OPTIMIZATION OF SMART WATER COMPOSITION FOR THE POTENTIAL SYNERGY WITH POLYMER FLOODING

by

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Originality Statement

I, Damir Karimov, hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgment is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation, and linguistic expression is acknowledged.

Signed on 15.04.2020

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ABSTRACT

Nowadays, different studies were conducted to design new methods to improve oil recovery efficiency. The study focuses on experimental work to evaluate synergy between low salinity water and polymer flooding in carbonate formations. The main objective of this thesis was to develop a hybrid method to enhance oil recovery by a possible combination of low salinity water and polymer flooding.

The Caspian Sea water was used as a base brine, and the water composition of the Caspian Sea was altered by diluting and adjusting the concentration of active ions such as Ca^{2+}, Mg^{2+}, SO_4^2, to observe the impact of modified seawater on wettability through contact angle measurements. The compatibility of the modified seawater and partially hydrolyzed polyacrylamide (HPAM) based polymer solutions is investigated by performing different rheological experiments. Different governing parameters such as water salinity, the concentration of active ions, and HPAM solutions concentration were experimentally studied to achieve the optimized rheological behavior.

The different diluted water compositions of Caspian Sea water were prepared to identify the best solution in terms of wettability alteration. Later, the diluted solutions were modified by adding active ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}. The wettability alteration to the more water-wet condition was observed when the concentrations of Ca^{2+} and SO_4^{2-} have been increased four times, respectively. However, no significant change in wettability was observed by only increasing the concentration of Mg^{2+} due to low-temperature conditions. The effect of modified seawater on polymer performance compatibility was studied by conducting a series of rheological experiments for various salinity levels in smart water composition, temperature range from 25-80°C, and polymer concentration at 1000 and 3000 ppm. All the polymer solutions showed typical non-Newtonian rheological characteristics with shear thinning behavior. Further, the results based on contact angle measurement and rheological experiments were combined to identify proper optimal conditions for the potential synergy of modified seawater and polymer. Our results showed a clear dependence of the polymer viscosity on the divalent ions concentration and temperature. The target viscosity of 4 cP at a shear rate of 10 s^{-1}, which approximately corresponds to the shear rate in porous media, was obtained with 500 ppm Flopaam 5115 polymer concentration in 20 times diluted Caspian Sea Water having four times increased concentrations of Ca^{2+} and SO_4^{2-}.

Through the series of experiments, we determined the optimum concentration of active ions in water that results in wettability alteration without compromising the effectiveness of polymer in the hybrid low salinity water-polymer flooding technique. The combination of low salinity water and polymer flooding was found useful to improve the performance of both methods. This hybrid low salinity/polymer flooding veils the drawbacks of each method, such as unfavorable mobility ratio for low salinity water and polymer degradation under high salinity conditions.

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ABBREVIATIONS AND SYMBOLS

EOR	Enhanced Oil Recovery
IOR	Improved Oil Recovery
BP	British Petroleum
OOIP	Original Oil in Place
MIE	Multi-ion Exchange
CT	Computed Tomography
PV	Pore Volume
HPAM	Hydrolyzed Polyacrylamide
LSW	Low Salinity Water
WAG	Water Alternating Gas
RF	Recovery Factor
WF	Water Flooding
k	Permeability
μ	Viscosity
S	Saturation
SSW	Synthetic seawater
SWF	Smart Water flooding

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1. INTRODUCTION

1.1 BACKGROUND

Approximately, only 40% of crude oil is extracted, and 60% of oil remains in the reservoirs (Campbell & Laherrere, 1998). For instance, during the primary stage of oil recovery, only 20-30% could be produced. In the primary stage of recovery, the oil is produced by the natural displacement energy of the reservoir. This primary drive mechanism includes such forces as solution gas drive, gas cap drive, compaction, gravity drainage, natural water drive, or the combination of these mechanisms. The production of oil starts to decline after a primary stage of recovery after a particular timeline in the oilfield life cycle. Then, some additional forces are applied to improve oil recovery. This method is called improved oil recovery, which consists of secondary and tertiary stages. During the secondary stage of oil recovery, these external forces help to maintain the pressure in a reservoir by supporting one of the mechanisms in a primary stage. One of the most commonly used methods in the secondary stage of oil recovery is waterflooding, gas injection, or injection of both methods for pressure maintenance.

A large amount of oil remains in a reservoir when incremental oil cannot be recovered anymore after the primary and secondary stages of oil recovery. This oil is entrapped in the pores, and conventional methods could not increase the oil recovery. Consequently, some processes and methods are needed to be implemented to recover trapped oil. This method is called tertiary oil recovery. However, three stages of oil production are not implemented in chronological order. There are many factors that impact production operation stages. These factors are governed by the nature of crude oil, availability of chemicals, or location of the wells. For instance, tertiary oil recovery is the only method to produce highly viscous oil in one of the most well-known and largest in-situ combustion projects in Suplacu de Barcau, Romania (Panait-Patica, et al., 2006). Therefore, tertiary oil recovery is used prior to the primary and secondary stages of oil production. Sometimes the term "tertiary oil recovery" is used interchangeably with "enhanced oil recovery" or EOR. This recovery technique includes methods that increase oil recovery when primary and secondary recovery stages are not useful anymore by the injection of fluids or chemicals that commonly do not present in the reservoir (Lake, 1989). Tertiary recovery stage consists of different types of enhancing oil recovery: thermal, chemical, miscible/immiscible displacement, and others. Different methods of oil recovery are shown in Figure 1. In this paper, two different and independent recovery enhancement techniques, such

as low salinity water and polymer flooding, are combined to examine a positive effect on oil recovery.
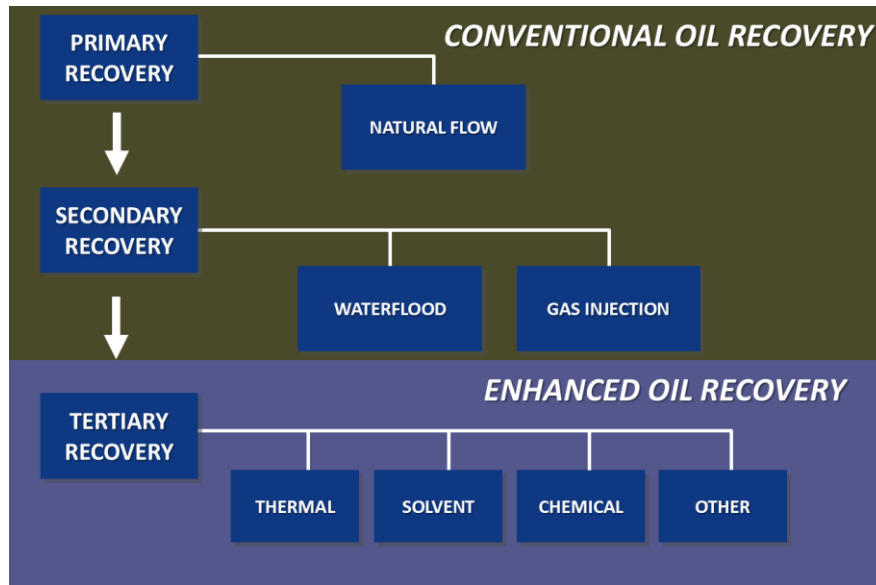
Figure 1. Different oil recovery mechanisms

1.2 PROBLEM DEFINITION

Since the discovery of oil, oil has been the primary contributor to the energy source in the world. Living in the XXI century, the demand for energy is increasing due to the development of many industrial and technological projects. Therefore, many laboratory experiments are conducted to find the best and optimal way to recover oil from the reservoirs. Recently extensive studies have been performed to examine the synergy between low salinity water and polymer flooding. Low salinity water and polymer flooding have already proved their benefits in increasing oil recovery in many laboratory studies (Fani, et al., 2018; Nasralla & Nasr-El-Din, 2011; Yang, et al., 2004; Wassmuth, et al., 2007). However, these methods sometimes are not considered viable due to the limitations in low salinity water, such as unfavorable mobility ratio and a high cost of polymer and its inability to work under high temperature-high salinity conditions. For that reason, it was suggested to combine these two EOR methods in order to eliminate the drawbacks and to achieve better performance from economic and technological perspectives. The research on the combination of low salinity water and polymer flooding has already caught the attention of the scientific community. The abovementioned results of laboratory studies showed a positive response for the successful implementation of this hybrid EOR method on laboratory and field scales. Many experimental findings demonstrate the efficiency of this technique in terms of oil recovery enhancement. However, the area of

research for hybrid low salinity/polymer flooding is not sufficiently understood to make any conclusions. Thus, in my thesis, I would like to overcome the challenges and spill the beans on the unexplored area related to this topic.

This thesis considered the typical Kazakhstani oilfield condition as a reference. Most of the large oil reservoirs in Kazakhstan, such as Tengiz, Kashagan, Karachaganak, are carbonates in nature. In addition, most of the research on hybrid low salinity/polymer flooding was conducted for sandstones due to the complexity of rock/fluid interactions and heterogeneity problems in carbonate reservoirs. Therefore, it was suggested to conduct the experiment on carbonate outcrops to overcome the challenging and unexplored issues related to this topic. Moreover, artificially synthesized Caspian Sea Water and formation water from Tengiz oilfield was used as a base water solution due to their geographical proximity to Kazakhstani reservoirs. Thus, in my experimental part, the effect of active ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} in Caspian Sea Water was determined on the potential impact on wettability alteration of the system through contact angle measurements. Then, the effect of these ions on viscoelastic properties of different HPAM-based polymers was investigated for the potential hybrid low salinity/polymer flooding method.

1.3 OBJECTIVES OF THE THESIS

The main objective of this thesis is to combine and discuss the potential synergy between low salinity water and polymer flooding in order to observe suitable conditions that help to improve oil recovery. The parameters such as temperature, concentration of active ions in the water composition, concentration of the polymer and its thermal and mechanical stability are examined to investigate suitable conditions for Hybrid Low Salinity Water/Polymer Flooding.

2. LITERATURE REVIEW

2.1 LOW SALINITY WATER

One of the most recent and promising EOR methods that caught the attention of global oil companies is low salinity water injection. The first studies of low salinity water injection were conducted at the University of Wyoming (Jadhunandan & Morrow, 1991). Low salinity water injection has many designations to this technology depending on the company such as Advanced Ion Management by ExxonMobil, Smart WaterFlood by Saudi Aramco, LoSal by BP, and Designer Waterflood by Shell (Shalabi, 2017). This method also shows great potential as a new and effective EOR technique due to efficiency in enhancing oil recovery, high water availability, low production, and capital costs. During low salinity water injection, the composition of injected water is changed by reducing the salinity level of injected water. This is the main difference comparing to conventional waterflooding in the secondary stage of oil recovery. This reduction in salinity level helps to mobilize trapped oil and increase oil recovery.

Low salinity water is a general term for water flooding with low salinity composition, which further could be classified into two categories. In the first case, the studies on low salinity water are conducted using only different water dilution samples. In another case, this diluted water is modified by adding different active ions to increase the potential for oil recovery. This water sample with modified ions is defined as a SmartWater. However, this SmartWater could have a negative and irreversible impact on a recovery process during the synergy with polymer flooding. This effect is discussed further in the thesis.

Different laboratories and field tests have already proved the effectiveness of low salinity water on oil recovery for both carbonate and sandstone reservoirs. Most of the laboratories studies confirmed the overall increase in oil recovery in the range of 5-25% of OOIP after secondary and tertiary injection modes (Morrow & Buckley, 2011; Nasralla, et al., 2013; Lager, et al., 2008; Austad, et al., 2012).

Some field applications have been already implemented a low salinity water injection technique for sandstone and carbonate reservoirs. For instance, low salinity water flooding was successfully applied for more than 40 years in the sandstone reservoir at the Pervomaiskoey oil field, Republic of Tatarstan. Deficiency of produced water caused to take water from the

nearest Kama River. Constant displacement of oil by low salinity water through 96 wells resulted in a 5-9% incremental oil recovery (Akhmetgareev & Khisamov, 2015). Field development history is shown in Figure 2.
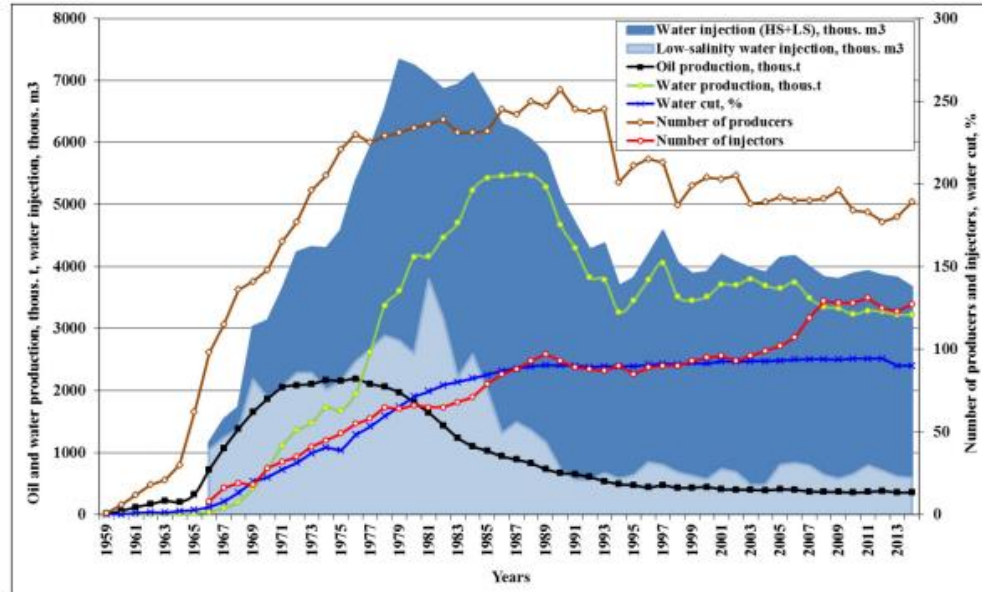
Figure 2. Oil and water production data in Pervomaiskoye field *(Akhmetgareev & Khisamov, 2015)*

There are different mechanisms behind low salinity water injection that were proposed for enhancing oil recovery in carbonate and sandstone reservoirs. The main mechanism for low salinity water injection is a controversial and debatable topic in the scientific area. Scientists still argue which mechanism is responsible for low salinity water injection due to the complex and incomprehensible interactions between oil, water, and rock surface. Several mechanisms have been already presented that explain and underlie the oil recovery process in both sandstone and carbonate rocks in Figure 3 (Rotondi, et al., 2014; Wang & Fu, 2018).

In sandstones, fines migration could be proposed as one of the possible mechanisms for low salinity water injection. The prerequisite for this mechanism to occur is the presence of clay minerals. During the low salinity water injection, clay fragments disperse from the rock, changing the wettability of the system. Thus, the released fines cause the initial pore throats to block. This blockage stimulates the development of new flow channels, diverting the water flow into non-swept pores and increasing oil recovery, respectively (Tang & Morrow, 1999). Nevertheless, this complex mechanism is not fully understood due to complex interactions on the microscopic level, depending on the clay content and brine composition.
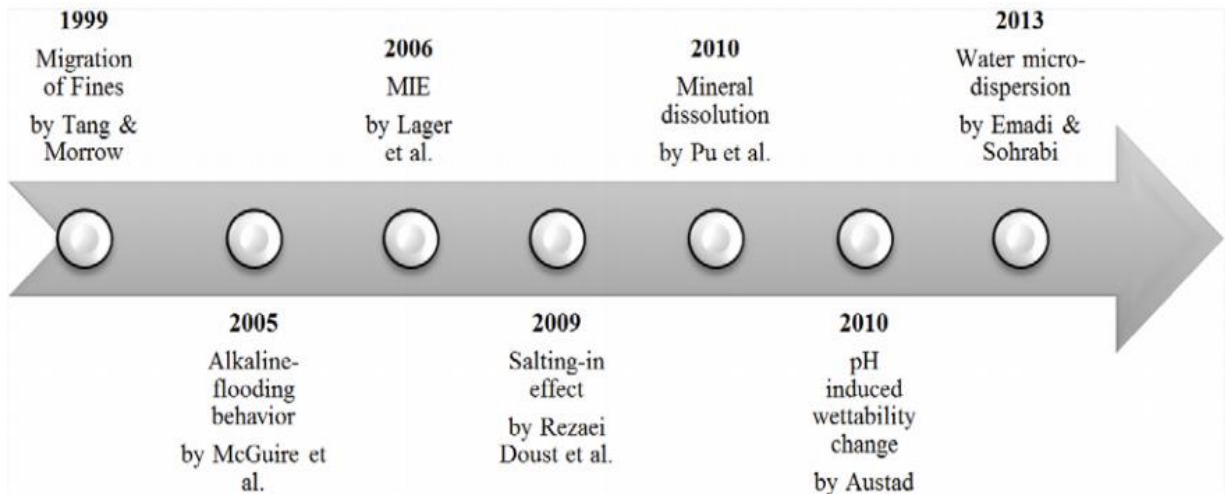
Figure 3. Proposed mechanisms for low salinity waterflooding *(Rotondi, et al., 2014)*

Another interesting observation was found by McGuire and coworkers. They conducted several core flooding experiments and suggested that the increase in pH is responsible for the increase in oil recovery by forming alkaline-flooding behavior during low salinity water injection (McGuire, et al., 2005). Further, Austad, et al. (2010) supported and explained this phenomenon by proposing a possible chemical mechanism. This mechanism is shown in Figure 4.
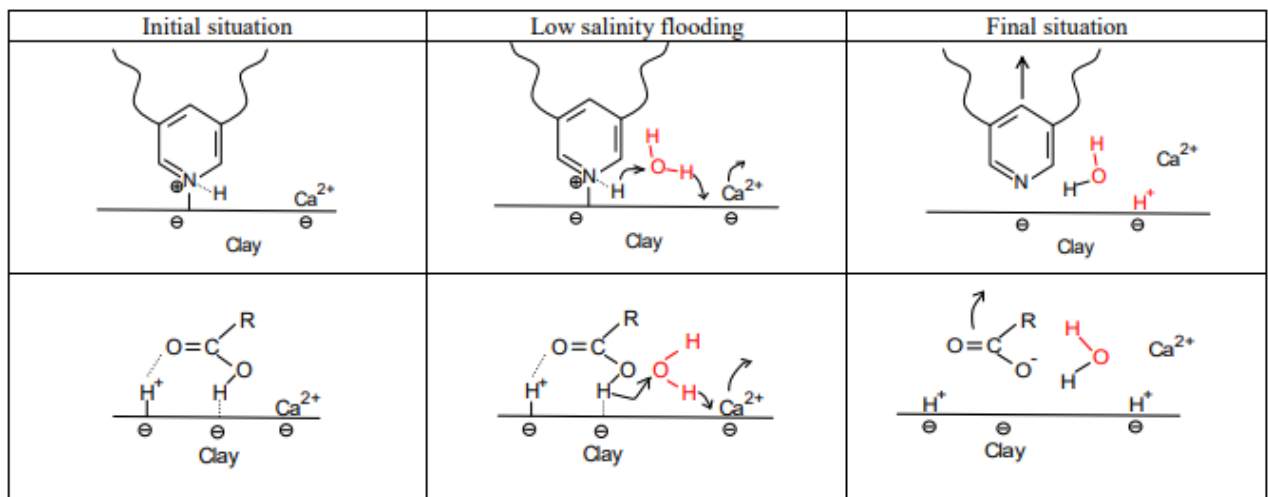
Figure 4. The mechanism for pH inducted wettability change. Top: Desorption of basic compound. Bottom: Desorption of acidic compound *(Austad, et al., 2010)*.

Both studies stated that low pH nature in the reservoir contributes to the disturbance of thermodynamic equilibrium during the injection of low salinity water. As at low pH values, the acidic and basic compounds readily absorb on the rock surface. During this process, H^+ ions interact with a clay content on the surface of the rock in order to compensate for the loss of

Ca^{2+} in low salinity water. This interchange of ions leads to the local increase of pH. The overall process could be described in the following reaction:

$$[Clay^- \, Ca^{2+}] + H_2O \rightarrow [Clay^- \, H^+] + Ca^{2+} + OH^-$$
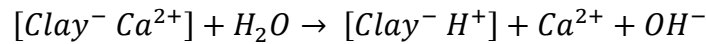
Lager, et al. (2008) proposed a multi-ion exchange (MIE) mechanism that changes the wettability of the system toward more water wetness in sandstone reservoirs. During the low salinity water injection, the effluent analysis showed that the concentration of divalent ions such as Ca^{2+} and Mg^{2+} significantly decreased. As a result, these ions strongly absorbed on the rock surface. In the proposed MIE model, Ca^{2+} and Mg^{2+} act as a bridge between the negatively charged rock surface and the polar functional group of the oil, increasing overall oil recovery.

For carbonate rocks, Pu and coworkers (2010) performed coreflooding experiments to investigate the effect of mineral dissolution on oil recovery. The experiment has been conducted on different rock formations that were rich in anhydrite, dolomite, and calcite components. X-ray CT imaging and effluent analysis demonstrated the evidence of anhydrite dissolution in all cases, resulting in a substantial increase in oil recovery (Pu, et al., 2010). The results of the experiment are shown in Figure 5.
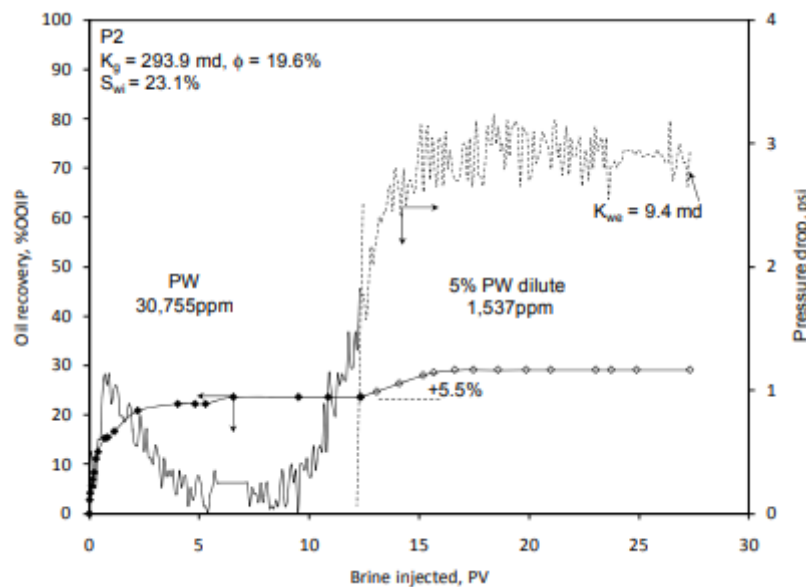
Figure 5. OOIP and pressure drop vs PV brine injected *(Pu, et al., 2010)*.

Recent studies on the possible mechanisms for low salinity waterflooding has been investigated by Emadi and Sohrabi. They performed a comprehensive visual analysis using a novel reservoir-condition micromodels. The models showed that the interaction between low salinity

water and oil phase results in the formation of water microdispersion at the oil/water interface (Emadi & Sohrabi, 2013). Figure 6 illustrates the visual image of this model.
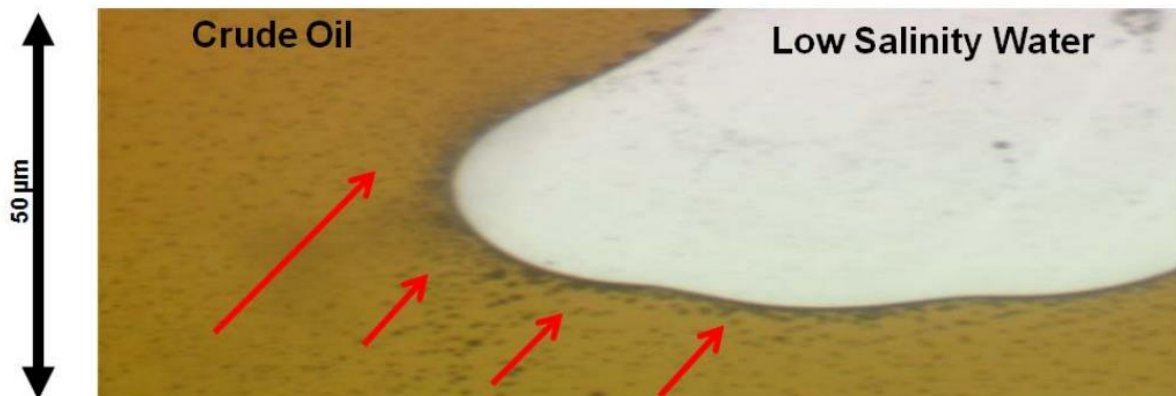
Figure 6. The formation of water micro-dispersion at the oil/water interface *(Emadi & Sohrabi, 2013)*

Consequently, this large number of formed microdispersions are responsible for the wettability alteration and increase in oil recovery (Emadi & Sohrabi, 2013).

Extensive studies showed that multi-ion exchange, which results in wettability alteration, is the most probable and acceptable mechanism in carbonate rocks. It was found that wettability alteration and enhancement in oil recovery can be achieved by modifying the ion composition during low salinity water injection. Sulfate, magnesium, and calcium are the most active ions that are responsible for this process. Some experiments have already been performed to investigate the effect of sulfate ions in injected water on wettability concentration (Hognesen, et al., 2005). The attraction of negatively charged sulfate ions towards positively charged rock surface results in the reduction of an overall positive charge. In addition, during this interaction, sulfate ions replace the negatively charged organic materials from the rock surface. Due to lower electrostatic repulsion on the rock surface, calcium and magnesium ions approach towards the surface and come in contact with organic material. Consequently, the desorption of organic material by sulfate ions and its further interaction with calcium and magnesium ions results in increasing the water wetness of the system (Tawfik, et al., 2019). The overall process of wettability alteration in carbonate rock is illustrated in Figure 7. Comprehensive research on the effect of increasing sulfate ions was performed using a spontaneous imbibition process (Romanuka, et al., 2012).
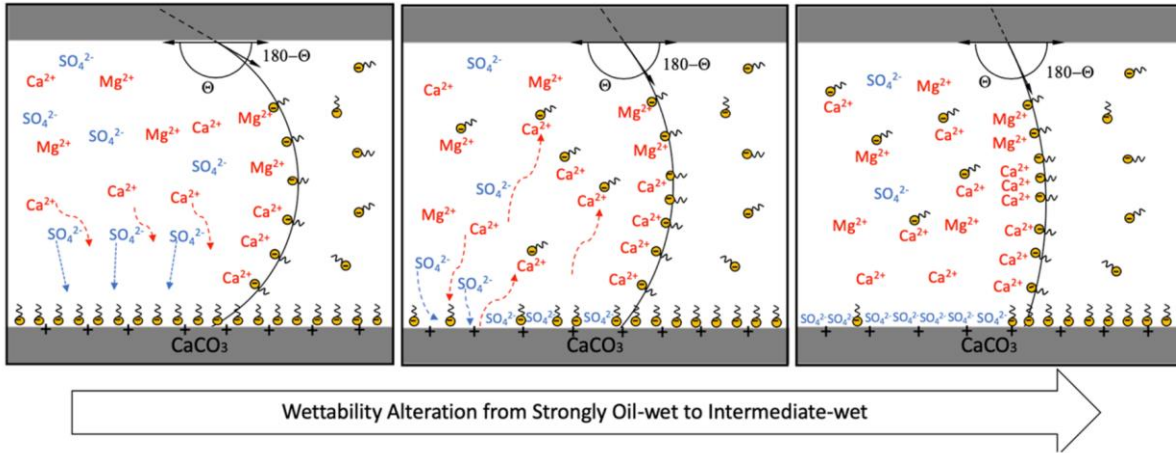
Figure 7. Schematic representation of the MIE mechanism in carbonate rocks *(Tawfik, et al., 2019)*

This effect was found to be more prominent under high-temperature conditions in another study (Zhang, et al., 2007). Unfortunately, high-temperature conditions limit the application of polymer. Therefore, it is essential to consider the reservoir depth and temperature. At the temperature higher than 60 °C acrylamide group in HPAM structure starts to rapidly hydrolyze (Dovan, et al., 1997). Due to this rapid hydrolysis, the viscosity of polymer decreases because of the interaction of hydrolyzed polyacrylamide with divalent ions.

The affinity of calcium and magnesium ions towards the rocks surface increases when the initial positive charge of rock surface decreases as the absorption of sulfate ions occurs (Zhang, et al., 2007). The overall process of wettability alteration in carbonate rocks could be described in the following equation:

$$RCOO^- - Ca - CaCO_3(s) + Ca^{2+} + SO_4^{2-} = RCOO - Ca^+ + Ca - CaCO_3(s) + SO_4^{2-}$$
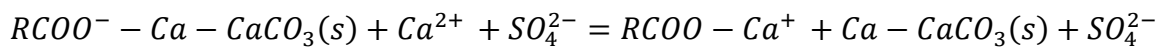
The presence of magnesium ions in injected water during this process is vital for the enhancement of oil recovery. Magnesium being more reactive than calcium ion, is capable of substituting calcium under high temperature. This chemical substitution process can be described in the following reaction:

$$RCOO^- - Ca - CaCO_3(s) + Mg^{2+} + SO_4^{2-} = RCOO - Ca^+ + Mg - CaCO_3(s) + SO_4^{2-}$$
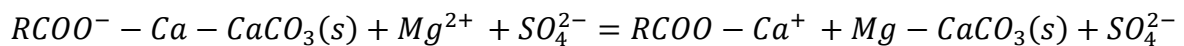
In another case, an excess of calcium ions will react with sulfate and produce unfavorable and destructive precipitation form of CaSO4. Consequently, it is essential to maintain proper and suitable initial conditions and concentrations of active ions in injected water. The simplified version of the multi-ion exchange reaction for carbonate rocks in the presence of active ions is described in Figure 8.
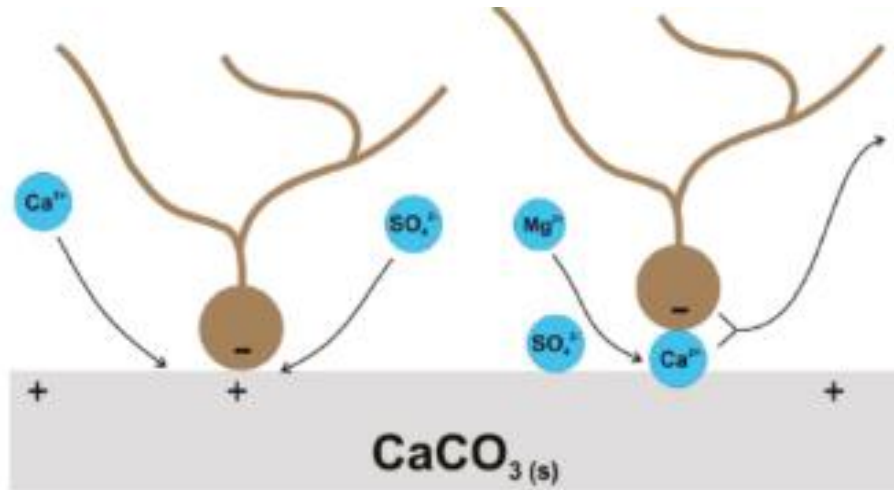
Figure 8. A probable mechanism for wettability alteration in carbonate rocks *(Jalilian, et al., 2017)*

However, one of the significant drawbacks of low salinity water injection is the unfavorable mobility ratio. The difference in viscosities of injected water and oil causes the viscous fingering, and the flow becomes unstable during the displacement process. This unstable flow of water results in an early breakthrough and affects oil recovery. At high mobility ratios, the displacing fluid moves through the path of minimum flow resistance and creates unstable channels along with the flow path from injection to the production well. The concept of mobility ratio can be defined as the ratio of displacing over displaced fluid and can be visualized in the equation below (Guo, et al., 2006):

$$M = \frac{k_{rw}}{\mu_w} \Bigg/ \frac{k_{ro}}{\mu_o}$$

The displacement process for different mobility ratio is presented in Figure 9.
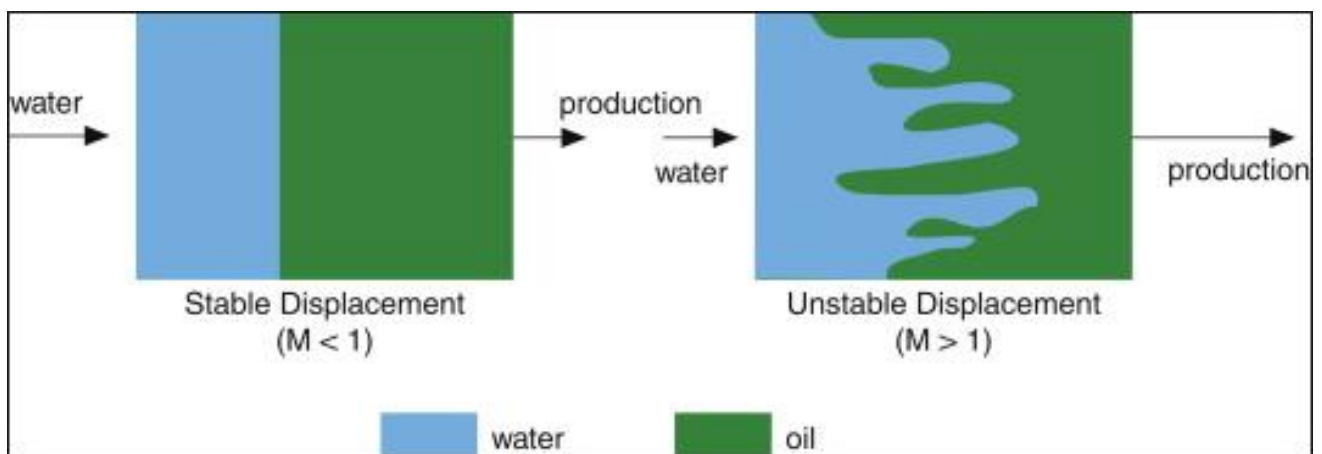
Figure 9. Displacement front at different mobility ratios *(Jahn, et al., 2008)*

2.2 POLYMER FLOODING

Polymers are used to overcome the problem of high mobility ratio by increasing the viscosity of displacing fluid. The decrease in the mobility ratio helps to improve sweep efficiency and increase oil production by providing a stable displacement flow. Mobility control at favorable conditions may significantly enhance the effectiveness of a combination between low salinity water and polymer. There are several proved experiments that showed a potential in hybrid polymer/ low salinity water injection to increase oil recovery. (Alsofi, et al., 2016; Almansour, et al., 2017)

Injection of polymer helps to increase the viscosity of displacing fluid and to decrease the mobility ratio. The problem with unfavorable mobility ratio can be solved using polymer flooding (Qi, et al., 2017). There are two types of polymer used for polymer flooding: synthetic polymer and biopolymer. Hydrolyzed polyacrylamide (HPAM) is a synthetic polymer that has been widely used in polymer flooding due to its highly productive and costly efficient properties. The chemical structure of HPAM is shown in Figure 10. However, this polymer is not stable under high temperature and high salinity conditions (Zhu, et al., 2013).

$$-[CH_2-CH]_x \, [CH_2-CH]_y-$$

with side groups $C=O$ and NH_2 on the x unit, and $C=O$ and O^-Na^+ on the y unit
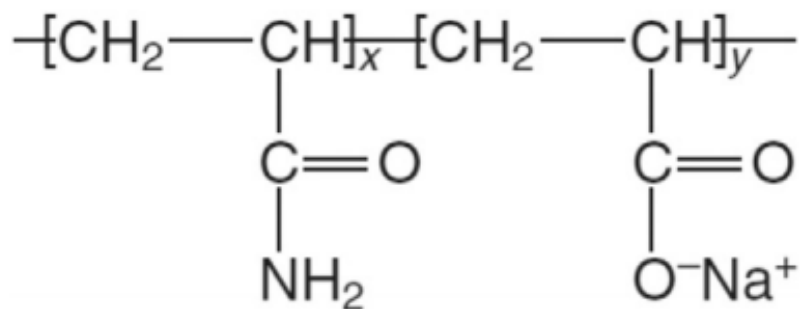
Figure 10. Chemical structure of HPAM polymer *(Choi, et al., 2014)*

At low salinity conditions, the repulsion of the negatively charged carboxylic groups stimulates the elongation of the polymer backbone chain. In addition, the repulsion between negatively charged anions increases as the degree of hydrolysis increases. Consequently, the fractional number of a carboxylic group within a polymer structure is directly proportional to the degree of hydrolysis and viscosity of polymer solution. This effect is more prominent with the increase of temperature, as the degree of hydrolysis increases at higher temperatures. During this reaction, amide groups convert to negatively charged carboxylic groups (Zaitoun & Potie, 1983). However, under high salinity conditions, the concentration of active cations such as Ca^{2+} and Mg^{2+} in water increases. Thus, it stimulates a higher affinity for the interaction with

the negatively charged carboxylic group. As a result, this interaction promotes a coiling effect on the polymer chain due to the attraction of positively and negatively charged ions (Dang, et al., 2015). This process is shown in Figure 11.
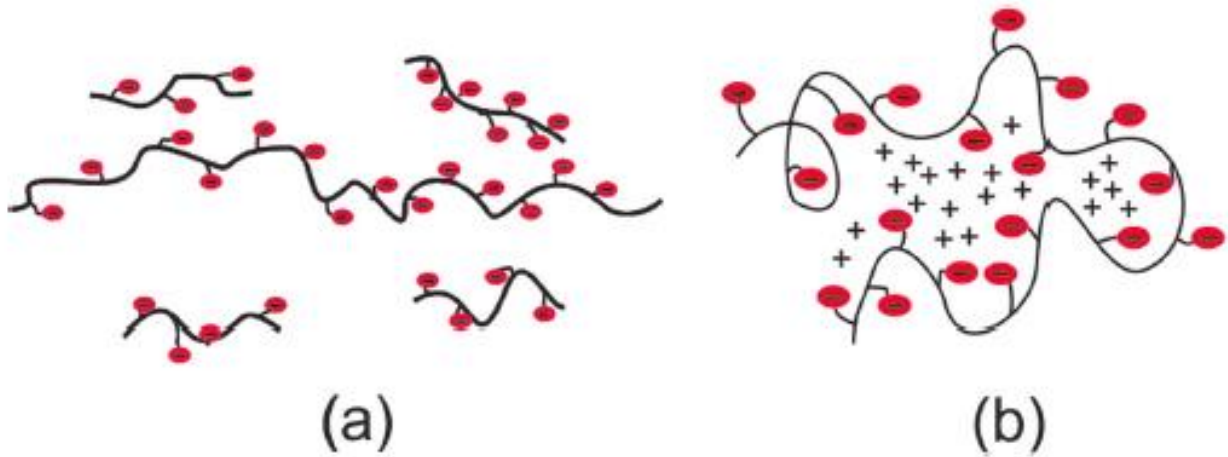
Figure 11. The polymer structure without (a) and with (b) the presence of divalent ions *(Rellegadla, et al., 2017)*

The high presence of these divalent ions is detrimental to polymer stability. Due to this strong interaction, the efficiency of polymer solution dramatically decreases, and the solution viscosity also reduces. There are many studies that investigated the effect of divalent ions on the polymer solution. The optimum concentration of divalent ions at which the viscosity of polymer remains unaffected is 200ppm (Ryles, 1988).

Another major disadvantage of HPAM polymer is its mechanical degradation. During the injection, the polymer passes a complex path through the pumps, chokes, and pipes until it reaches a near-wellbore zone and porous media. Thus, during this flow, HPAM-based polymers are subjected to withstand extensional and compressional stresses. This process leads to the excessive elongation of the polymer backbone chain. Consequently, as the shear rate increases, it results in the active deformation of polymer macromolecules, breaking the larger molecules into smaller parts (Noik, et al., 1995).

Moreover, polymer retention has a substantial impact on the technical and economic feasibility of polymer flooding projects. It may dramatically affect the rate of propagation of polymer and oil displacement through a porous medium. Green & Willhite (1998) conducted an experiment to study the effect of polymer retention on a delay factor for different polymer concentration to illustrate oil movement behavior. According to Figure 12, the polymer concentration of 200ppm and polymer retention of 15μg/g corresponds to the delay factor of 0.5. The delay

factor of 0.5 means that an additional 50% of polymer should be reinjected to restore initial concentration and reach the target location in a porous medium.
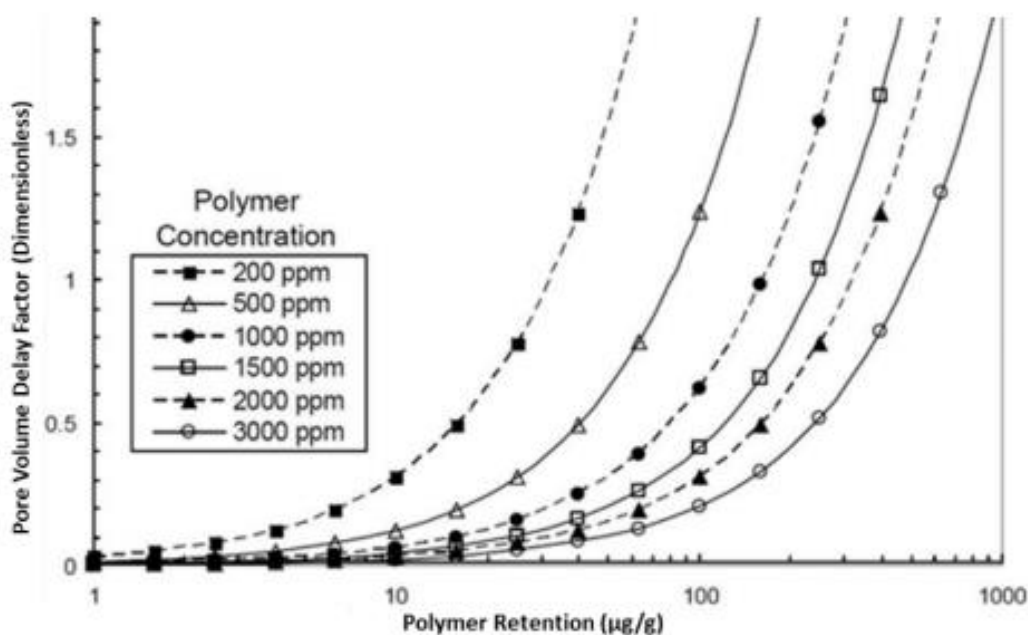
Figure 12. Delay factor caused by polymer retention under different concentrations *(Green & Willhite, 1998)*

Different mechanisms of polymer retention, such as adsorption, mechanical entrapment, and hydrodynamic retention, should be carefully evaluated for the design of a successful polymer project. These mechanisms are explained and illustrated in more detail in Figure 13.
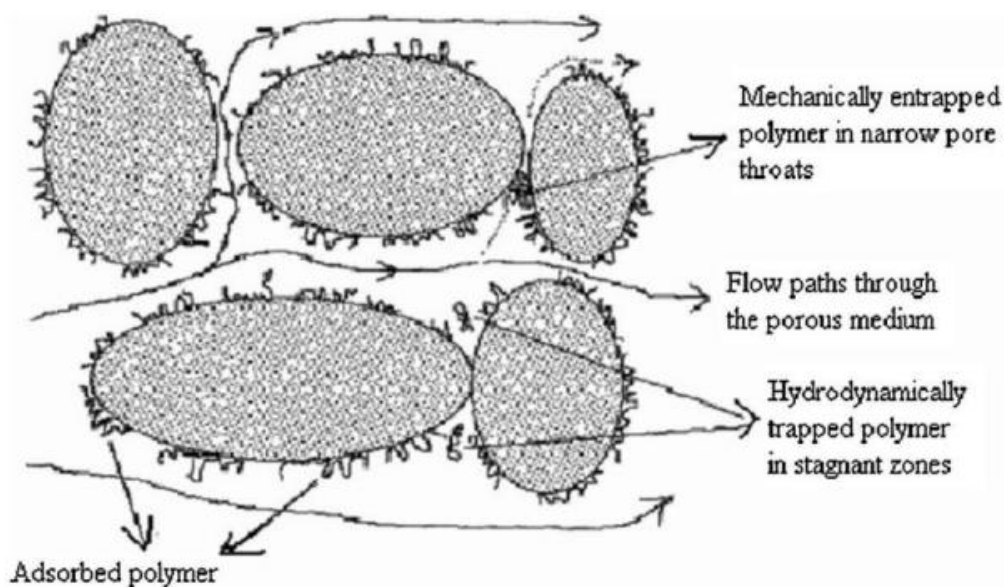
Figure 13. Polymer retention mechanisms *(Sorbie, 2013)*

There are many chemical and physical properties of injected agents and rock surface that affect polymer retention. Many laboratory studies reported the impact of polymer, fluid, and rock characteristics on the adsorption and retention capabilities of polymers. These factors are summarized in Figure 14.
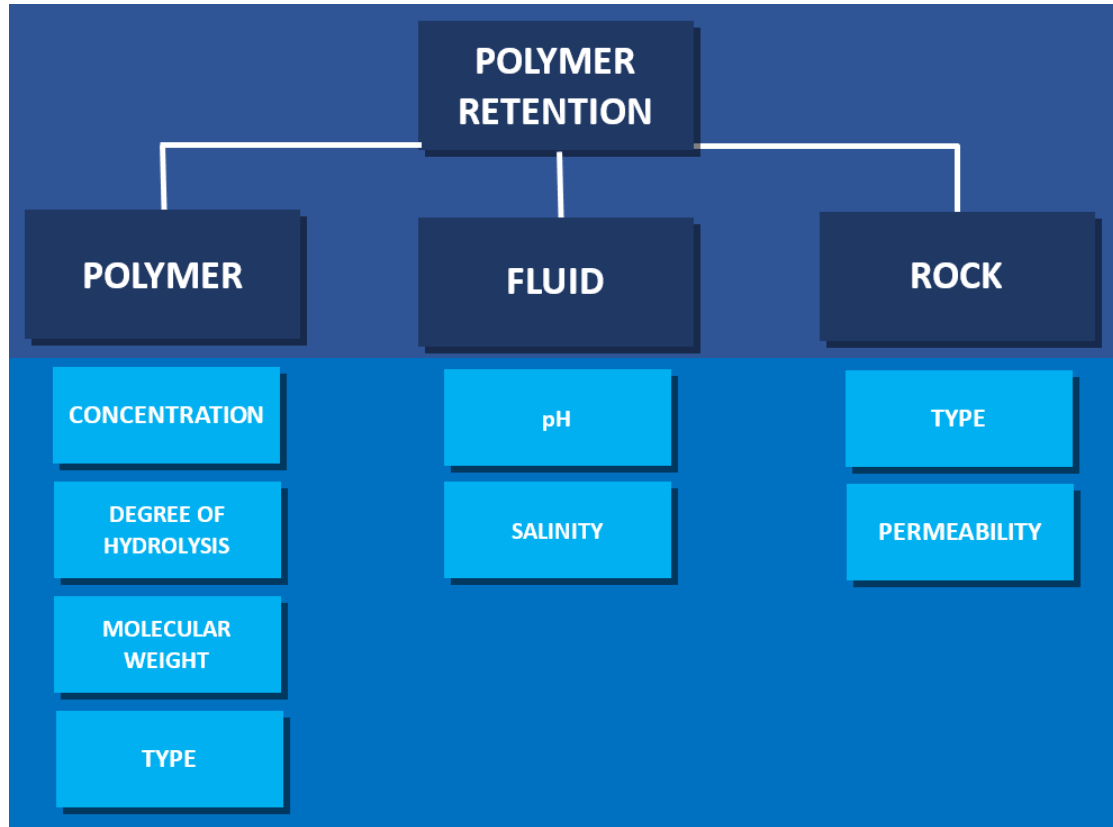
Figure 14. Factors that affect polymer retention

Szabo carried out an experiment on Berea sandstone cores to measure the retention factor for different types of polymers, including HPAM-based, bio, and other polymers. Biopolymers retained the lowest value of measured retention, followed by 2-acrylamido-2-methyl propane sulfonate (AMPS) and HPAM (Szabo, 1975). Figure 15 illustrates the difference in adsorption for different types of polymer.
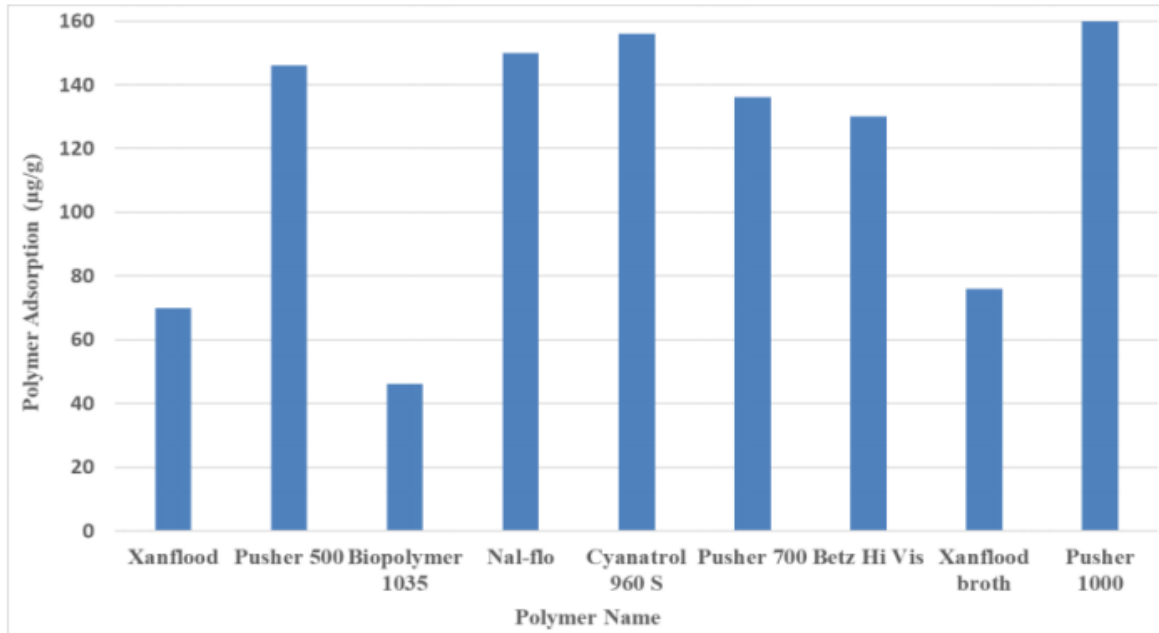
Figure 15. Polymer absorption as a function of the type of the polymer *(Szabo, 1975)*

Other extensive studies showed a straight dependence of polymer properties such as concentration, molecular weight and degree of hydrolysis on polymer retention (Green & Willhite, 1998; Huang & Sorbie, 1993; Zheng, et al., 1998; Rashidi, et al., 2009; Lakatos, et al., 1981). All these studies claimed that polymer retention increases with the increase of these fundamental features regardless of the polymer type. The results of the dependency of polymer adsorption on concentration are summarized in Table 1. The degree of hydrolysis is proportional to the temperature. Consequently, the increase of temperature increases the negative charge on the rock surface and degree of hydrolysis by converting amide groups to negatively charged carboxylic groups. As a result, the electrostatic repulsion between the carboxylic group and the rock surface leads to a decrease in polymer retention (Sheng, 2010).

Table 1. Polymer concentration effect on retention *(Al-Hajri, et al., 2018)*

Polymer Concentration (ppm)	Type of Polymer	Retention (µg/g)
10–6000	HPAM	20–420
20–1000	HPAM	21–30
250–1500	HPAM	40–58
50–200	Scleroglucan	8.2–11.7

Rock surface and its characteristics are other parameters that affect the disturbance of polymer behavior. HPAM absorption in carbonates is significantly higher than in sandstones due to the interactions between positively charged rock surface (Ca^{2+}) and negatively charged carboxylic group on a polymer backbone chain (Lakatos, et al., 1981). In addition, the wettability of the rock surface should be considered for a proper design of polymer flooding. Broseta and coworkers estimated through coreflooding experiments that the retention depends on the wettability of the system. The polymer flooding in the oil-wet system shows significantly lower retention values comparing to water-wet due to limited contact with the adsorbing oil surface (Broseta, et al., 1995).

In addition, reservoir intrinsic properties play a crucial role in polymer retention capability. The reservoir permeability should be examined foremost because these criteria cannot be regulated during the flow of fluids. For the benefit of polymer flooding, the pore size and permeability is a key factor for the economic success of the project due to the high cost of the polymer. These parameters should be sufficiently large in order to prevent pore blockage. Figure 16 represents how pore size and permeability can be reduced due to polymer retention. Polymer retention significantly increases with the decrease of pore size and permeability (Rellegadla, et al., 2017). Table 2 shows the variations of rock type and permeability on the retention.

Table 2. The dependency of rock type on retention *(Al-Hajri, et al., 2018)*.

Rock Type and Permeability	Polymer Type	Retention (µg/g)
Vosges sandstone 2100 md	HPAM	155
Vosges sandstone 520 md	HPAM	140
Reservoir sandstone 137 md	HPAM	12
Reservoir sandstone 12 md	HPAM	130
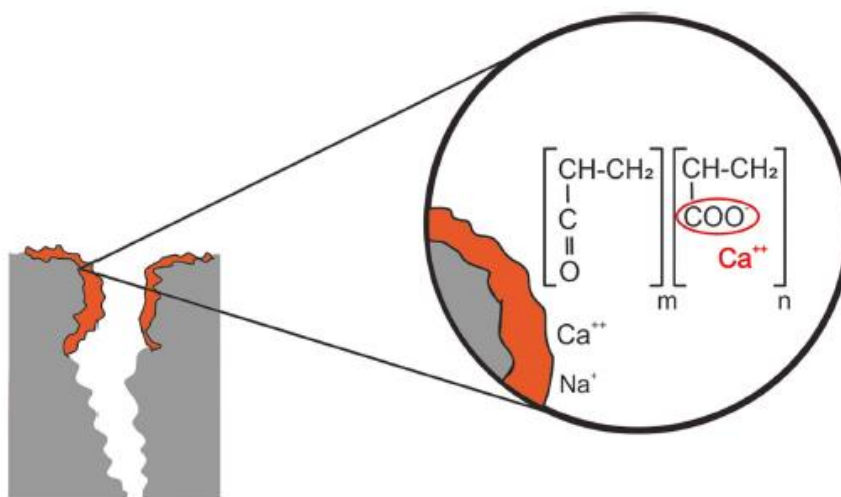
Figure 16. The effect of polymer retention on permeability *(Rellegadla, et al., 2017)*

The change in a flow rate may also contribute to the loss of polymer in a porous media, which results in polymer retention. This type of retention is called hydrodynamic retention (Manichand & Seright, 2014). Different studies on hydrodynamic retention evaluated the effect of flow rates on permeability change in porous media (Zhang, et al., 2015; Chen, et al., 2016). Chen, et al. (2016) performed comprehensive rheological studies in sandstone formations to evaluate the effect of retention at different injection rates. The results indicated a clear dependence of polymer retention with the increase of flow rate. The results of this experiment are shown in Figure 17.
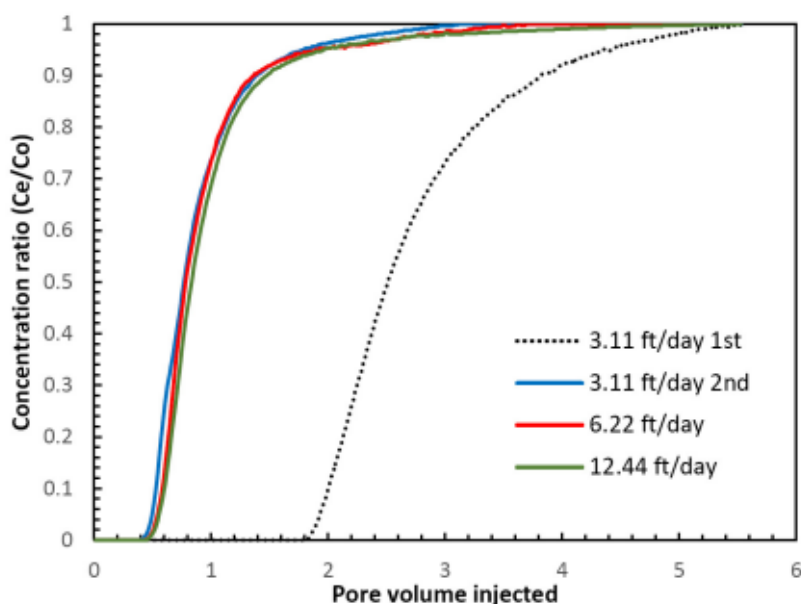
Figure 17. Flopaam 3230S breakout curves at different injection rates *(Chen, et al., 2016)*

pH and salinity play an important role in polymer behavior in terms of its retention capability and viscoelastic properties. For instance, under acidic conditions, the rock surface becomes more positive, and it may attract anionic parts of polymer which can further strongly absorb on the surface of rocks. In addition, the change in water salinity level disturbs the charge of the rock surface (Aronofsky, 1952). Generally, divalent ions such as Ca^{2+} and Mg^{2+} facilitate the interaction between the polymer and rock surface and increases absorption under high-salinity conditions. This absorption dramatically impacts the ability of the fluids to flow through a porous media due to the blockage of the pores and causes a loss of polymer, respectively. This process is shown in Figure 18.
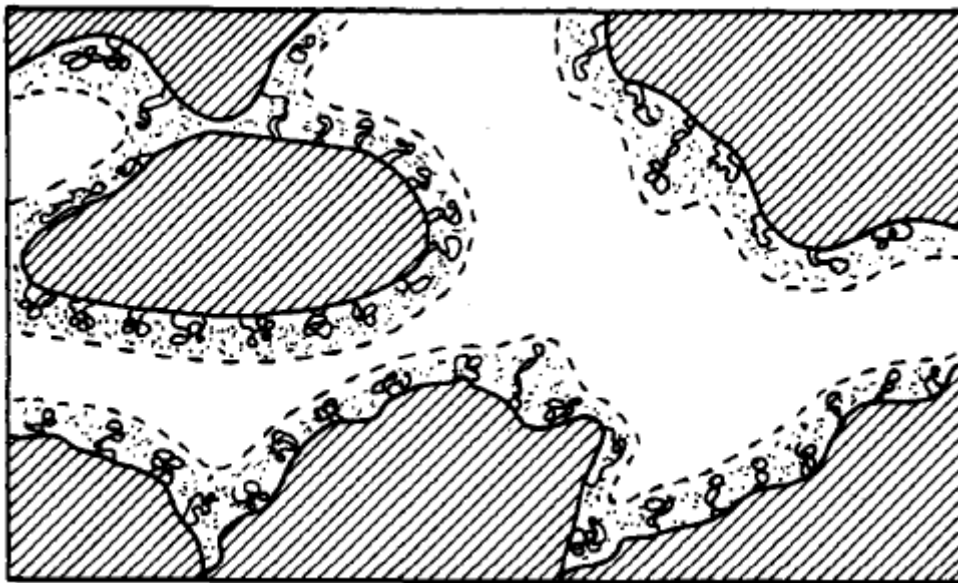
Figure 18. The absorption of polymer that reduces the diameter of pore size *(Litmann, 1988)*.

2.3 LABORATORY STUDIES ON THE SYNERGY OF LOW SALINITY WATER AND POLYMER FLOODING

Due to the nature of polymers, most commonly used polymers behave as non-Newtonian fluids because of their reduction in viscosity with increasing shear rate (Zhao, et al., 2018). Consequently, it is essential to achieve the optimum range of polymer viscosity with a preferable mobility ratio. Mobility control at favorable conditions may significantly improve the effectiveness of low salinity water injection. Therefore, the combination of low salinity water injection and polymer flooding is key to obtain the highest oil recovery from the reservoirs. Different studies have already investigated the potential of this combination.

Shiran and Skauge (2013) conducted an experiment on Berea and Bentheimer core plugs to investigate the positive effect of the synergy of low salinity water injection and polymer flooding. Results showed an enhancement of oil recovery after low salinity water injection in both cores. After conventional water flooding, followed by low salinity water injection, the oil recovery factor was increased by 2-5%. However, incremental oil recovery was obtained after the addition of polymer. The recovery factor was increased by 10% even at a low concentration of polymers during a secondary mode of low salinity water injection and polymer flooding. In addition, cores with initial intermediate wetting state showed a higher response on oil recovery comparing to water-wet cores. The results of their experiments are shown in Figure 19.
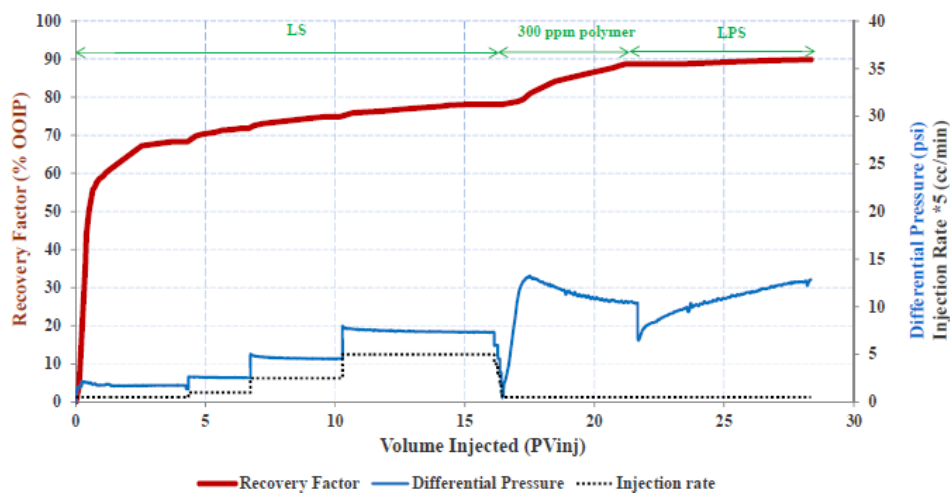
Figure 19. The oil recovery and differential pressure curve at a secondary mode of low salinity water injection
(Shiran & Skauge, 2013)

Also, Almansour, et al. (2017) confirmed the results obtained from previous studies by comparing two sandstones with the intermediate and water wet states to observe the wettability effect on oil recovery. The highest oil recovery was obtained for Berea sandstone with intermediate water-wetness of the system. The obtained results of this experiment are shown in Figure 20.
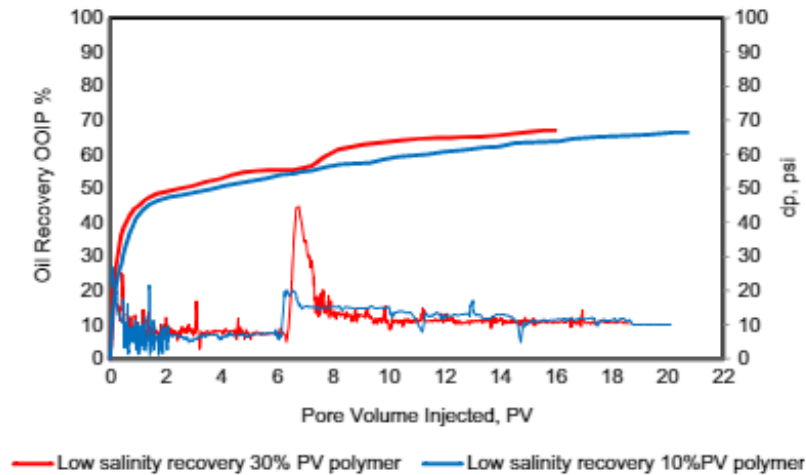
Figure 20. Oil recovery and differential pressure curve at different polymer slug concentrations *(Almansour, et al., 2017)*

In another study, the potential effect of the synergy of low salinity water injection and polymer flooding was analyzed in Bentheimer core plugs by optimizing and diluting brine composition (Tahir, et al., 2018). Ten times diluted seawater, and even a small concentration of polymer solution (500ppm) showed a significant enhancement in oil recovery under different injection modes. The results of this study are shown in Figure 21.
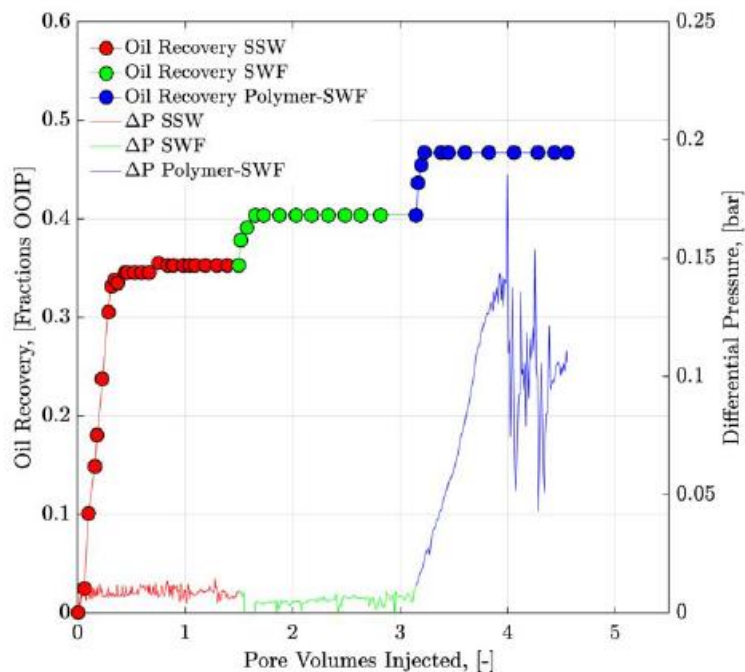
Figure 21. Oil recovery and differential pressure under different injection stages *(Tahir, et al., 2018)*

Alsofi, et al. (2016) investigated the combination of low salinity water and polymer flooding in a slightly viscous crude oil in a carbonate reservoir. The authors reported additional oil

recovery when they either combined or applied both methods independently. The effect of the synergy of low salinity water injection and polymer flooding was undeniable due to more than 10% in oil recovery. The results of this experiment are shown in Figure 22.
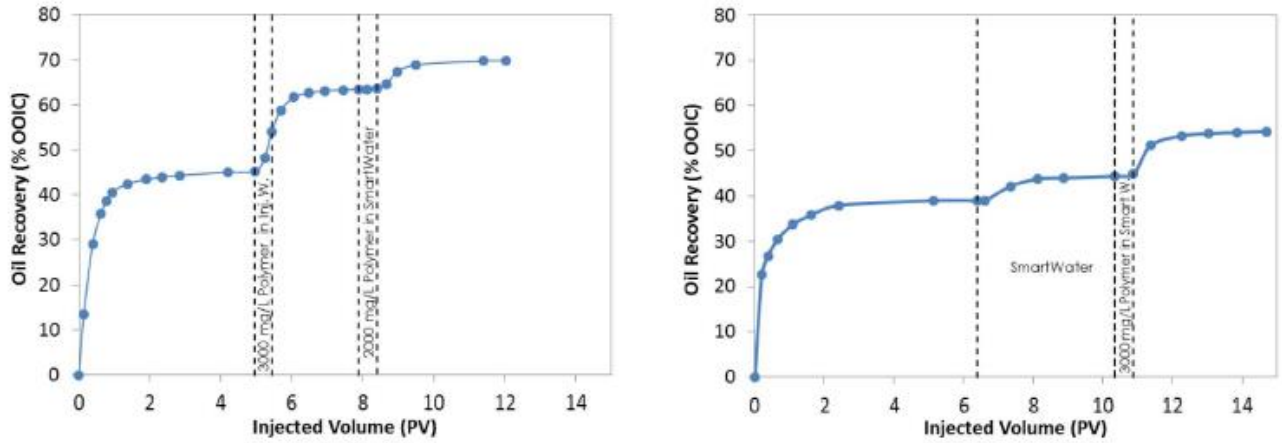
Figure 22. Oil recovery versus pore volume injected under different injection stages *(Alsofi, et al., 2016)*

Pinerez Torrijos, et al. (2016) performed the experiment, which showed the impact of low salinity water injection on polymer flooding. In their study, they conducted a core flooding experiment in sandstone cores to confirm a positive effect between low salinity water injection and polymer flooding. Figure 23 shows that the ultimate recovery was obtained at 86% and an additional 20% in oil recovery after polymer flooding in tertiary mode.
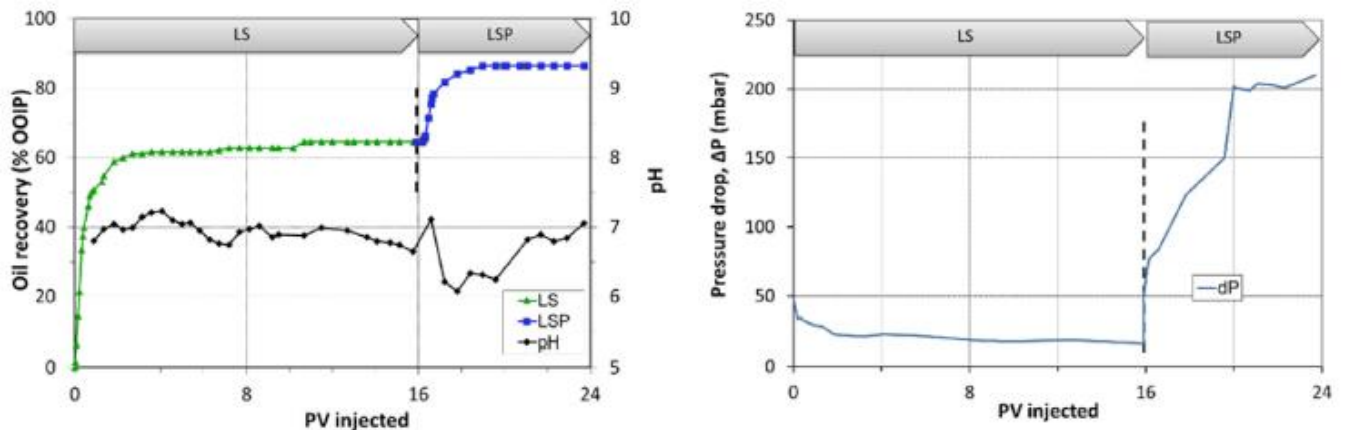
Figure 23. Oil recovery and pH versus pore volume injected under different injection stages *(Pinerez Torrijos, et al., 2016)*

Recent studies on the synergy of low salinity water and polymer flooding also have shown a positive response in terms of oil recovery. Moghadasi, et al. (2019) conducted comprehensive research on mixed-wet sandstone core plugs at 76ºC and 90ºC to investigate the effect of the combination of these EOR techniques. In their experiment, polymer compatibility (Flopaam

5205 SH) was initially evaluated on different screening parameters such as concentration, salinity, temperature, mechanical degradation, and adsorption. This step was performed to observe polymer properties and their compatibility with low salinity water under reservoir conditions. Then, the coreflooding experiment was conducted to estimate the potential increase in oil production. According to the results of the coreflooding experiment, in Figure 24 and Figure 25, low salinity-polymer water flooding improved the oil recovery by 8%.
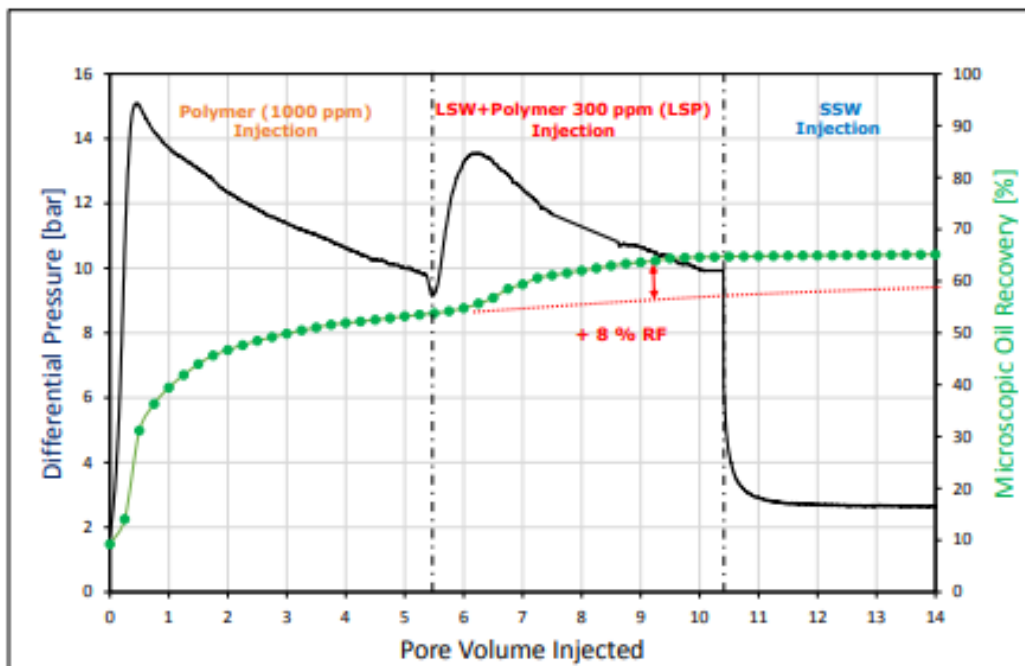
Figure 24. Oil recovery and differential pressure vs pore volume injected at 76 ºC(*(Moghadasi, et al., 2019)*
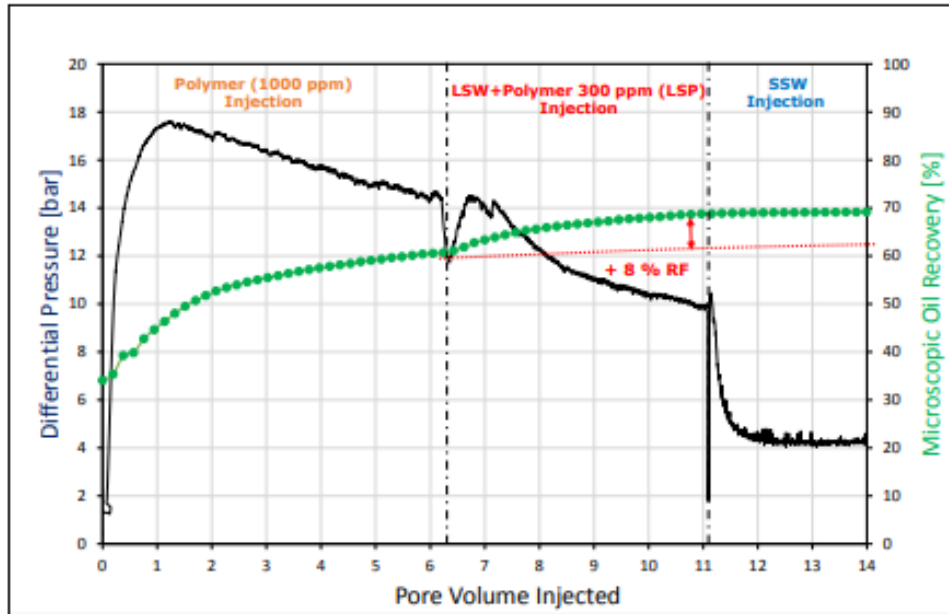
Figure 25. Oil recovery and differential pressure vs pore volume injected at 90 ºC *(Moghadasi, et al., 2019)*

Al-Murayri, et al. (2019) investigated the feasibility of low salinity water and polymer flooding in carbonate rock under harsh reservoir conditions such as low permeability(10mD), high temperature(>100ºC), high salinity(239000ppm). Firstly, the thermal and chemical stability of the polymer (SAV10) was evaluated to obtain the desired concentration and viscosity for injectivity experiments. Despite the abovementioned challenging conditions, coreflooding tests showed promising results in terms of oil recovery for hybrid low salinity/polymer flooding. According to Figure 26, an 11% increase in OOIP has been observed in this experiment.
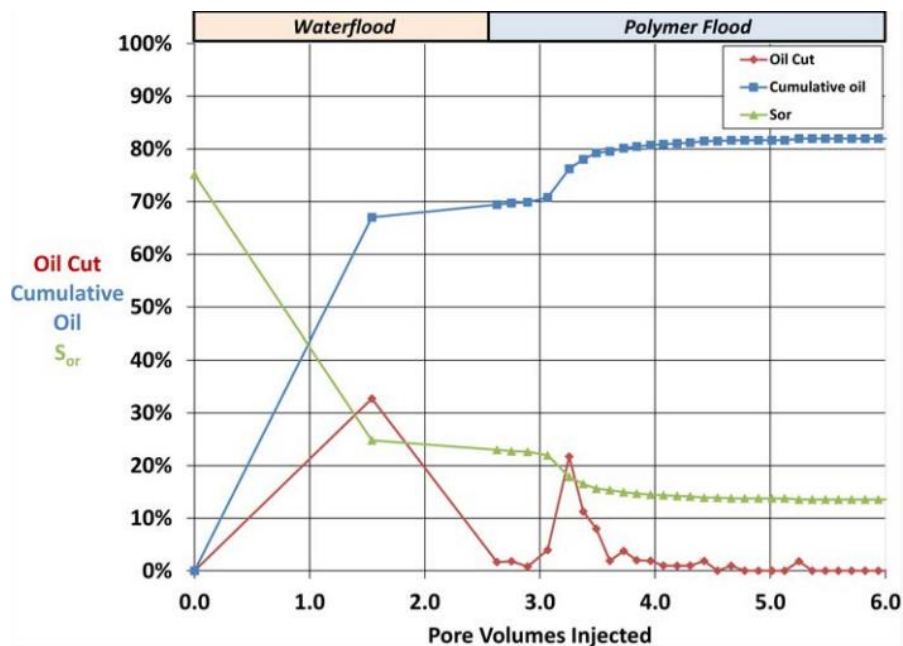
Figure 26. Cumulative Oil, Oil Cut, and Oil Saturation vs pore volume injected *(Al-Murayri, et al., 2019)*

Lee, et al. (2019) conducted an experiment to design appropriate composition of low salinity for the synergy with the polymer in carbonate reservoirs. The purpose of the experiment was to determine suitable pH and concentration of ions (SO_4^{2-} and Ca^{2+}) in injection water that would not disturb the stability of the polymer. The stability of polymer and its retention for different water samples was investigated through contact angle and coreflooding experiments. Based on the results (Figure 27), the highest oil recovery was obtained in neutral water solution (pH=7) with the highest concentration of SO_4^{2-} (4000ppm).
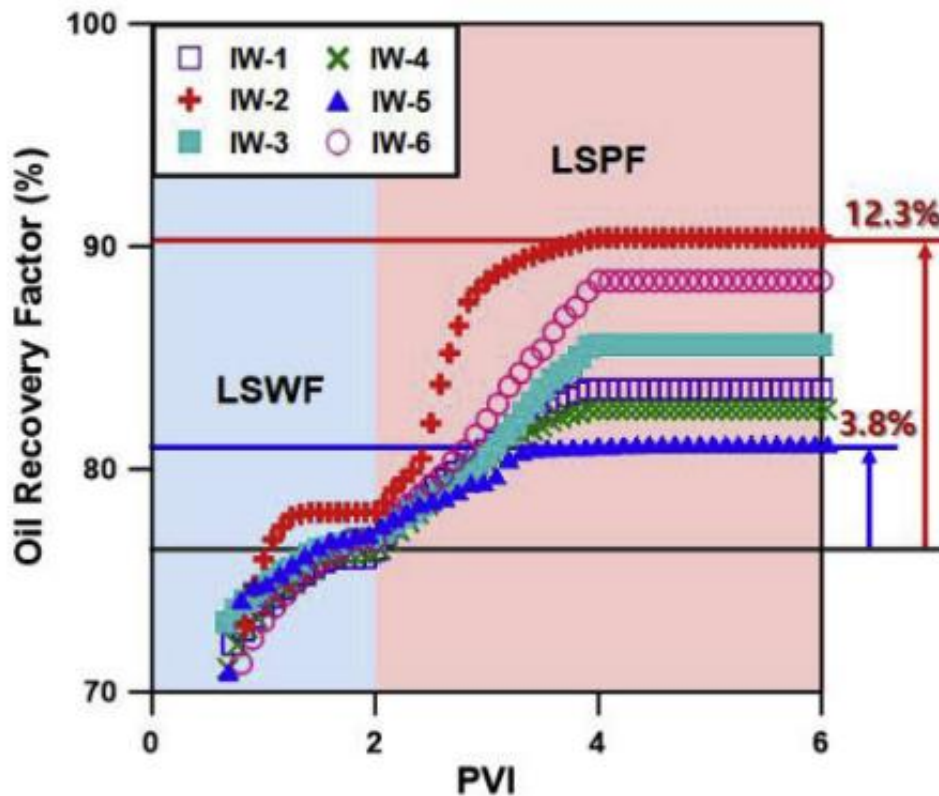
Figure 27. Oil recovery vs pore volume injected for different water solutions *(Lee, et al., 2019)*

Also, some simulation methods have been developed to investigate the impact of the combined polymer-low salinity water flooding process. Different simulation models were designed to compare the effect of water composition under a different range of salinities with polymer flooding. Figure 28 clearly indicates that the oil recovery significantly increased for more than 20% for all reservoir models from 1000ppm to 30000ppm water salinity levels (Santo & Muggeidge, 2018).
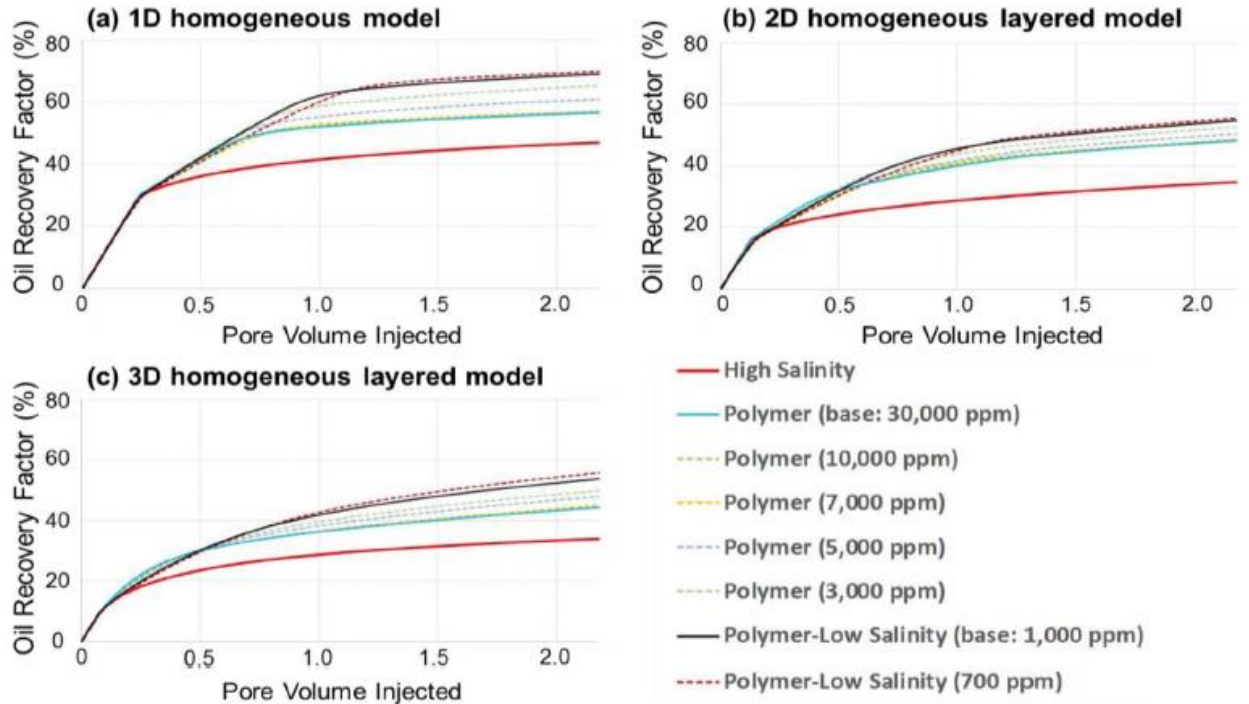
Figure 28. Effect of different water salinity levels on combined low-salinity water injection and polymer flooding *(Santo & Muggeidge, 2018)*

However, some studies did not show a positive response to the synergy of low salinity water injection and polymer flooding. Alfazazi, et al. (2018) showed no positive response on oil recovery for low salinity water injection, and only the injection of the polymer showed a higher production of oil. The injection of low salinity water (20000ppm) prior to polymer flooding helped to increase oil recovery by 8%. Figure 29 shows the results from the core flooding experiment at different stages of injections. Thus, it was suggested that low salinity water could be used as a preconditioning method in high-temperature and high salinity reservoirs. The main objective of preconditioning is to decrease the initial salinity of water to maximize the potential of polymer flooding because polymers could not operate under harsh conditions.
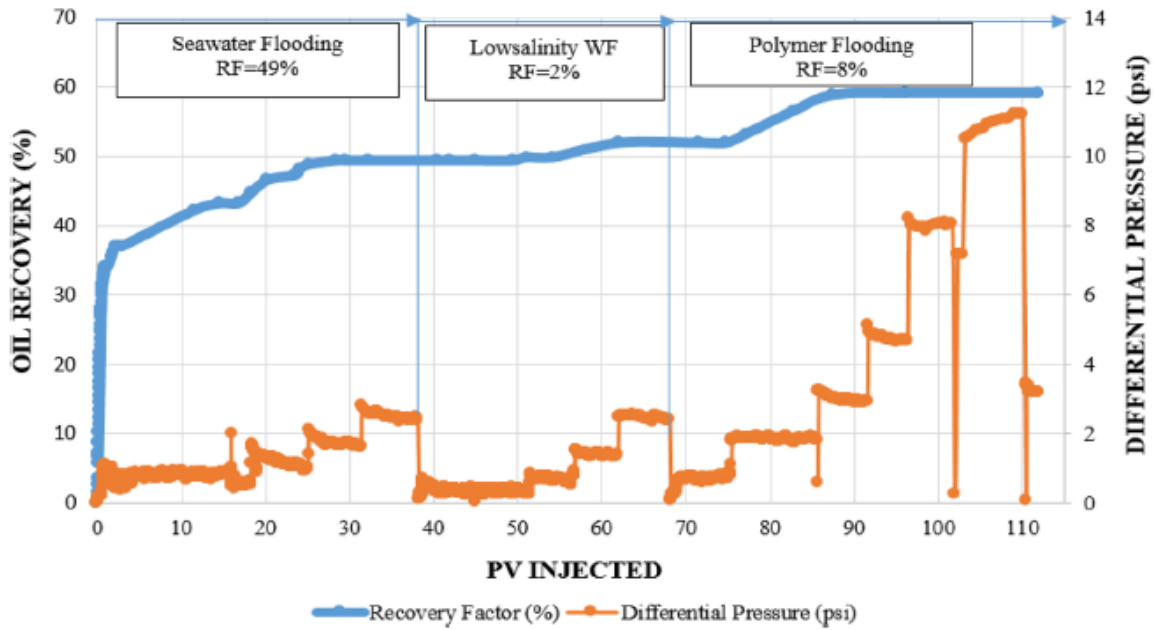
Figure 29. Oil recovery and differential pressure under different injection stages *(Alfazazi, et al., 2018)*

2.4 POTENTIAL SYNERGY OF LOW SALINITY WATER WITH DIFFERENT IOR PROCESSES

The effect of low salinity water injection on oil recovery has been investigated due to its highly efficient productivity and low operational costs. Furthermore, the studies on low salinity water were extended towards the potential synergy of low salinity water with different IOR processes. The potential combination of low salinity water with different IOR techniques such as a polymer, surfactant, and CO_2 allows to combine the effect of these processes for the improvement of both methods. Figure 30 summarizes the current applications and combined effects of low salinity water with different IOR techniques.
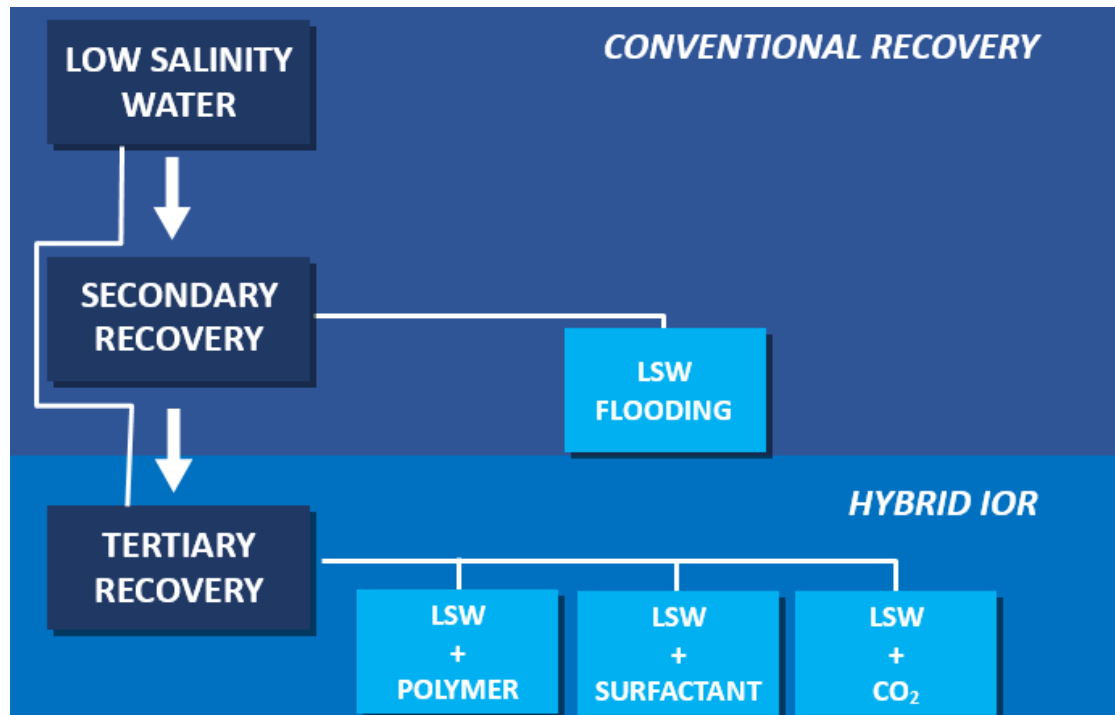
Figure 30. Applications of low salinity water in different stages of oil recovery

Different laboratory experiments evaluated the performance of the synergy between low salinity water and polymer flooding. Most of these experiments focused on analyzing the benefits of this combination in terms of oil recovery. The increase in oil recovery in the range of 5-10% OOIP has been observed (Ayirala, et al., 2010; Kozaki, 2012). In addition, low salinity water, in combination with polymer, has a pronounced effect on the viscoelastic properties of the polymer. Low salinity water provides additional higher thermal and mechanical stability. As a result, it significantly improves project economics due to lower polymer consumption (Vermolen, et al., 2014).

The combination of low salinity water with surfactant also shows auspicious results in terms of oil recovery. Surfactants play an important role in this synergy as they allow to decrease the capillary forces and interfacial tension in the oil/water system. Spildo, et al. (2012) became the pioneers who examined the potential synergy between low salinity water and surfactant. The results of the experiment (Figure 31) have shown an additional 12% OOIP and low surfactant retention at intermediate wet conditions on Berea sandstone cores.
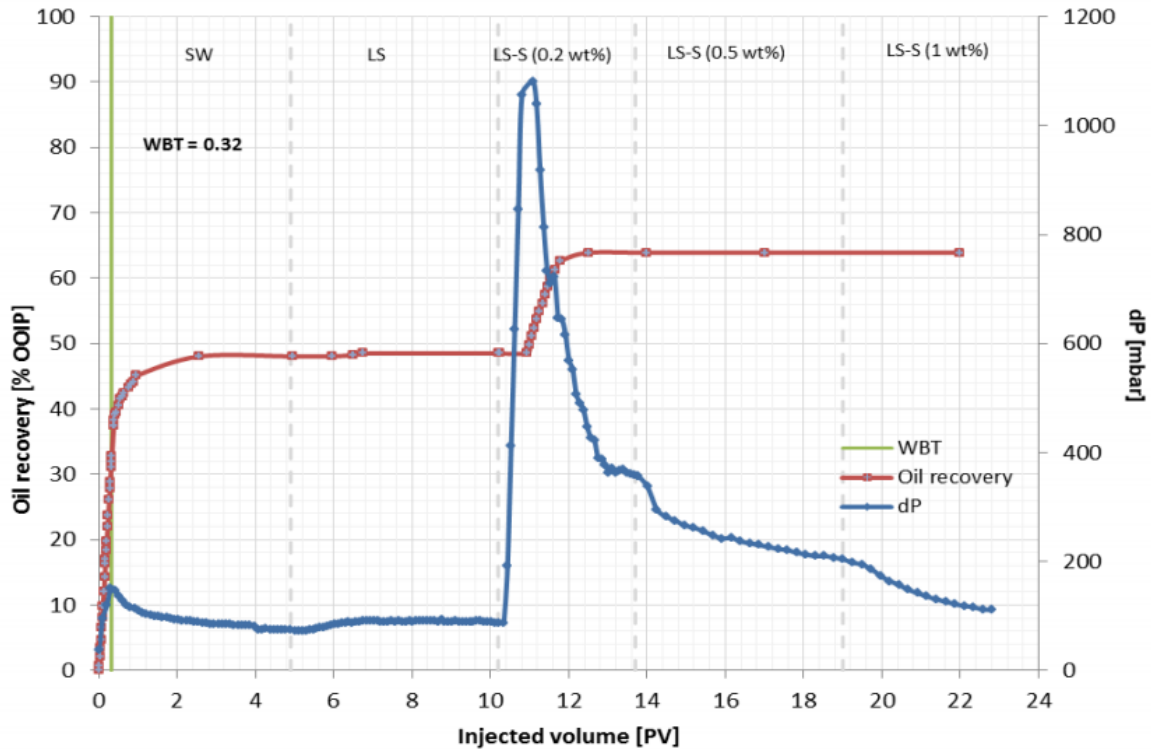
Figure 31. Oil recovery and pressure drop vs pore volume injected *(Spildo, et al., 2012)*

The combination of CO_2 and water plays a vital role during the water alternating gas (WAG) process. In this process, the water flooding followed by CO_2 injection helps to mobilize bypassed oil after CO_2 slug (Aleidan & Mamora, 2010). Therefore, the fluid and rock properties, as well as WAG parameters such as time of injection, fluid/gas ratio, significantly affect the level of residual oil saturation and oil recovery, respectively. Another critical parameter in the WAG process is the solubility of CO_2 in water. The solubility of CO_2 increases with the decrease in the salinity level. Figure 32 represents the relationship between CO_2 solubility and water salinity level.
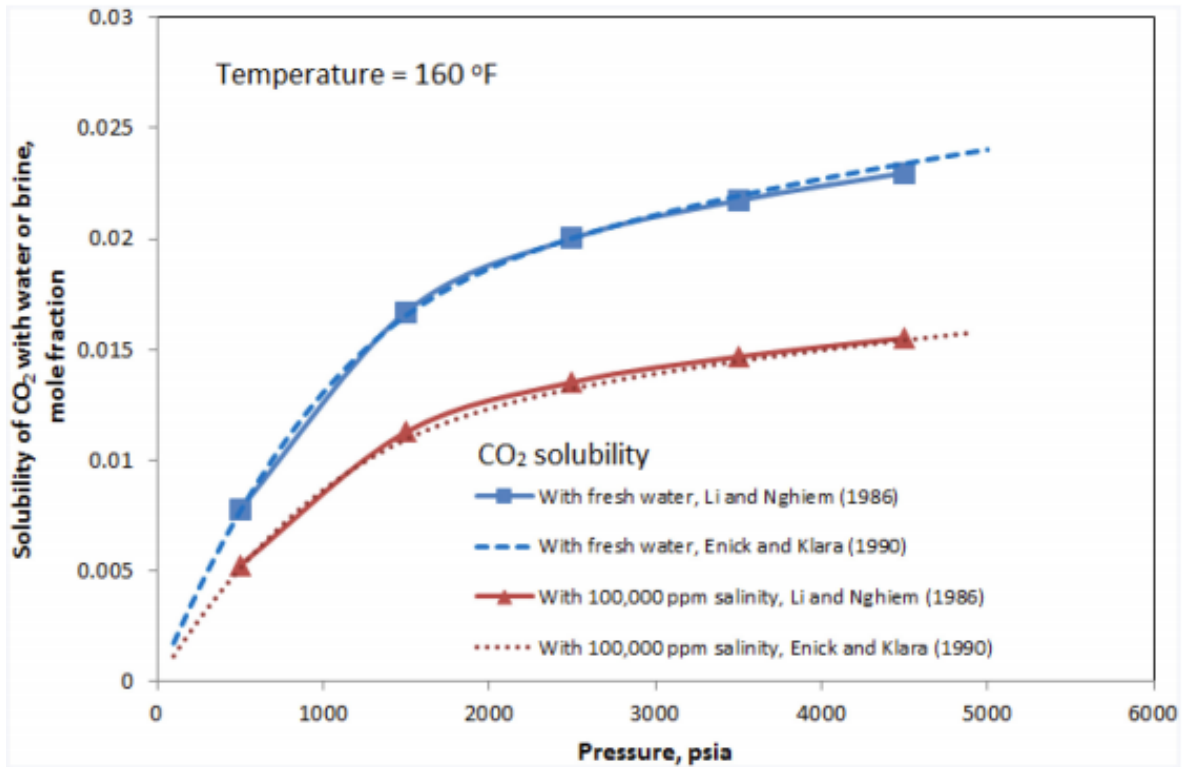
Figure 32. The solubility of CO_2 in fresh and 100000ppm salinity brine *(Teklu, et al., 2014)*

Therefore, a new hybrid EOR method, which involves the combination of low salinity water and water alternating CO_2 gas, was proposed to combine the effect of both methods (Aleidan & Mamora, 2010). In addition, Teklu, et al. (2014) also investigated the combined effect of low salinity water and CO2 on the rock, fluid, and gas properties by performing IFT, contact angle, and injectivity experiments. Based on their experiments, the hybrid low-salinity-water-alternate-CO_2 gas (LS-WAG) technique was proposed to be an effective technique in terms of oil recovery and optimized sweep efficiency. The results of coreflooding experiments, in Figure 33, showed a dramatic increase in OOIP(55%) after the addition of low salinity water in secondary mode followed by CO_2 gas injection in tertiary mode.
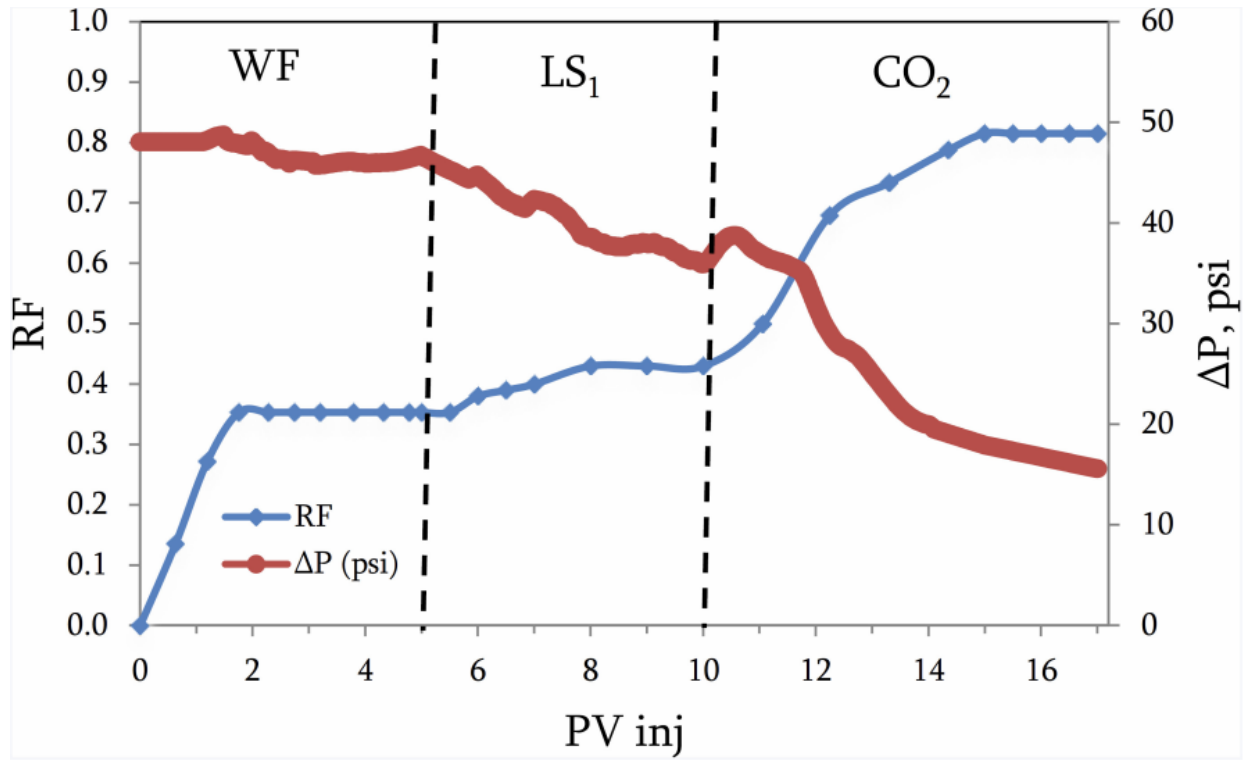
Figure 33. Oil recovery and pressure drop vs pore volume injected *(Teklu, et al., 2014)*

3. PROJECT PLAN

3.1 PROJECT SCHEDULE

The thesis schedule was created to control the progress and to monitor the activities until the end of the project.
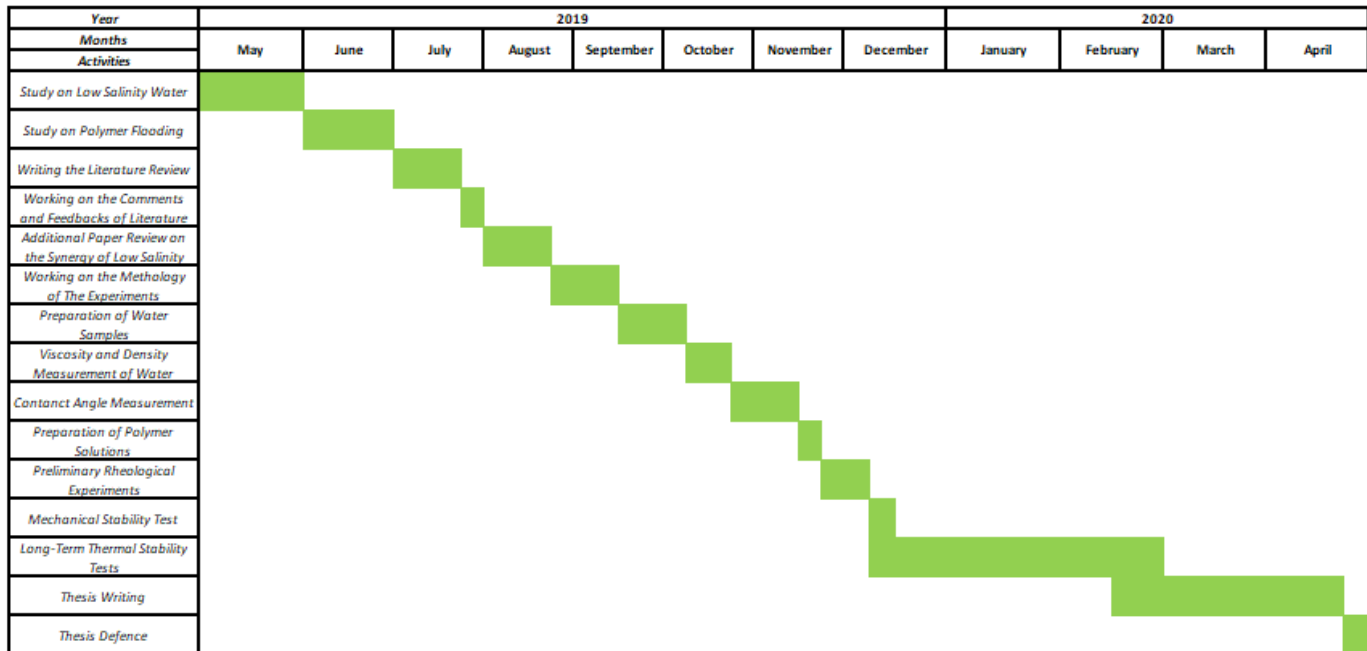
Figure 34. Thesis schedule

3.2 RESOURCE REQUIREMENTS

The essential materials for successful project completion are shows in Table 3.

Table 3. Required resources

Device/material	Function
Laptop	My own laptop or PC from 4.322 was used to write the thesis
OCA 15EC	To perform contact angle measurements
Viscometer	To perform the measurement of fluid properties
Rheometer	To perform rheological experiments on polymer solutions
Printer	To print out needed materials
Access to the internet	To read and to download the articles related to my work

3.3 RISK MANAGEMENT

Risk management is a tool that is needed to monitor the probability of failure. The risk of failure could be avoided through a proper plan to achieve the expected results. Therefore, the risk mitigation plan was established to monitor the possible risks and ways to control them. WRAC analysis that consists of 5x5 likelihood-consequence matrix is one of the common risk assessment tools. Table 4 demonstrates the risk ranking matrix for different cases.

Table 4. Risk ranking matrix

Risk matrix		Consequence						Risk rating	
		Negligible	Minor	Moderate	Major	Catastrophic			
Likelihood		1	2	3	4	5		Risk rating	
Almost certain	5	6	7	8	9	10		Extreme	≥ 8
Likely	4	5	6	7	8	9		High	7
Possible	3	4	5	6	7	8		Medium	5-6
Unlikely	2	3	4	5	6	7		Low	≤ 4
Very unlikely	1	2	3	4	5	6			

3.3.1 Physical hazards

A physical hazard is one of the ways that may threaten mental or physical conditions with no physical contact. Potential physical hazards that can happen during this project and the ways to control them are demonstrated in Table 5.

Table 5. Physical hazards

Physical Hazard	Description	Risk rating	Risk Control
Eye-strain	Fatigue of the eyes due to the prolonged presence in front of the computer screen	7 High	Regular exercise for eyes, frequent breaks while using the computer
Injury during physical activities in the gym	Injuries from lifting heavyweights	7 High	An accurate and proper technique during the heavy weight lifting, training under the supervision
Mental stress	Frustration and stress from the overwork	5 Medium	Good time management and balance between study and relax
Illness	Disease from mild colds to flu	5 Medium	Proper medical treatment and sustain immunity of the body

3.3.2 Project hazard

Project hazard is the term that defines the features that may impact the provision of the thesis on a long time scale due to unforeseen circumstances. The list of project hazards is described in Table 6.

Table 6. Project hazards

Project hazard	Description	Risk level / rating	Risk control
Unexpected computer or software crash	Sudden failure of computer	3 Low	Proper maintenance of the computer
Document loss	The loss of files due to sudden computer crash	5 Medium	Constant control of antivirus software, use of cloud services
Change of thesis supervisor or topic	Unexpected conditions that lead to the inability of the supervisor to monitor the student's progress	5 Medium	Be in touch with other faculty members who are competent with the thesis topic
Problem with the equipment	Sudden breakage of viscometer or rheometer	5 Medium	Work with other suitable equipment

4. METHODOLOGY

Different laboratory experiments have been conducted to achieve research objectives. The combination of low salinity water and polymer flooding requires comprehensive laboratory studies to ensure effective synergy between these techniques. The primary purpose was to find the optimum concentration of active ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} in Caspian Seawater that will show the best results in terms of wettability alteration. Also, this Smart Water composition should not disturb the polymer stability under reservoir conditions. Furthermore, different polymer solutions were examined on different screening parameters such as temperature, concentration, thermal, and mechanical degradations. These rheological experiments allowed to find the most stable polymer with the highest viscosity at the lowest concentration under high salinity, high-temperature conditions. Based on these criteria, the best suitable polymer was chosen for the potential synergy with Smart Water. Thus, the results from contact angle measurement and polymer screening tests would be combined to find the most suitable polymer solution for further investigation. The target viscosity of 4cP was determined for effective sweep efficiency in this hybrid method. The following steps were suggested to obtain my thesis objectives and to ensure the efficiency of hybrid EOR method for oil recovery enhancement:

- the effect of salinity of different diluted Caspian Seawater samples on density and viscosity at different temperatures was evaluated using a viscometer.

- performance and effect of active ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} in Caspian Sea water was investigated through contact angle measurements

- based on contact angle measurements, the Smart Water sample with an adjusted concentration of active ions that showed the highest tendency to water wetness was determined

- different rheological experiments helped to select the most suitable polymer that is less sensitive to chemical and mechanical degradation

- the target viscosity of 4cP was obtained with Smart Water composition with the best wettability alteration effect and the most stable polymer under reservoir conditions

More detailed information about the materials and procedure steps is provided in the subsections below.

4.1 MATERIALS

This section provides information about the materials used in this study, including Caspian Sea water, HPAM based polymers, and carbonate outcrop core samples.

4.1.1 Core Sample

An outcrop core sample, which was carbonate in nature (Indiana), was used for contact angle measurements. Figure 35 shows the disks of the core sample used for the experiments.

Figure 35. Core sample used for contact angle measurements

4.1.2 Brine

The water composition of the Caspian Sea was synthesized to imitate the condition of the typical injection water to Kazakhstani fields (Tuzhilkin, et al., 2005). Formation water was prepared based on the data from Tengiz oilfield (Isabaev, et al., 2015). Table 7 shows the chemical water composition of the Caspian Sea with dilutions, and Table 8 represents the mass of chemicals required to prepare these solutions.

Table 7. Chemical composition of the water used in the experiments

Ions (ppm)	Caspian Sea	2x	5x	10x	20x
Na	3240	1620	648	324	162
Ca	350	175	70	35	18
Mg	740	370	148	74	37
Cl	5440	2720	1088	544	272
SO_4	3010	1505	602	301	151
HCO3	220	110	44	22	11
Total	13000	6500	2600	1300	650

Table 8. Mass of salts needed to prepare different water compositions

Salts	Formation brine (FW) g/L	Caspian Sea Water (SW) g/L	0.5*SW g/L	0.2*SW g/L	0.1*SW g/L	0.05*SW g/L
NaCl	207.42	4.36	2.18	0.872	0.436	0.218
Na₂SO₄	-	4.45	2.225	0.89	0.445	0.2225
CaCl₂.2H₂O	34.98	1.28	0.64	0.256	0.128	0.064
MgCl₂.6H₂O	12.28	6.18	3.09	1.236	0.618	0.309
KCl	1.32	-	-	-	-	-

4.1.3 Polymers

Four HPAM-based polymers were used in this work. These polymers were provided in a powder form by SNF Floerger. The chemical characteristics of each polymer are shown in Table 9. Flopaam 3330S belong to standard polyacrylamide polymers, which are suitable for reservoir temperatures up to 70 ᵒC, and water salinity of 35000 ppm. The other polymers, i.e., Flopaam AN113, Flopaam 5205, Flopaam 5115, are sulfonated HPAM-based polymers. Therefore, they are less sensitive to temperature, salinity, and divalent ion concentrations. The chemical structures of simple polyacrylamide and sulfonated polyacrylamide polymers are shown in Figure 36.
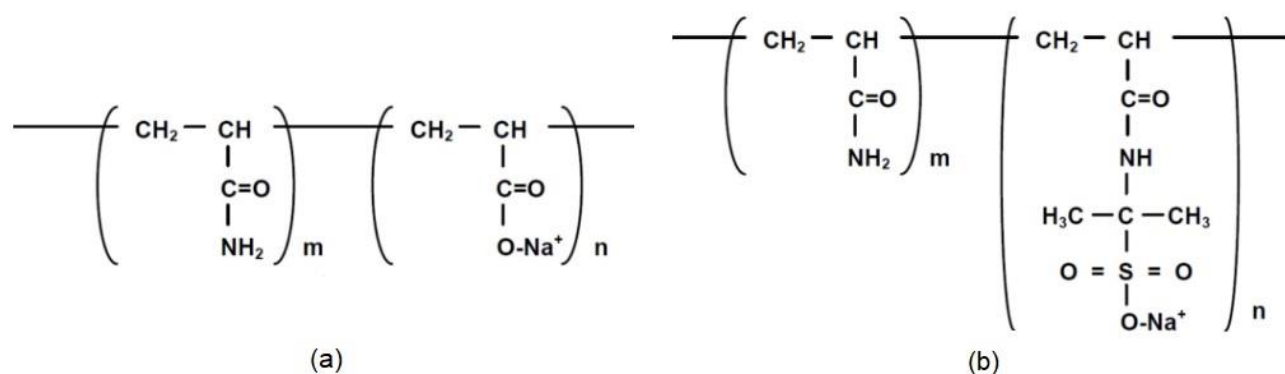
Figure 36. The chemical structures of polymers. (a) HPAM, hydrolyzed polyacrylamide; (b) AMPS, 2-acrylamido-2methylpropane sulfonated polymer *(Chen, 2016)*

Table 9. Chemical properties of polymers used in the experiment

	Flopaam 3330S	Flopaam 5205	Flopaam 5115	Flopaam AN113
Chemistry	Acrylamide/Acrylate	Acrylamide/ATBS/Acrylic acid	Acrylamide/ATBS/Acrylic acid	ATBS/Acrylic acid
Anniocity	Medium to High	Medium	Medium	Low
Molecular Weight	Low	Medium	Medium	Low

4.2 PROCEDURE

4.2.1 Brine and Polymer Preparation

Water composition for the middle part of the Caspian Sea region was synthesized in the laboratory as the base water to represent the injection water to oil fields in Kazakhstan. Formation and Caspian Sea water compositions were prepared by adding and mixing the required amount of different salts such as NaCl, Na_2SO_4, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$. After the preparation of base brine, the synthetic water composition of the Caspian Sea was diluted two, five, ten, and twenty times in order to decrease salinity level in initial water composition.

Then, the compatibility of the modified seawater with different polymer solutions was investigated. Initially, recommended API standard procedure for laboratory polymer preparation was used (Skauge, et al., 2014). The details on polymer solution preparation are clearly illustrated in Figure 37. According to Table 10, the specified amount of polymer, based on the concentration, was weighted.

Table 10. Mass of polymer needed for polymer preparation

Concentration of polymer	500ppm	1000ppm	1500ppm	2000ppm	2500ppm	3000pppm
Mass of polymer	0.1g	0.2g	0.3g	0.4g	0.5g	0.6g
Volume of water	200mL	200mL	200mL	200mL	200mL	200mL

Constant mixing was adjusted using a magnetic stirrer at 600rpm to get a vortex while the polymer was sprinkled on the shoulders of the vortex. Rapid addition of the polymer may result in the formation of large slugs or "fish-eyes". The fisheye is a common term for granules of unhydrated particles, which prevents the completion of the hydration process in polymers. Therefore, slow addition of the polymer and then stirring at low speed (80rpm) is a crucial step to fully dissolve the polymer in water.
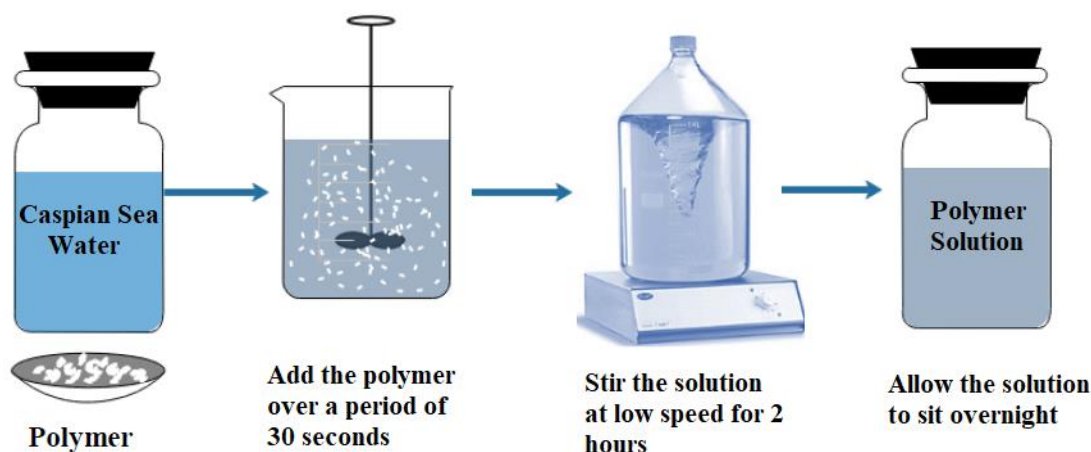
Figure 37. Polymer preparation process

4.2.2 Fluid Properties Measurements

The effect of salinity change and dilution on the physical properties of water, such as density and viscosity at different temperatures, has been investigated. For this part of the experiment, different diluted Caspian Seawater samples (2x, 5x, 10x, 20xSW) were artificially synthesized to measure the fluid properties. Kinematic Viscometer Anton Paar SVM 3001, as shown in Figure 38, was used to measure the fluid properties of Caspian Sea Water solutions at different temperatures. Before the experiment, all necessary calibrations and cleaning procedures were performed for the proper functionality of the equipment. For each trial, only 1.5mL of each predetermined water sample was measured using a syringe to collect the data. Integrated thermostatic technology of Anton Paar SVM 30001 Viscometer allowed to adjust specific temperature control without additional equipment. As the water sample was injected, multiple different parameters such as kinematic and dynamic viscosities, density for a specific temperature were displayed on the monitor.

Figure 38. Anton Paar SVM 3001 Viscometer

4.2.3 Contact Angle Measurements

As mentioned previously, the contact angle measurements helped to quantify the effect of different diluted water samples on wettability alteration. Firstly, the cores were aged in formation water for one week and in oil for one month to imitate initial reservoir conditions. Later, after aging the core in oil, the initial contact angle was measured using OCA 15EC optical contact angle measuring device, which is shown in Figure 39. Following the measurement of the contact angle, the cores were aged in predetermined low salinity water compositions for one week. Thus, previously specified diluted water samples were used as a bulk fluid for all contact angle measurements. Finally, the contact angle was measured again to quantify the wettability alteration and to determine the most effective solution. This video-based contact angle measurement apparatus OCA 15EC allowed to reproduce highly accurate and precise results. Consequently, each trial for contact angle measurement was repeated three times for the reproducibility of the results. For each trial, the same steps were used to measure the contact angle. In all cases, a medical syringe was used to produce a droplet of oil on the rock surface, which was imbibed in water. Then, a high-performance zoom lens on a video measuring system captured this droplet on the rock surface. Finally, DataPhysics Software connected to OCA 15EC assisted to calculate the captured contact angle of the droplet on PC.

Figure 39. OCA 15EC

4.2.4 Rheological Preliminary Characterization

The obtained polymer solutions were evaluated for different screening parameters. The effect of modified seawater on polymer performance compatibility was studied by conducting a series of rheological experiments at various salinity levels, temperature range from 25-80 $^{\circ}$C, and polymer concentration of 1000 and 3000 ppm. Therefore, a set of rheological experiments was used to select the optimum salinity of the diluted seawater for the potential synergy with polymer flooding. Anton Paar MCR 301 rheometer with different measuring systems was used to conduct all rheological experiments, as shown in Figure 40.

Figure 40. Anton Paar MCR 301 Rheometer

4.2.5 Long Term Thermal Stability Experiment

Long term thermal stability experiment was conducted for obtained polymers solutions to observe the degradation effect in terms of viscosity over time. This experiment allowed us to investigate the effect of high temperature for a long period of time on the polymer rheological properties. The polymers were prepared using the API standard in the Caspian Sea water solution (13000ppm) with a polymer concentration of 3000ppm. Firstly, the polymer solutions were placed in small cylindrical jars and were stored in an oven at $80^{\circ}C$ for aging. Then, after a particular time period, the polymers were taken out from the oven, and the high-temperature effect on viscosity was measured immediately at ambient temperature using Anton Paar MCR 301 rheometer.

4.2.6 Mechanical Stability Experiment

After rheological and long-term thermal stability experiments, the polymers were further screened on mechanical stability to select the best suitable polymer for the potential investigations. The polymer solution of 3000ppm was exposed to the overhead stirrer at 23900rpm for a different time period (5, 10, 15, 30minutes). After each time interval, the mixing was stopped, and the viscosity of the polymer was measured at $25^{\circ}C$. Hamilton Beach Single Spindle Drink Mixer HMD 200 Series was used as a stirrer for conducting mechanical stability experiment, and it is shown in Figure 41.

Figure 41. Hamilton Beach Single Spindle Drink Mixer

5. RESULTS

This section focuses on the obtained results based on the methodology described above. Each step of the experiment helped to identify the suitable conditions for hybrid EOR method. The results from contact angle measurement helped to determine the best diluted Caspian Seawater solution in terms of wettability alteration. Then, this diluted solution was further modified by adding active ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} that would further change the wettability of the system. Thus, based on contact angle measurements, the most efficient water solution with modified active ions would be chosen for further potential combination with a polymer. The effect of these ions on wettability alteration will be discussed in this chapter.

On the other hand, four different HPAM-based polymers were characterized under rheological experiments for different screening criteria. The evaluation of polymer stability after exposure in different environments was performed by measuring viscoelastic properties using a rheometer. All polymers samples were subjected to pass the same rheological tests under the same conditions. Thus, the most suitable polymer out of four was selected based on the following criteria:

- the highest viscosity values under two extreme conditions (low salinity/low temperature, high salinity/high temperature)

- the highest viscosity at different concentration in the range of 1000-3000ppm

- minimum viscosity decrease at different temperatures in the range of 25-80ºC

- the highest viscosity and lowest long-term thermal degradation

- the highest viscosity and lowest mechanical degradation

Finally, the modified Caspian Seawater solution that showed the best result in terms of wettability alteration and polymer solution that retained maximum viscosity and lowest degradation under different abovementioned conditions were combined for the successful implementation of this hybrid EOR technique. The target viscosity of 4 cP was chosen to avoid injection problems associated with pump capacity and to obtain efficient sweep efficiency in porous media. In addition, it is essential to consider the effect of active ions (Ca^{2+}, Mg^{2+}, SO_4^{2}) on polymer performance. As it was mentioned above, a high concentration of Ca^{2+}, Mg^{2+} in water has a detrimental effect on the viscoelastic properties of the polymer and leads to the overall degradation of the polymer backbone chain.

5.1 VISCOSITY AND DENSITY MEASUREMENTS

Table 11 indicates the results on density and viscosity measurements of the fluids at different temperatures. As can be seen in the data presented, there is a clear correlation of density with a salinity level of water and temperature. The results of density and viscosity variations for different diluted water samples are shown in Figures 42 and 43, respectively. As expected, temperature and salinity have a significant effect on fluid properties. The density of water increases as the salinity level in water increases due to a higher amount of dissolved salts in water composition. On another extent, the density of water decreases with the increase of temperature. This trend corresponds to the expansion of water in volume at higher temperatures. Correspondingly, the viscosity of water decreases with the increase of temperature due to the increase in distance between molecules. As a result, low intermolecular attraction leads to a decrease in viscosity. The effect of the salinity level on viscosity is small. Nevertheless, the viscosity of water increased with an increasing number of dissolved salts.

Table 11. Brine density and viscosity at various temperatures

Brine	Density (g/cm^3)		Viscosity (cP)	
	T = 25ºC	T = 50ºC	T = 25ºC	T = 50ºC
SW	1.0067	0.9962	0.8888	0.5681
0.5*SW	1.0021	0.9921	0.8812	0.5605
0.2*SW	0.9992	0.9895	0.8744	0.5530
0.1*SW	0.9980	0.9881	0.8694	0.5477
0.05*SW	0.9976	0.9871	0.8668	0.5416
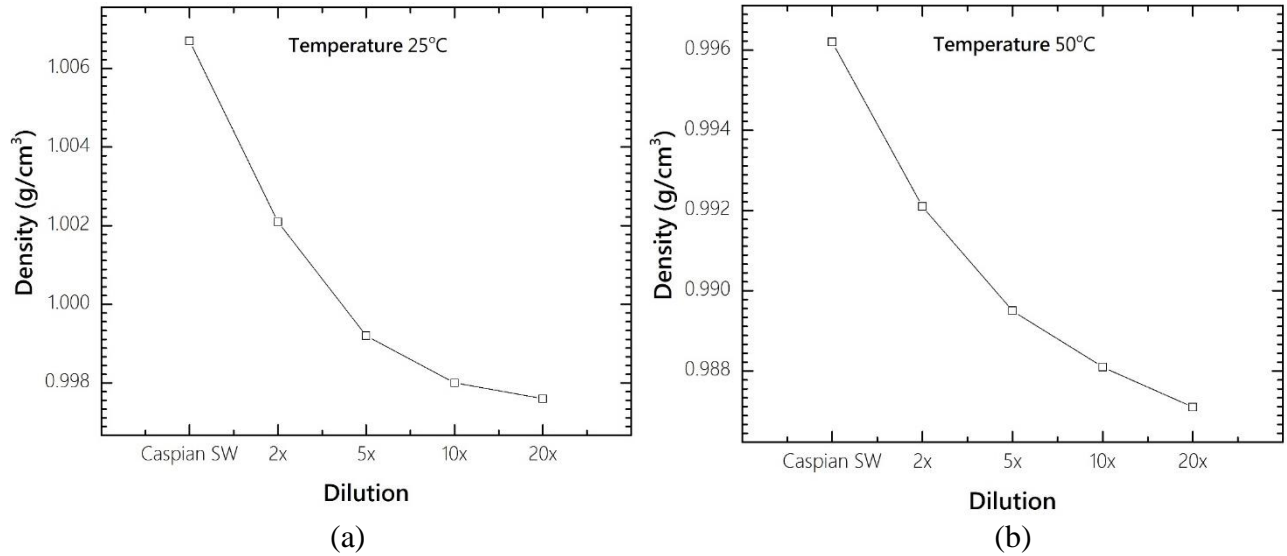
Figure 42. Density variation for different dilutions. (a) at 25ºC; (b) at 50ºC
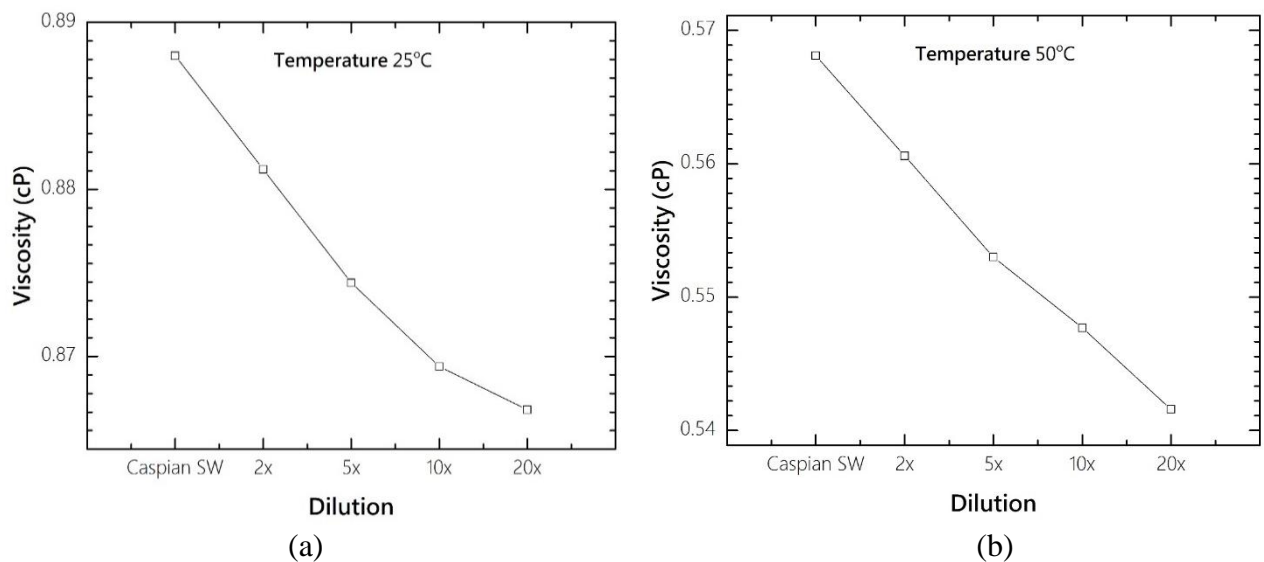
Figure 43. Viscosity variation for different dilutions. (a) at 25ºC; (b) at 50ºC

5.2 CONTACT ANGLE MEASUREMENTS

Wettability is a crucial parameter that plays an important part in reservoir engineering. According to Dandekar (2013), wettability is defined as the ability of fluid to maintain contact with the rock surface in the presence of other fluids. Consequently, the investigation of wettability preference helps to understand the interactions between reservoir fluid and rock surface. Wettability preference could be classified in terms of contact angle into three different categories:

- water-wet, contact angle varies from 0º to 75º

- oil-wet, contact angle varies from 105° to 180°
- intermediate-wet, contact angle varies from 75° to 105°

Figure 44 shows a schematic illustration of different wettability states on a pore scale.
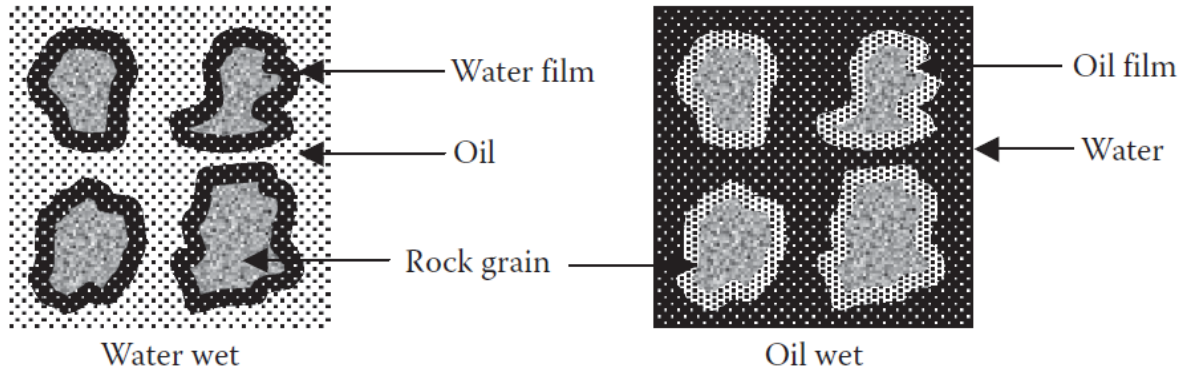
Figure 44. Representation of water and oil-wet states *(Dandekar, 2013)*

Initially, the water composition of the middle Caspian Sea region was diluted two, five, ten, and twenty times to obtain low salinity water samples. At different dilution levels, contact angles of water/oil/rock were measured to study the effect of low salinity water on wettability alteration toward more water-wet conditions.

As expected, as the salinity decreases, the solutions become more water wet. However, a significant change in contact angle was not observed in this experiment, as shown in Table 12 and Figure 45. Hence, to achieve a better design of the Smart Water, the ion composition of 20 times diluted water sample was adjusted to increase the presence of active ions such as Ca^{2+}, Mg^{2+}, $SO4^{2-}$. These active ions play an important role in the determination of wettability preference due to their reactivity towards the carbonate surface. Different studies have already examined the positive effect of active ions in terms of oil recovery and wettability alteration.

Table 12. Contact angle measurement for different diluted samples

Contact Angle	Caspian Sea	2x	5x	10x	20x
Initial	45	45	45	45	45
Final	42	41	41	41	40
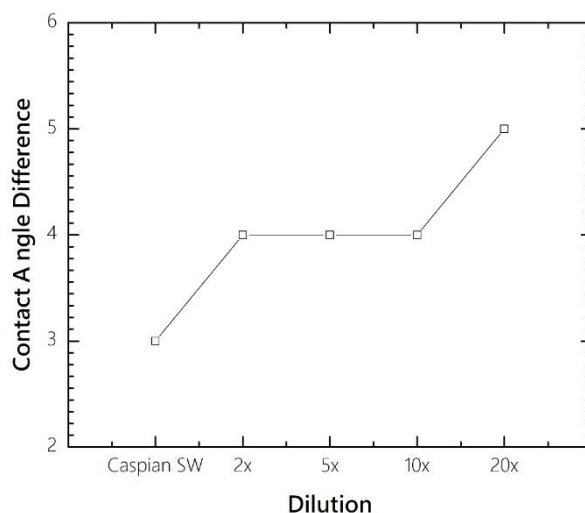
Figure 45. Contact angle difference for different diluted water samples

Furthermore, the impact of modified seawater on oil/water/rock interactions was also investigated by contact angle measurements to characterize the wettability preference of fluid/rock system, as shown in Table 13. Contact angle measurement helped to examine the effect of active ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} on wettability alteration. Based on the results from Table 14 and Figure 46, it could be suggested that the increase in the concentration of active ions improved the water-wet conditions of the system. High presence of negatively charged sulfate ions catalyzes the exchange reaction with positively charged rock surface. The reaction leads to the detachment of carboxylic groups from the surface which makes the approach of positively charged calcium and magnesium ions to react more readily. However, in the case of $6xCa^{2+}$, $6xSO_4^{2-}$, excess of Ca^{2+}, and SO_4^{2-} ions may result in the formation of anhydrite precipitation ($CaSO_4$), which decreases surface absorption. Consequently, 20x diluted Caspian Sea with $4xCa^{2+}$, $4xMg^{2+}$, and $4x SO4^{2-}$ ions, and the same diluted brine with $4x Ca^{2+}$ $4x SO4^{2-}$ ions showed the best results in terms of wettability alteration. These two solutions showed the highest contact angle difference comparing to others. Therefore, these two water compositions were used for further investigations.

Table 13. Composition of ions for modified 20x Caspian Seawater

Ions (ppm)	20x	20x 2xCa 2xMg 2xSO4	20x 2xMg 2xSO4	20x 2xCa 2xSO4	20x 4xCa 4xMg 4xSO4	20x 4xMg 4xSO4	20x 4xCa 4xSO4	20x 6xCa 6xMg 6xSO4	20x 6xMg 6xSO4	20x 6xCa 6xSO4
Na	162	162	162	162	162	162	162	162	162	162
Ca	18	36	18	36	72	18	72	108	18	108
Mg	37	74	74	37	148	148	37	222	222	37
Cl	272	272	272	272	272	272	272	272	272	272
SO4	151	302	302	302	604	604	604	906	906	906
HCO3	11	11	11	11	11	11	11	11	11	11
Total	650	857	839	820	1269	1215	1158	1681	1591	1496

Table 14. Contact angle measurement for modified Caspian Sea Water

Contact Angle	20x	20x 2xCa 2xMg 2xSO4	20x 2xMg 2xSO4	20x 2xCa 2xSO4	20x 4xCa 4xMg 4xSO4	20x 4xMg 4xSO4	20x 4xCa 4xSO4	20x 6xCa 6xMg 6xSO4	20x 6xMg 6xSO4	20x 6xCa 6xSO4
Initial	45	45	45	45	45	45	45	45	45	45
Final	40	35	40	33	24	30	24	33	33	35

(a)

(b)

(c)

(d)
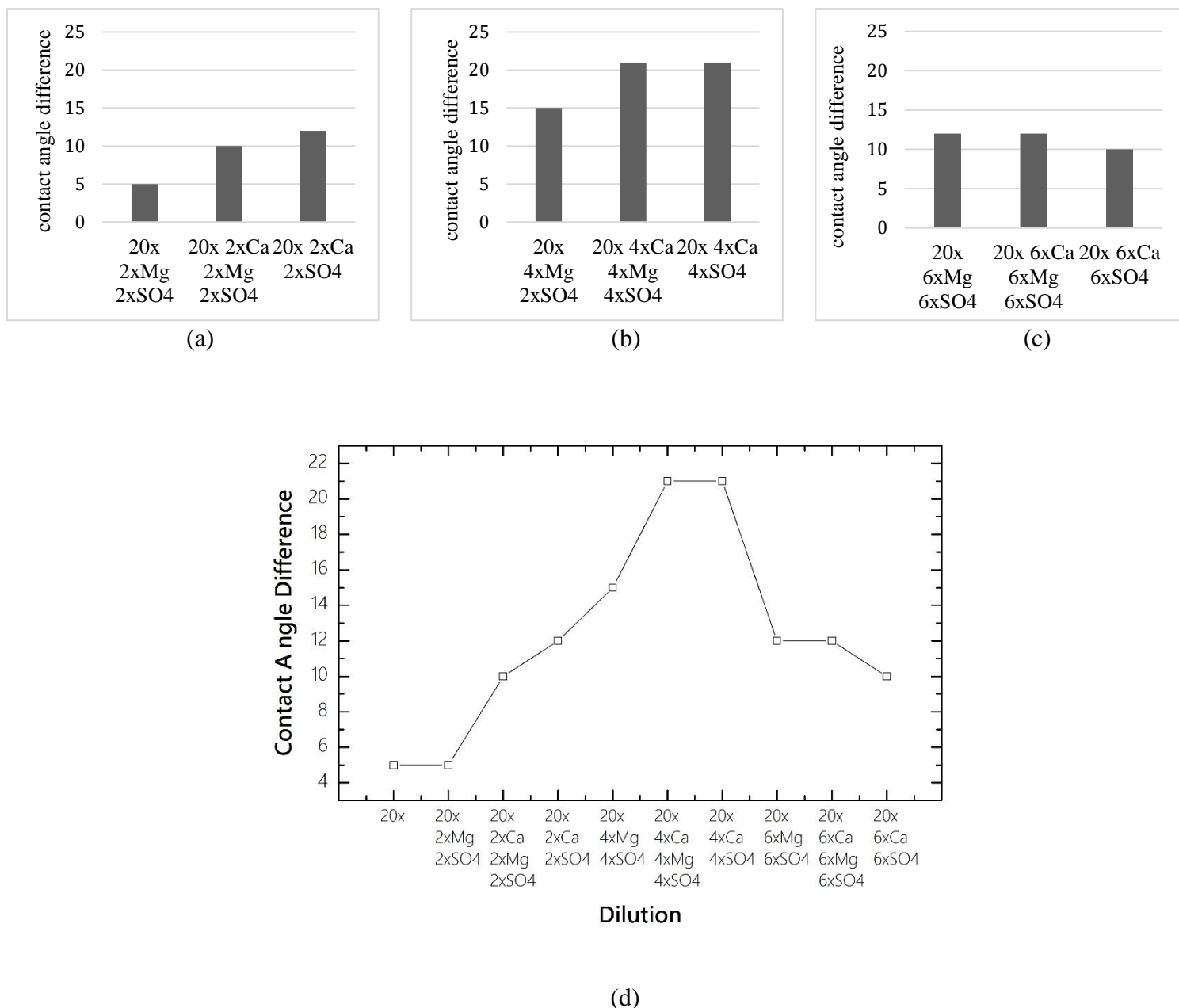
Figure 46. Contact angle difference for modified water compositions. (a) for 20xCaspian seawater, 2x modified active ions; (b) for 20xCaspian seawater, 4x modified active ions; (c) for 20xCaspian seawater, 6x modified active ions; (d) for all solutions

5.3 RHEOLOGICAL EXPERIMENTS

Investigation of rheological properties of the polymer is a fundamental step for the successful implementation of polymer flooding on a field. Therefore, polymers are firstly screened based on rheological experiments. The primary purpose of these experiments is to find the solution that retains maximum viscosity under different conditions such as temperature, salinity, shear rate. In our case, HPAM-based polymers were used in this experiment. Generally, HPAM-

based polymers behave as Newtonian fluids at low shear rates and as non-Newtonian at high shear rates. Any fluid in which viscosity changes with shear rate is considered as Non-Newtonian. The non-Newtonian region also includes both shear thinning and shear thickening behaviors. Thus, polymer normally shows shear-thinning behavior, in which the viscosity decrease with the increase of shear rate. In contrast, the polymer exhibits shear-thickening behavior only under a critical shear rate, where the apparent viscosity starts to increase. This value of critical shear rate mostly depends on the chemical properties of the polymer such as molecular weight, concentration, degree of hydrolysis. The flow curve for different flow behaviors is depicted in Figure 47.
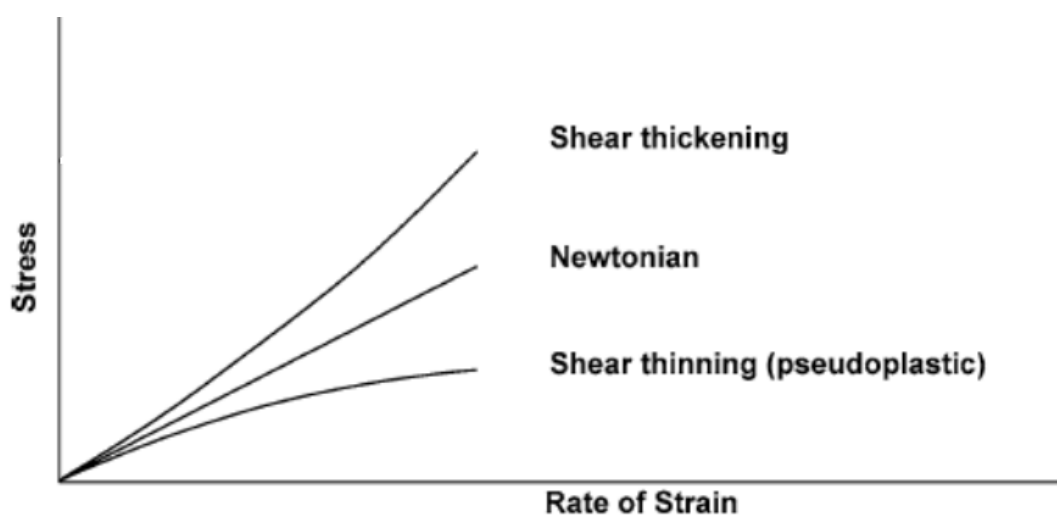
Figure 47. Shear-stress variation with the rate of strain

5.3.1 Initial Screening

As mentioned previously, different rheological experiments have been conducted to investigate the efficiency of four different HPAM polymers. These polymers were kindly provided by SNF Floerger due to their compatibility for low salinity conditions. Different screening criteria, such as salinity, concentration, and temperature, were evaluated. For this part of rheological experiments, two different scenarios at extreme conditions were established to compare the performance of all polymers and select the most suitable polymer for further steps. Table 15 shows the conditions of extreme conditions (low salinity low temperature, high salinity high temperature at two opposite concentrations) as screening cases. Viscosity values of polymers at different shear rates were measured in both extreme cases and are shown in Figure 48. At Case #1, all four polymers showed a stable non-Newtonian thinning behavior. Only the AN113 shows more shear sensitive behavior with slightly lower viscosity values due to the lower anionicity degree comparing to the other three polymers. At Case #2, under harsh conditions,

only Flopaam 5115 showed a clear shear-thinning behavior with the highest viscosity values in the range of 1-100s^{-1} shear rates. Three other polymers showed a dramatic decrease in viscosity with the increase of shear rate and behaved like a typical Newtonian fluid under higher shear rate. The lowest viscosity was observed for Flopaaam 3330S due to the absence of a sulfonated structural group in its structure. This phenomenon is related to the initial harsh conditions such as the low concentration of polymer (1000ppm), high salinity level (13000ppm), and high temperature (80°C) that led to the degradation of the polymer.

Table 15. Two different cases for polymer screening

Conditions	Case #1	Case #2
Concentration	3000ppm	1000ppm
Brine Salinity	650ppm, 20x Caspian Water	13000ppm, Caspian Water
Temperature	25 °C	80 °C
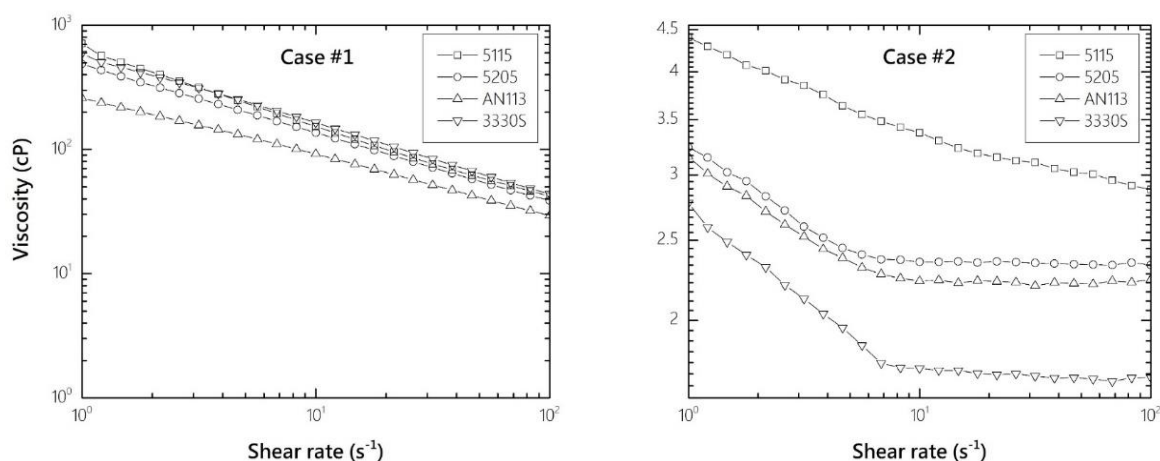
Figure 48. HPAM solutions viscosity vs. shear rate for Case #1 and Case #2

5.3.2 Effect of Concentration on Polymer

All four polymers exhibited strong Non-Newtonian flow characteristics with clear thinning behavior at the predetermined concentration. Figure 49 shows a straightforward relationship of viscosity with the concentration and shear rate. In all cases, the viscosity of polymer increased with the increase of concentration. Based on the results, in Figure 50, Flopaam 5115 showed the highest viscosity with the increase of concentration and shear rate, comparing to three other polymers. However, too high viscosities at relatively high concentrations may cause plugging problems in the pores, reducing its initial permeability. The reduction in permeability occurs due to the absorption of the polymer on the rock surface and results in the opposite effect on polymer efficiency and oil recovery, respectively. In this case, the surface of the rock is covered

by the polymer molecules, and it has an adverse effect on the concentration. The extensive research on polymer retention in porous media is beyond the scope of this thesis, but it has been widely investigated in different papers (Zhang, et al., 2013; Choi, et al., 2016; Chen, et al., 2016). In addition, the high concentration of the polymer leads to the excess amount of spendings on polymer purchasing, which makes the project economically unfeasible. Consequently, the primary purpose during the polymer flooding is to maintain high viscosity at low concentrations. Therefore, it is essential to consider the effect of concentration on the successful polymer injection in terms of injectivity and economic perspectives.
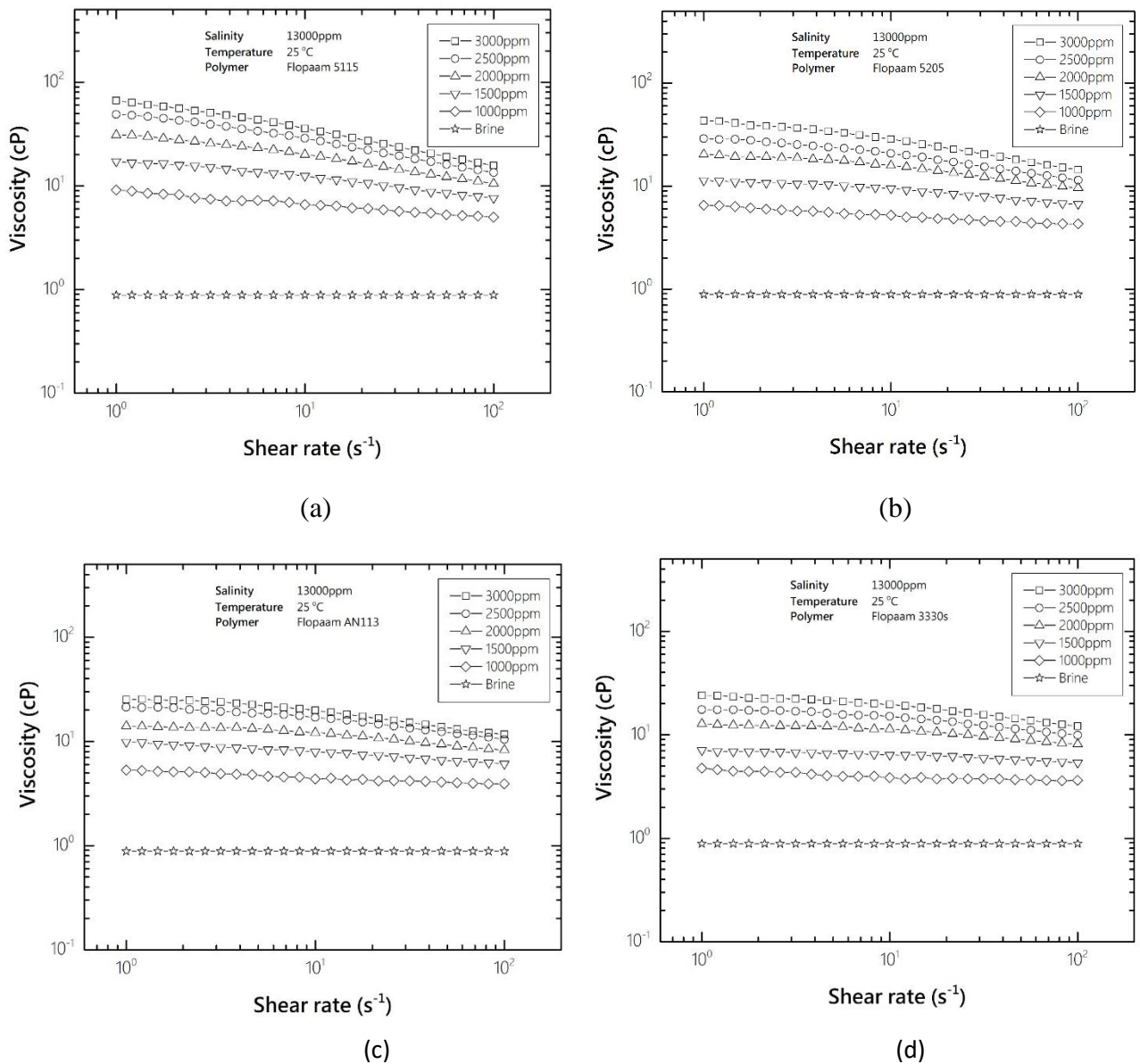

Figure 49. Viscosity vs shear rate for different polymer concentrations.
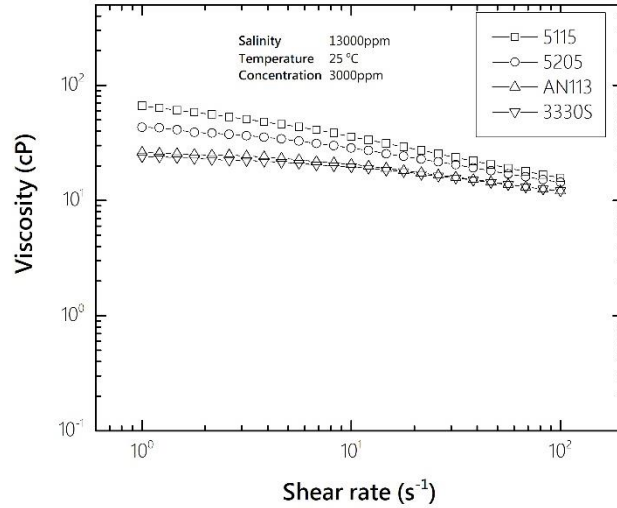(a) Flopaam 5115; (b) Flopaam 5205; (c) Flopaam AN113; (d) Flopaam 3330S

Figure 50. Comparison of the different polymers at predetermined conditions

5.3.3 Effect of Temperature on Polymer

The temperature has an adverse effect on the viscosity of the polymer. Polymer loses its original viscosity under high-temperature conditions. The loss of polymer viscosity with the increase of temperature is caused by the reduction of the intermolecular forces in the polymer chain. Figure 51 clearly indicates the effect of temperature on the viscosity of the polymers. The degradation degree of the viscosity was calculated using the formula:

$$Degradation\ factor = \left| \frac{\mu_{test} - \mu_{ref}}{\mu_{ref}} \right| * 100\%,$$

where μ_{test} is the testing viscosity of the solution (cP), and μ_{ref} is the initial viscosity of the solution. In this case, the measurements of the degradation factor were examined at a shear rate of $10s^{-1}$, which is close to $7.3s^{-1}$. This shear rate matches the shear rate experienced in pipelines through the injection and porous media in the reservoir (Lake, 1989). Based on this factor, as can be observed in Figure 52, Flopaam 5115 showed the highest temperature stability with the minimum decrease in viscosity comparing to other polymers. In contrast, Flopaam 3330S showed the highest thermal degradation with the dramatic decrease in viscosity after 60°C. These results correspond to chemical characteristics of the polymers, as Flopaam 5115, 5205 and AN113 are copolymers of acrylamide and ATBS, and Flopaam 3330S belongs to regular HPAM, respectively.

(a)
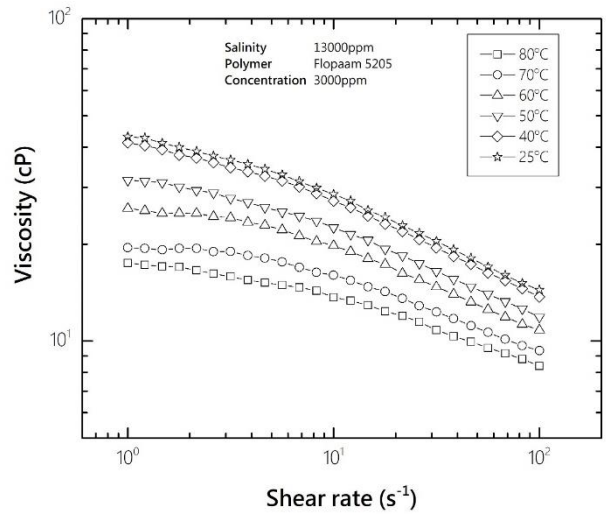
(b)
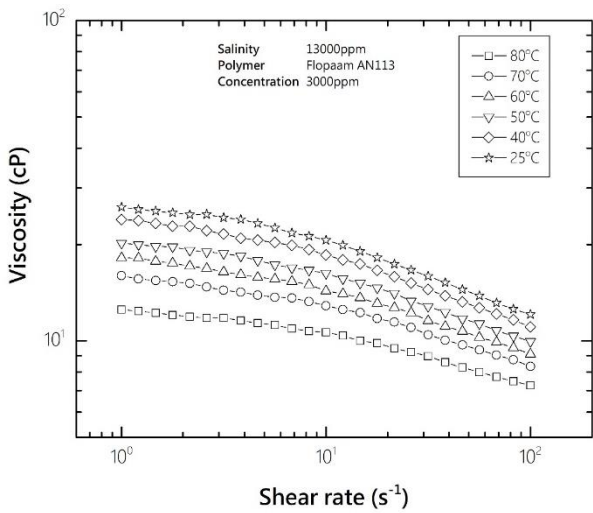
(c)
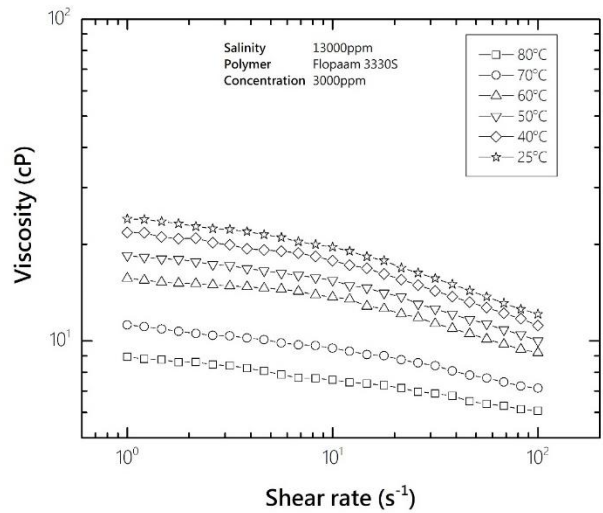
(d)

Figure 51. Viscosity vs shear rate at different temperatures
(a) Flopaam 5115; (b) Flopaam 5205; (c) Flopaam AN113; (d) Flopaam 3330S
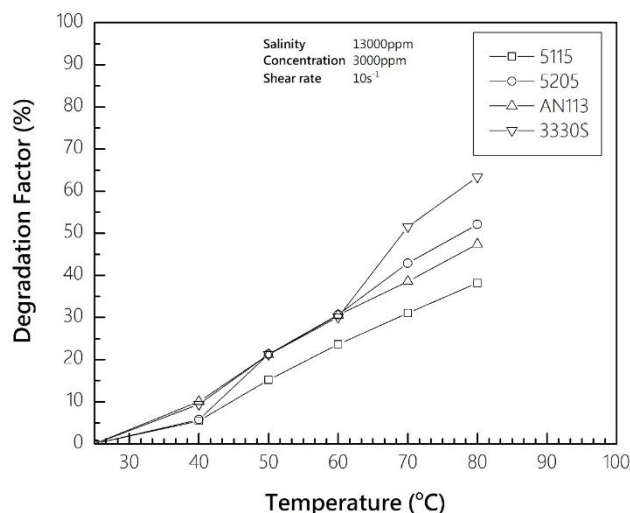
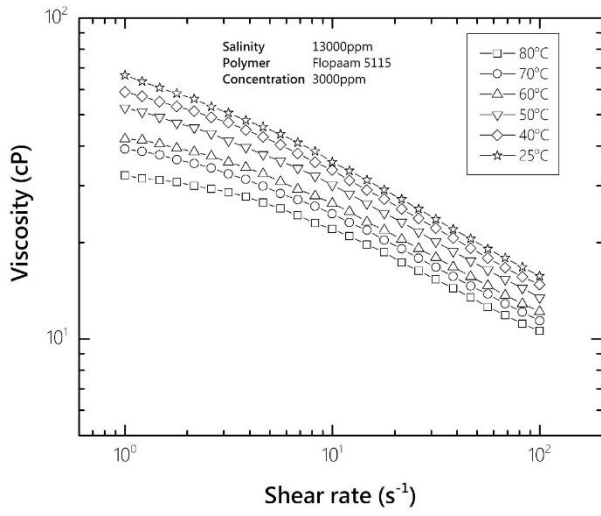Figure 52. Degradation factor of the polymers as an effect of temperature.

5.3.4 Effect of Long-Term Thermal Stability to Polymer

Another screening criteria was based on the long thermal stability of polymers. Long-term thermal stability is an important screening factor for the determination of the most suitable polymer. The polymer should maintain its thermal stability under reservoir conditions for a long time period. At elevated temperature, the degree of hydrolysis increases, and HPAM-based polymers rapidly precipitate. As a result of the precipitation, the rate of polymer viscosity loss increases too. This effect is more prominent in the presence of a high concentration of divalent ions in the solution. The suitable polymer should maintain 50% of its original viscosity over a period of 6 months to be considered as a good candidate for the polymer flooding (Han, et al., 2014). Consequently, laboratory thermal stability data of polymer is a necessary and important factor in designing polymer flooding.

Figure 53 shows the viscosity dependence versus time at a specific temperature of 80°C in an oxygen-free environment for different polymer solutions with predetermined polymer concentration and brine salinity at 3000ppm and 13000ppm, respectively. All four polymers struggled to maintain its original viscosity over a period of 100 days at 80°C. The viscosity was presented in terms of relative viscosity. According to the equation, relative viscosity is equal to:

$$\mu_{rel} = \frac{\mu}{\mu_s},$$

where μ is the viscosity of the solution (cP) and μ_s is the viscosity of solvent (cP). In our case, Caspian Sea water with a salinity level of 13000ppm was used as a solvent. The viscosity of

the Caspian Sea at specific conditions water was determined and was equal to 0.888 cP. As mentioned above, the same approach to calculate the degradation factor was used. Figure 54 shows the degradation of the HPAM-based polymers at 80ºC, losing its viscoelastic properties with the increase of time. Based on the results, the original viscosity of the polymers has decreased by 50% for Flopaam 5115, 5205, and almost by 70% for Flopaam AN113, 3330S, respectively. Consequently, Flopaam 5115 and 5205 retained the maximum viscosity and lowest thermal degradation degree comparing to other polymers.

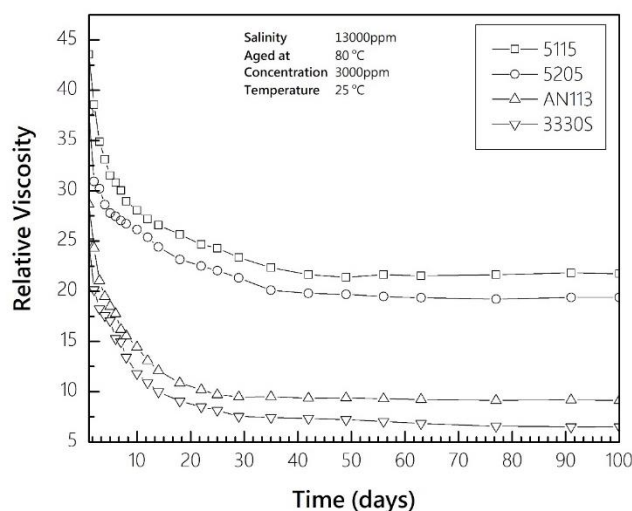Figure 53. Long term thermal degradation degree for different polymer solutions
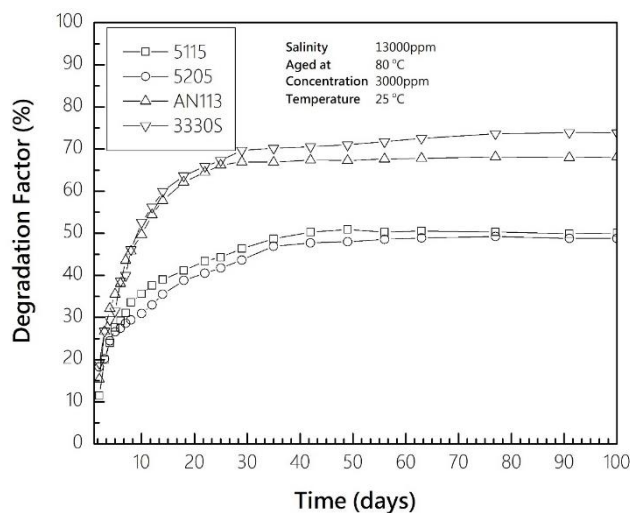
Figure 54. Degradation factor of the polymer as an effect of long term thermal degradation

5.3.5 Effect of Mechanical Stability to Polymer

Molecular weight significantly affects the mechanical stability of the polymers. The polymers become more shear sensitive with the increase of molecular weight. Therefore, some

modifications are made to the polymer backbone chain to improve the performance and stability of the polymer. For instance, the introduction of the special functional groups such as acrylate, N-vinyl pyrrolidone acrylamide, or acrylamide tertiary butyl sulfonic acid helps to increase the stiffness and rigidity of polymer backbone chain (Zaitoun, et al., 2012).

The mechanical stability test was carried in a rheometer using a cone plate at 25°C. Figure 55 demonstrates the mechanical stability of the polymers with a predetermined shear rate range (1-100s^{-1}) under different time intervals. Normally, the pumping of the polymer through the pipes and its passage near the wellbore area incorporates high shear rates conditions. Subsequently, the sheared rate at 23900rpm (max. speed of device) was chosen to imitate the worst scenario conditions of polymer injection through the wellbore. According to the results, Flopaam 5115 maintained the highest viscosity after 30minutes of shearing at 23900rpm. However, based on the overall performance, Flopaam 5115 and AN113 shows identical results in terms of mechanical degradation, as shown in Figure 56. This result corresponds to the effect of the ATBS group that provided additional mechanical stability to the polymer structure. A similar approach to calculate the degradation factor was used as for previous cases.

(a)   (b)

(c)   (d)
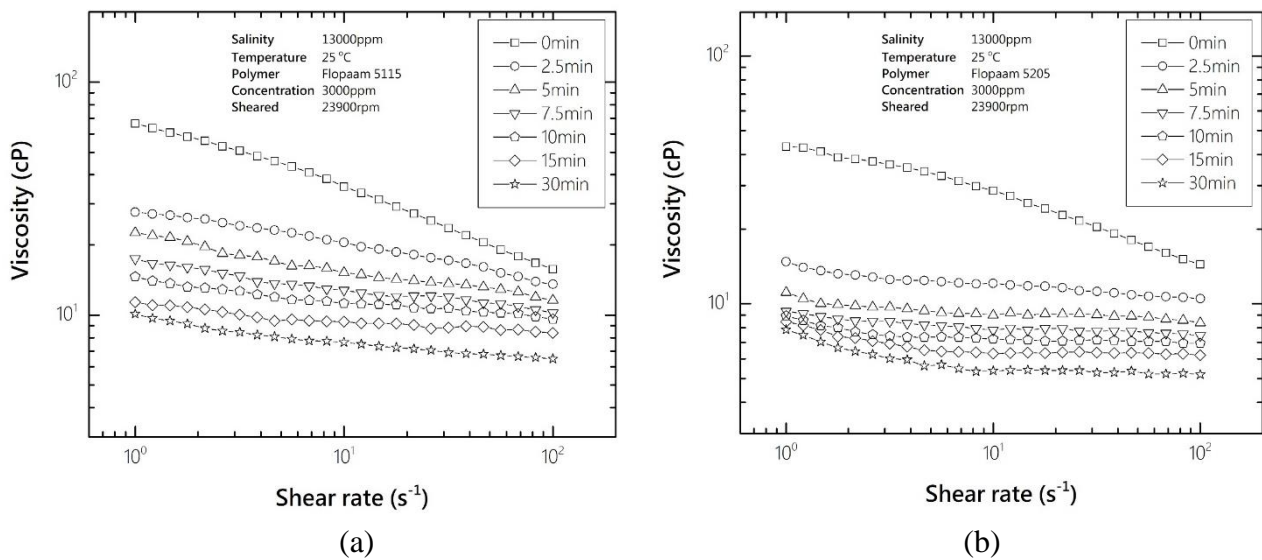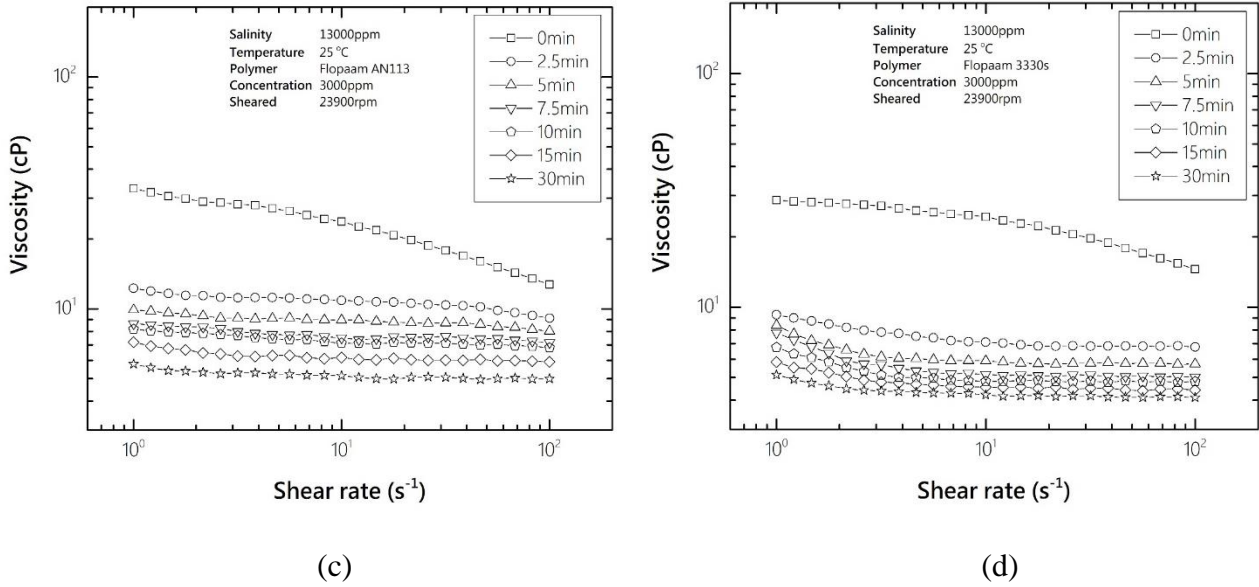
Figure 55. Viscosity vs shear rate at different time after shearing at 23900rpm.

(a) Flopaam 5115; (b) Flopaam 5205; (c) Flopaam AN113; (d) Flopaam 3330S
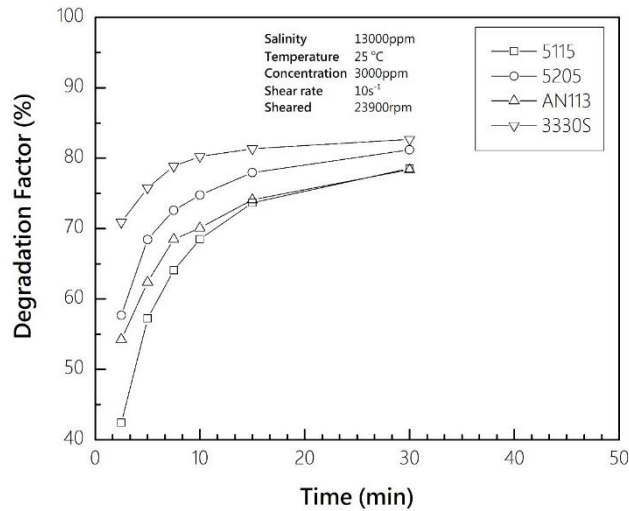
Figure 56. Degradation factor of the polymer as an effect of mechanical degradation

5.4 POTENTIAL SYNERGY OF LOW SALINITY WATER AND POLYMER FLOODING

The results from the contact angle and rheological experiments were combined to determine the optimal conditions for the potential synergy of low salinity water and polymer. Table 16 shows the ranking of polymers based on rheological experiments that have been performed for different screening parameters. The following polymers were ranked corresponding to their capacity to retain the maximum viscosity and lowest degradation degree. Consequently, based on previous results, Flopaam 5115 was prepared in two adjusted Caspian Seawater solutions that showed the best effect in terms of wettability alteration.

Table 16. Ranking of the polymers for different screening parameters

Polymer	Ranking Criteria					
	Initial screening	*Effect of concentration*	*Effect of temperature*	*Long-Term Thermal Stability*	*Mechanical Degradation*	*Overall*
Flopaam 5115	1	1	1	2	1	**1**
Flopaam 5205	2	2	3	1	3	**2**
Flopaam AN113	3	3	2	3	2	**3**
Flopaam 3330S	4	4	4	4	4	**4**

Through the numerous rheological tests, the target viscosity of 4 cP has been obtained with 500 ppm Flopaam 5115 and a modified water composition of 0.05*SW 4xCa 4SO$_4$ at 80°C. This target viscosity was chosen in order to decrease the mobility ratio in order to obtain a stable displacement process and avoid viscous fingering. At the same conditions, another polymer solution showed a slightly lower viscosity value of 3cP. This result corresponds to the higher concentration of Mg^{2+} in water composition that is detrimental to the polymer stability. Figure 57 shows a shear rate dependence of viscosity for two prepared Flopaam 5115 solutions with different modified ion composition. In addition, the application of hybrid polymer/low salinity water should be investigated further by conducting infectivity tests to understand the process to the full extent.
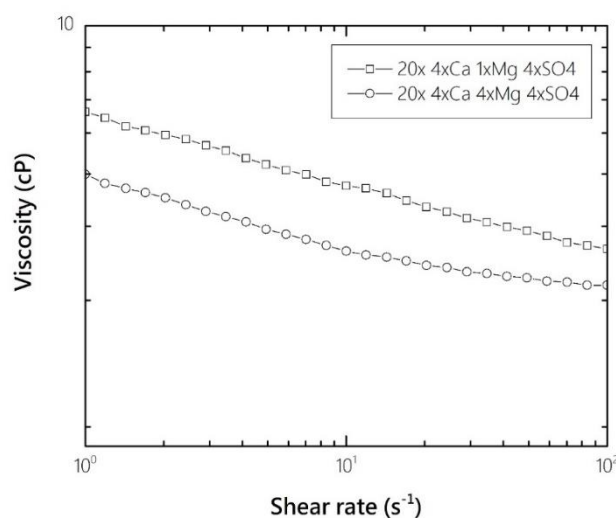

Figure 57. Effect of shear on viscosity for different polymer solutions

6. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the potential synergy between low salinity water and polymer flooding has been investigated as the primary objective. Potential combination between these EOR techniques was examined by performing rheology and contact angle measurements. Based on the results, the following conclusions could be found:

- The potential synergy between low salinity water and polymer flooding was found to be successful as the target objectives have been obtained.

- The limitations of low salinity water and polymer flooding were faded by combining them together.

- Contact angle measurements showed a small effect of low salinity water on wettability alteration. The small difference in contact angle could be a result of the low affinity of oil towards the core sample. In addition, the aging temperature could be raised to 120°C for a more substantial effect.

- Rheological experiments helped to screen and identify the best solution out of four different HPAM based polymer in terms of concentration, temperature, and salinity level. Flopaam 5115 showed less shear sensitive behavior under high temperature-high salinity conditions.

- The results of contact angle measurement and rheological experiments were combined to find the optimal conditions for the combination between low salinity water and polymer. The viscosity of 4 cP has been obtained with 500 ppm Flopaam 5115 with modified water composition of 0.05*SW 4xCa 4SO$_4$ at 80°C.

- Overall, hybrid low salinity/polymer flooding technique showed notable improvements in wettability alteration for low salinity water and viscoelastic properties of the polymer.

- This work can further be expanded to perform additional screening criteria for polymers and coreflooding experiments to observe the retention and recovery factor values.

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