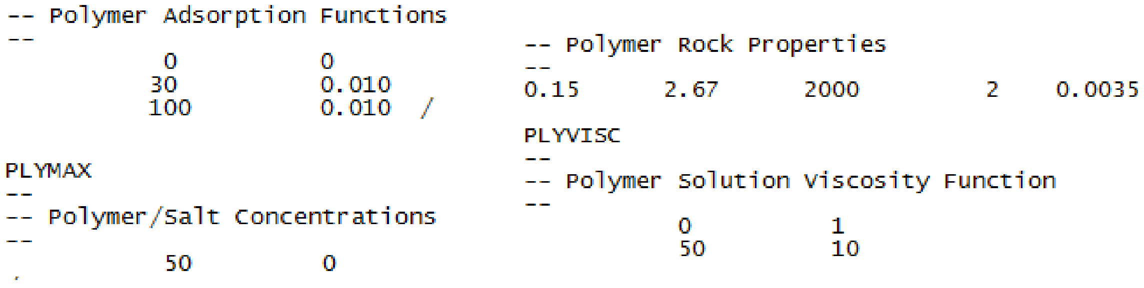


```
ECLMC
BRINE
 NACL  KCL  CACL2  MGCL2  NA2CO3  CACO3  MGCO3  NA2SO4  K2SO4  CASO4  MGSO4  /
```

Figure 1.5 BRINE Function

Figure 1.5 designates that salt option is switched on and hereby enables to correlate the salinity effect to stability of polymer solution. Elements listed in this figure represent different types of salts that will be used in a multi-component system (ECLMC).

After this it becomes possible to start creating the Properties Section (PROPS).



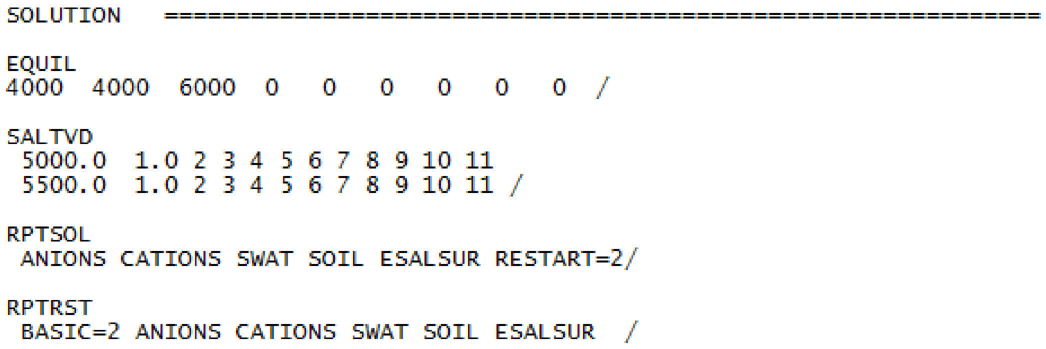
```
-- Polymer Adsorption Functions
--
           0            0
          30            0.010
          100           0.010   /


PLYMAX
--
-- Polymer/Salt Concentrations
--
           50           0
```

```
-- Polymer Rock Properties
--
0.15       2.67       2000          2     0.0035

PLYVISC
--
-- Polymer Solution Viscosity Function
--
           0           1
           50          10
```

Figure 1.6 Polymer Properties

All the properties described in Figure 1.6 are important in order to correlate the Eclipse model mathematically to the real life process inside the reservoir as precise as possible.

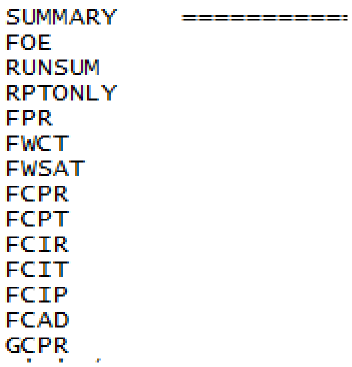
Solution section will perform enumeration and equilibration, as described before, in order to correlate all the numbers, properties and multipliers to respective formulas integrated inside the software and perform the calculation (Figure 1.7). In this part of simulation only salinity effect is to be calculated. This can be seen according to the keyword SALTVD, which is included in the Solution Section.



```
SOLUTION   ==========================================================

EQUIL
4000  4000  6000  0   0   0   0   0   0  /

SALTVD
 5000.0  1.0 2 3 4 5 6 7 8 9 10 11
 5500.0  1.0 2 3 4 5 6 7 8 9 10 11 /

RPTSOL
 ANIONS CATIONS SWAT SOIL ESALSUR RESTART=2/

RPTRST
 BASIC=2 ANIONS CATIONS SWAT SOIL ESALSUR  /
```

Figure 1.7 Solution Section

The solution section is followed by the summary where it is required to specify all the outputs that the engineer needs to see and analyze upon the completion of the simulation (Figure 1.8). As can be seen below all the output parameters are specified with abbreviations. Likewise, for example, FOE stands for Field Oil Efficiency, FWCT – Water Cut, FCIT – Field Chemical Injected Total and so on.



```
SUMMARY    ===========
FOE
RUNSUM
RPTONLY
FPR
FWCT
FWSAT
FCPR
FCPT
FCIR
FCIT
FCIP
FCAD
GCPR
```

Figure 1.8 Summary Section

After the Summary Section is completed the Data File is to be saved and then run in Eclipse for simulation. If the simulation results with minor or no errors, then it means that it has been successfully completed and now there is access to results section. In case if there are errors, then it is required to return to the data file and adjust the errors that the software will point out.

5.2.4 Simulation Results

After the simulation has been successfully completed it becomes possible to check the results and have a graphical representation and all the relevant correlations.

It is required to open Eclipse Launcher and select Flow Wiz section. The window with graph screen will be opened and in the window on the left side there becomes possible to select the desired outputs to be visualized on the graph screen. All the parameters that have been specified in the Summary section are now available for visualization.

In order to have a graphical representation that will clearly present the dependence of polymer solution stability with respect to variations in salinity it is decided to track the increase in Recovery Factor (or Field Oil Efficiency - FOE); then compare the amount of the polymer injected into the reservoir (Field Chemical Injected Total - FCIT) with the amount of oil produced (Field Oil Produced – FOP). Then the price of the polymer is to be multiplied with the total injected amount and that, in return, is to be compared with the revenue that is obtained by multiplication of oil price by total oil produced. The results will clearly show the degree of effectiveness and efficiency of polymer flooding and will demonstrate how polymer should be expected to behave inside the reservoir in order to result with maximum recovery.

Figure 1.8 below shows the injection rate of the polymer inside the formation.

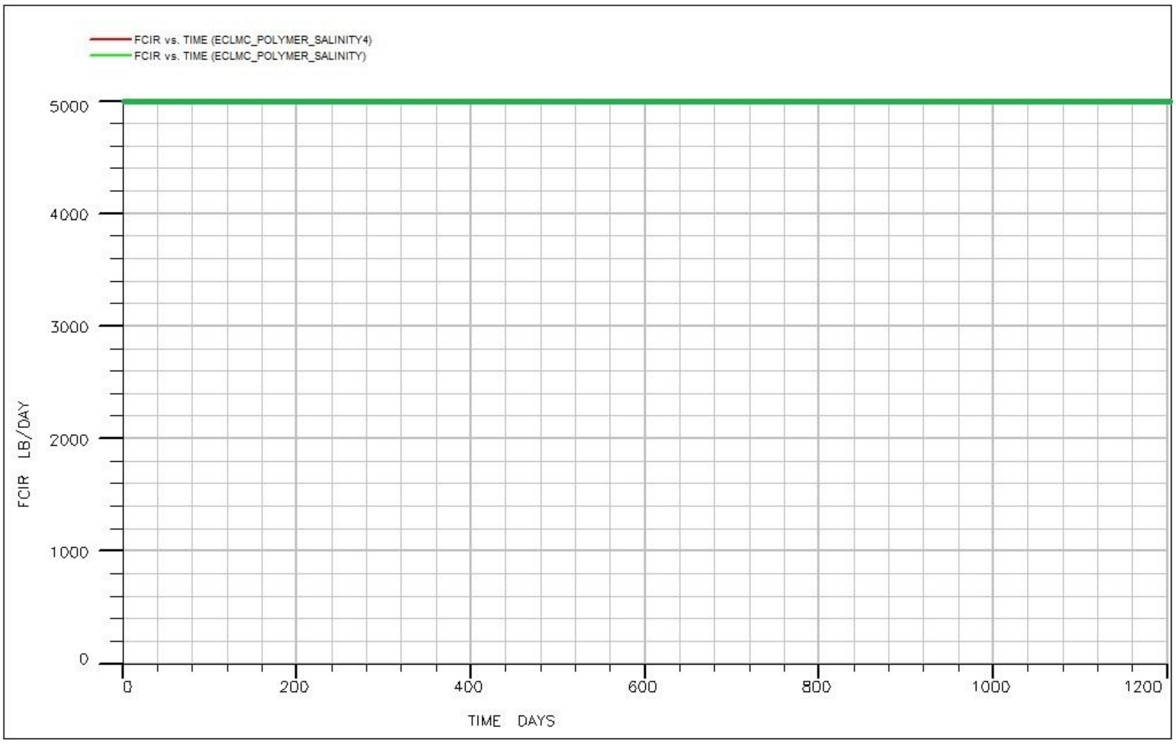


Figure 1.8 Field Polymer Injection Rate

FCIR stands for Field Chemical Injection Rate and has the dimensions of Lb/Day. From the Figure it becomes obvious that the polymer solution injection rate is being kept at the constant rate of 5000 Lb/Day. It has been decided to maintain the injection rate as constant in order to ensure that the polymer solution is being injected continuously within the preset period of 1200 days and solution stability is not being affected by any other external parameters, such as Shear Rate. Shear Rate also contributes to degradation of polymer solution; however it is not the part of the scope of this study, because Shear is related to Mechanical Degradation of the polymer. Mechanical Degradation is another factor that has an impact on stability of polymer solution. However it is not included in objectives of this stud. The time frame of 1200 days has been selected in order to make sure that the entire reservoir has been flooded with polymer solution.

The next step is to visualize the total amount of polymer injected into the formation. It can be done with help of FCIT functions, which stands for Field Chemical Injected Total (Figure 1.9).

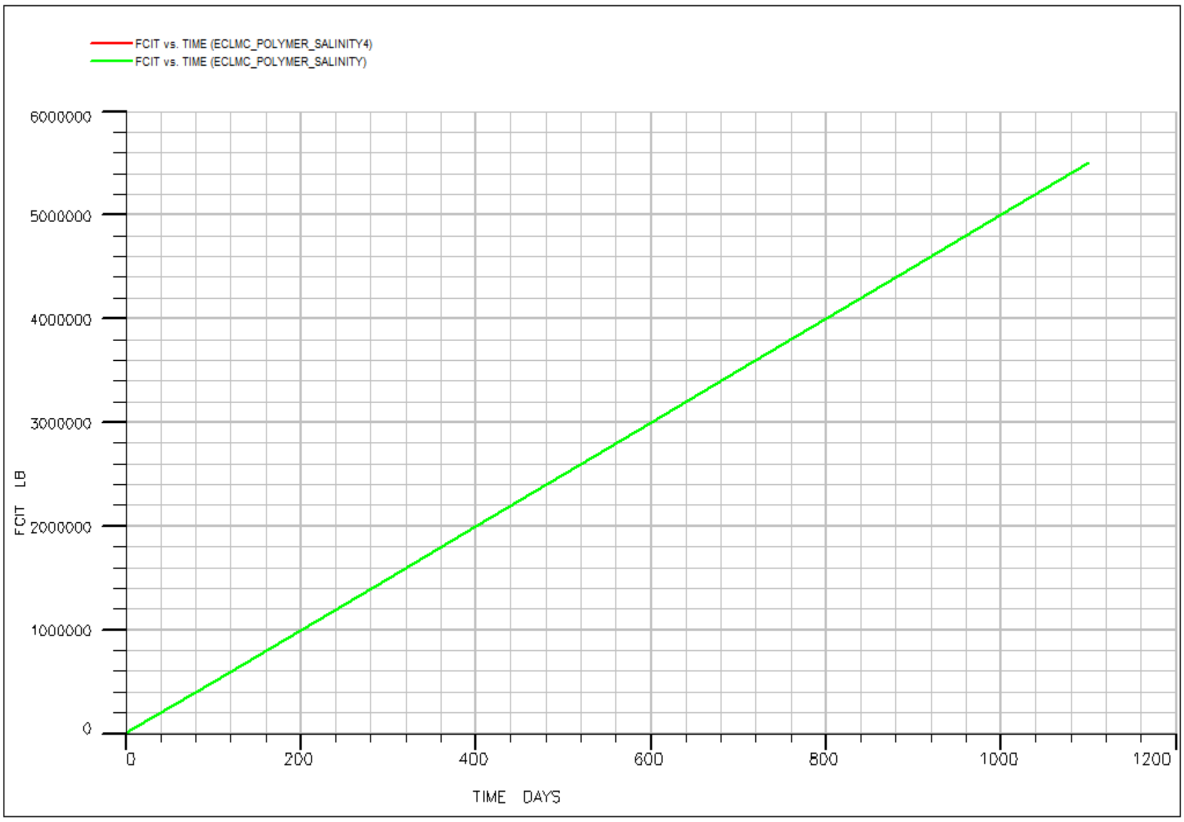
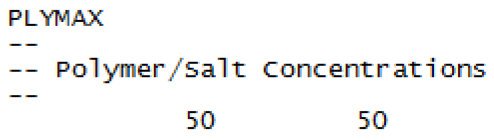


Figure 1.9 Total amount of polymer injected into reservoir.

From the Figure above it is clear that approximately 55000 lb of polymer solution have been injected into reservoir within 1100 days. This value is to be used for economical feasibility later on. The value keeps increasing linearly as the injection rate in maintained at the constant rate.

Another important factor is that this simulation has been completed in the isothermal mode, i.e. there is no influence of the temperature on the polymer solution. This was one of the conditions under which the simulation would run correctly. Another reason to run the simulation in isothermal mode is to investigate the stability of the polymer solution due to variation only in one parameter.

All these values have been obtained at high value of salinity, which is designated in the figure below.



```
PLYMAX
--
-- Polymer/Salt Concentrations
--
              50          50
```

Figure 2.0 Salt Concentration

The first value corresponds to the concentration of the polymer in the solution (i.e. polymer viscosity), while the second value corresponds to the amount of salt contained in the polymer solution.

Since the salt concentration directly corresponds to salinity, then it becomes obvious that at this value of salinity, the recovery factor reaches up to 32%, which is described in the figure below.

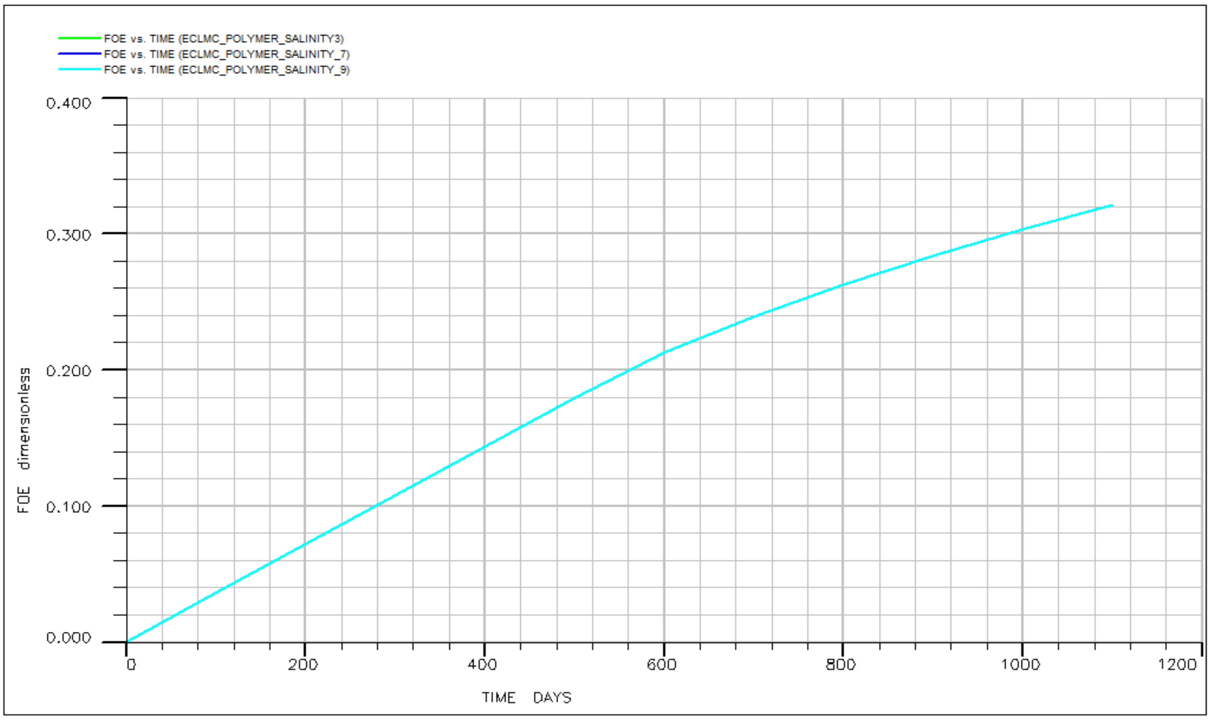
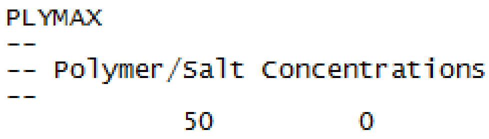


Figure 2.1 Recovery Factor at high salinity value

On the contrary, the next alteration in simulation values corresponds to lowering of the salinity. The updated file is to be saved and the simulation is to be repeated again for the low salinity case.

This can be observed in the figure below:



```
PLYMAX
--
-- Polymer/Salt Concentrations
--
               50          0
```

Figure 2.2 Salt Concentration

This in return will alter the viscosity of the polymer solution and hence will influence the recovery factor. This can be clearly seen from the figure below:

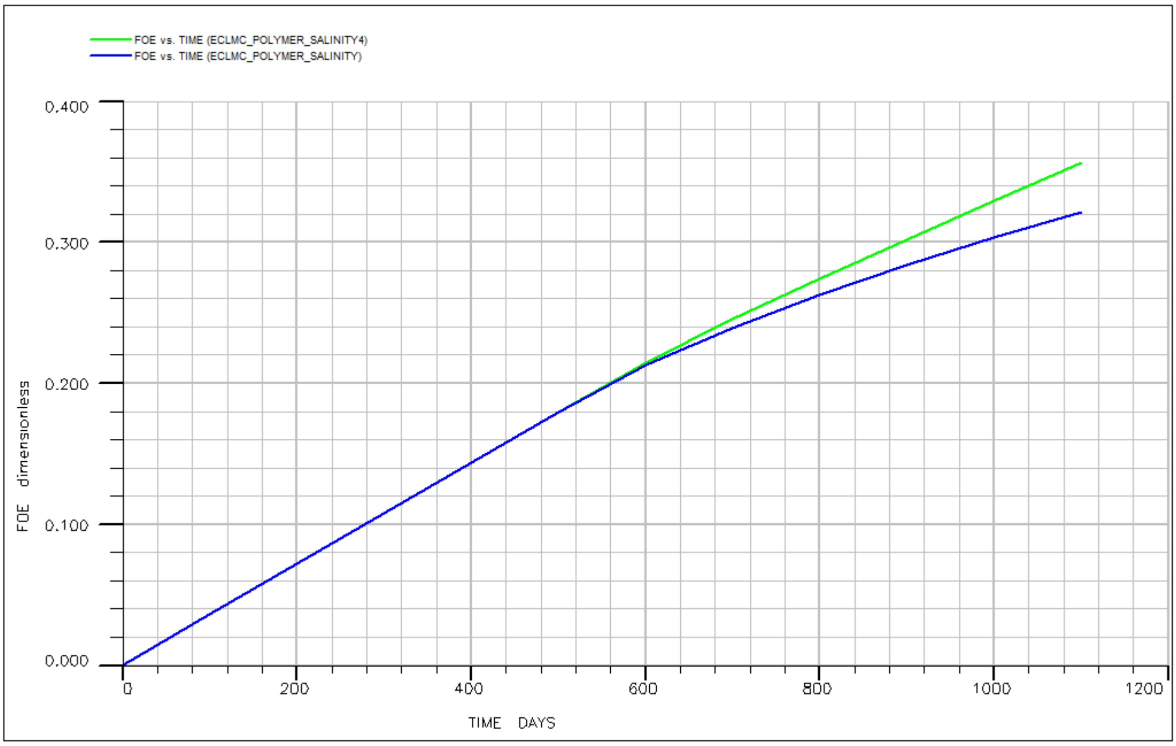


Figure 2.3 Recovery Factor at different salinity values

As can be seen in the figure above the polymer solution results in increase in Recovery Factor due to low values of salinity. The blue line represents the recovery factor at high salinity values, while the green line corresponds to recovery factor at low salinity level. Hence it can be seen that polymer solution performs better in low salinity environment.

Hereby the theoretical statement regarding this rule has been proved on practice. The value of new recovery factor reaches up to 36% and that clearly proves the main objective of the study.

The change in recovery factor directly affects the change in the total amount of oil produced to the surface. In order to trace down the change in oil production the results section has been checked for FOPT (Field Oil Production Total) and the outcomes are presented in the figure below.

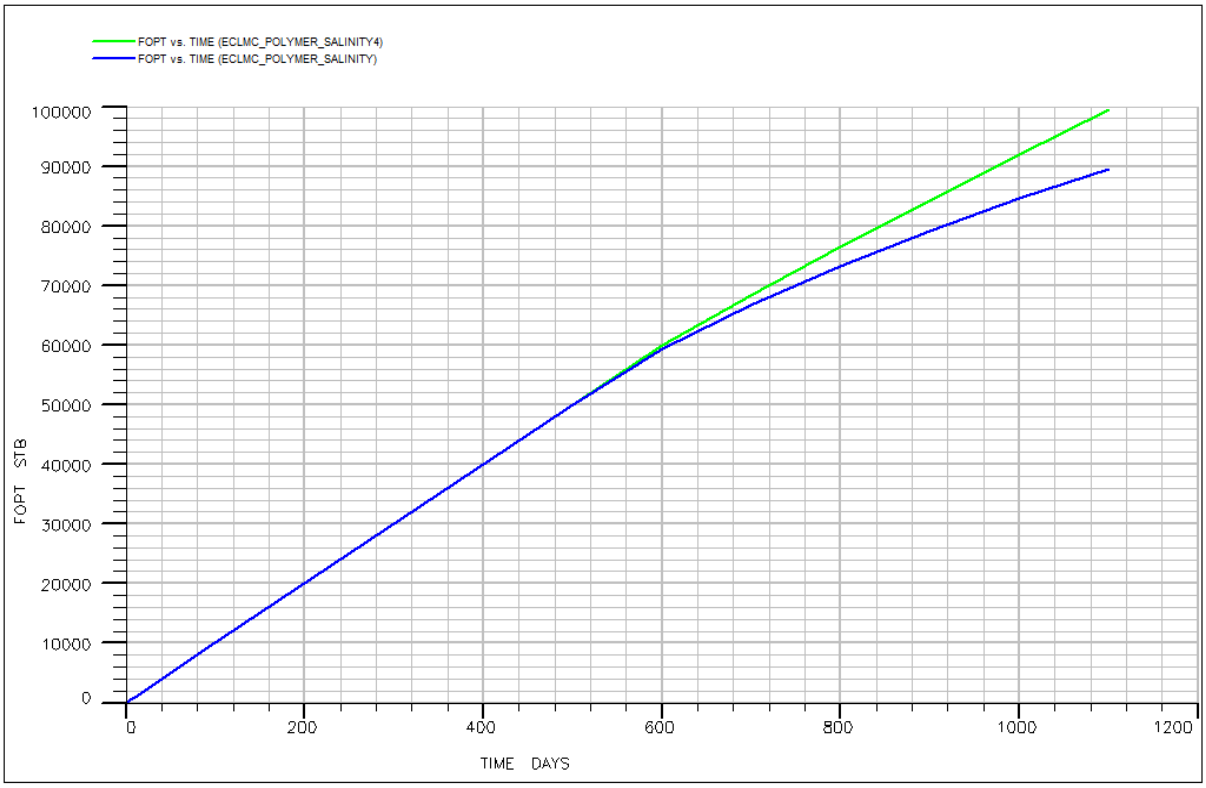


Figure 2.4 Field Oil Production Total (FOPT) values at different Recovery Factors

As can be seen from the figure above initial FOPT value has resulted in approximately 90,000 STB after 1,100 days of flooding and production, while after the salinity has been reduced, the FOPT value has increased up to 100,000 STB during the same flooding period. This clearly shows and proves that salinity effect is very crucial for polymer flooding and results in big difference in total amount of produced oil.

In addition to the simulation in Eclipse an additional simulation has been completed using another Simulation Software from Schlumberger, called Petrel. This software is designed for assistance in increasing the reservoir performance by improving asset team productivity. Geophysicists, geologists, and reservoir engineers can develop collaborative workflows and integrate operations to streamline processes.

The figure below corresponds to the simulation model of a reservoir section with variation in salt concentration with change in time.

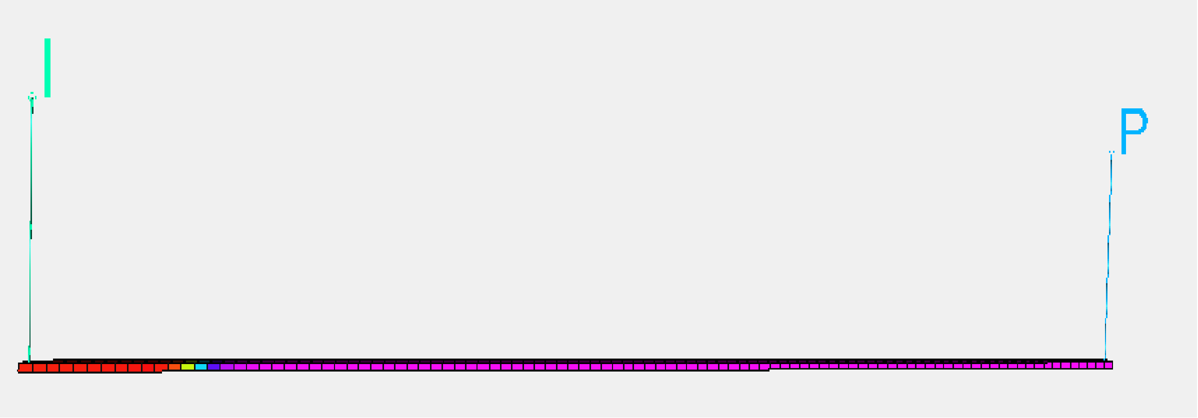


Figure 2.5 Polymer cell concentration at the last time step, i.e. 1200 days

As can be seen from the figure above the salt concentration has decreased from the maximum level (designated with red color) within 1200 days until the lowest value (designated with purple color).

This is another proof of the fact that this particular stage of simulation has been successfully accomplished and the obtained results are reliable.

5.2.5 Economics of Polymer Flooding

In addition to results of the simulation, those results have also to be justified from the economical point of view. Hereby the economical analysis is to be conducted in order to prove the effectiveness of Polymer Flooding as well as the effect of salinity on economical efficiency of the Polymer Solution. It represents a simple calculation on the basis of current average prices of polymer solution per barrel and price of crude oil per barrel.

- Polymer Cost = $2/lb
- Polymer Injected = 55,000 lb
- Cost of Polymer = $110,000
- Incremental oil produced (incremental over the previous polymer flooding) = 10,000 STB

- Income from oil production = $ 1,050,000 (taking average crude oil price = $105/bbl)
- Profit = $ 940,000

This simple calculation shows that slight variation in salinity may result in six-zero-digit amount of money gain or loss. In this case due to increase in Recover Factor the Profit has also increased up to $ 940,000. Hereby it is very crucial to design and select the proper type of polymer that would be able to withstand the external factors and result in high production.

5.2.6 Polymer Flooding vs Water Flooding

In order to prove that the Polymer Flooding is more effective for Enhanced Oil Recovery, another simulation has been conducted, where polymer flooding was compared with water flooding.

The key effect that investigation targets, is the influence on change in recovery factor. Another simulation has been run in order to compare the change in Recovery Factor due to Polymer Flooding comparing to Water Flooding. The results can clearly be seen from the figure below.

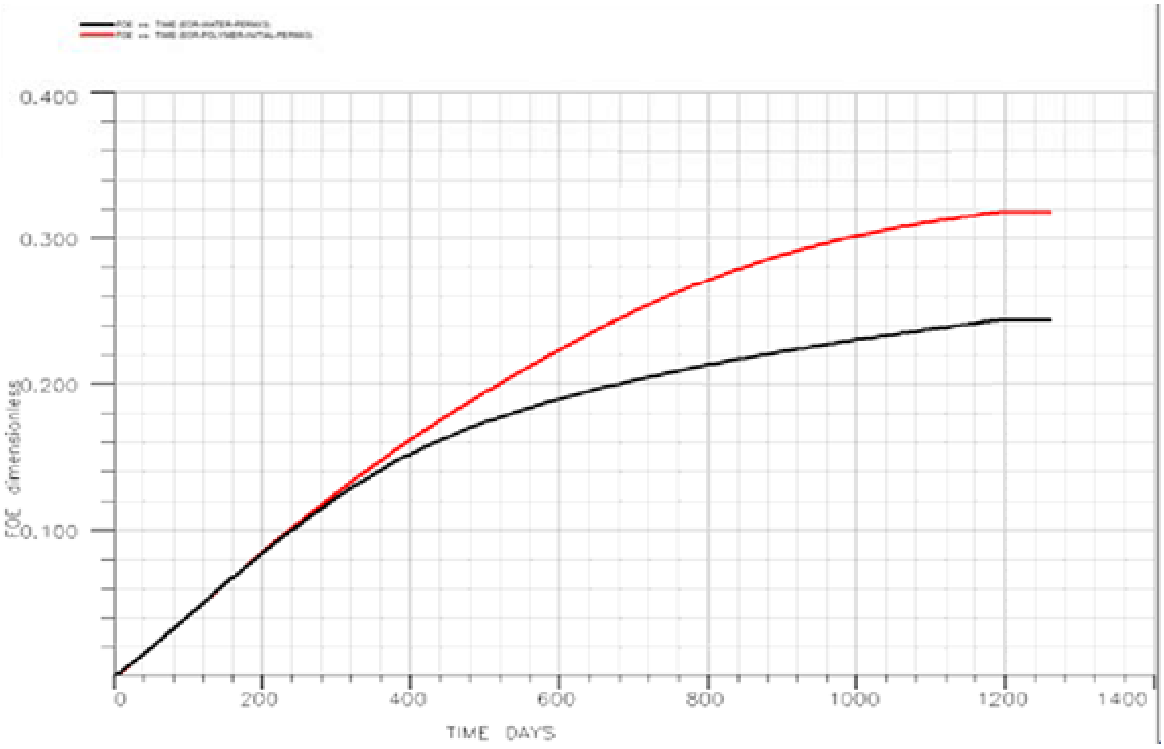


Figure 2.6 Polymer Flooding vs Water Flooding

As can clearly be seen from the figure above, Water Flooding (black curve) results in FOE equal to approximately 24%, while Polymer Flooding (red curve) results in 32%. This directly proves the fact that Polymer Flooding has more impact on increase in Recovery Factor and hence results in higher amount of oil produced to the surface.

Now in order to investigate the influence of temperature on stability of the polymer solution, it is required to conduct another simulation and create another data file in order for simulator to give corresponding results.

Unfortunately the Temperature Effects can be simulated only in the latest versions of Eclipse software (2012 versions and above). Hereby another data file is to be used for that and the data file is to be accordingly updated with new keywords, which are responsible for correlation and influence of temperature on viscosity of polymer solution and, as result, on Field Oil Efficiency or Oil Recovery Factor.

Older versions of Eclipse did not include the dependence of polymer viscosity on temperature. Likewise default and initial condition was that polymer flooding is being simulated at isothermal conditions. This puts restrictions to simulation of influence of temperature on polymer solution during polymer flooding process.

Hereby the analyzed correlations between temperature and polymer viscosity are to be used for purposes of reliability of the simulation results. Another simulation had to be run in order to verify the influence of temperature on stability of polymer solution. As the results had been obtained, it has become clear that temperature has also got an effect on viscosity of polymer solution and on recovery factor as well. The simulation had been run at different values of viscosity, which have been altered by variations in temperatures.

The values of polymer viscosity have been verified against the real experiments and real results in order to make sure that simulation process results in desired outcomes. The same format (i.e. FOE vs Time) has been chosen in order to keep the flow of the simulation in the same manner and in order to make it easier to compare the results. Likewise the results are presented in the figure below:

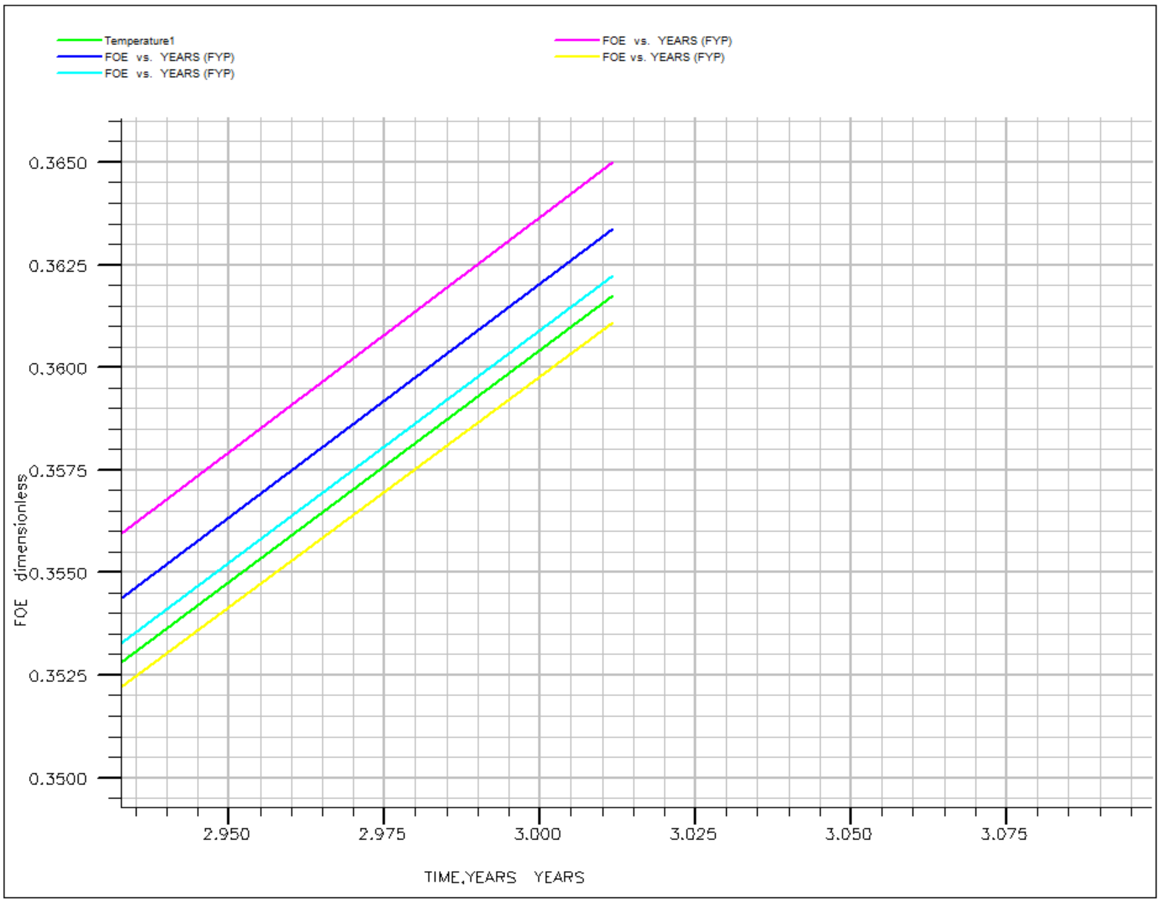


Figure 2.7 Influence of Temperature on Recovery Factor

Likewise, a number of runs have been conducted and the temperature did not have effect of recovery or polymer viscosity until it had reached approximately 50˚C. Starting from 90˚C the changes were obvious. After the temperature went beyond 90˚C and reached up to 120˚C, then the recovery has decreased.

The main problem that has been encountered during simulation is that the simulator could not provide viable results. All the results from the graph above are obtained at high values of viscosity, which is not economically efficient. Hereby the stud of temperature effect on stability of polymer solution had to be changed to be based on laboratory experiments.

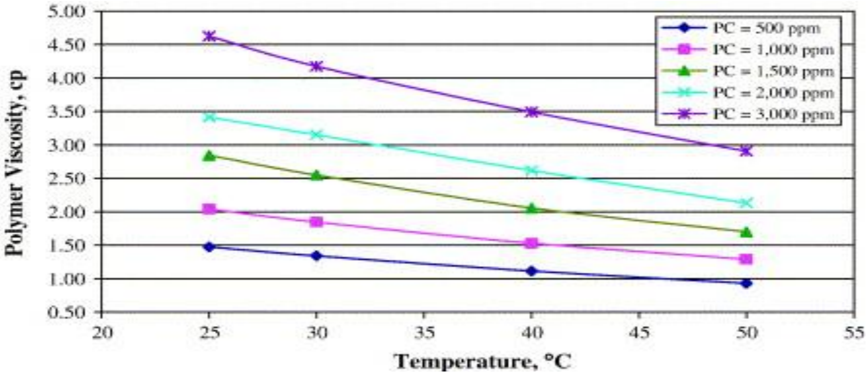
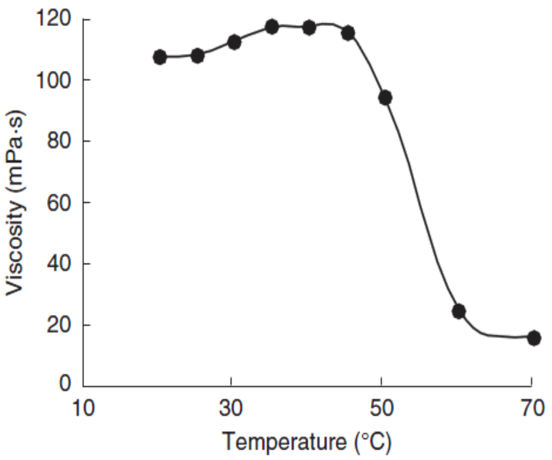


Figure 2.8: Influence of Temperature on Polymer Viscosity

The figure above shows and proves that temperature has an effect on the polymer stability, because polymer viscosity keeps changing at different temperature values. These results were taken as a reference from the literature. One of the sources is James J. Sheng; 2011; Modern chemical enhanced oil recovery: theory and practice; pp (119-225).

Figure below shows another correlation between temperature and viscosity of polymer. The type of polymer used was PAMOA75 with 0.75 mol% octylacrylate (OA) with polymer concentration of 2800mg/L. The results are presented below:



Below 35°C, as the temperature increased, the viscosity increased slightly

•Between 35°C and 45°C, the viscosity was almost constant

•Above 50°C, the viscosity has abruptly decreased

• At 70°C, the viscosity was 15.8% of viscosity value at 20°

Figure 2.9

PAMOA75 viscosity versus temperature.

Source: Zhou and Huang (1997)

From figure above it can be clearly observed that PAM does not withstand high temperatures and looses the viscosity after the temperature exceeds 50°C.

Likewise the economical analysis could not be concluded as the recovery factors did not change at slight variations in polymer viscosity, which has been affected by different temperatures.

So as conclusion polymer solution has demonstrated to have higher viscosity retention in case of gradual increase in temperature, rather than starting the simulation straight forward from high temperature value. In that case the viscosity did decrease. That is the reason why there is only the last part of the graph being shown in Figure 2.7, because in the beginning the values of FOE are more or less the same and do not change much. So it shows that polymer would be more stable under thermal degradation, i.e. when temperature is being increased gradually.

Hereby polymer was able to withstand small temperatures, but at high values started degrading, resulting in decrease in Recovery. Figure 2.9 has clearly demonstrated that after temperature has reached more than 50°C , the viscosity started decreasing drastically and at 70°C, the viscosity was 15.8% of viscosity value at 20°. On the other hand the simulation has shown that the slight changes in temperature result in recovery factor variation from 36% to 36.5%. This shows that temperature effects should be studied during the lab experiments, not by using simulation and will yield better results.

CHAPTER6: CONCLUSION

The simulation of polymer flooding at variations in salinity has showed good results and has approved the effectiveness of polymer flooding as well as highlighted the importance of stability of polymer solution from engineering side as well as from economic side.

The stage of investigation of salinity effect on stability of polymer solution has provided reliable results and has underlined the significance of maintaining polymer structure irresistible to external factors. The variation in salt concentration from minimum to maximum specified level has resulted in change in Recovery Factor by approximately 4%, which is significant, when it comes to Enhanced Oil Recovery stage.

On contrary, the effectiveness of polymer flooding has been approved by comparing the outcomes of simulation of waterflooding against polymer flooding, which has resulted in increase by approximately 8% in favor of polymer solution.

In addition the economic feasibility of polymer stability has been approved to be crucial, as 4% difference in recovery factor has resulted in approximately $ 940,000 of profit, which is a significant number.

Thermal influence on stability of polymer solution has shown that polymer is being affected by temperature and that, in return, has an effect on final recovery as well. However the study on polymer stability at high temperature will yield better results during laboratory experiments, rather than simulation, as the simulator so far cannot provide viable results and correlations.

All the conducted tests demonstrate that the evaluation of salinity affects the viscosity of the polymeric surfactant. Multi-component brine system has an effect on salinity and has to be studied further on through laboratory experiments.

A comparative study on the effect of high salinity and high temperature should be investigated further and by using more complex geological structures and specialized laboratory experiments.

Nomenclature

S_w = Saturation of water

S_g = Saturation of CO_2

f_w = Fractional flow of water

f_g = Fractional Flow of CO_2

f_o = Fractional Flow of Oil

k_{rw} = Relative Permeability of Water

Ap = frequency factor

k_{ro} = Relative Permeability of Oil

μ_g = Viscosity of CO_2

μ_w =Viscosity of Water

μ_o = Viscosity of Oil

R = Universal Gas Constant

C = Concentration

F = Flux

T = Absolute Temperature

T_{ref} = Reference Temperature

H = Heterogeneity Factor

k_z=Vertical Permeability Gravitational Acceleration

W = Thickness of the Rectangular Reservoir Perpendicular to Flow

E_w = Exponent for Water Relative Permeability

E_o = Exponent for Oil Relative Permeability

$S_{wf\,1}$ = Initial Water Saturation

S_{ow} = Residual Oil Saturation

K_o = Relative Permeability of Oil at Residual Saturation

REFERENCE

1. James J. Sheng (2011). Modern chemical enhanced oil recovery: theory and practice.
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3. Kulicke, W. M., Kniewske, R., & Klein, J. (1982). Preparation, Charaterization, Solution Properties and Rheological Behavior of Polyacrylamide.
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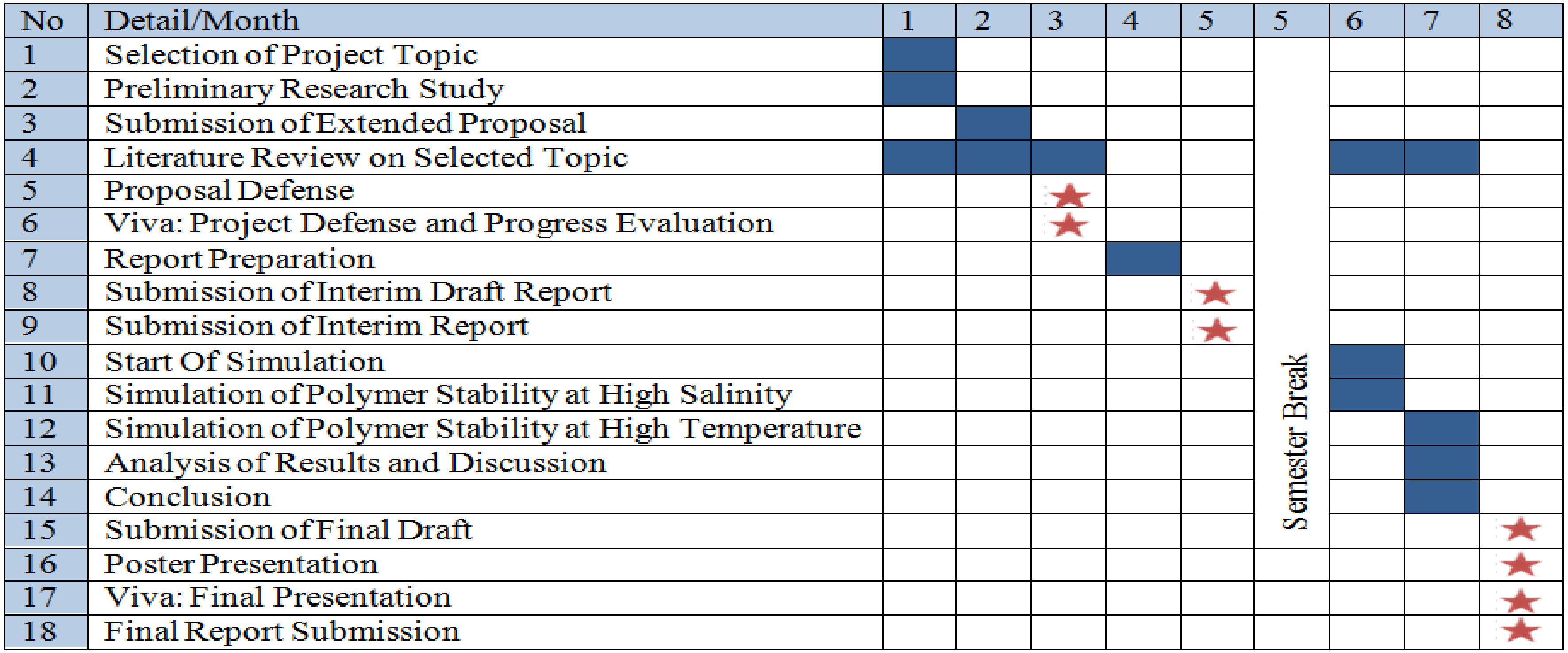
7. Zhang, Y., Gao, P., Chen, M., & Huang, G. (2008). Rheological Behavior of Partially Hydrolyzed Polyacrylamide Hydrogel Produced by Chemical Gelation. *Journal of Macromolecular Science, Part B* .

APPENDIX

Appendix 1 – Gantt Chart for Final Year Project



No	Detail/Month	1	2	3	4	5	5	6	7	8
1	Selection of Project Topic	🟦					Semester Break			
2	Preliminary Research Study	🟦								
3	Submission of Extended Proposal		🟦							
4	Literature Review on Selected Topic	🟦	🟦	🟦				🟦	🟦	
5	Proposal Defense			★						
6	Viva: Project Defense and Progress Evaluation			★						
7	Report Preparation				🟦					
8	Submission of Interim Draft Report					★				
9	Submission of Interim Report					★				
10	Start Of Simulation							🟦		
11	Simulation of Polymer Stability at High Salinity							🟦		
12	Simulation of Polymer Stability at High Temperature								🟦	
13	Analysis of Results and Discussion								🟦	
14	Conclusion								🟦	
15	Submission of Final Draft									★
16	Poster Presentation									★
17	Viva: Final Presentation									★
18	Final Report Submission									★

🟦 Processes

★ Milestones