DELFT UNIVERSITY OF TECHNOLOGY

ROCK-FLUID INTERACTION DURING LOW-SALINITY POLYMER FLOW IN POROUS MEDIA

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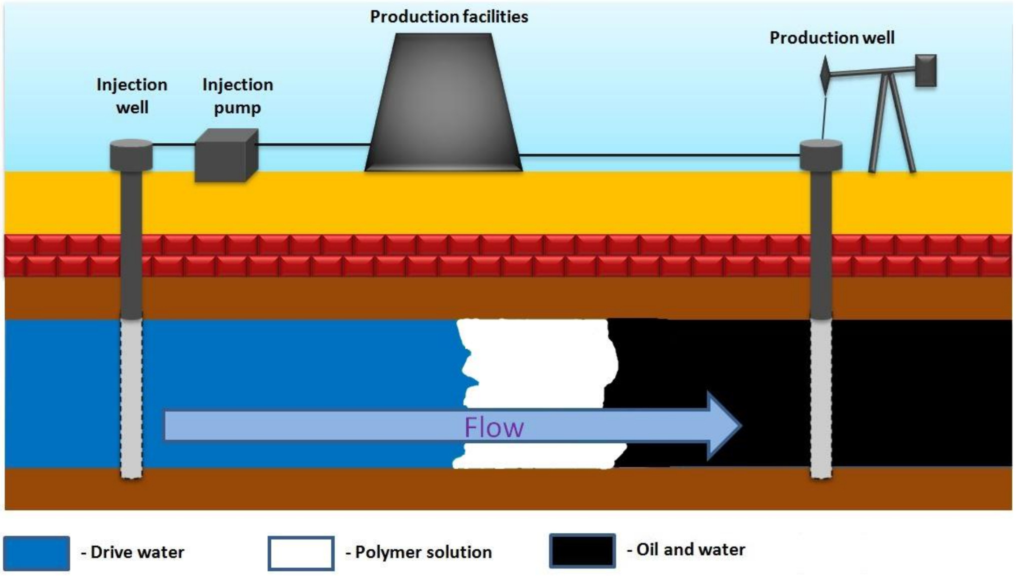

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Abstract

Usually, oil fields are developed over three stages. First is the primary oil recovery, where the natural underground pressure is used to drive the oil to the surface. Afterwards is the secondary oil recovery, usually by water flooding or gas injection. However, the water flood yields lower sweep efficiency in heterogeneous reservoirs, contrary to homogeneous reservoirs. Tertiary flooding methods are applied to increase the oil sweep efficiency, hereby improving the efficiency of the extraction process. These methods include injection of gas and chemical solutions. This study focusses on the polymer flooding method. Polymers are used to adjust the mobility ratio (M) between oil and the displacing fluid, where the viscosity of the displacing fluid is increased significantly. However, rock-fluid interaction might affect the viscosity of the polymer, which in turn affects the mobility ratio.

A series of core flood experiments were conducted, where rock-fluid interaction likely affects the viscosity of the polymer. Hydrolyzed polyacrylamide (HPAM) is used as the polymer, which is injected in a sandstone core with brine. The produced fluids are analyzed afterwards, where its ion concentration, rheology, pH, and carbon content are measured. The results of the effluent analysis shows no change in viscosity compared to the injected polymer. There is however, a decrease in the divalent cations in the Low-salinity fluids, which can be explained by these cations getting stripped from the fluid at attaching to the rock surface. An increase in the effluent High-Salinity Brine is observed, which may be the cause of mechanical degradation, or by the influence of dissolved Ca^{2+} or Mg^{2+} cations due to leaching.

1. Introduction

After the primary oil recovery and secondary oil recovery methods, where reservoir energy and reservoir depressurizing with gas or water respectively, are no longer applicable, oil companies head towards the improved or enhanced oil recovery process (IOR/EOR). This process focuses mainly on the remaining oil in the reservoir, estimated to be around 70% of the original resource. The enhanced oil recovery process is categorized in four groups (Terry, 2001):

- Miscible flooding processes
- Chemical flooding processes
- Thermal flooding processes
- Microbial flooding processes

The focus of this study is put on the chemical flooding processes, where polymer is used as the flooding agent. Polymer is used for a more stable displacement of oil, than when using water. Adding polymer to brine causes the solution to be more viscous, improving the macroscopic sweep and preventing viscous fingering (Lohne, et al.). A visual comparison of water and polymer injection is given with Figure 1.1.

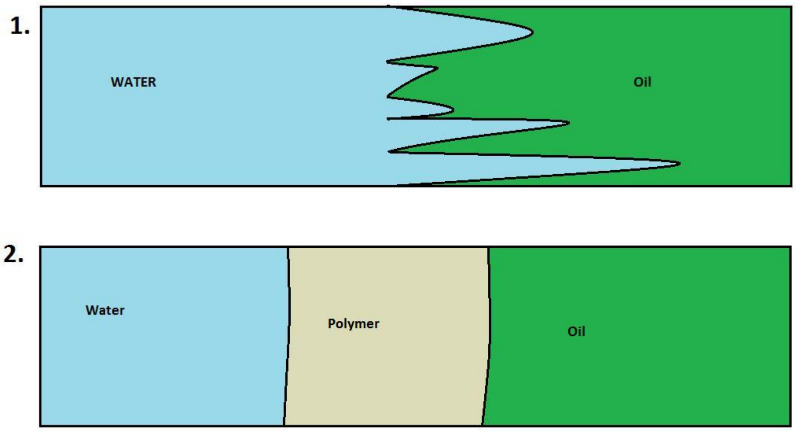


Figure 1.1- *Schematic visualization of Polymer flooding. (1) shows the water injection and (2) shows the water and polymer injection.*

Rheology of the polymer is one of the main characteristics that affects the propagation of polymer in porous media. The cause of this is the fact that the polymer is dissolved as a 3D-coil in the solvent, which can be easily deformed during the flow. The polymer can therefore adapt a shear-thinning behaviour or a shear-thickening behaviour. Shear-thinning behaviour flow happens when the viscosity decreases with increasing shear rate. On the contrary, shear-thickening flow occurs when the viscosity increases with increasing shear rate. Polymer molecules have the ability to be retained during flow by retention mechanisms. This can cause the concentration of the polymer to decrease along the porous media (Denys, 2003).

However, the polymer may experience a decrease in viscosity due to rock-fluid interaction. This decrease in viscosity may affect the mobility ratio of the polymer, which decreases the efficiency of the polymer injection. The goal is thus to obtain the same mobility as that of oil, so that the mobility ratio of $M \leq 1$ is achieved (equation 1.1). The mobility ratio is the ratio between the displacing phase over the displaced phase (Sorbie, 1991).

$$M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o/k_o}{\mu_w/k_w} \tag{1.1}$$

where λ, μ and k are mobility, viscosity and permeability respectively. The subscripts o and w refer to oil and water (Sorbie, 1991). The change in viscosity of the polymer takes place due to rock fluid interaction where present cations in the reservoir interact with the polymer. The reservoir is usually made up of porous sandstone or carbonate rocks (Sun, Saleh, & Bai, 2012), typically containing clay particles such as Illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)$, Kaolinite $Al_2Si_2O_5(OH)_4$, Feldspar ($KAlSi_3O_8$-$NaAlSi_3O_8$-$CaAl_2Si_2O_8$) and other silicates. The quantity of cation exchange between the polymer and reservoir is called the Cation Exchange Capacity (CEC) and it is an interfacial process where cations are replaced by other cations (Farajzadeh, Guo, Winden van, & Bruining, 2017). The main cations associated with CEC are calcium (Ca^{2+}), sodium (Na^{+}), magnesium (Mg^{2+}), and potassium (K^{+}) (Rayment & Lyons, 2011). The leaching of the cations may influence the size of the polymer molecules, which in turn may cause the viscosity of the polymer to decrease.

1.1 Scope of the Study

The goal of this study is to understand the behaviour of the rock-fluid interaction between rock and low salinity polymer. Hydrolyzed polyacrylamide (HPAM) is used for the polymer flow tests. The project is approached by conducting core flood experiments, performed by my supervisor, Nikita Lenchenkov, and carrying out a series of bulk experiments on the produced fluids from the core flood, conducted by myself. The laboratory techniques used are Inductive Coupled Plasma (ICP) analysis, viscosity measurements using a rheometer, pH measurements and Total Organic Carbon (TOC) measurements. This thesis focuses mainly on the bulk experiments and its results, which are conducted in the petroleum-engineering laboratory located at the Civil engineering & Geoscience faculty (CEG).

1.2 Outline of the Thesis

Chapter 2 describes the procedures and materials used for the experiments. The purpose of every procedure is explained in this chapter. Chapter 3 discusses the results of the experiments. Chapter 4 closes the thesis with the conclusions obtained after the project.

2. Experimental Procedure and Materials

The analysis of rock-fluid interaction is done through a core-flood experiment method. This experiment is performed under selected P-T (pressure-temperature) conditions. Brine and polymer are injected into the core. After the injection, fractions of fluids are collected in the outlet, which then are used for further analysis. Different characterization techniques were used during the experiments to analyze the fluids, prior to- and after the injection. The samples underwent pH-and weight measurements, Total Organic Carbon (TOC) analysis, where carbon content in polymer concentrations is measured. Furthermore, polymer samples are treated with a chemical package, which breaks down the polymer to conduct an Inductively Coupled Plasma Spectrometry (ICP) analysis for ion content measurement. The rheology of the produced polymers is measured with a rheometer. The procedure of the experiments is shown in the flowchart depicted in Figure 2.1.

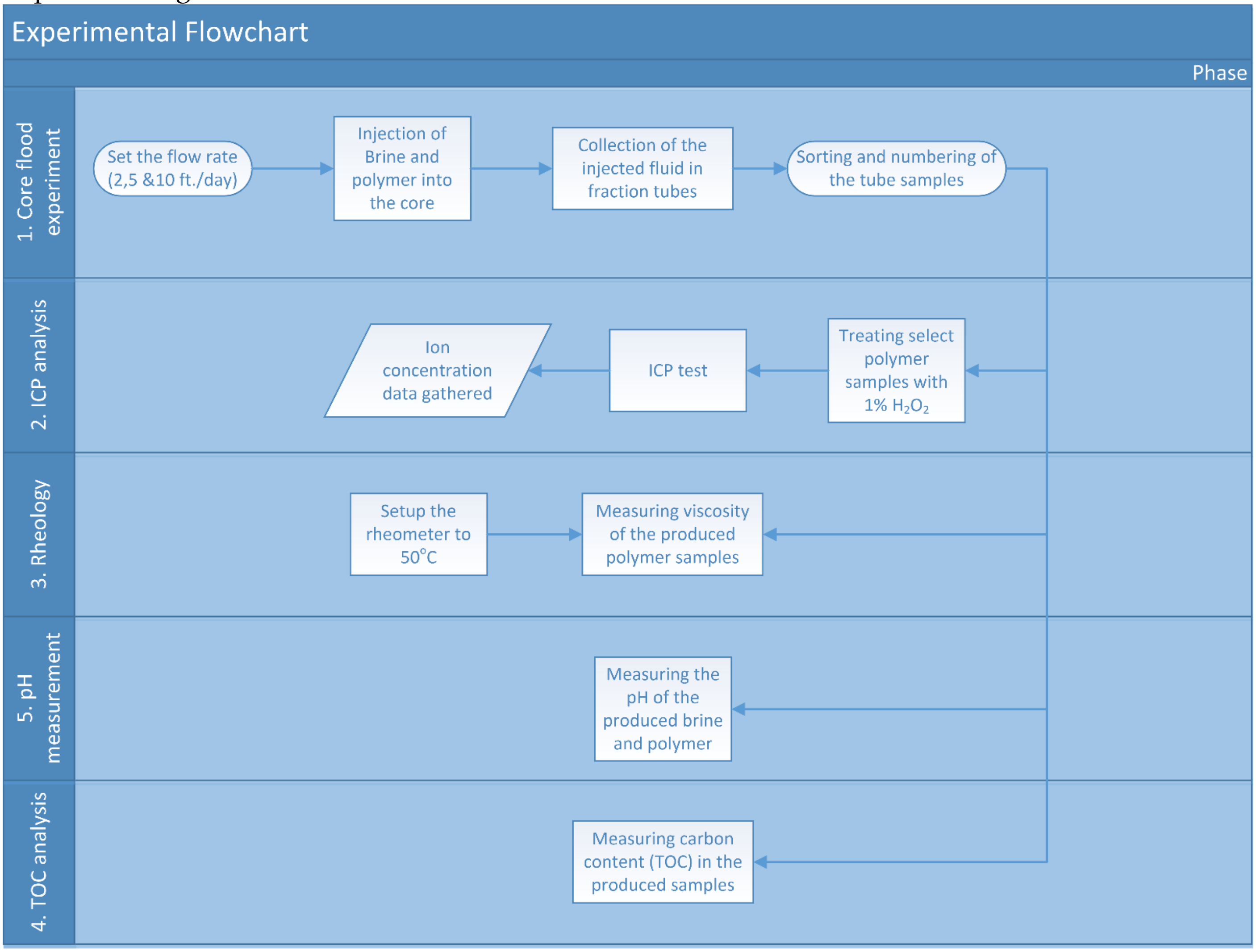


Figure 2.1- *Flowchart overview of the experiments conducted for the study.*

2.1 The Core Flood Setup

The core flood experiments are conducted using a core flood setup; build up in the petroleum-engineering lab at the CEG faculty. The schematic of the setup is demonstrated in Figure2.2.

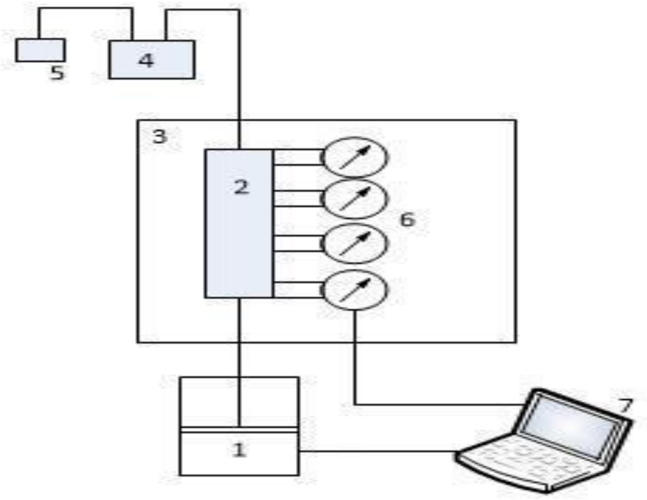


Figure 2.2 *- Schematic diagram of the core flood setup with (1) the pump; (2) core holder; (3) oven; (4) backpressure; (5) fraction collector; (6) pressure transducers; (7) laptop & data acquisition system.*

(1) The pump is used to inject the fluids, such as brine and polymer, into the core, which is located in the (2) core holder. The core is glued in the core holder with special adhesive glue, which holds the core in place, but it also excludes influences such as axial or radial pressure during the injection. (3) The core flood experiments are conducted in in-situ P-T conditions of 50^{o}C temperature and 6 bar pressure. (4) The purpose of the backpressure is to increase the pressure in the core to prevent any back-flow of the fluids back to the core sample. (5) The fraction collector collects the fluids after the injection in sample tubes. These samples are analyzed to see the changes compared to their initial conditions prior to injection. (6) The pressure transducers measure the differential pressure in four different ranges of the core. These measurements are important for accurate permeability and other calculations. (7) With a software on the laptop the flow rate can be set, the acquired results is displayed here.

2.2 pH measurement and Inductively Coupled Plasma Spectrometry analysis

A pH measurement, carried out on the injected samples, to find a relationship between the cation concentration and pH of these samples. The measurement was conducted with an electronic pH meter consisting of an electrode. The use of the pH meter is straightforward; the electrode is put in the sample tubes and the pH value is shown on the screen. For a more accurate value, the electrode should be put in the sample for a couple of seconds until the pH value stops fluctuating. The pH of the polymer samples were measured with pH strips, because the electrode of the pH meter is not suitable for the sticky polymer. The concentration of the ions in the samples was obtained through an Inductive Coupled Plasma (ICP) test. Inductive Coupled Plasma is an analytical technique used to detect trace ions in environmental samples, with the primary goal to get elements to emit characteristic wavelength of specific light, which can then be, measured (Planas, 2002). Ranges of samples were selected and brought to another laboratory were the test was conducted. The measured unit is mg/L. With the achieved values, the apparent change in concentration of each ion can be compared. This comparison can show wether there is an increase or decrease of the present ions. Before the ICP analysis can be started, the samples, especially the polymer samples, need to be treated with a chemical package. The purpose of this chemical package is to breakdown polymer in the samples, so that only ions are available in the sample for the ICP analysis. The chemical package used for breaking down the polymer is hydrogen peroxide (H2O2), specifically, 1% H_2O_2. The available concentration of H_2O_2 in the lab was 30 mole%; this means that this compound needed to be diluted to 1mole% to be able to use it for the experiment. The ratio in which the polymer and this chemical compound were mixed is 1:1, where 5mL of polymer sample and 5mL of 1% H_2O_2 are put together.

2.3 Rheology

The rheology of the polymer was measured with the Modular Compact Rheometer (MCR 302) as shown in Figure 2.3. With this rheometer, the viscosity behavior of a sample can be followed. It gives a spectrum of the viscosity at increasing shear rates. This device consists of a concentric cylinder and a measuring cup. The device has to be first initialized and setup through its respective program, where temperature is set to 50°C and a shear rate range is set 1-50 s^{-1}. The measurement is done in an interval of 3 seconds and in steady state conditions. After initializing, the sample is poured in the measuring cup, and the cylinder is lowered into the measuring cup. After the temperature stabilizes around 50°C, the test is started. The results are in-situ measured and displayed on a monitor to the right of the device. There is a hood, not displayed in the picture, which encloses the measuring cup and the cylinder preventing any heat loss, thus creating a stable environment of 50°C for the tests to take place.

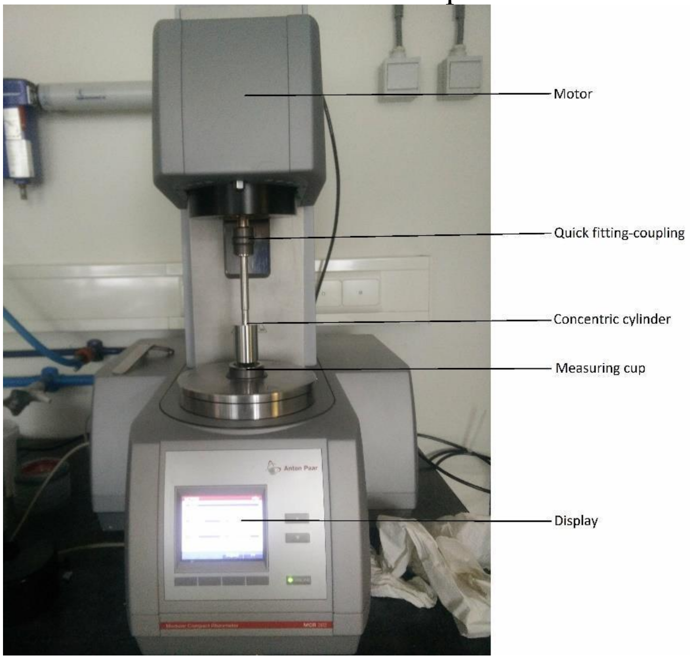


Figure 2.3- *Modular Compact Rheometer (MCR 302), with the concentric cylinder and the measuring cup mounted.*

2.4 Preparation of Brine

For the experiment, two concentrations of brine was prepared and used. The first one was a Low-Salinity Brine (LS Brine) with a concentration of 5 g/L (5070 ppm). The second one was High-Salinity Brine (HS Brine) 10g/L (10143 ppm). The concentrations of the ions in HS,-and LS Brine are given in Table 2.1. These ion concentrations are the expected values when preparing the brines. However, these values may differ due to human error, for example by inaccurately weighing out the salts. The used concentrations of the ions were measured. These values are later displayed in Table 3.2.

Table2.1 *- Ion concentrations in high salinity and low salinity Brine.*

Ions	**Conc. in HS Brine (mg/L)**	**Conc. in LS Brine (mg/L)**
Na^+	3319	1659
Mg^{2+}	137	68
Ca^{2+}	304	152
Cl^-	5133	2566
SO_4^{2-}	1250	625
Total	10143	5070

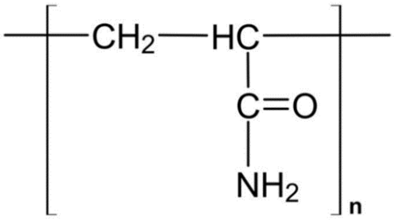
Before injecting the brine, the batch needs to undergo a degassing process. During this process, the brine is stirred under vacuum to extract all air from the solution. The purpose of degassing the brine is to prevent any injection of air, which may block pathways in the core.

2.5 Total Organic Carbon (TOC) analysis

Total organic carbon measurement is used to determine the organic content in the effluent polymer. A laboratory staff member conducted this analysis. The purpose of this analysis is to measure the CH content in the effluent polymer. This analysis can show the breakthrough where polymer is injected for the first time.

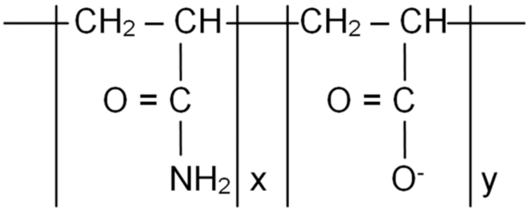
2.6 Preparation of Hydrolyzed Polyacrylamide (HPAM)

For the experiments, polyacrylamide (PAM), in its partially hydrolyzed form, Hydrolyzed Polyacrylamide (HPAM), is used. HPAM is a widely used polymer in the oil industry for improved oil recovery. It is a synthetic, flexible, straight chain polymer consisting of acrylamide monomers, some of which have been hydrolyzed. The hydrolyzed part of the backbone of the polymer may have established through potentiometric titration, where negative charges are attached to the backbone of the polymer. These charges have a large effect on the rheological properties of the polymer solution. The structure of the polyacrylamide and its hydrolyzed form are shown in Figure 2.4 and Figure 2.5. Due to the flexible chain structure, polyacrylamide responds differently in low salt concentration and high salt concentration. This behavior is shown in Figure 2.6. In low salt concentrated solutions, electrostatic repulsion exists between the carboxylate groups causing a flexible backbone, hence increasing the viscosity of the solution. In high salt concentrated solutions, a shielding of double layered electrolytes takes place, minimizing the charge repulsion, causing a balling-up of the polymer, making the solution less viscous (Sorbie, 1991). For the preparation of polymer, as seen in Table 2.2, an ITW package is added to the solution. The ITW package is a preservative package (ITW-Thiourea an isopropyl alcohol) which avoids deterioration of the rheology during storage and usage (Khodaverdian, Sorop, Postif, & Hoek van der, 2010). The polymer should be transferred into the brine in small quantities to prevent the polymer from clinging together or else it may cause the polymer to not expand fully, resulting in a change in concentration than initially intended.



$$\left[-CH_2-HC(C{=}O)(NH_2)-\right]_n$$

Figure 2.4- Polyacrylamide (PAM).



$$\left[-CH_2-CH(C{=}O)(NH_2)-\right]_x\left[-CH_2-CH(C{=}O)(O^-)-\right]_y$$

Figure 2.5- partially hydrolyzed polyacrylamide (HPAM).

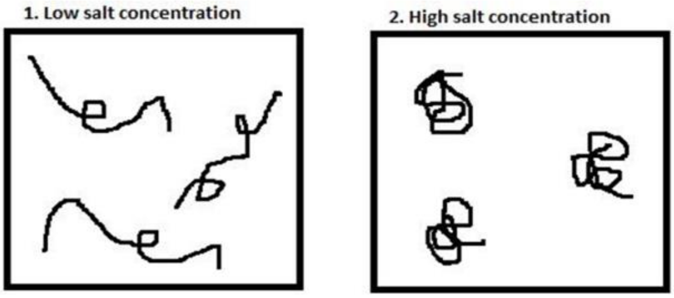


Figure 2.6 -Schematic overview of the behavior of HPAM in low salt concentration (1) and high salt concentration (2).

Table 2.2- Necessities for preparing High Salinity polymer.

Necessities	To weigh (g)
HS Brine	988.33
ITW package	6.675
HPAM	5.000

The following steps are following for preparing the HS polymer:

- Wash and clean the bottle in which the polymer solution will be made
- Weigh out carefully the HS brine on a scale in mass into the bottle
- Weigh carefully the ITW package and pour this into the bottle
- Weigh out carefully 5.0 grams of polymer
- Put a magnetic bar into the bottle and put the bottle on a magnetic stirrer
- While stirring, gently put the polymer into the solution
- Let the solution as a whole stir for at least 48 hours

At first glance, the last step seems a bit out of place considering the homogenizing time of the polymer. The reason for this time is the degree of hydrolysis. The degree of hydrolysis affects some physical properties of HPAM, such as adsorption, shear stability and thermal stability (Sorbie, 1991). the molarity of the polymer, because it reflects directly to the amount of carboxylate groups presents in the polymer, which influences the molarity of the polymer. In commercial use of polymer, such as HPAM, the degree of hydrolysis is 25%. By knowing the amount of carboxylate groups, the normality of the polymer can be calculated as well. Normality is a measure of concentration equal to the gram equivalent weight per liter of solution (Weber).

The application of the degree of hydrolysis and its relation to the normality of the polymer is explained more in detail in chapter 3. After the polymer is thoroughly stirred, it is then filtered. The filtering is done under pressure due to the high viscosity of the polymer, using nitrogen gas as the pressure source and a filter paper of 8μm in pore diameter. Nitrogen gas is used as it does not deteriorate the polymer. The set-up of this filter is shown in Figure 2.7. The purpose of filtering is to purge the polymer from impurities. This is also displayed on the right-hand side of Figure 2.7. If the polymer has to be diluted, this diluted batch needs to be degassed as well to prevent any injection of air in the core.

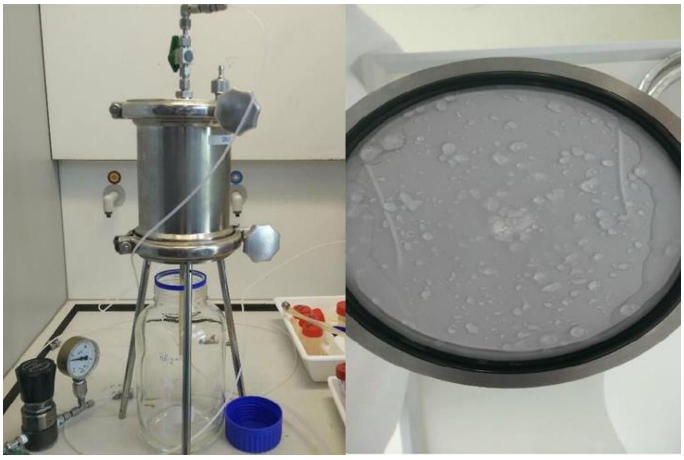


Figure 2.7- *Filter setup to filter polymer (left), filter(right).*

3. Results and Discussions

In this chapter, the results and calculations of each test used are explained in detail. Starting with the permeability calculations for the core sample, the data of which we have collected from the core flood experiments, using the Darcy's Law (equation 3.1). The results correspond to the permeability calculated earlier by N. Lenchenkov for a core sample originated from the same sandstone. The results of the ICP, and TOC analysis is graphically displayed along with the pH correlation. At last, the rheologies of the samples with various polymer concentrations are compared.

3.1 Permeability Test

Permeability refers to the rock property, which indicates its ability for gas or fluid to flow through. This property is one of the most important factors for determining the mobility ratio of a fluid (for example oil, water, polymers) in the porous media. To calculate the permeability, Darcy's Law is used (Bird, Stewart, & Lightfoot, 2006), given by equation 3.1.

$$Q = -\kappa \frac{A\Delta P}{\mu L} \tag{3.1}$$

Here, Q is the flowrate (m^3/s, k is the permeability (m^2), A is the cross sectional area of the flow (m^2), ΔP (Pb-Pa) is the total pressure drop, μ is the viscosity (Pa·s) and L is the length of the flow path (m). Rewriting equation 3.1 in terms for permeability, equation 3.2 is obtained

$$\kappa = -Q \frac{\mu L}{A\Delta P} \tag{3.2}$$

The core used during the experiment is a Boise Berea sandstone. For determining the permeability of the core, brine was injected at various flow rates and the resulting pressure changes were measured in-situ by four pressure transducers installed at different distances at the core. The pressure transducers were installed at the following distances: L_1=0.047m, L_2=L_3=0.133m and L4=0.066m. The total length and diameter of the core is 0.382m and 0.037m, respectively. For the calculation of the permeability of the sandstone, the total pressure drop observed at the second pressure transducer is used, because the measurement on this transducer is done on a large part of the core. The permeability obtained at each flow rate in tabulated in Table 3.1. Averaging all the permeability gives the permeability of the sandstone.

Table 3.1*- Permeability results at each tested flow rates.*

Flow rate(mL/min)	K_dP2(mD)
0.12	3855.23
0.3	4037.78
0.6	4051.69
1	4431.14
1.6	4153.46
Total	4105.86

As seen in Table 3.1, the permeability of the core is around 4105 mD, which is expected as the Boise Berea is a high permeable sandstone.

3.2 Polymer Dilution

For the injection of polymer into the core, a specific viscosity was needed for that, namely 48 mPa · s at a shear rate of 8 s^{-1}. This shear rate is approximately equal to 1 ft/day, which is a typical reservoir flow rate. This test was conducted with the rheometer depicted in Figure 2.3. The tests show that at increasing shear rate, the viscosity decreases. This is a characteristic of a shear thinning behaviour.

To achieve the target value, the initially prepared batch of 5000ppm needed to be diluted. First, the polymer was diluted to 71%, 62% and 50%. These specific dilutions were determined by plotting a trend line through the values achieved at 100% and 50% and using its linear equation to figure out the dilution percentage. It was determined that the polymer needed to be diluted to 62% to achieve the ideal viscosity of 48mPa · s. The dilution trend is displayed in Figure 3.1. Through this graph, it is clear that the dilution follows a linear trend, meaning the viscosity is linear dependent on the HPAM concentration, but seeing how it does not intersect the origin, it is irrespective of the shear rates. Therefore, it is advised to use more than two points to plot the trend line for dilution calculation. Because of diffusion effect, it is advisable to stir the diluted polymer for an extended period of time.

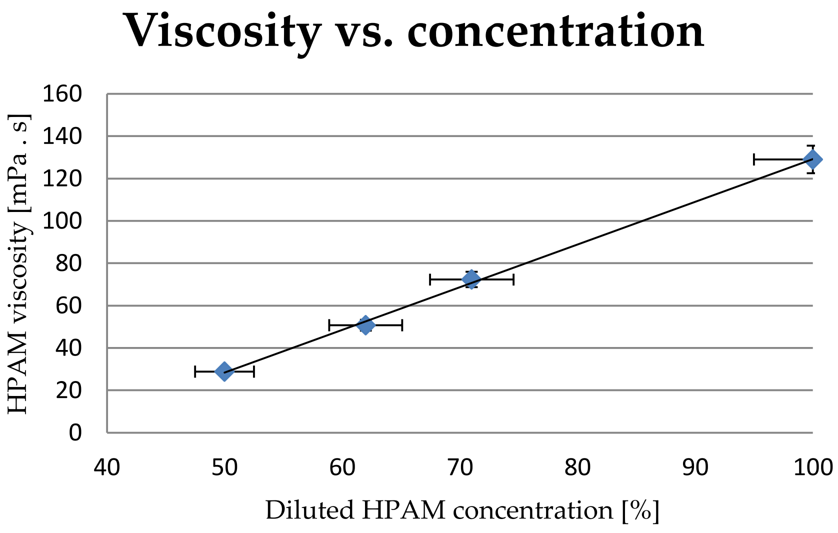


Figure 3.1- Denotes the viscosity change when diluting the 5 g/l in concentration HPAM to a specific viscosity.

3.3 ICP Analysis and pH Correlation

Figure 3.2 displays the ion concentration with respect to the porous volume (PV) added, obtained with the ICP analysis of the rock-fluid interaction experiment (RFI). The pH of some these samples were measured as well. These results are also plotted in Figure 3.3. The samples used in this figure were purely brine, in other words polymer was not yet injected at this stage. It is noticeable that the trend of the pH and the trend of the Na^+ ion concentration are correlated inversely of on another; where the Na^+ ion concentration increases, the pH decreases and vice versa. When the polymer is injected, initially the pH drops to around 5, but again increases to a value of around 6. The pH of the polymer was measured using pH strips, because the electrode of the pH meter was not suable for polymer. Although, the pH strips give a value in a wide range, the colour change on the strips shows that all the measurements in the same range.

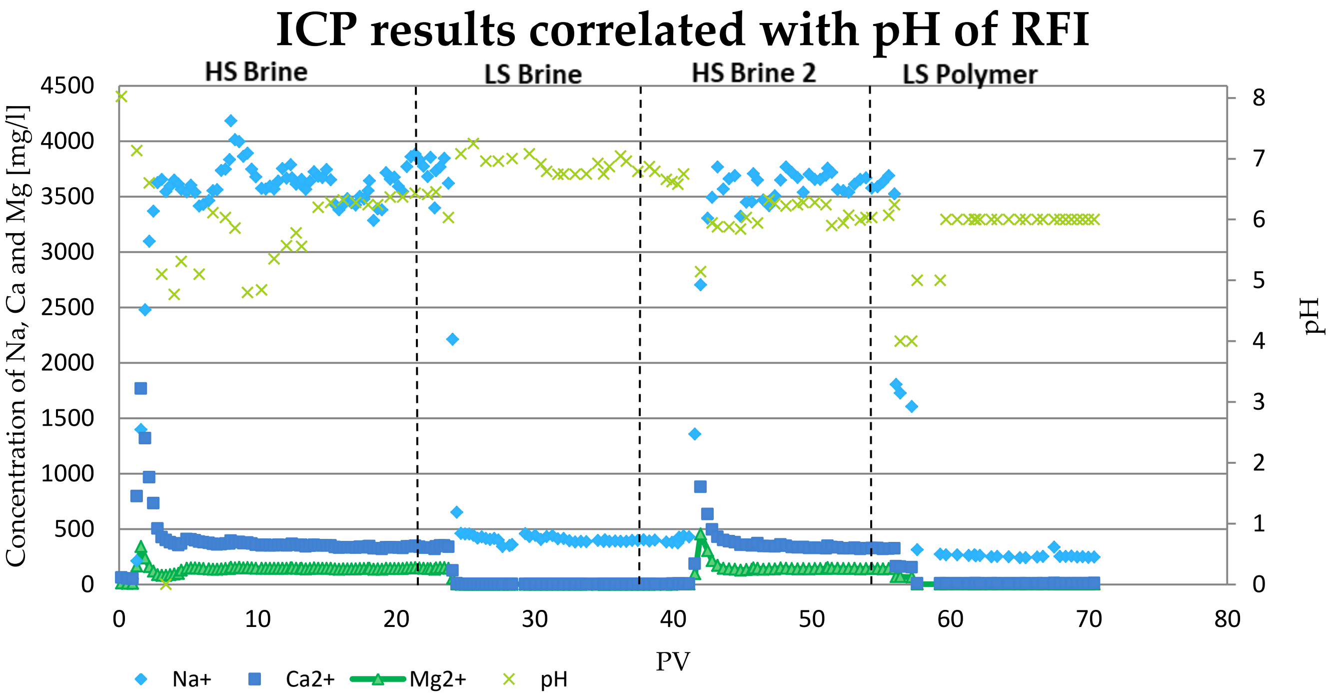


Figure 3.2- This graph shows the concentration fluctuation of the cations in the injected brine. The pH of these samples is plotted as well.

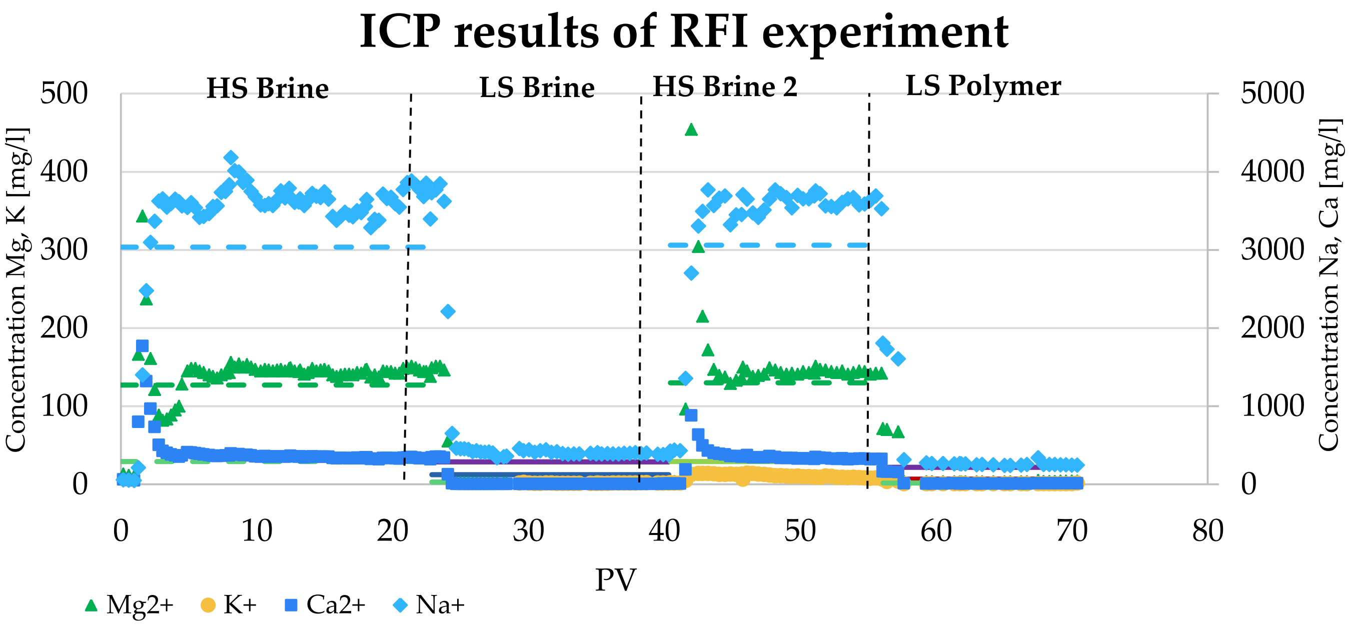


Figure 3.3- This graph depicts the ICP result of the whole experiment, including the brine and polymer samples.

Figure 3.3 shows the total trend of the ion concentrations throughout the first rock-fluid interaction experiment. First, HS Brine was injected with flow rates of 2 ft./day, 5 ft./day, and 10 ft./day respectively. Afterwards, LS Brine was injected at the same flow rates. Then, HS Brine was injected again, then lastly, LS polymer. The injected concentration of HS,-and LS Brine and LS polymer measured with the ICP are given in Table 3.2. In the first injection of HS Brine, we see that the concentrations of NA^+, Ca^{2+} and Mg^{2+} have noticeably increased compared to their initial concentration. This can be the result of leaching, where ions are extracted from the soil and dissolves in the fluid. The average of the ion concentration measured with the ICP test and the change are tabulated in Table 3.3 and Table 3.4.

A better representation of the effluent LS brine results in given in Figure 3.4. This graph shows a clear reduction in the divalent cation concentration, compared to their initial concentration given by the horizontal lines. On the contrary, the Na^+ ion concentration increased. The results of the change in concentration is found in table 3.4.

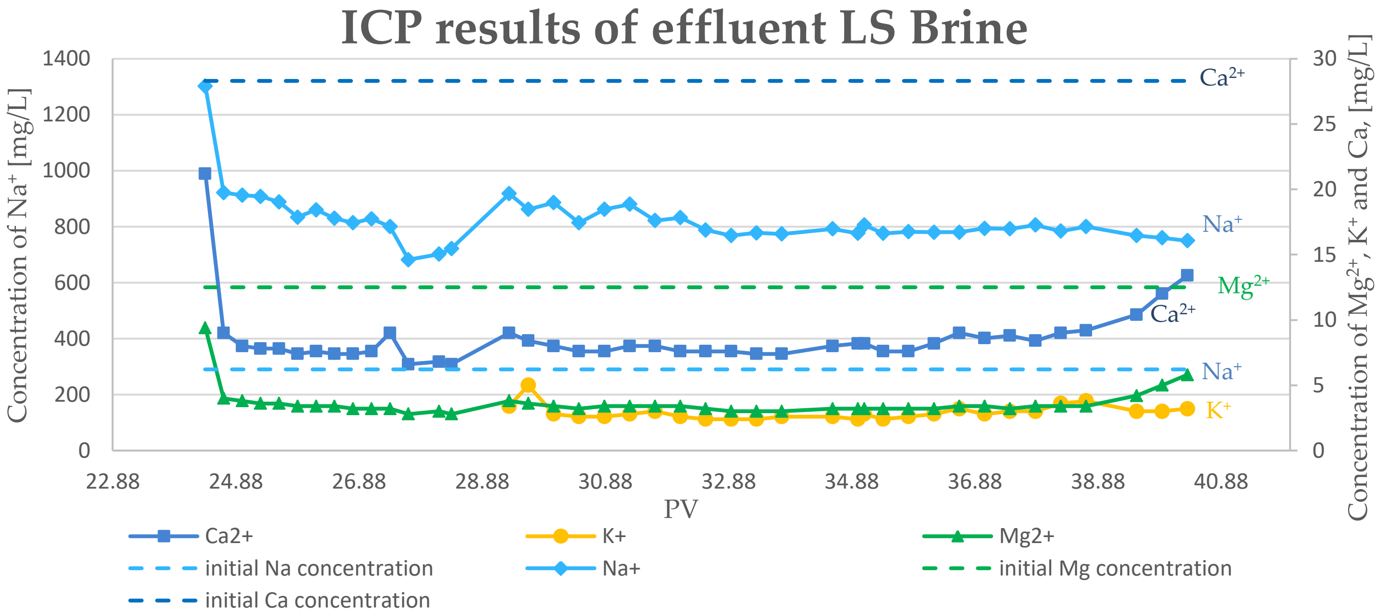


Figure 3.4*- ICP results of the effluent LS Brine (from 22.88 PV to 40.34 PV, Ref. Figure 3.3).*

Figure 3.5 displays the Mg^{2+} and Ca^{2+} divalent ion concentration in the effluent LS Polymer. Figure 3.6 represents the concentration of the monovalent ions Na^+ and K^+. There is a noticeably decrease in concentration of the divalent cations and K^+ ions, with exception of Na^+, which increased in concentration. The specific values of the change are tabulated in Table 3.4. It is noticeable that there is little to change in the concentration of the divalent cations.

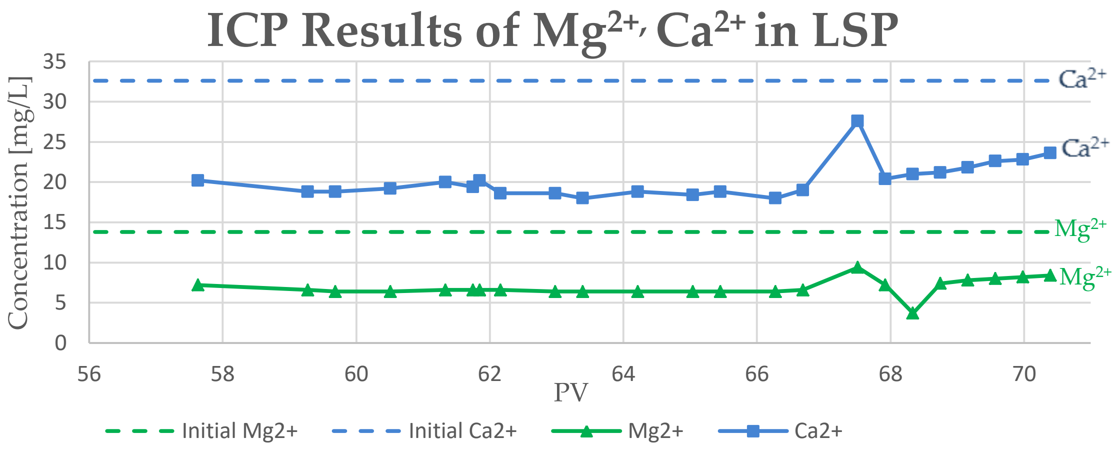


Figure 3.5- *ICP results of Ca^{2+} and Mg^{2+} in the effluent LS Brine (from 56.08 PV to 70.40 PV, Ref. Figure 3.3).*

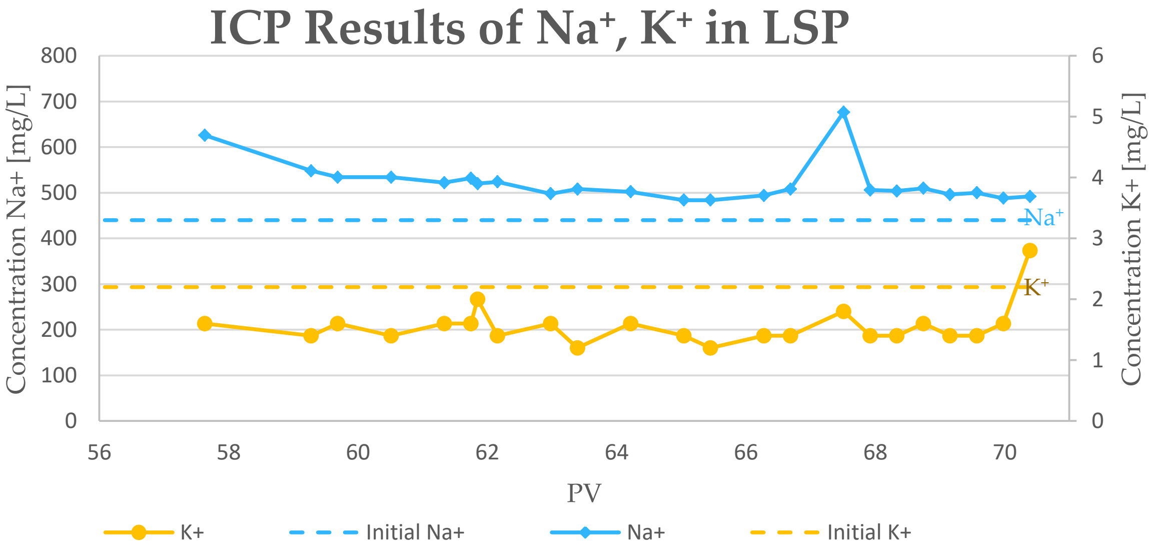


Figure 3.6- *ICP results of Na+ and K+ in the effluent LS Brine (from 56.08 PV to 70.40 PV, Ref. Figure 3.3).*

Table 3.2- *Initial concentration of the ion measured with ICP.*

	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)
HS Brine	127	293	3034	-
LS Brine	12.5	28.3	290	-
HS Brine 2	130	292	3062	0.8
LS Polymer	14	32	440	2.2

Table 3.3- *Average concentration of the ions at each injection.*

	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)
HS Brine	145.12	346.52	3649.13	-
LS Brine	1.79	4.28	411.39	1.46
HS Brine 2	157.95	370.92	3574.05	10.81
LSP	6.87	20.25	521.30	1.56

Table 3.4- Difference in ion concentration between the collected fluid and its initial concentration.

	Mg^{2+} (mg/L)	Ca^{2+}(mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)
HS Brine	8.12	53.52	615.13	
LS Brine	-10.71	-24.02	121.39	1.46
HS Brine 2	27.95	78.92	512.05	10.02
LS Polymer	-6.39	-12.35	81.30	-0.64

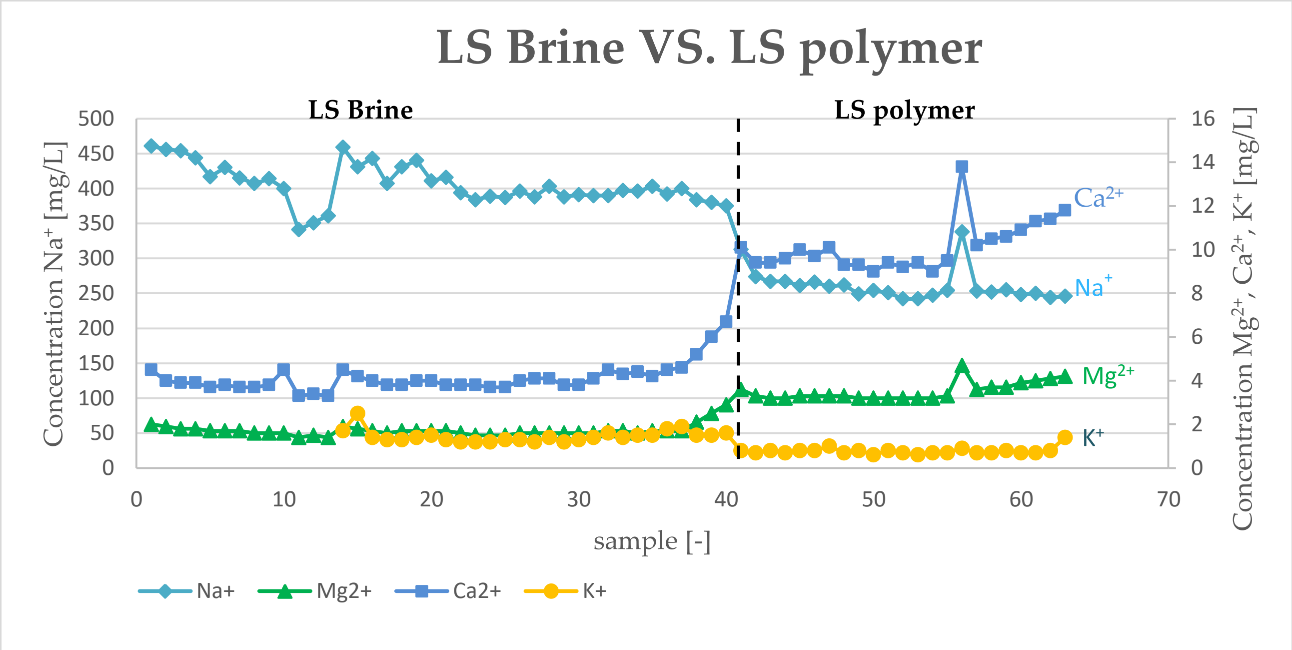


Figure 3.7- This graph compares the ICP results of LS Brine and LS polymer.

Figure 3.7 displays the ion concentration change between LS Brine and LS polymer. There is a clear increase in the divalent ion concentration, whereas the monovalent ions decreases in concentration. Compared to the LS Brine injection, the LS polymer lost less divalent cations due to stripping.

3.4 Total Organic Carbon analysis and rheology

Figure 3.8 depicts the TOC breakthrough results. The measurement was performed on the first low-salinity polymer injected into the core. From the curve behaviour, it can be said that there is a very low polymer retention as the inclination of the breakthrough steep. According to (Almansour, 2017) the high salinity brine will be stably displaced in the core, because of a low salinity buffer that is created between the two fluids due to polymer adsorption. The impact the polymer retention can have on the delay in polymer propagation is explained in appendix A.

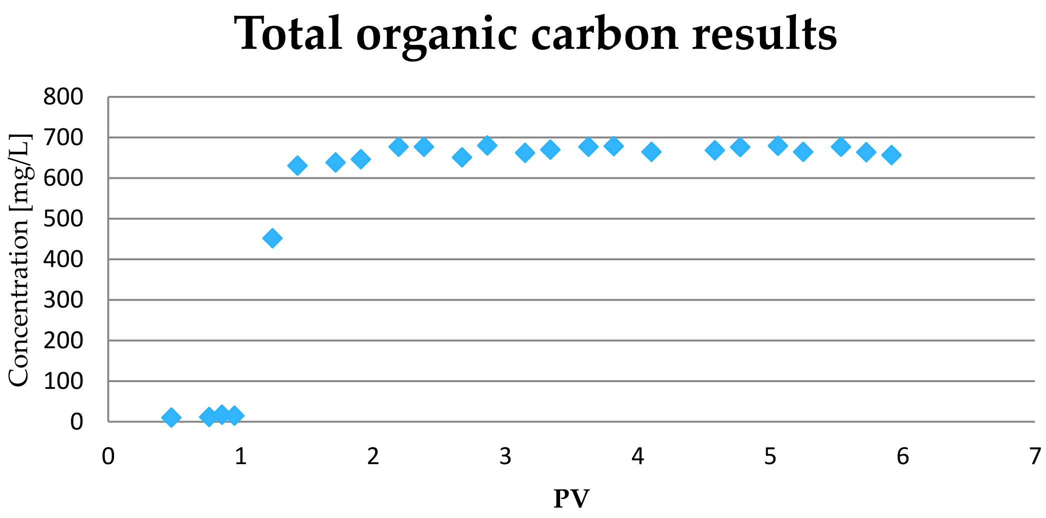


Figure 3.8- TOC results conducted on the first polymer sample produced from the core. The polymer injected was of low-salinity, injected at a flow rate of 2ft/day. (At 56.08 PV, ref. Figure 3.3)

The pH of the TOC samples was measured as well. The first samples showed a pH in the range of 4-5 and in the samples where the breakthrough is observed, the pH increases to a range of 5-6. A reason for the increase of the pH may be due to leaching of the cations present in the fluid.

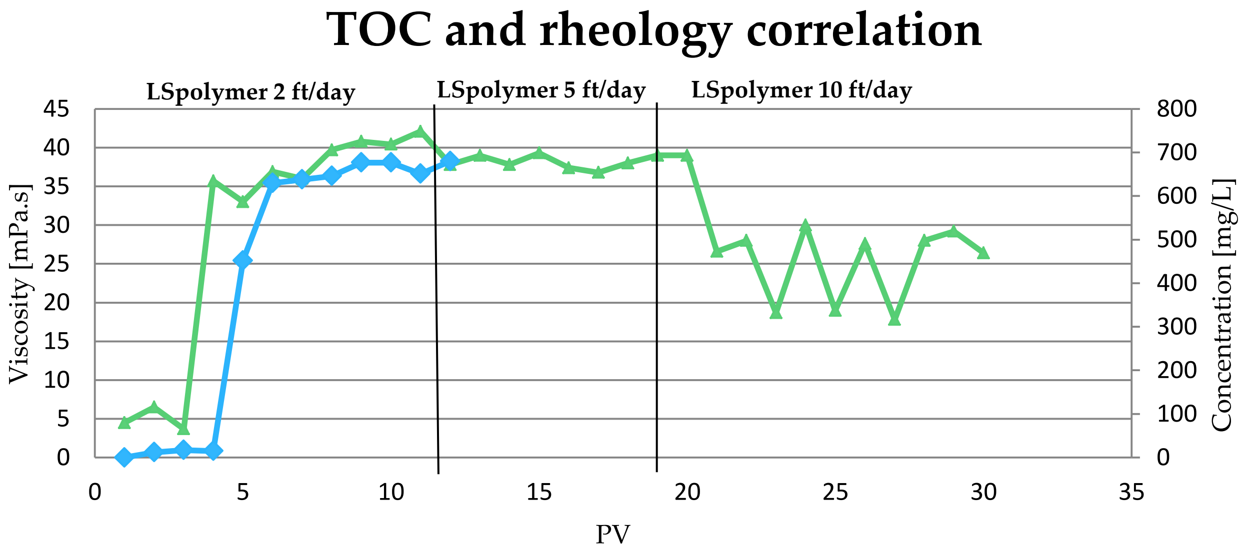


Figure 3.9- TOC correlated against the measured rheology of the effluent polymer.

Figure 3.9 displays the graph of the rheology results (in green) with the TOC results (in blue). A line plot is used in this graph for a better view of the rheology. The value of the viscosity was taken at the shear rate of 8 s^{-1}. There is a clear correlation of the two graphs at the breakthrough. This was expected, because the effluent polymer concentration would increase in the early samples.

The rheology graph shows a decrease in viscosity and fluctuations when LS polymer is injected at a flow rate of 10 ft./day. A possible theory for this behaviour could be due to mechanical degradation. Mechanical degradation is the result of high mechanical stress on the molecules or high flow rates, where the molecules are broken down (Puls, Clemens, Sledz, Kadnar, & Gumpenberger, 2016). Another possibility could be that during the rheology test the measuring cup was not filled such that the concentric cylinder as entirely under the fluid. Each sample had a volume of approximately 9 mL whereas a volume of 20 mL is needed for the concentric cylinder to be completely immersed. The lack of fluid for this measurement might be the reason for this fluctuation.

3.5 Cation Exchange Capacity

Cation exchange is an interfacial process during which cations on a clay surface are replaced by other cations (Farajzadeh, Guo, Winden van, & Bruining, 2017). The minerals present in the Boise Berea sandstone core is given in Table 3.5. Considering the available ions in the core, it is clear that the increase in Na^+ ions during RFI came from dissolution of Na^+ holding minerals, such as K feldspar and plagioclase. The dissolution of illite and K feldspar are the cause for the presence of K^+ ions, as sees in Figure 3.4, because in the injected Brine no potassium containing salts were present. The CEC of illite is 20-40 meq/100g (mindat, 2017). The effect of Ca^{2+} and Mg^{2+} change in concentration can also be explained due to dissolution of these minerals, where these cations are freed in the fluid. The reason for the decrease of the divalent ions when LS Brine is injected may occur because in the previous HS Brine injection, the rock surface lost its cations resulting in a negative charged rock surface. This may have cause the cations in the LS Brine to attach itself on this negatively charged surface. The exact changes in ion concentration is seen back in Table 3.4.

Table 3.5- Present minerals in the Boise Berea sandstone core and their respective formulae.

Boise Berea Sandstone	Formula	% mineral present [%]
Illite & Mica	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)$	4
Illite-Rich, Illite-Smectite		1
Quartz	SiO_2	76
K feldspar	$KAlSi_3O_8$-$NaAlSi_3O_8$-$CaAl_2Si_2O_8$	9
Plagioclase	$NaAlSi_3O_8 – CaAl_2Si_2O_8$	9
Calcite	$CaCO_3$	1
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	1

3.6 Molarity and Normality of HPAM

The molarity of the HPAM is calculated by equation 3.3

$$\text{Molarity} = \frac{m}{M \cdot V} \tag{3.3}$$

where m is the mass of the dissolved polymer, M is the molecular weight of the polymer and V is the volume of the solution.

Dissolving 5grams of HPAM with a molecular weight of 20 million Dalton (20 × 106 g/mole) in 1 liter of HS Brine, the molarity of this solution becomes $2.5 \cdot 10^{-7}$mole/L

The degree of hydrolysis is calculated with the simple equation (3.4)

$$\text{Degree of Hydrolysis} = \frac{y}{x+y} \tag{3.4}$$

where x is number of acrylamide in the mole, and y is the number of carboxylate groups in the mole. The sum of x and y gives the total number of groups in the HPAM as shown in Figure 2.7. The total number of groups is calculated by equation 3.5

$$x + y = \frac{\text{Mw\_HPAM}}{\text{Mw\_monomer}} \tag{3.5}$$

where Mw_HPAM is the molecular weight of the HPAM.
Mw_monomer is the molecular weight of one monomer, which is 71 g/mole.
The total number of groups is then $x + y = 2.85 \cdot 10^5$.
The number of carboxylate groups can now be calculated, simply by multiplying the total number of groups by the degree of hydrolysis, which, as mentioned in chapter 2.6, is 25%
The number of carboxylate groups is hence, $y = 0.25 \times 2.85 \cdot 10^6 = 71{,}250$ carboxylate monomers

Now that the number of carboxylate groups and the molarity of the polymer are known, the normality can be calculated by equation 3.6.

$$N = \text{Molarity} \cdot y \tag{3.6}$$

The unit of the normality is milliequivalents/liter, in short, meq/L.
The normality of the carboxylate groups in HPAM is 1.78×10^{-2} meq/L

Besides HPAM, the normality of the ions present in the solvent can be calculated.

However, instead of the number of ions, the valence number of the ions is multiplied my its molarity. The normality of the cation is given in table 3.6. According to (Lopes, Silveira, & Moreno, 2014), divalent cations such as Mg^{2+} and Ca^{2+} have a more significant effect on polymer solution, despite that monovalent cations, like Na^+, are much more present in the solution. The divalent cation should still be present in an equivalent mass percentage as the polymer. Working with this theory, we see that the normality of HPAM and the normality of the present divalent cations are in the same magnitude. Thus, it can be concluded that the carboxylate monomers are shielded by the cations.

Table 3.6 *- Normality values of the cations present in high-salinity brine used as solvent for the polymer.*

Ions	**Concentration (mole/L)**	**Ion charge**	**Normality(meq/L)**
Na	$1.44 \cdot 10^{-1}$	1	$1.44 \cdot 10^{-1}$
Mg	$5.64 \cdot 10^{-3}$	2	$1.13 \cdot 10^{-2}$
Ca	$7.60 \cdot 10^{-3}$	2	$1.52 \cdot 10^{-2}$

The same approach is used to check whether the LS polymer is shielded or not. The LS polymer was prepared in LS brine, the cation concentrations of which are found in table 2.1. The same amount of HPAM (5 grams) was used to prepare the LS polymer, meaning the amount of monomers present in this solution is the same as in HS polymer. The molarity of LS polymer is found to be $5{\cdot}10^{-08}$ mole/L. Subsequently, the normality is $3.56{\cdot}10^{-03}$ meq/L. The cation concentrations in this solution are tabulated in table 3.7.

Table 3.7- *Normality values of the cations present in low-salinity brine used as solvent for the polymer.*

Ions	Concentration (mole/L)	Ion charge	Normality(meq/L)
Na	$1.44{\cdot}10^{-2}$	1	$1.44{\cdot}10^{-2}$
Mg	$5.64{\cdot}10^{-4}$	2	$1.13{\cdot}10^{-3}$
Ca	$7.60{\cdot}10^{-4}$	2	$1.52{\cdot}10^{-3}$

Similarly as the previous case, the normality of the carboxylate groups HPAM and the normality of the divalent cations in LS polymer, meaning that the carboxylate monomer groups are shielded in LS brine as well.

4. Conclusions

From Table 3.4, it is noticeable that concentration of the monovalent and divalent cations increase in the effluent HS Brine. On the contrary, in the effluent LS Brine and LS Polymer, the concentrations of the ions have decreased in comparison to the injected concentrations. This decrease in ion concentration, as seen in Figure 3.4, Figure 3.5 and Figure 3.6, may be because stripping of ions took place during the flow in the core. Stripping occurs when ions from the fluid attaches itself to the rock surface.

The difference of the divalent cations between the effluent and the injected LS polymer is not as large as the difference between the effluent and injected LS Brine (Table3.4). The higher concentration of the divalent ions during the polymer injection may have occurred due to leaching effect. In other words, the divalent cations in the LS polymer solution were more attracted to the HPAM molecules than in the LS Brine solution.

The TOC analysis from Figure 3.8 showed low polymer retention. Low polymer retention means high propagation of the polymer through the core, which is favorable as it improves the sweep in the core (PRRC). This also means that for IOR, the oil displacement will not be delayed substantially during polymer flooding, where this LS polymer is used.

Through Figure 3.9 it can be concluded that the viscosity change is not significant, till 5 ft./day flow rate at least. This might be explained by mechanical degradation, where molecules may have broken down due to high mechanical stress or the high flow rate.

5. Recommendations

This study can also be simulated in PHREEQC. A possible further study can therefore be a modelling of the rock-fluid interaction in PHREEQC, where polymer can be included as a species. This can possibly define the rock-fluid interaction process better.

A more defined method on rheology can be used to obtain more precise results. This can be measured with a low shear rate viscometer. A big advantage here is that little polymer is needed for these measurements.

Another recommendation is to perform this experiment in carbonate rocks, as Mg^{2+} and Ca^{2+} ions in carbonate rocks are higher, which can affect the characteristic of the effluent polymer.

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Appendix A- Delay in polymer propagation due to polymer retention

Polymer propagation through porous media is delayed by polymer retention. This delay is given by equation A1. (PRRC, n.d.)

$$PV_{ret} = \left[\frac{\rho_{rock}(1-\emptyset)}{\emptyset}\right]\left[\frac{R_{pret}}{C_{inj}}\right] - IAPV \qquad (A1)$$

Where,

- PV_{ret} is the additional pore volumes of polymer solution that must be injected to contact one pore volume
- ρ_{rock} is the rock density
- $\emptyset$ is the porosity
- R_{pret} is the polymer retention is µg/g
- C_{inj} is the polymer concentration in mg/L
- $IAPV$ is the inaccessible pore volume

The IAPV is calculated by equation A2. For calculating the polymer retention, equation A3 is used.

$$IAPV = \sum[\left(\frac{C_{poly}}{C_{polyo}} * \Delta PV\right) - (\frac{C_{trac}}{C_{traco}} * \Delta PV)] \qquad (A2)$$

$$R_{pret} = \{\left[\sum[\left(\frac{C_{poly}}{C_{polyo}} * \Delta PV\right) - (\frac{C_{trac}}{C_{traco}} * \Delta PV)]\right] + IAPV\right\} * C_{polyo} * \frac{PV}{M_{rock}} \qquad (A3)$$

C_{poly} is the effluent polymer concentration, C_{polyo} the injected polymer concentration, C_{trac} is the effluenttracer concentration, C_{traco} the injected tracer concentration, ΔPV is the pore volumer increment and M_{rock} is the rock mass in the core.

Assuming that the IAPV is zero, the delay factors of polymer concentrations between 200-3000ppm is measured. The porosity of the core is 0.3 and ρ_{rock} is 2.56g/cm^3. The results are given in Figure A.1. (Adapted from (PRRC, n.d.))

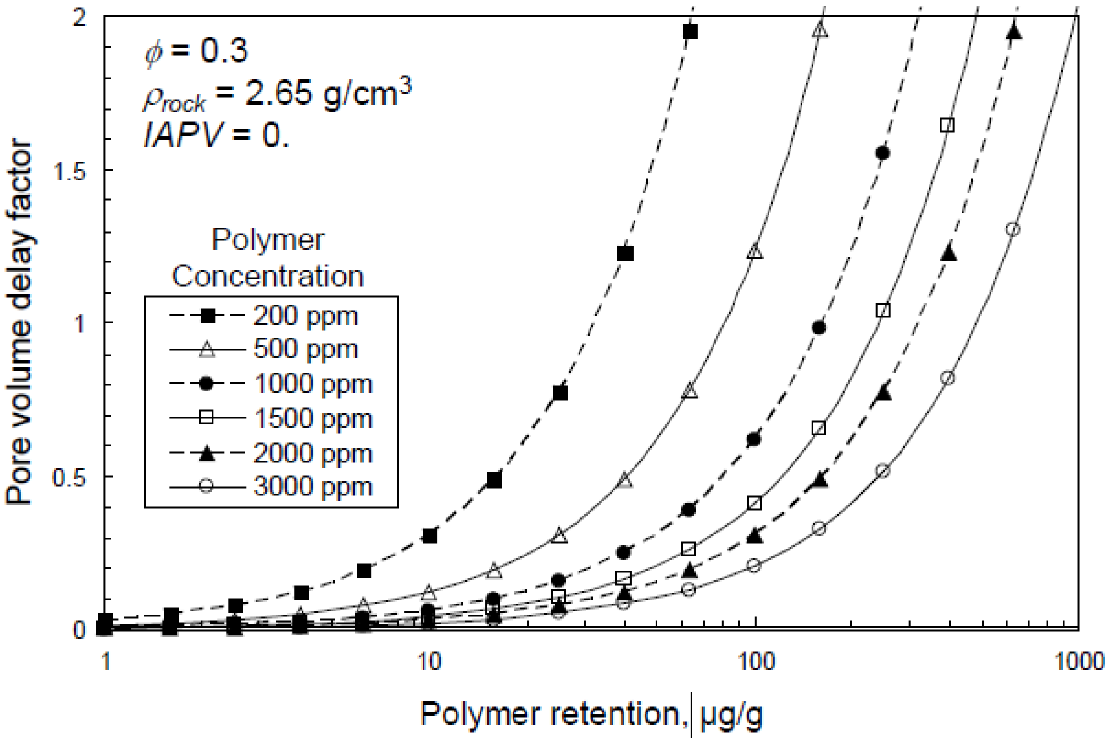

Figure A.1-*Polymer retention delay at different polymer concentration.*

For example, at low polymer retention of 10 µg/g and a polymer concentration 2000 ppm, the delay factor is 0.03 (3%). At high polymer retention of 100 µg/g and a polymer concentration of 1240 ppm, the delay factor is about 0.5 (50%), which means that 50% more polymer should be injected to reach the case for no polymer retention.

Nomenclature

Symbol	Unit	Description
ΔP	[Pa]	Total pressure drop
μ	[Pa·s]	Viscosity
A	[m^2]	cross-sectional area of the flow
κ	[mD]	permeability
L	[m]	Length of flow path
m	[g]	mass of dissolved polymer
M	[g/mole]	molecular weight
N	[meq/l]	Normality
Q	[m^3/l]	flow rate
V	[m^3]	volume of solution
x	[-]	number acrylamide
y	[-]	number of carboxylate groups

Acronyms

CEC	Cation Exchange Capacity
EOR	Enhanced Oil Recovery
HPAM	Hydrolyzed Polyacrylamide
HS	High Salinity
IAPV	Inaccessible pore volume
ICP	Inductively Coupled Plasma Spectrometry
IOR	Improved Oil Recovery
LS	Low Salinity
M	Mobility ratio
MCR	Modular Compact Rheometer
PAM	Polyacrylamide
PV	Pore Volume
RFI	Rock-Fluid Interaction
TOC	Total Organic Carbon

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