



جامعة خليفة
Khalifa University

Effect of Water Chemistry on Polymer Retention in Carbonate Reservoirs under Harsh Conditions

Anoo Sebastian

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by

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Abstract

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Polymer flooding is one of the most effective chemical EOR method and has been successfully applied in many sandstone reservoirs worldwide. In this process, a water-based solution containing long-chain polymer molecules is injected into the reservoir to reduce the mobility ratio between the injected fluid (water) and the displaced fluid (oil); thus, improving the sweep efficiency and increasing the amount of oil recovered. In recent years, polymer flooding has emerged as a promising enhanced oil recovery technique in carbonate reservoirs of the Middle East due to the development of novel polymers that can withstand the harsh conditions in these reservoirs. One of the significant challenges of polymer flooding is polymer retention affecting the economics and the performance of a polymer-flooding project.

The main objective of this research is to investigate the effect of water chemistry (salinity and ionic compositions) to reduce polymer retention in carbonates at representative reservoir conditions. SAV10, an ATBS based polymer that showed significant stability at high temperature and salinity, was considered. The water chemistry of the make-up brine was altered by reducing the salinity of both typical formation water and seawater in carbonates under harsh conditions. Furthermore, varying the ionic composition of Ca^{2+} , Mg^{2+} , and SO_4^{2-} was also investigated to reduce polymer adsorption. A significant aspect of the study was the assessment of polymer adsorption when oil was present, and the influence of temperature on polymer retention. Furthermore, polymer adsorption was quantified using both static adsorption tests on crushed Indiana limestone outcrop and dynamic retention test on the same Indiana limestone outcrop core plugs. Finally, a correlation was developed between static adsorption and dynamic polymer retention.

Twelve proposed brine recipes including both water dilution and ion manipulation effects were selected. The rheology of the polymer was closely studied, emphasizing shear ramp-up tests, varied polymer concentration, salinity, ionic compositions, and temperature to study their effects on polymer solution viscosities. The hydrodynamic size and polydispersity index of the polymers were determined at varying conditions. Various analytical methods including UV-Vis, TOC-TN, and viscosity, employed for determining polymer concentrations were compared to identify the most accurate and consistent technique. Static and dynamic retention studies were conducted to study the effect of salinity, ionic compositions, and temperature on polymer retention. Moreover, additional static adsorption experiments were performed at the same experimental conditions including surface access, liquid-to-solid ratio, retention time, make-up water salinity and temperature as that of dynamic retention tests. Based on these results, a correlation was developed between static adsorption and dynamic retention with the application of Machine Learning algorithms and symbolic regression.

To investigate the effect of salinity on polymer retention, dilutions of formation water salinity (167,114 ppm) and seawater salinity (42,507 ppm) were first studied, which are

representative of a Middle East reservoir. Initially, static adsorption studies were conducted as the preliminary screening study. This was followed by dynamic retention studies in the absence of oil as well as in the presence of oil on oil-wet cores to obtain representative polymer retention values. All the experiments were performed at ambient temperature conditions. Both static and dynamic polymer retention studies showed reduced retention levels below a salinity of 10,000 ppm in the absence and presence of oil. Moreover, in the presence of oil, the polymer retention was less compared to its absence. The dynamic polymer retention was 14 $\mu\text{g/g-rock}$ for seawater dilution of 425 ppm salinity compared to 26 $\mu\text{g/g-rock}$ for high salinity formation water (167,114 ppm) in oil wet cores.

Furthermore, the effect of ionic compositions on polymer retention was studied using brines derived from seawater of salinity 8,502 ppm with varying concentration of Ca^{2+} , Mg^{2+} , and SO_4^{2-} . The investigation included static adsorption studies as well as dynamic retention experiments in the absence and presence of oil at ambient conditions. A reduction in static and dynamic polymer retention was observed with reduced hardness levels. The dynamic polymer retention for complete softened brine (0 ppm of $\text{Ca}^{2+} + \text{Mg}^{2+}$) in the presence of oil was 20 $\mu\text{g/g-rock}$, whereas the dynamic retention value for the brine composition with hardness ions (425 ppm of $\text{Ca}^{2+} + \text{Mg}^{2+}$) was 26 $\mu\text{g/g-rock}$. Analyzing the low polymer retention values obtained based on water dilution and ion-modification, diluted brine compositions showed lower retention (14 $\mu\text{g/g-rock}$) compared to softened brine composition (20 $\mu\text{g/g-rock}$) in the presence of oil. When considering large-scale applications, it is simpler to formulate a diluted brine recipe than to vary ionic compositions at the field scale. Hence, diluted brine composition was recommended as preferred solution.

In high-temperature conditions, the study investigated the static and dynamic retention of polymer in low salinity brine (425 ppm) compared to high salinity (167,114 ppm). Static adsorption showed decreasing polymer adsorption with increasing temperatures in both salinity levels. However, dynamic polymer retention remained stable across various temperatures (25, 40, 60, 80, and 90°C) for both salinities, attributed to the stability of polymer at high temperature. Despite this stability, the polymer's hydrodynamic size reduction at high temperatures leads to increased retention. On the other hand, high temperatures weaken the intermolecular forces between polymer and rock, reducing retention, which is more apparent in static adsorption due to greater surface area. In dynamic coreflooding, where surface area is less, these effects balance out, resulting in minimal temperature impact on retention. At 90°C, mimicking reservoir conditions, polymer retention in low salinity (425 ppm) was 12 $\mu\text{g/g-rock}$.

For effective polymer flooding design, precise polymer retention measurement is crucial. The final objective aimed to correlate static and dynamic retention values. Using crushed rock powder, static adsorption experiments were conducted, ensuring similar surface access to that of the core plugs used for dynamic retention studies. Predicting dynamic retention involved machine learning and symbolic regression, initially focusing on static adsorption values. All tree-based models exhibited superior performance in predicting dynamic retention demonstrating R^2 values of 0.95 – 0.98 and 0.91 – 0.95 for training and testing, respectively, with respective mean absolute error (MAE) and root mean square (RMS) error values in the range of 6.13 – 8.17 and 8.10 – 9.83. Further analysis included variables like TDS, pore throat size, residual oil saturation, and temperature. This holistic approach, encompassing more parameters, improved accuracy, as evidenced by high R^2 values (0.98 – 1.00 for testing, 0.97 – 0.98 for training) and lower MAE and RMS ranges of 2.97 – 4.26 and 3.71 – 5.31, respectively. Symbolic regression, applied for the two distinct approaches, yielded explicit equations with

R^2 values of 0.95 and 0.98, though the latter had a higher RMS (19.82 vs. 6.84). Nevertheless, the second approach using different influential variables captured a broader range of influencing factors, rendering it more valuable for practical applications.

This research is among the very few works that investigate the effect of injection water chemistry, including both water dilution and ion-modification, on polymer adsorption in carbonates under harsh conditions of high temperature and high salinity. Furthermore, the developed correlation could determine representative polymer retention levels at reservoir conditions based on static tests, which save the time and efforts spent in dynamic retention tests.

Indexing Terms: Static Polymer Adsorption; Dynamic Polymer Retention; Low Salinity Polymer Flooding; Carbonates; Correlation

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Declaration and Copyright

Declaration

I declare that the work in this Dissertation was carried out in accordance with the regulations of Khalifa University of Science and Technology. The work is entirely my own except where indicated by special reference in the text. Any views expressed in the dissertation are those of the author and in no way represent those of Khalifa University of Science and Technology. No part of the dissertation has been presented to any other university for any degree.

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NOMENCLATURE

Symbols

C	=	Concentration (ppm)
K	=	Absolute permeability
k_r	=	Relative permeability
M	=	Mobility ratio
ΔP	=	Differential pressure
S	=	Saturation
V	=	Volume (ml)
W	=	Weight (gram)

Subscripts/Superscripts

e	=	Effluent
i	=	Initial
or	=	Residual oil
wi	=	Initial water

Abbreviations

AA	=	Acrylic Acid
AdaBoost	=	Adaptive Boosting
AM	=	Acrylamide
AMPS	=	2-Acrylamido-2-MethylPropane-Sulfonate
ATBS	=	Acrylamido-Tertiary-Butyl Sulfonate
BET	=	Brunauer-Emmett-Teller
CF	=	Coreflood
EOR	=	Enhanced Oil Recovery
EPV	=	Excluded Pore Volume
ET	=	Extra Trees
FR	=	Filtration Ratio
FW	=	Formation Water
GB	=	Gradient Boosting

HPAM	=	Hydrolyzed Polyacrylamide
HTHS	=	High Temperature High Salinity
IPV	=	Inaccessible Pore Volume
LSP	=	Low Salinity Polymer
MAE	=	Mean Absolute Error
MICP	=	Mercury Injection Capillary Pressure
ML	=	Machine Learning
MSE	=	Mean Squared Error
NF	=	Nanofiltration
NVP	=	N-Vinyl Pyrrolidone
PDI	=	Polydispersity Index
PV	=	Pore Volume
RF	=	Resistance Factor or Random Forest
RMSE	=	Root Mean Squared Error
RO	=	Reverse Osmosis
RRF	=	Residual Resistance Factor
SW	=	Seawater
TDS	=	Total Dissolved Solids
TOC-TN	=	Total Organic Carbon – Total Nitrogen
UV	=	Ultraviolet
XGBoost	=	Extreme Gradient Boosting

CHAPTER 1: INTRODUCTION

1.1 Problem Statement

Carbonate reservoirs account for more than 60% of the global petroleum reserves. Oil recovery from these reservoirs is challenging due to their complexity, particularly in the Middle East region, which includes mixed-to-oil wettability, low permeability with high heterogeneity, high temperature (above 90 °C), and high salinity (over 150,000 ppm). Also, carbonate rocks are typically characterized by being either mixed-wet or predominantly oil-wet. Water injection in these reservoirs usually results in low oil recovery due to the early breakthrough of water in the high permeability streaks and bypassing the oil in the low permeability matrix. Hence, several enhanced oil recovery (EOR) techniques have been proposed over the years to improve oil recovery from carbonate reservoirs beyond conventional waterflooding. One of the most widely applied EOR techniques is chemical EOR, which incorporates different chemicals into the injection water including surfactants and alkali to reduce interfacial tension for improving the microscopic displacement and polymers to control injection water mobility thereby improving volumetric sweep efficiency.

Polymer flooding is among the most widely applied chemical EOR techniques, which primarily targets unswept or bypassed oil. During polymer flooding, water-soluble polymers propagate through the porous media and get retained onto the rock surface by combined mechanisms of adsorption, mechanical entrapment, and hydrodynamic retention. The retention of polymers causes a delay in oil breakthrough, also increased consumption of the chemical. Therefore, it is essential to properly characterize and reduce polymer retention in porous media for the success of polymer flooding projects.

Two types of polymers are used for polymer flooding: synthetic- and biopolymers. The most widely used synthetic polymer is the Partially Hydrolyzed Polyacrylamide (HPAM) due to its low cost. However, this polymer has limited applications in harsh reservoir conditions due to its instability at high temperatures (above 90 °C) and high salinities (above 100,000 ppm). Biopolymers have a higher tolerance to temperature and salinity than HPAM-based polymers. Nonetheless, their use in large-scale field applications is constrained due to several issues. Firstly, these polymers often face significant injectivity challenges, rendering them difficult to use effectively in porous media. Additionally, biopolymers are more prone to bacterial degradation, which can compromise their performance in field conditions. The

manufacturing process also poses challenges; the concentrated broth produced by bacterial fermentation is typically laden with debris, such as bacterial cells and proteins, as well as polymer aggregates, commonly referred to as microgels. These impurities necessitate advanced filtration techniques prior to injection, further escalating the production costs and complicating their application in large-scale operations.

To overcome salinity and temperature challenges, new HPAM-based polymers were manufactured by incorporating unique monomers such as N-vinylpyrrolidone (NVP) and Acrylamide tertiary butyl Sulfonate (ATBS). These groups can enhance chemical stability under harsh conditions of high temperature and high salinity (HTHS). Although the new polymers may withstand the harsh conditions in carbonate reservoirs, their high production costs present a significant challenge to the project's economics. The case worsens when these polymers have high retention. This adds further to the cost as these polymers cannot be recovered and might even affect the polymer flooding performance. One solution to this problem is understanding water chemistry, including salinity and ionic composition, and applying it to reduce polymer retention. This approach can transform a previously screened-out polymer into a viable candidate.

Furthermore, accurately determining polymer retention is crucial for the effective implementation of a polymer flood project. While both static adsorption and dynamic polymer retention measurements characterize these interactions, the former is notably simpler and more convenient to execute. Given that static adsorption tests are easier to perform, it becomes valuable to establish a reliable correlation between static and dynamic retentions. Possessing such a correlation simplifies the process of predicting dynamic retention, rendering it feasible and more efficient, thereby enhancing the overall success of the polymer flooding operation.

1.2 Research Objectives

The main objectives of this research study are as follows:

1. To investigate the effect of water chemistry (salinity and composition) on the retention of a synthetic ATBS-based polymer (SAV10) in carbonates under harsh conditions of high temperature and high salinity.
2. To perform a thorough investigation of the effect of oil presence on polymer retention through two-phase dynamic retention tests.
3. Establish a correlation between static and dynamic polymer retentions to predict dynamic polymer retention from static adsorption values.

1.3 Framework of this Dissertation

This dissertation consists of nine chapters, and each chapter's content is structured as follows:

Chapter 1 is the introductory chapter that outlines the problem statement, research objectives, and framework of this dissertation.

Chapter 2 compiles comprehensive literature, discussing the extensive background of polymer retention in carbonate reservoirs. This chapter provides an in-depth review of existing knowledge on retention mechanisms and the factors influencing retention. This chapter also integrates insights from machine learning (ML), exploring important concepts and methodologies relevant to petroleum engineering, which set the theoretical foundation for implementing ML approaches in subsequent chapters.

Chapter 3 details the materials and methodologies employed to achieve the objectives. It includes the protocols for fluid preparation, static adsorption tests, and dynamic retention studies. The procedures to evaluate uncertainties in measurements are also described to ensure the reliability and validity of the experimental data. The last part of this chapter explores the construction, training, validation, and testing of ML models relevant to the research.

Chapter 4 describes rheological investigations, particularly focusing on the shear ramp-up tests, variation of polymer viscosities with varied polymer concentration, salinity, ionic compositions, and temperature. Furthermore, the chapter also presents findings related to the hydrodynamic size and polydispersity index of various polymer solutions. To ensure precise evaluations, the chapter compares different analytical methods employed for determining polymer concentrations.

Chapter 5 presents investigations on the specific impact of salinity on polymer adsorption in both static and dynamic conditions. This chapter thoroughly examines the interactions between polymers and carbonate reservoirs in varying salinity levels, discussing the implications, and drawing relationships to understand the influence of salinity on polymer retention mechanisms more cohesively.

Chapter 6 describes how varying ionic compositions influence polymer adsorption, exploring their effects under static and dynamic conditions. Detailed experiments and analyses are presented to reveal how different ionic compositions alter the interactions between polymers and carbonate reservoirs, thereby affecting retention.

Chapter 7 presents the importance of temperature in controlling polymer adsorption for both static and dynamic conditions. This chapter meticulously examines the temperature-

related aspects of polymer retention, providing in-depth insights into how temperature impacts the adsorption of polymers in carbonate reservoirs. The chapter also provides conclusive insights, bridging the gap between laboratory studies and field scenarios.

Chapter 8 discusses tree-based machine learning models and symbolic regression equations, aiming to predict dynamic retentions based on static adsorption values, average pore throat size of the cores, total salinity, presence of oil, and temperature. It also provides insights into how the models are rigorously trained and tested to ensure their robustness and reliability in predicting dynamic retention under different conditions. Therefore, the chapter illustrates the applicability and effectiveness of machine learning in understanding and resolving issues related to polymer retention.

Chapter 9 summarizes the main findings and conclusions based on the conducted work. This chapter also highlights the shortcomings of the conducted research and the recommended future work. The recommendations target improvements in both the experimental work as well as the developed ML model for polymer retention predictions.

CHAPTER 2: LITERATURE REVIEW

This chapter briefly reviews the polymer flooding process, the mechanisms responsible for polymer retention in the porous media, the effects of IPV and adsorption on polymer propagation in the reservoir and the effects of polymer type, temperature, water salinity, ionic composition, and oil presence on polymer retention. Furthermore, this chapter describes fundamental concepts integral to the approach of machine learning, beginning with comparison metrics that act as evaluative standards for model performance. It then proceeds to discuss the bias-variance tradeoff, a crucial balance that prevents model overfitting and underfitting. To ensure the developed models are robust and validated effectively, the K-cross validation technique is discussed. Regularization is another pivotal concept explored, helping to prevent overfitting by introducing penalties to more complex models. Moreover, this chapter provides insights into the use of Heatmap and Pearson correlation coefficient, which demonstrate the relationships between features or input parameters. Additionally, various tree-based modeling techniques are explored, from the foundational Decision Tree Algorithm to a range of ensemble methods. These ensemble methods, including Bagging, Stacking, and Boosting, offer advanced techniques to improve model accuracy and robustness.

2.1 Polymer Flooding

Global energy demand is surging, with oil being one of the leading energy sources, and many of the reservoirs are on the verge of depletion. Therefore, enhanced oil recovery (EOR) techniques are becoming more significant to satisfy this energy demand. Polymer flooding is a proven chemical EOR technology that can be applied at the early stages of waterflooding (Chang, 1978; Zhong *et al.*, 2017; Khalilinezhad *et al.*, 2019; Chen *et al.*, 2021a). Polymers are added at varying concentrations to the injected water to increase its viscosity (Gao *et al.*, 2014; Saboorian-Jooybari *et al.*, 2016; Panthi *et al.*, 2016). The polymer solution improves the water-oil mobility ratio, which reduces viscous fingering and results in a better sweep efficiency of the reservoir (Sandiford, 1964; Rashidi *et al.*, 2009; Han *et al.*, 2014; Yoo *et al.*, 2020; Lamas *et al.*, 2021).

In addition to increasing the viscosity of the injected water, polymers also alter the permeability of the reservoir (Vossoughi and Buller, 1991; Vasquez *et al.*, 2009), which lowers the mobility of the water injected. Mobility ratio (M), which is defined as the ratio of the

displacing phase mobility to displaced phase mobility (**Equation 2.1**), is the most crucial parameter for polymer flooding operations.

$$M = \frac{\lambda_w}{\lambda_o} = \frac{\frac{k_{rw}}{\mu_w}}{\frac{k_{ro}}{\mu_o}}, \quad (2.1)$$

where λ_w is the mobility of the displacing phase (water) and λ_o is the mobility of the displaced phase (crude oil). k_{rw} and k_{ro} are the relative permeability to water and oil, respectively. μ_w and μ_o refer to the water viscosity and oil viscosity, respectively. Based on the value of mobility ratio (M) relative to unity, the displacing process is considered to be either favorable and a piston-like displacement when $M \leq 1$, or unfavorable and instable when $M > 1$ (Aronofsky, 1952; Skauge *et al.*, 2014). To attain a favorable mobility ratio (M) and improve the sweep efficiency, increasing the viscosity of the water phase is considered to be the most common way (Assunção *et al.*, 2011).

Juárez *et al.* (2020) conducted coreflooding experiments on sandstone cores with varying concentrations (1,500 to 3,000 ppm) of HPAM polymer to achieve a viscosity ratio of oil to polymer in the range of 2 to 18 corresponding to mobility ratio of 0.5 to 4. They concluded that the highest recovery efficiency is achieved at a mobility ratio of 1 ($M = 1$), corresponding to a viscosity ratio of 5. Polymer flooding has been widely used in sandstone reservoirs with mild conditions of low temperature (below 60 °C), low salinity (less than 100,000 ppm), and high permeability (greater than 200 mD). Nevertheless, its application is limited in carbonate reservoirs, particularly in the Middle East region, due to the prevailing harsh reservoir conditions. Sheng *et al.* (2015) surveyed about 700 polymer projects across 24 countries, of which only 14% were conducted in carbonate reservoirs.

2.2 Harsh Conditions of Middle East Carbonate Reservoirs

Carbonate rocks are a class of sedimentary rocks that are composed mainly of carbonate minerals. The two main types of carbonate rocks are limestone, composed of calcite or aragonite (different crystal forms of CaCO_3), and dolostone, composed of dolomite ($\text{CaMg}(\text{CO}_3)_2$). Carbonate reservoirs are characterized by varying porosity and permeability due to varying depositional conditions of these reservoir rocks (Jardine and Wilshart, 1982). Carbonate reservoirs are also characterized by complex heterogeneities related to the rock

mineral compositions, rock properties, matrix pore systems, and fracture densities (Olairewaju, 1997; Ehrenberg and Nadeau, 2005; Brigaud *et al.*, 2014).

Harsh reservoir conditions indicate the combination of two or more conditions, including complex heterogeneity, mixed-to-oil wettability, low permeability values less than 100 mD, high reservoir temperatures above 85 °C, high salinity above 100,000 ppm, and hardness over 1,000 ppm (Chen and Mohanty, 2013; Diab and Al-Shalabi, 2019; Adila *et al.*, 2020). The significant challenges of polymer flooding in these conditions are the poor performance of synthetic polymers in high salinity and high temperature conditions as well as the poor polymer injectivity in low permeability porous media (Ghosh *et al.*, 2019). In addition, the presence of fractures and high permeable streaks tend to complicate the application of EOR. High permeability zones are essential conduits for oil production in the early stage of the reservoir. However, as the field matures, these same high permeable streaks become the conduits for the early breakthrough of water. Therefore, in EOR projects involving the injection of expensive fluids, precautions need to be taken to avoid the early breakthrough of these expensive chemicals (Manrique *et al.*, 2007).

2.3 Overview of Polymer Retention in Carbonate Reservoirs

Polymer retention is considered one of the critical parameters in deciding the economic viability of a polymer flood. Thus, the success of a polymer flood depends on determining the exact retention levels and designing the polymer flood accordingly. Polymer retention is defined as the loss of polymer molecules in the porous media due to mainly the interactions between the injected polymer molecules and the porous rock. As a result, the viscosity of the injection fluid decreases with polymer adsorption, leading to a reduction in the polymer flood efficiency (Sorbie, 1991). Zhang and Seright (2014) demonstrated the economic impact of adsorption in terms of delay factor, for which they considered a range of polymer adsorption values and polymer concentrations of 9-700 µg/g of rock and 500 to 3,000 ppm, respectively. They calculated the delay factor using **Equation 2.2** and plotted it versus the polymer adsorption as presented in **Figure 2.1**. They concluded that higher adsorption causes higher economic impacts on polymer flooding as more polymer is consumed to achieve the desired efficiency (Zhang and Seright, 2014; Yoo *et al.*, 2020; Wartenberg *et al.*, 2021).

$$PV_{ret} = \left[\rho_{rock} \frac{1-\phi}{\phi} \right] \left[\frac{R_{pret}}{c} \right], \quad (2.2)$$

where PV_{ret} is the pore volume delay per pore volume injected, ρ_{rock} is the density of rock (g/cc), ϕ is the porosity, R_{pret} is the polymer adsorption levels ($\mu\text{g/g}$ of rock), and C is the polymer concentration (ppm).

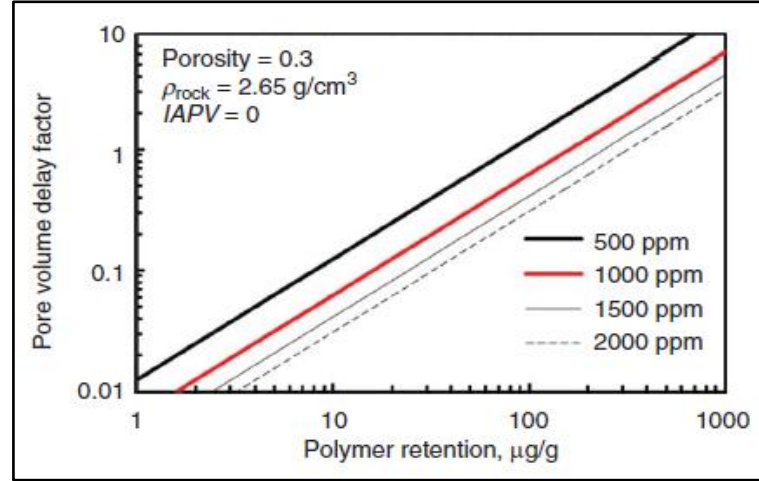


Figure 2.1: Polymer bank delay factors associated with polymer adsorption (Zhang and Seright, 2014).

2.3.1 Polymer Retention Mechanisms

Polymer retention mechanisms include adsorption, mechanical entrapment, and hydrodynamic retention. These mechanisms are ordered in terms of their significance where adsorption is the most significant and hydrodynamic retention is the least significant. The mechanism of physical adsorption of polymers onto the pore surface is due to the high affinity of polymers to many reservoir rocks, as a result of van der Waal's forces in the case of synthetic polymers and hydrogen bonding forces for biopolymers (**Figure 2.2**). Polymer adsorption mainly depends on the rock surface area available for the polar groups of long-chain polymer molecules to get adsorbed on; a larger surface area leads to a higher absorption rate (Grattoni *et al.*, 2004; Cheraghian *et al.*, 2014; Banerjee *et al.*, 2017; Al-Hajri *et al.*, 2018; Berg *et al.*, 2019). Mechanical entrapment is observed in lower permeability reservoirs, where the polymer molecules get trapped in the pore spaces with smaller throat sizes. Mechanical entrapment can be reduced to some extent in low permeable rocks either by considering low molecular weight polymers or by pre-shearing and filtrating the high molecular weight polymers (Choi *et al.*, 2014; Ghosh *et al.*, 2019; Ghosh and Mohanty, 2020; Loaiza *et al.*, 2020; Khalilinezhad *et al.*, 2021).

Hydrodynamic retention is the polymer solution flow rate-dependent retention. Once the retention reaches equilibrium, an increase in flow rate results in loss of additional polymer to the porous media. However, this flow rate dependent retention is assumed to be reversible, i.e., when the flow rate is brought back to the initial rate or flow is completely stopped, the retained polymer molecules are released back to the main flow channels (Marker, 1973; Zhang and Seright, 2015; Idahosa *et al.*, 2016). In case of high shear rates in restricted flow regions, the polymer molecules change from coiled form to an elongated shape, thus easing its flow through small diameter pores and gets trapped in these pores (Marker, 1973). AlSofi *et al.* (2017a) conducted single-phase coreflood experiments on carbonate cores with varying permeabilities from 45.2 to 12,836 mD. The polymer dynamic adsorption values ranged from 0.155 to 0.530 mg/g-rock, showing a decreasing trend in polymer adsorption with increasing permeability, which is mainly due to the entrapment of polymer molecules in low permeable carbonate rocks.

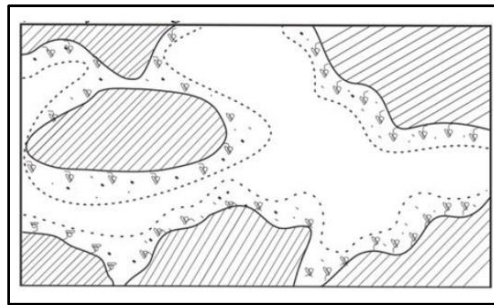


Figure 2.2: Polymer adsorption in porous media (Al-Hajri *et al.*, 2018).

2.3.2 Inaccessible Pore Volume

The fraction of pore spaces in the reservoir rocks that the polymer molecules cannot access is defined as the inaccessible pore volume (IPV). This fractional pore volume has two kinds of impact on the polymer flooding efficiency. In case of higher amount of residual oil saturation with less percentage of IPV, it accelerates the polymer propagation through the porous medium resulting in an early breakthrough of the polymer solution (Dawson and Lantz, 1972; Idahosa *et al.*, 2016; Akbari *et al.*, 2019). Hence, the polymer displaces more crude oil to obtain higher recovery. Further, in case of low residual oil saturation with higher amount of IPV, the polymer cannot access the trapped oil in these pores (Wu *et al.*, 2017). Inaccessible pore volume positively affects the polymer flooding efficiency as it reduces the amount of polymer being

contacted with the rock surface, thus reducing the amount of polymer adsorbed onto rock surface in the porous medium (Dawson and Lantz, 1972).

Dawson and Lantz (1972) demonstrated the combined effect of polymer adsorption and IPV through polymer breakout curves for four cases: (A) No retention and no IPV, (B) No retention and 0.25 PV IPV, (C) 0.25 PV retention and no IPV, and (D) 0.25 PV retention and 0.25 PV IPV (**Figure 2.3**). The ideal case is expected with neither retention nor IPV, where the polymer breakout occurs after injecting 1PV (Case A). However, an early breakthrough occurs in Case B with no retention and an IPV of 0.25. On the contrary, a delay in breakthrough of the front edge without affecting the back edge resulting in a smaller polymer bank is observed in Case C with no IPV and retention of 0.25 PV. Lastly, in Case D polymer bank shifts forward indicating a reduction of polymers in the effluents and showing a lower adsorption in the porous media, where both retention and IPV are combined (Dawson and Lantz, 1972; Al-Hajri *et al.*, 2018).

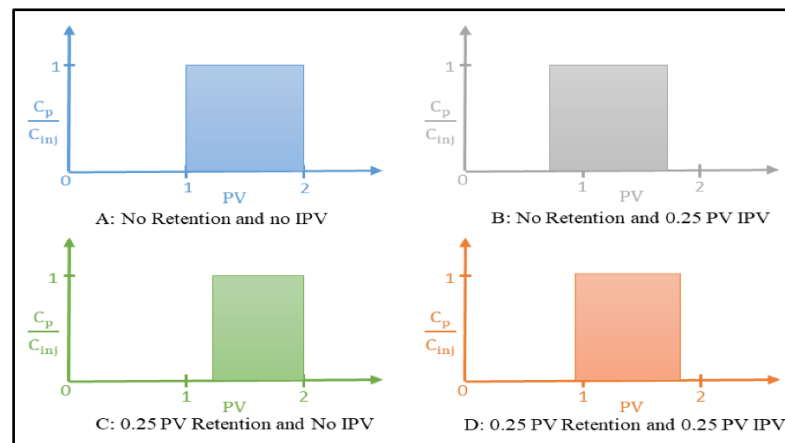


Figure 2.3: Polymer breakout curves (Dawson and Lantz, 1972; Al-Hajri *et al.*, 2018).

Akbari *et al.* (2019) explained the two mechanisms contributing to the inaccessible pore volume; size exclusion and wall exclusion. Size exclusion effects include the dependency of the inaccessible pore volume on the hydrodynamic radius of polymer molecules, permeability to porosity ratio, and pore-size distribution of the porous medium. A more pronounced IPV effect occurs in the case of high molecular weight polymers and lower permeability to porosity ratios. The wall exclusion effect explains the flow through porous media, which follows the parabolic Poiseuille velocity profile, i.e., central layer flows with maximum velocity, and the layers close to the wall have zero velocity. Hence, the polymer molecules will flow freely in the center, and their movement is restricted across the boundary of the pore walls. There is a

higher entropy in the center due to depleting polymer molecules; hence, polymer molecules near the pore wall in the pore volume tend to move towards the central region. This depleted layer is called the Excluded Pore Volume (EPV). EPV contributes to the velocity enhancement effect and is most dominant in large pore sizes. Bennetzen *et al.* (2014) determined IPV values varying from 15 – 20% from their coreflooding experiments on oil-wet limestone rocks with low permeability ranging from 0.3 – 20 mD using HPAM polymers. AlSofi *et al.* (2017b) also obtained an IPV in the same range of 17% from their coreflooding experiment on a carbonate core.

2.4 Factors Affecting Polymer Retention

Polymer retention in porous media is a complex phenomenon, and many factors need to be considered while dealing with this issue. Therefore, this section extensively reviews the effects of polymer type, reservoir temperature, water salinity and composition, and the presence of oil on polymer retention.

2.4.1 Effect of Polymer Type

As was previously mentioned, the two most widely used polymer types are synthetic partially hydrolyzed polyacrylamide (HPAM) and biopolymer Xanthan Gum.

HPAM is relatively cheap and hence used in most field projects (Smith, 1970; Zhang *et al.*, 2011; Zaitoun *et al.*, 2012; Aalaie *et al.*, 2014; Sheng *et al.*, 2015). However, HPAM polymers have limited applications in harsh reservoir conditions of high temperature and high salinity due to their instability at these conditions. The acrylamide groups within the HPAM polymer hydrolyze to form acrylate groups and this is accelerated at high temperature and high salinity conditions resulting in precipitations (Diab and Al-Shalabi, 2019; Jouenne, 2020). Polymers containing N-Vinylpyrrolidone (NVP) are developed to improve thermal stability in harsh conditions. NVP, being a neutral monomer, decreases the polymer's anionicity and protects neighboring acrylamide units from hydrolysis. Despite their improved stability, these polymers have certain drawbacks, such as limited molecular weight leading to decreased viscosifying power, higher cost, and potential raw material supply issues (Jouenne, 2020). Polymers containing 2-Acrylamido-2-Methyl Propane Sulfonate (AMPS) are highlighted for their ability to withstand temperatures above 95 °C, particularly when the AMPS content is high. Jouenne (2020) discusses various studies and aging tests demonstrating that AMPS-rich

copolymers, especially those with high AMPS content, show excellent thermal stability, retaining significant viscosity even at high temperatures and salinities. Acrylamido Tertibutyl Sulfonate (ATBS) is an alkyl acrylamide monomer that also has a sulfonic acid group attached to it. The acrylic functional group in the molecule allows the monomer to polymerize easily with other comonomers. ATBS inhibits acrylamide (AM) hydrolysis, the rate of AM hydrolysis decreases with an increase of the ATBS content (Jouenne, 2020). Masalmeh *et al.* (2019) conducted studies on SAV10, an ATBS based polymer, concluded that these polymers could be efficient in harsh reservoir conditions of Middle East carbonate reservoirs.

However, synthetic anionic polymers show higher tendency to get adsorbed on positively charged carbonate rocks. Wang *et al.* (2021) studied polymer retention in carbonate cores with a formation water salinity of 213,723 ppm and a temperature of 100 °C using a sulfonated polyacrylamide polymer, a copolymer of acrylamide and acrylamido-tert-butyl sulfonate (ATBS), with a sulfonation degree of about 25%. The polymer was stable under these harsh conditions and led to dynamic retention in the range 21 - 61 µg/g of rock. Dynamic adsorption studies of sulfonated polyacrylamide on low permeability carbonate reservoirs were determined in the range of 100 to 200 µg/g of rock (Han *et al.*, 2014; Jabbar *et al.*, 2019). Polymer dynamic adsorption for the polymers SAV 333 and SAV 225 with a balanced ratio of ATBS and NVP on carbonate rocks was found in the range 28 to 84 µg/g of rock (Gaillard *et al.*, 2014).

Xanthan gum is a high-molecular-weight polysaccharide biopolymer commonly used in the oil and gas industry. These polymers are relatively insensitive to salinity. The main disadvantages of Xanthan gum are formation plugging characteristics and susceptibility to bacterial attack. Furthermore, Xanthan gum polymers are unstable in presence of oxygen at high temperatures (Chang, 1978). Contrary to Xanthan gum, Schizophyllan and Scleroglucan are advanced biopolymers stable at high temperature and salinity conditions (Fournier *et al.*, 2018; Mukherjee *et al.*, 2018). Schizophyllan and Scleroglucan showed shear thinning behavior with good thermal stability up to 120 °C and salt tolerance up to 220,000 ppm (Elhossary *et al.*, 2020; Shoaib *et al.*, 2020). However, these polymers show injectivity issues in low permeability cores and have high manufacturing cost. Hence its field applications are very limited.

In the case of biopolymers, their helical structure and existence as a semi-rigid rod structure in solution impart higher viscosity at lower concentrations. Also, their nonionic structure leads to lower retention rates (Jouenne, 2020). Static adsorption studies of biopolymer Schizophyllan on calcite, dolomite, kaolin, and silica were determined to be 1.18, 1.58, 0.046,

and 1.40 mg/m², respectively. Coreflooding experiments on Scleroglucan polymers on high-permeability sandstone rock and low-permeability carbonate rocks at residual oil saturation showed acceptable polymer retention values of 12 and 8 µg/g of rock, respectively (Fournier *et al.*, 2018).

2.4.2 Effect of Temperature

The influence of temperature on polymer retention in porous media is a complex phenomenon that has been the subject of numerous studies. Some investigations suggest a positive correlation between temperature and polymer retention. At high temperatures, the polymer molecules may become unstable and undergo precipitation leading to increased polymer retention with temperature (An *et al.*, 2014; Hassan *et al.*, 2022). However, other studies have shown a negative relationship between temperature and polymer retention (Wiśniewska, 2012; Sodeifian *et al.*, 2015; Omini *et al.*, 2019). At higher temperatures, polymer solubility in brine is relatively higher, leading to a decrease in adsorption quantity (Jouenne, 2020). Further, for anionic polymers, the thermal motion of ionic groups increases, which weakens the electrostatic interaction responsible for holding polymer molecules onto the rock surface (Liu *et al.*, 2016). Other binding forces responsible for polymer adsorption, including Vander Waals forces and hydrogen bonding, also weaken at high temperatures decreasing polymer retention (Hollander *et al.*, 1981). Shoaib *et al.* (2020) studied the adsorption of Scleroglucan biopolymer on calcite mineral and observed a downward trend in polymer adsorption values from 1.2 to 0.84 mg/m² with an increase in temperature from 25 to 80 °C. Static adsorption studies by Thomas *et al.* (2020) on Scleroglucan biopolymer and SAV10 synthetic polymer at varying temperatures from 20 to 70 °C showed retention values from 309 to 160 µg/g of rock for Scleroglucan and 236 to 95 µg/g of rock for SAV10, respectively.

Overall, the effect of temperature on dynamic polymer retention for synthetic polymers is a complex phenomenon. Therefore, it is important to carefully consider the temperature and other reservoir conditions when designing and optimizing polymer flooding operations.

2.4.3 Effect of Water Salinity and Composition

Salinity can significantly affect polymer retention in polymer flooding in carbonate and sandstone reservoirs. In carbonate reservoirs, high salinity can increase the retention of polymers by reducing the permeability of the reservoir rock. This is because high salinity brines

can cause precipitation of minerals, such as calcium carbonate, which can clog the pore throats of the reservoir rock, reducing the effective permeability and increasing the retention of polymers (Masalmeh *et al.*, 2019). In addition, high salinity brines can also cause salting-out of the polymer, leading to a decrease in its solubility and an increase in its retention. In sandstone reservoirs, in the presence of divalent ions, such as calcium or magnesium, the anionic polymers can form bridges between the negatively charged sandstone reservoirs, increasing the retention of polymers. However, the effect may be less pronounced in sandstones than that in carbonates. This is because sandstone rocks are negatively charged and have relatively larger pore sizes and higher porosity than carbonate rocks, which can limit the extent of pore plugging and polymer retention (Manichand and Seright, 2014; Al-Shajalee *et al.*, 2021).

To minimize the effect of salinity on polymer retention in both carbonate and sandstone reservoirs, it is essential to select the appropriate polymer type and suitable concentration for the specific reservoir conditions, as well as to optimize the injection water salinity and composition. In some cases, pre-flushing the reservoir with low-salinity water before polymer injection can also help reduce the effect of salinity on polymer retention. Studies have also shown that lower adsorption is achieved for lower salinity polymer flooding for sandstone and carbonate rocks (Brantson *et al.*, 2020; Ramkissoo *et al.*, 2020; Chen *et al.*, 2021b). In low salinity polymer flooding, due to the reduced amount of hardness ions, i.e., both calcium and magnesium, the electrostatic repulsion between the carboxyl group in the polymer and the negatively charged sandstone rock surface is enhanced, which reduces the adsorption of the polymer onto the rock surface (Smith, 1970; Al-Murayri *et al.*, 2019; Wang *et al.*, 2020). Unsal *et al.* (2018) studied dynamic polymer adsorption on sandstone reservoir core plugs in single-phase conditions with a low salinity polymer solution of 785 ppm salinity and a synthetic formation brine polymer solution of 6400 ppm salinity. The polymer adsorption was found to be lower in low salinity polymer flooding, i.e. 53 µg/g compared to 271 µg/g for high salinity polymer flooding.

In carbonate rocks, the low adsorption from low-salinity polymer flooding is due to the expansion of polymer molecules at the lower salinities. These expanded polymer molecules in smaller quantities will satisfy the adsorption sites (Sorbie, 1991). Also, the low salinity polymer flooding with a higher concentration of negatively charged SO_4^{2-} ions reduces polymer adsorption as these negatively charged SO_4^{2-} ions adsorb onto positively charged carbonate rock surface (Al-Shalabi *et al.*, 2014; Al-Shalabi and Sepehrnoori, 2016; Sharma and Mohanty, 2018; Tetteh *et al.*, 2020); thus, reducing the adsorption sites for polymers. Lee *et al.* (2019)

conducted polymer flooding studies on carbonate cores with a salinity of 6000 ppm consisting of HPAM polymer and potential determining ions (SO_4^{2-} and Ca^{2+}) at varying concentrations and varying pH. They reported that adsorption was lower in high SO_4^{2-} concentration (4000 ppm), absence of Ca^{2+} ions, and a neutral pH. Additionally, polymer adsorption reduction by low salinity polymer flooding was further supported by AlSofi *et al.* (2018) where they observed adsorption values between 133 to 230 $\mu\text{g/g}$ of rock for high salinity polymer flood of 69,000 ppm salinity as opposed to 84 to 102 $\mu\text{g/g}$ of rock for low salinity polymer flood of 7000 ppm salinity.

2.4.4 Effect of Oil Presence

Residual oil affects polymer adsorption depending on the wettability of the rock surface and the polymer type. In oil-wet reservoirs, polymer adsorption values are usually less in the presence of oil regardless of the polymer type as the residual oil forms a wetting film around the rock particles and smoothens the irregularities in the rock grain particles. The latter leads to a reduction in the total surface area and the oil-water interfacial area available for the polymer molecules to get adsorbed onto (Hughes *et al.*, 1990; Broseta *et al.*, 1995; Hatzignatiou *et al.*, 2015; Wang *et al.*, 2020 and 2021). On the contrary, in water-wet reservoirs, the oil droplets get trapped inside the large pore spaces, and additional adsorption sites are formed, causing an increase in adsorption in case of non-ionic polymers in the presence of oil (Broseta *et al.*, 1995).

Studies have shown that in oil-wet reservoirs, retention values are reduced by a factor of 4 to 6 in the presence of oil (Skauge *et al.*, 2020). Furthermore, in low permeability oil-wet rocks, the combined effect of a reduced surface area in the presence of oil and a high inaccessible pore volume reduces the polymer adsorption onto the rock surface in the porous medium (Wever *et al.*, 2018). Coreflooding experiments conducted on low permeability oil-wet limestone rocks, with HPAM polymer at varying concentrations from 500 to 1,000 ppm led to dynamic adsorption values in the range of 10 to 20 $\mu\text{g/g}$ of rock. The latter is considerably low when compared to dynamic adsorption of 530 $\mu\text{g/g}$ for a low permeability limestone rock in a single-phase experiment (Al Sofi *et al.*, 2017).

2.5 Desalination Methods

Low salinity and chemistry alteration of the injection water is gaining more attraction for chemical EOR applications. These low salinity brines consume fewer chemicals to achieve the target in-situ viscosity than higher salinity brines, thus leading to significant cost reduction (Shiran and Skauge, 2013; Vermolen *et al.*, 2014; Kakati *et al.*, 2020). Brine recipes of varying compositions are achieved by varying injection water salinity and ionic composition. Commonly used desalination techniques include chemical precipitation technologies, thermal-based methods, and membrane-based methods. Chemical precipitation technologies involve the addition of chemical reagents to remove divalent cations (Ca^{2+} and Mg^{2+}) and it is achieved by raising the pH of the water by different techniques to values greater than 10. Different chemical precipitation technologies include lime/soda ash and caustic soda softening techniques. In lime/soda ash softening techniques as the name indicates, lime is added to remove the carbonate hardness and soda ash is added to remove non-carbonate hardness. Whereas, in caustic soda softening technique, caustic soda is added to raise the pH thus removing both carbonate and non-carbonate hardness. However, these methods are economically non-viable for field-scale use due to the high cost of the chemicals required and the obstacles related to removing and disposing of the precipitated sludge (Zadhaitari and Asr, 2013). Thermal technologies heat the saline feed water to collect salt-free pure water as a condensed vapor from the distillation process (Velarde and Alejandro, 2018). On the other hand, membrane-based technologies apply pressure to force the desalted water to pass through the membrane and leave the selective salts behind (Nair *et al.*, 2019).

Ayirala *et al.* (2010) concluded in their review of various seawater desalination methods that thermal-based methods are not suited for offshore fields due to the difficulty of accommodating the ample space, weight, and steam requirements. Nonetheless, this study proposes that membrane-based reverse-osmosis is an attractive option in offshore environments, given its relatively compact space and lower energy requirement than thermal methods. Reverse osmosis (RO) and nanofiltration (NF) are the two membrane-based desalination methods. In Reverse osmosis, the partially permeable membrane is much tighter with pore sizes less than or equal to 0.0005 microns. Furthermore, these partially permeable membranes are capable of efficiently rejecting both monovalent and divalent ions from seawater. Hence, the product from RO membranes is essentially freshwater, and the rejected water is highly concentrated in both monovalent and divalent ions. On the contrary, the partially permeable membranes in Nanofiltration units are relatively larger, with pore sizes

ranging from 0.005 to 0.05 micron and a 200 Dalton molecular weight cut-off. Moreover, nanofiltration membranes selectively reject only divalent cations and sulfates with high rejection efficiencies. Hence, these product waters are rich in monovalent ions, whereas the reject water contains only divalent ions.

Yousef and Ayirala (2014) developed a new water-ionic technology combining the two-membrane-based process nanofiltration and reverse-osmosis in a parallel configuration to obtain different streams of water with varied ionic strengths and compositions. The different streams of water obtained are mixed effectively to yield a required brine recipe. Nair *et al.* (2016) developed a low salinity brine formulation with varying ionic compositions for EOR applications in carbonate reservoirs where a combination of pressure-based membrane process reverse osmosis and nanofiltration was used to develop these recipes. The following dilution options were considered: a) Nanofiltration retentate and reverse-osmosis membrane permeate, b) Nanofiltration retentate with multi-flash distillation (MSFD) of seawater c) Nanofiltration retentate, and naturally fresh water. Although these mentioned technologies yield a feasible solution, they still have limitations in altering the water chemistry of the injection water, especially when it comes to incorporating selected ions and providing efficient water management for large-scale field applications. Ayirala and Yousef (2016) conducted a comprehensive review of some emerging and existing desalination technologies to propose a potential water treatment solution that can efficiently tune the injection water chemistry for smart waterflooding in carbonate reservoirs. Their review concluded that there is no commercial technology available yet to selectively remove specific ions from seawater in one-step and meet the desired water chemistry requirements for smart-water flooding. However, a combination of different technologies can produce the desired combination of low salinity brine recipes.

2.6 Economics of Low Salinity Polymer Flooding

In general, studies have shown that the economics of polymer flooding is governed by the amount of oil recovered and cost of the polymer. For commonly used HPAM polymers, the cost of the polymer is \$1.50/lb (Alusta *et al.*, 2012; Vermolen *et al.*, 2014). Further, polymer injection cost and polymer production are \$0.50/bbl and \$0.50/bbl, respectively (Alusta *et al.*, 2012). Wang *et al.* (2003) in their study has shown that operational costs for polymer flooding appear higher by \$0.58 per barrel compared to waterflooding. Also, the treatment costs for both

water and produced fluids are higher in polymer flooding by \$0.14 and \$0.316 per barrel, respectively.

Application of low salinity polymer flooding can reduce the cost of polymer flooding projects in various ways. Vermolen *et al.* (2014) have analyzed the economic aspects of using low salinity brine in polymer flooding for enhanced oil recovery (EOR). This evaluation considered the impacts of polymer stability and adsorption on the overall economics of the project. The study concluded that application of low salinity brine reduces the cost through reduced polymer concentration, as the low salinity water reduces the polymer concentration needed to achieve the desired viscosity. This reduction can be substantial, especially in high salinity reservoirs. For example, in reservoir with 260,000 ppm Total Dissolved Solids (TDS), polymer concentration can be reduced by 3-4 times by lowering the make-up brine salinity to 1,500 ppm TDS. Further, this study demonstrated that the shear sensitivity of polymers decreases with lower salinity, which is beneficial as it reduces the viscosity loss during mechanical processes. Moreover, lower salinity also leads to fewer issues with scaling, souring, and oil/water separation, enhancing overall operational efficiency and potentially reducing costs related to these issues. The latter study emphasized that while using low-salinity polymer flooding, polymer adsorption can be minimized. Hence, the delay in the oil recovery can be reduced, lowering the overall cost. For harsh reservoir conditions which require a more expensive polymer, then the polymer cost saving associated with the low salinity injection water would increase significantly.

Further, in the low salinity polymer flooding. The production of low salinity brine comes at a cost. Reverse osmosis desalination costs were USD 0.80/m³ of treated water (onshore), and greater than USD 2.2/m³ of treated water (offshore) (Yousef and Ayirala, 2014). Onshore-treatment costs of produced water from the North Sea differ from 0.19 to 3.40 USD/bbl of produced water (Nair *et al.*, 2019). Nair *et al.* (2016) has performed economic analysis of smart water production for enhanced oil recovery (EOR) in chalk reservoirs with various scenarios: a) Nanofiltration retentate and reverse-osmosis membrane permeate, b) Nanofiltration retentate with multi-flash distillation (MSFD) of seawater c) Nanofiltration retentate, and naturally fresh water. They showed that a combination of NF and RO in parallel configuration can be considered as the most economic feasible option when compared to other advanced desalination technologies. The membrane costs factored into the economic analysis were \$726 for a reverse osmosis membrane and \$335 for a nanofiltration membrane.

The research conducted by Ayirala *et al.* (2010), which involved an advanced facility engineering analysis utilizing reverse osmosis desalination, evaluated the cost-effectiveness of

using low salinity water in offshore polymer flooding operations relative to traditional seawater polymer flooding. The study examined two scenarios based on different injection capacities 10,000 m³/d and 45,000 m³/d and two levels of polymer solution viscosity of 3 cP and 6 cP. Findings from this study indicate that low salinity water polymer flooding stands out as a cost-efficient method when compared to its seawater counterpart. The study estimates that the additional investment in desalination technology could be recovered within a period ranging from 1.6 to 4 years, due to the substantial cost reductions in chemical usage and polymer processing facilities attributed to the low salinity approach. Moreover, the time required to recover the costs was observed to be shorter for high viscous polymer solution, as these conditions typically necessitate higher polymer concentrations and more extensive facilities when using seawater, thus leading to enhanced operational expenditure savings.

2.7 Correlation between Static and Dynamic Retentions

Accurately determining polymer retention is pivotal in ensuring the efficacy and operational success of a polymer flood project. The precision in these determinations is crucial as it governs the optimal performance of the injected polymer solution, subsequently impacting the oil recovery rates and the overall economic viability of the project. In this context, polymer retention studies including static adsorption and dynamic retention studies become crucial tools in evaluating polymer behavior within reservoir conditions.

Static adsorption method is comparatively more accessible, faster, and cheaper than those involving the dynamic adsorption approach. Static adsorption tests are mainly used as a preliminary screening method for polymers. Experiments are conducted on crushed rock, to which a known polymer concentration is transferred and mixed well. Subsequently, the polymer solution is separated from the crushed core, and polymer concentration loss due to adsorption is determined (Szabo, 1975; Ogunberu and Asghari, 2005).

Dynamic retention measurements are obtained by different methods. One of the methods uses mass balance principle to determine polymer retention. In this method, a slug of known polymer concentration is injected through the core, and the effluent polymer concentration is analyzed. The polymer injection is continued until the effluent polymer concentration equals the injected polymer concentration, indicating no more polymer retention is occurring. Then brine post-flush is conducted to flush out all the mobile polymer molecules, and the polymer amount released in the effluent is measured. The difference in amount of polymer injected and polymer produced will give the amount of polymer retained (API RP 63,

1990; Wang *et al.*, 2021). This method was applied in this research. Another method has been discussed in the literature known as the double slug injection method, where two polymer slugs containing a tracer are injected separately, and a thorough brine flush is performed between them. When the first slug is injected, the process of polymer retention prevails, slows down the polymer's movement, and results in a late breakthrough. In addition to adsorption, IPV also leads to an early polymer breakthrough. However, at this point, we cannot differentiate between the relative delays related to adsorption and IPV. When the second polymer slug is injected, the polymer front is accelerated due to the IPV, as the adsorption has already been satisfied during the previous polymer slug, leading to an early breakthrough. Once the displacement is complete, the effluent is collected and analyzed for the tracer and the polymer. One can calculate the retention by determining the delay between two polymer fronts. This method can also be applied at field scale to determine polymer retention (Manichand and Seright, 2014).

Dynamic polymer retention values, a combination of adsorption and mechanical entrapment, results in differing shapes of the normalized polymer concentration profile, as depicted in **Figure 2.4**, assuming that no dispersion is occurring. In scenarios lacking mechanical entrapment, the normalized polymer concentration (illustrated as curve b in **Figure 2.4**) remains at zero until the point of breakthrough, at which it abruptly rises to and maintains a level of unity. Conversely, in the presence of mechanical entrapment, the breakthrough is observed to occur with a slight delay (represented by curve c in **Figure 2.4**), with the concentration at the time of breakthrough rising from zero to approximately 0.5. Following this, there is a gradual increase in concentration until it finally reaches unity, necessitating the injection of numerous pore volumes (Farajzadeh *et al.*, 2016; Akbari *et al.*, 2019). In dynamic retention experiments that utilize a tracer, it is possible to distinguish between adsorption and mechanical entrapment by analyzing the concentration profiles of both the tracer and the polymer. The difference in positioning (or shift) between these profiles indicates adsorption, while the variation (or deviation) in their profiles points to mechanical entrapment (Farajzadeh *et al.*, 2016). Conversely, in experiments conducted without a tracer, differentiating between adsorption and mechanical entrapment becomes significantly more challenging.

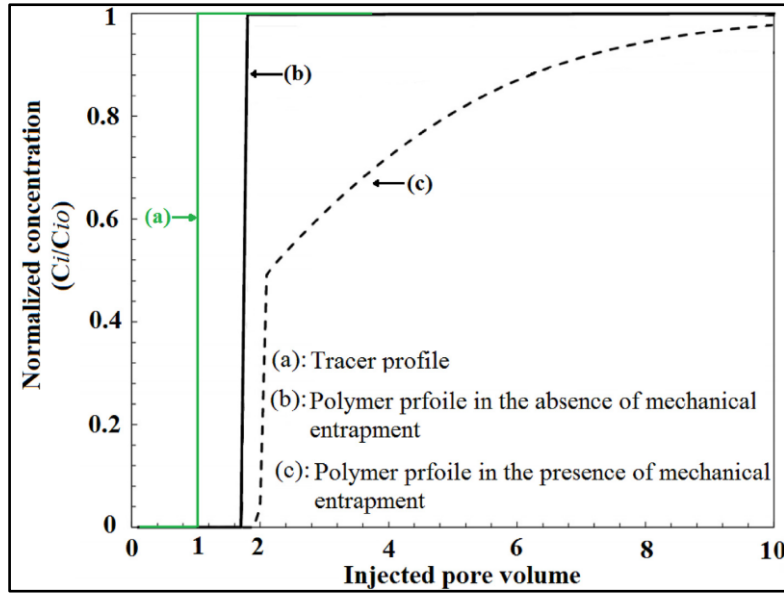


Figure 2.4: Normalized polymer concentration profile with and without mechanical entrapment (Akbari *et al.*, 2019).

The results obtained from the static tests are not representative of field values due to factors including differences in the surface area exposed, the inconsistency in the residence time, and varying solid to liquid ratio. In addition, mechanical entrapment cannot be predicted, and there are disagreements in wettability on disintegrated rock and the reservoir rock (Szabo, 1975; API RP 63, 1990; Al-Hajri *et al.*, 2020; Thomas *et al.*, 2020; Hernández-Morales *et al.*, 2023). Nevertheless, researchers are currently undertaking initiatives to control these parameters in order to make static adsorption as representative as dynamic adsorption. Al Hajri *et al.* (2020) made a significant contribution to this area by developing a correlation between static and dynamic retentions within sandstone reservoirs. Their work is pivotal as it seeks to bridge the gap between static adsorption measurements and dynamic retention predictions. However, the correlation presented has its limitations. Notably, it falls short in addressing the influence of mechanical entrapment and the presence of oil in the reservoir. These elements are crucial as they could significantly affect the accuracy of retention predictions. Afolabi *et al.* (2021) introduced an innovative approach designed to quantitatively map various retention mechanisms specifically in sandstone reservoirs. This methodology underscores the evolving intricacies of understanding retention in enhanced oil recovery scenarios, providing a clearer lens to discern how different mechanisms play out within the confines of sandstone reservoirs. One of the primary drawbacks of their model is the omission of considerations related to the

presence of oil in the reservoir. This is a crucial aspect, as the oil presence can significantly affect retention mechanisms.

These limitations necessitate further refinements to the correlation to incorporate these unconsidered parameters, paving the way for a more comprehensive and robust predictive model suitable for a wider range of reservoir conditions.

2.8 Machine Learning Techniques

Machine learning (ML) is a specialized area within artificial intelligence (AI) that utilizes data and mathematical algorithms to perform certain tasks. The process starts with “training data”, which is the initial set of data used to help the machine recognize patterns between input and output variables. After training, the model is tested with new data, which has not seen before, known as “test data”. This helps to check if the machine learning model has been trained well enough to make accurate predictions or decisions (Meyes *et al.*, 2018; Sarker, 2021).

Depending on the data and the goal, ML is usually grouped into three main types: supervised learning, unsupervised learning, and semi-supervised learning. First, supervised learning involves training models using a labelled dataset, where both input and corresponding output are provided. In this case, the primary goal of the model is to learn the underlying relationship between the input and output, enabling it to make predictions when presented with new, unseen data. In contrast, unsupervised learning does not rely on labelled data. Instead, it aims to identify patterns, relationships, or structures within the data, often leading to tasks like clustering or dimensionality reduction, where data is grouped based on inherent similarities or differences. Bridging the gap between these two is semi-supervised learning, which utilizes a mix of both labelled and unlabeled data for training. This approach leverages the large volume of often-available unlabeled data to enhance the learning process, benefiting from the underlying structure of the data while also making use of the known labels to guide the learning (Brunton *et al.*, 2020; Jhaveri *et al.*, 2022). In this study, the primary emphasis is on supervised machine learning, a technique where algorithms are trained using labelled data to make predictions or determinations. Within supervised learning, there are two main tasks: regression, which predicts a continuous value, and classification, which categorizes data into predefined labels. While both tasks have their unique applications and characteristics, this work will particularly concentrate on the regression aspect.

2.8.1 Different Concepts in Machine Learning Application

2.8.1.1 Regression Metrics

In regression analysis, various metrics assist in evaluating the accuracy and robustness of predictive models. Often, a combination of these evaluation metrics is needed to assess the performance of the model.

The Mean Absolute Error (MAE) offers insight into the model's performance by calculating the average absolute difference between predicted and true values, ensuring a straightforward linear penalty for every unit of error (Varshini *et al.*, 2021). The MAE is calculated based on the **Equation 2.3** as follows:

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad (2.3)$$

where y_i are the actual values, $\hat{y}_i$ are the predicted values, and n is the number of observations.

Mean Squared Error (MSE) is a widely adopted metric in regression studies that gauges the discrepancy between real and forecasted values. It signifies the mean of the squared variances between the true observed outcomes and the estimations made by the model. The squaring in the formula ensures that each term is positive, so errors in opposite directions do not cancel each other out. It also emphasizes larger errors over smaller ones, meaning that the model is penalized more for making bigger mistakes than for making smaller ones (Ahmad *et al.*, 2021; Yafouz *et al.*, 2022). **Equation 2.4** represents the formula for computing the MSE.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2. \quad (2.4)$$

Root Mean Squared Error (RMSE) is a widely used metric in regression analysis that quantifies the model's prediction error. It represents the square root of the Mean Squared Error (MSE). By taking the square root of MSE, the RMSE gives a more interpretable measure of error in terms of the original units of the dataset, providing an idea of the average magnitude of the error between predicted and actual values (Chai and Draxler, 2014). The RMSE is computed using **Equation 2.5** as follows:

$$RMSE = \frac{1}{n} \sqrt{\sum_{i=1}^n (y_i - \hat{y}_i)^2}. \quad (2.5)$$

The Coefficient of Determination, often denoted as R^2 (R-squared), is a statistical measure that represents the proportion of the variance for a dependent variable that is explained by independent variables in a regression model. It provides an indication of how well the model fits or explains the observed data. An R^2 value of 1 indicates that the regression predictions perfectly fit the data, meaning that all the variability of the dependent variable is accounted for by the independent variables (Sapra, 2014; Chicco *et al.*, 2021). Conversely, an R^2 value of 0 indicates that the model does not explain any of the variance in the dependent variable. The R^2 is determined using **Equation 2.6**.

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - y_{mean})^2}, \quad (2.6)$$

where y_i are the actual values, $\hat{y}_i$ are the predicted values, y_{mean} is the mean value of the data set and n is the number of observations.

2.8.1.2 Bias – Variance Tradeoff

The Bias-Variance Tradeoff encapsulates a core dilemma in machine learning, addressing the delicate balance between two primary error sources in models: bias and variance. Bias arises when a model, due to its overly simplistic nature, fails to grasp the intricate patterns within data, leading to underfitting. This type of model cannot even perform adequately on its training data, let alone unseen data. On the other hand, variance highlights a model's tendency to be overly influenced by minute fluctuations in training data. Such a model, in its quest for perfect training data accuracy, ends up modeling noise and outliers, resulting in overfitting, which harms its performance on new data. In an ideal scenario, a model would simultaneously exhibit low bias and low variance. However, in practical applications, enhancing a model's complexity to reduce bias often inadvertently heightens its variance, and vice versa. Striving for equilibrium, practitioners employ various strategies: intricate models or added features to combat high bias, and data augmentation, feature reduction, or regularization to curb high variance. Ultimately, the art of machine learning hinges on this continuous calibration, ensuring models are adept at generalizing insights from training data to novel scenarios (Gudivada *et al.*, 2017; Guan and Burton, 2022). **Figure 2.5** represents the schematic of bias-variance trade off.

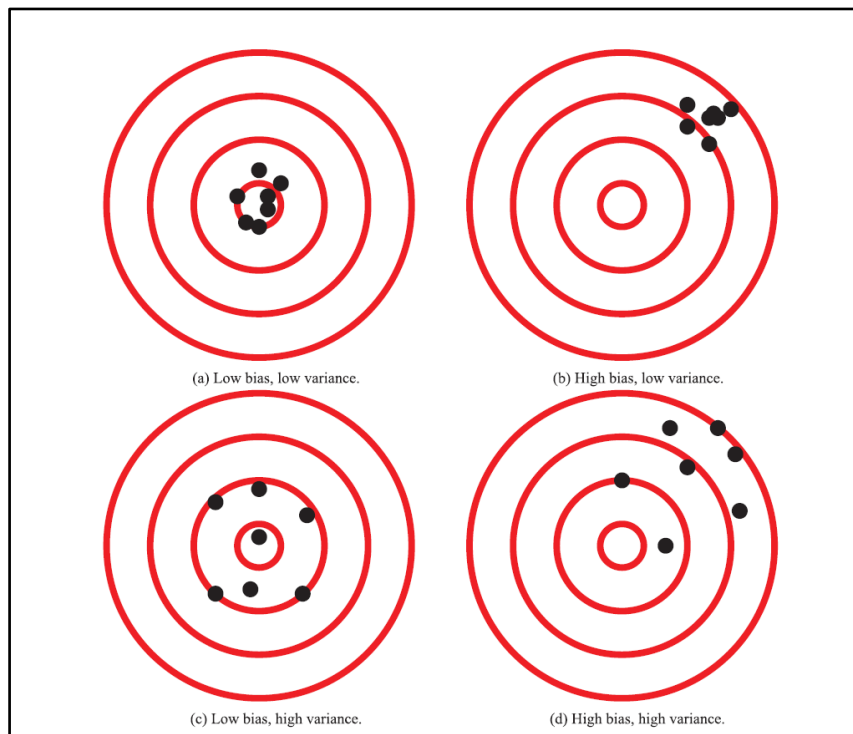


Figure 2.5: Schematic representing the bias-variance tradeoff (Doroudi, 2020).

2.8.1.3 Underfitting

Underfitting is a situation in machine learning where a model is too simple to capture the underlying relationships in the data (**Figure 2.6**). This inadequacy means that the model fails to represent critical aspects of the data, leading to poor performance on both training and unseen datasets. Often a result of overly simplistic algorithms, insufficient features, or premature termination of training, underfitting hinders the model's predictive capability. Essentially, an underfitted model has not learned enough from the training data, rendering it ineffective at generalizing to new, unseen data, and resulting in higher than necessary errors for both known and unknown inputs (Jabbar and Khan, 2014).

2.8.1.4 Overfitting

Overfitting occurs when a model is too complex and learns the training data too well, resulting in poor performance on unseen data. Instead of discerning just the general patterns, an overfitted model captures even the minor fluctuations and anomalies in the training data (**Figure 2.6**). Consequently, while it might perform exceptionally well on the training data, showcasing high accuracy, it struggles to maintain similar performance on new, unseen data. This is because the model has essentially memorized the training set rather than understanding

the underlying structure. Overfitting can result from overly complex models, insufficient training data, lack of proper regularization, or not using a diverse enough dataset during training. Addressing overfitting is critical, as models in real-world scenarios are valued for their ability to generalize to new data, not just their performance on known data (Ying *et al.*, 2019).

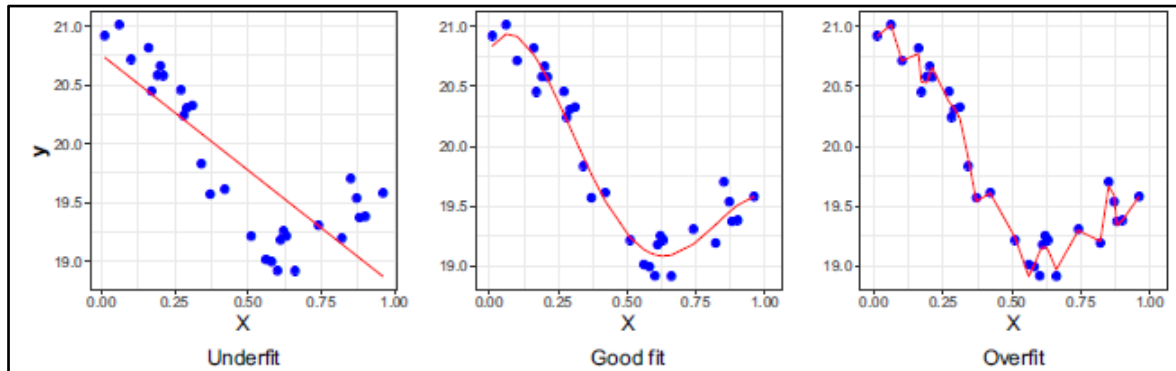


Figure 2.6: Schematic representing underfitting, good fitting, and overfitting (Badillo *et al.*, 2020).

2.8.1.5 K-fold Cross Validation

K-fold cross validation is a technique for evaluating the performance of a predictive model. It involves dividing the dataset into k subsets of approximately equal size. The model is then trained and evaluated k times, each time using a different subset as the validation set and the remaining subsets as the training set. The performance metrics obtained from each fold are averaged to provide a more robust estimate of the model's generalization performance. This approach offers two primary advantages: it utilizes the entire dataset for both training and validation, providing a more comprehensive evaluation, and it mitigates the risk of anomalies from a single random train-test split influencing the model's perceived performance (Little *et al.*, 2017). However, it is worth noting that K-fold cross-validation increases the computational burden, as the model needs to be trained multiple times. Common choices for k include 5 or 10 (Ghorbani and Ghousi, 2020; Nti *et al.*, 2020), but the optimal number can vary depending on the dataset size and specific use-case (Nti *et al.*, 2021).

2.8.1.6 Regularization

Regularization techniques are essential tools in machine learning to prevent overfitting. It works by adding a penalty term to the loss function during training. A loss function measures

how well a model's predictions align with the actual outcomes. The penalty term added to the loss function penalizes large parameter values, which helps to shrink the model and make it less complex. Two common types of regularization techniques are L1 regularization (also known as Lasso regularization) and L2 regularization (also known as Ridge regularization). Both techniques add a penalty term to the loss function that the model is trying to minimize during training. The penalty term is based on the model's weights, and its purpose is to discourage the model from assigning excessively large weights to certain features, which helps control the model's complexity.

L1 Regularization (Lasso) adds the absolute values of the weights to the loss function. This encourages the model to shrink the less important feature weights to zero. As a result, L1 regularization performs feature selection by effectively setting the coefficients of less relevant features to zero. This can lead to a sparse model where only the most important features are retained, rendering the model more interpretable (Nusrat and Jang, 2018; Emmert-Streib and Dehmer, 2019). L1 regularization is represented by **Equation 2.7** as follows:

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 + \lambda \sum_{i=1}^n |m_i| , \quad (2.7)$$

where y_i are the actual values, $\hat{y}_i$ are the predicted values, and n is the number of observations, and λ is the parameter selected depending on the output of cross-validation. As λ increases, MSE increases, which reduces the values of coefficients.

L2 Regularization (Ridge) adds the squared values of the weights to the loss function. Unlike L1 regularization, L2 regularization does not force the weights to become exactly zero. Instead, it encourages the model to have smaller but non-zero weights for all features (Hastie, 2020). This helps to prevent the weights from becoming too large and overemphasizing specific features. **Equation 2.8** can be used to depict L2 regularization.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 + \lambda \sum_{i=1}^n |m_i^2| . \quad (2.8)$$

2.8.1.7 Heatmap and Pearson Correlation Coefficient

The Pearson Correlation Coefficient (PCC) is a commonly used statistical metric that measures the strength and direction of a linear relationship between two input parameters. Its value ranges between -1 and 1, inclusive. A value of 1 indicates a perfect positive linear relationship: as one parameter increases, the other also increases at a consistent rate. A value of -1 indicates

a perfect negative linear relationship: as one parameter increases, the other decreases. A value of 0 suggests no correlation between the variables indicating that the input parameters are independent of each other, these leads to decrease in model's bias and prevents underfitting. The PCC is given by **Equation 2.9** as follows:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}}, \quad (2.9)$$

where r is the correlation coefficient, x_i is the first parameter, $\bar{x}$ is the mean value of the x -parameter, y_i is the second parameter, and $\bar{y}$ is the mean value of y -parameter.

A heatmap is a graphical representation of data where individual values contained in a matrix are represented as colors. In the context of machine learning, heatmaps are often employed to visualize the correlation between input parameters. When using heatmaps to represent correlations, for example, between features in a dataset, the color intensity and scale represent the Pearson Correlation Coefficient values. Bright colors (e.g., intense red or blue) typically indicate high positive or negative correlations, while colors closer to neutral (e.g., white or Gray) indicate weaker correlations (Coscia, 2021; Sami and Ibrahim, 2021; Lu *et al.*, 2023).

2.8.1.8 Feature and Permutation Importance

Feature importance is a critical concept in machine learning and data analysis. It helps understand which features (or variables) in the dataset have the most significant influence on the outcome or target variable. By identifying important features, one can make more informed decisions about model selection, feature engineering, and data interpretation. There are various ways to measure feature importance, and the choice of method depends on the type of data and machine learning model applied. Tree-based models have built-in mechanisms to compute feature importance. The two most common methods are Gini Impurity and Mean Decrease in Impurity. Gini Impurity is a measure of how often a randomly chosen element would be incorrectly classified. It gives an idea of the disorder or randomness of the labels. In the context of a decision tree, when evaluating a potential split, the Gini Impurity measures how mixed the labels are in the two groups created by the split. While Mean Decrease in Impurity (or Total Decrease in Impurity) refers to the total reduction of the impurity measure (often Gini Impurity, but it could also be entropy or other impurity measures) brought by a feature. It is computed as

the difference between the impurity of the parent node and the weighted average of the impurities of the child nodes. In ensemble models like Random Forests, this decrease is averaged over all trees to determine the feature's importance. This metric quantifies how much each feature contributes to decreasing impurity across all decision nodes in which it is used. So, while Gini Impurity helps in making individual split decisions, the Mean Decrease in Impurity gives a more holistic view of a feature's importance over the entire model or ensemble of trees. The Gini Impurity for a node is computed based on **Equation 2.10**.

$$\text{Gini Impurity} = 1 - \sum_{i=1}^n r_i^2, \quad (2.10)$$

where r_i is the proportion of instances in the node that belong to class i .

The feature that results in the greatest reduction in Gini Impurity when used for splitting the data is considered the most important. Specifically, the decrease in impurity (or improvement) is calculated for each feature when it is used for splitting, and this decrease is averaged over all nodes in the tree where the feature is used. The larger the decrease, the more important the feature is considered. This process is repeated for all features, and you end up with a ranking of features based on their contribution to reducing impurity. Features that lead to a more significant reduction in impurity are considered more important in the decision tree model.

Permutation Importance is a powerful method for assessing feature importance in machine learning models. It operates by disrupting the intrinsic relationship between a feature and the target variable, allowing us to gauge the feature's significance accurately. The procedure unfolds as follows: first, it measures the model's performance on a validation dataset, typically using metrics like accuracy or mean squared error, without any feature shuffling, which serves as a baseline performance level. Then, it introduces randomness by shuffling the values of a specific feature within the validation dataset, effectively erasing any meaningful connection between the feature and the target variable. Afterward, the model's performance is re-evaluated using the dataset with shuffled feature values. The degree of performance deterioration, compared to the baseline, quantifies how much the model relies on that feature. If there is a substantial decrease in performance, it indicates higher feature importance. This process is repeated for all features in the dataset, providing a comprehensive ranking of feature importance. Permutation Importance's advantage lies in its ability to directly assess each feature's contribution to the model's predictive capability, regardless of the

underlying relationships, rendering it adaptable and suitable for various types of machine learning models (Altmann *et al.*, 2010; Huang *et al.*, 2016; Saarela and Jauhiainen, 2021; Niu *et al.*, 2022).

2.9 Machine Learning Algorithms

2.9.1 Tree Based Models

Tree-based models are foundational tools in machine learning and they are commonly used in supervised learning for tasks such as prediction and classification. These models split data into groups, called nodes. The process begins with a “root node” and then branches into “decision nodes” based on feature conditions. As the data splits more, the model becomes more complex, improving its prediction accuracy. The goal is to end with “leaf nodes”. Initially, the root node has mixed features, rendering it less specific or “impure”. As the model works, it tries to make the decision nodes more specific or “pure” by choosing the best features for splitting. This continues until no more effective splits can be made. Details of the model, such as how many features to use or when to stop splitting, are determined by hyperparameters. After the model is trained, new data is passed through these decision nodes to get a prediction. A key strength of tree-based models is their simplicity and clarity in results (Banerjee *et al.*, 2019; Avand *et al.*, 2020).

Furthermore, recent advancements in tree-based models have positioned them as effective and intricate learning algorithms. Over time, various tree-based algorithms have emerged such as decision tree, random forests, extra trees, AdaBoost, gradient boosting, and XGBoost (Makhotin *et al.*, 2022). In this study, we employed all these six methods to forecast dynamic retention, using various parameters.

2.9.1.1 Decision Tree Algorithm

The decision tree (DT) is one of the most intuitive and popular machine learning algorithms used for both classification (categorizing items into groups) and regression (predicting numerical values). A decision tree represents decisions and their possible consequences in a tree-like model. The root of the tree is the initial decision, and each branch represents an outcome or decision based on conditions, leading to leaves which represent the outcome or decision. Decision tree models are easy to understand and interpret, require little data preprocessing (no need for normalization), and handle both numerical and categorical data.

However, these models are prone to overfitting, especially on small datasets or trees that are too deep. It can be sensitive to small changes in the data and are less accurate. **Figure 2.7** represents a schematic of DT algorithm (Zhu *et al.*, 2020; Huynh-Cam *et al.*, 2021).

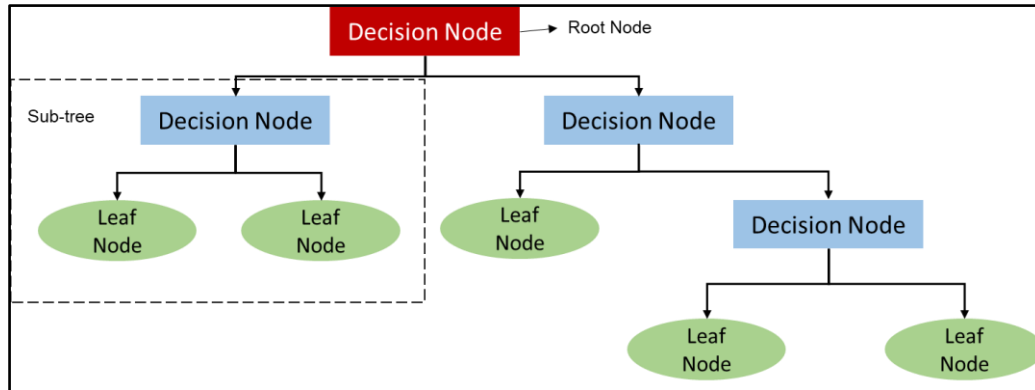


Figure 2.7: Structure of Decision Tree algorithm, modified from Hafeez *et al.* (2021).

2.9.1.2 Ensemble Models

Ensemble models in machine learning harness the power of multiple models to achieve better predictive performance than could be achieved by any of the constituent models alone. The underlying idea is that by combining several models, the individual weaknesses of each can be mitigated, resulting in improved overall accuracy, robustness, and generalization to new data.

Bagging or Bootstrap Aggregating is a technique used to enhance accuracy and reduce the overfitting of machine learning models. Bootstrap sampling involves taking several random subsets from a dataset, a process that is performed with “replacement”. This means the same data point might appear in different subsets. For each subset, a model, usually a decision tree, is trained. When it is time for predictions, the ensemble uses an average of the models’ predictions for regression tasks (**Figure 2.8**). One of the main advantages of this approach is the reduction of overfitting. Since each model only gets a portion of the data, they are less likely to overfit. Furthermore, the ensemble typically achieves better accuracy because the individual errors of the models tend to cancel out. A popular application of this method is the random forest algorithm. This not only uses the basic bagging principle but also adds an extra layer of randomness. For every decision a tree makes, only a subset of features is considered, resulting in a variety of trees. However, there are challenges faced by this method. The method can be computationally intensive due to multiple models being trained. While a single decision tree can be relatively easy to understand, an ensemble of trees can complicate interpretation. In

a nutshell, bagging trains multiple models on random data subsets, and by combining their outputs, it often provides more reliable results (Taser, 2021).

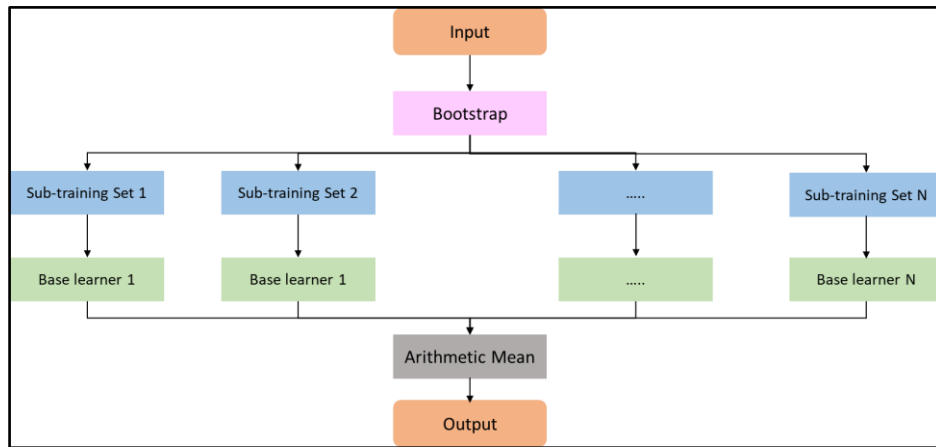


Figure 2.8: Schematic of bagging ensemble learning model, modified from Hafeez *et al.* (2021).

Stacking is a type of ensemble technique in which multiple machine learning models, known as first-level learners, are used together to make predictions. These individual predictions are then combined by a second-level model, or meta-learner. Unlike bagging methods like random forests, which use sampling and random feature selection, stacking uses the entire dataset for each model. This approach emphasizes the need for diverse machine learning models, ensuring varied predictions that can be averaged for better accuracy (**Figure 2.9**). The key challenge in stacking is determining the best way to combine individual model predictions. Some common methods for combining predictions include super ensemble and blending. While stacking can be applied to both classification and regression problems, it is not as commonly adopted as bagging or boosting. This is primarily because stacking does not introduce randomness in its learners, rendering it potentially more susceptible to high variance. Furthermore, some studies have found stacking models to perform slightly inferior to other ensemble methods. Overall, while stacking offers a unique approach to ensemble learning by leveraging the strengths of different models, its efficacy can vary based on the data and problem at hand (Zhu *et al.*, 2022a; Kalule *et al.*, 2023; Lu *et al.*, 2023).

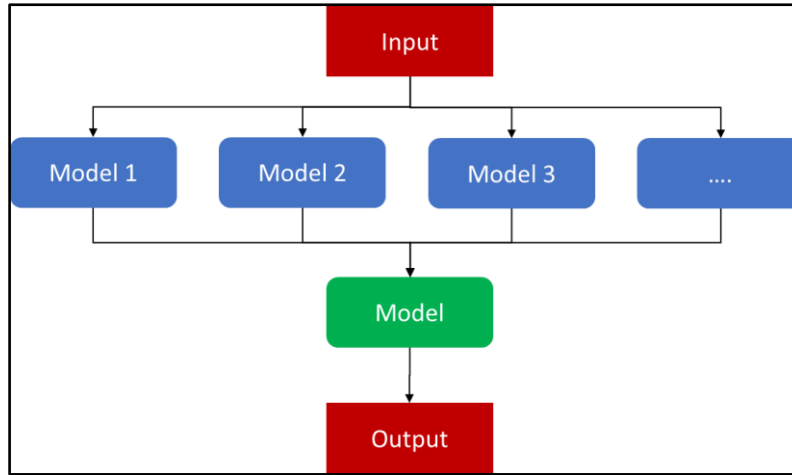


Figure 2.9: Schematic of stacking ensemble learning model, modified from Anđelić *et al.* (2022).

Boosting is an ensemble technique designed to convert weak learners into strong ones by focusing on training errors. Instead of training models independently like in bagging, boosting trains models sequentially. Each new model attempts to correct the errors made by its predecessor. In boosting, every instance in the training set is assigned a weight, indicating its importance. Initially, these weights are equal for all instances. However, as training progresses, instances that were misclassified by previous models are given more weight, rendering the next model in the sequence focus more on them. The final prediction is made through a weighted vote of all the models (**Figure 2.10**). Popular examples of boosting include AdaBoost, Gradient Boosting, and XGBoost. AdaBoost (Adaptive Boosting) works by adjusting the weights of misclassified instances in each iteration, ensuring that subsequent weak learners focus more on previously misclassified samples. After training, it combines these weak learners into a single ensemble model by weighing their predictions based on their overall accuracy. Gradient Boosting fits the new predictor to the residual errors of the previous predictor. Essentially, each new tree tries to correct the mistakes of its predecessor by fitting to the residual errors. The final prediction is an accumulation of predictions from all individual trees. XGBoost is an optimized implementation of gradient boosting. It offers parallel tree boosting to make the training faster and more efficient. Additionally, XGBoost includes regularization terms in its objective function, which can help in reducing overfitting, and it is equipped with additional features for handling missing values and improved tree-pruning logic. All three boosting algorithms combine multiple weak learners to create a strong ensemble model. The Boosting approach not only tends to improve accuracy but also reduces bias and variance, rendering it one of the most effective ensemble methods. Nevertheless, it is more computationally intensive

and can sometimes overfit, especially when there is noise in the data (Ferreira and Figueiredo, 2012; Sibindi *et al.*, 2023).

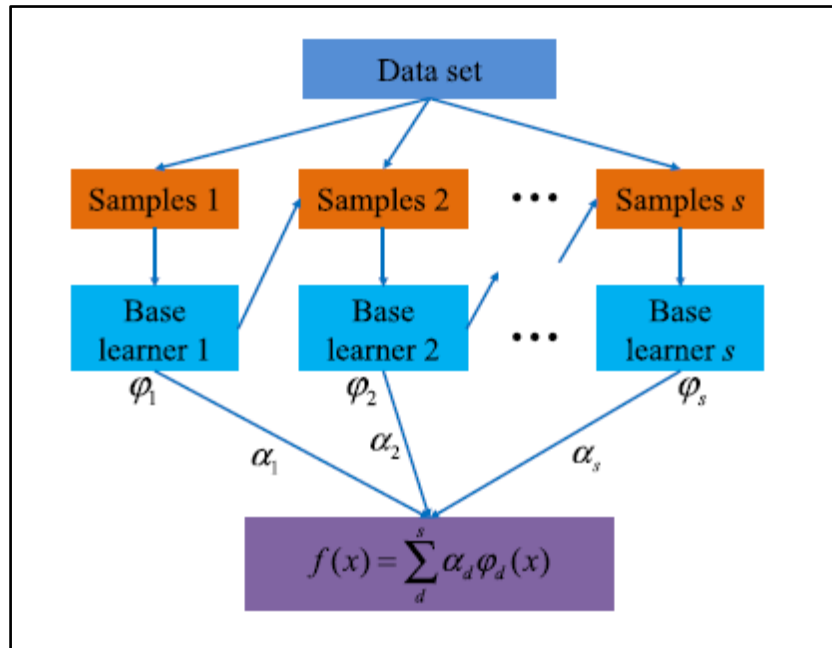


Figure 2.10: Schematic of boosting ensemble learning model (Liang *et al.*, 2020).

CHAPTER 3: MATERIALS AND METHODS

This chapter provides a comprehensive overview of the materials used, experimental setup, sample preparation, data collection procedures, analytical techniques, and software used to achieve the research objectives.

3.1 Materials

This section details the materials used for this study including makeup brines, crude oil, polymer, crushed rock, and core plug samples.

3.1.1 Makeup Brines

The study utilized twelve distinct makeup brines, encompassing synthetic formation water, synthetic seawater, various dilutions of formation water and seawater, as well as brine recipes with different concentrations of Ca^{2+} , Mg^{2+} , and SO_4^{2-} . The abbreviations FW and SW represent formation water and seawater, respectively. Additionally, FW-1, FW-2, and FW-3 denote 5-times, 10-times, and 20-times diluted formation water, while SW-1, SW-2, and SW-3 represent 5-times, 25-times, and 100-times diluted seawater, respectively. These dilutions were formulated to have a varied salinity range to study the effect of salinity on polymer retention. Furthermore, four brines, namely SW-1A, SW-1B, SW-1C, and SW-1D represent 5-times diluted seawater with different ionic composition, all with the same total dissolved salt content (8,502 ppm). These variations involved: eliminating Ca^{2+} while maintaining Mg^{2+} (SW-1A), eliminating Mg^{2+} while maintaining Ca^{2+} (SW-1B), eliminating both Ca^{2+} and Mg^{2+} ions (SW-1C), and maintaining both Ca^{2+} and Mg^{2+} ions while doubling the amount of SO_4^{2-} ions (SW-1D). In all instances, the overall total dissolved solids were consistently maintained by compensating for the altered ions with an equivalent amount of NaCl. The ionic compositions of all twelve synthetic brines are presented in **Tables 3.1 – 3.3**.

Table 3.1: Ionic composition of formation water and its different dilutions

Ionic Composition	FW (ppm)	FW-1 (ppm)	FW-2 (ppm)	FW-3 (ppm)
Na ⁺	52,952	10,590	5,295	2,648
Ca ²⁺	9,250	1,850	925	463
Mg ²⁺	1,446	289	145	72
K ⁺	744	149	74	37
Cl ⁻	102,722	20,544	10,272	5,136
TDS	167,114	33,423	16,711	8,356

Table 3.2: Ionic composition of seawater and its different dilutions

Ionic Composition	SW (ppm)	SW-1 (ppm)	SW-2 (ppm)	SW-3 (ppm)
Na ⁺	13,072	2,614	523	131
Ca ²⁺	539	108	22	5
Mg ²⁺	1,583	317	63	16
K ⁺	498	100	20	5
Cl ⁻	23,517	4,703	941	235
SO ₄ ²⁻	3,298	660	132	33
TDS	42,507	8,502	1,701	425

Table 3.3: Ionic composition of brine recipes with varying ionic compositions

Ionic Composition	SW-1 (ppm)	SW-1A (ppm)	SW-1B (ppm)	SW-1C (ppm)	SW-1D (ppm)
Na ⁺	2,614	2,708	3,084	3,192	2,530
Ca ²⁺	108	0	108	0	108
Mg ²⁺	317	317	0	0	317
K ⁺	100	100	100	100	100
Cl ⁻	4,703	4,717	4,550	4,550	4,127
SO ₄ ²⁻	660	660	660	660	1,320
TDS	8,502	8,502	8,502	8,502	8,502

3.1.2 Crude Oil

The light crude oil representative of Middle Eastern field was used for the studies with density of 0.84 g/cc and viscosity of 4.77 cP at ambient temperature (25 °C). The crude oil was filtered using a nitrocellulose 0.45 μm filter membrane under an applied pressure of 40 psi. Subsequently, the filtered crude oil was centrifuged at 2000 rpm for 2 hours to remove impurities, such as asphaltenes and waxes. The fluid properties of the crude oil, including density and viscosity, were measured using an Anton Paar viscometer. For each measurement, the crude oil sample was inserted into the viscometer, and the instrument was set to the required temperature. The viscosity and density measurements were then taken at different temperatures less than 70 °C, then extrapolated to 80 °C, and 90 °C. **Figure 3.1** shows viscosity of crude oil at different temperatures. The viscosity of crude oil decreases with an increase in temperature, following an exponential decay pattern. This is because as the temperature increases, the liquid molecules move more vigorously, reducing the intermolecular forces that contribute to viscosity. The exponential nature of this decrease is attributed to the non-linear relationship between temperature and the energy of the molecules within the liquid.

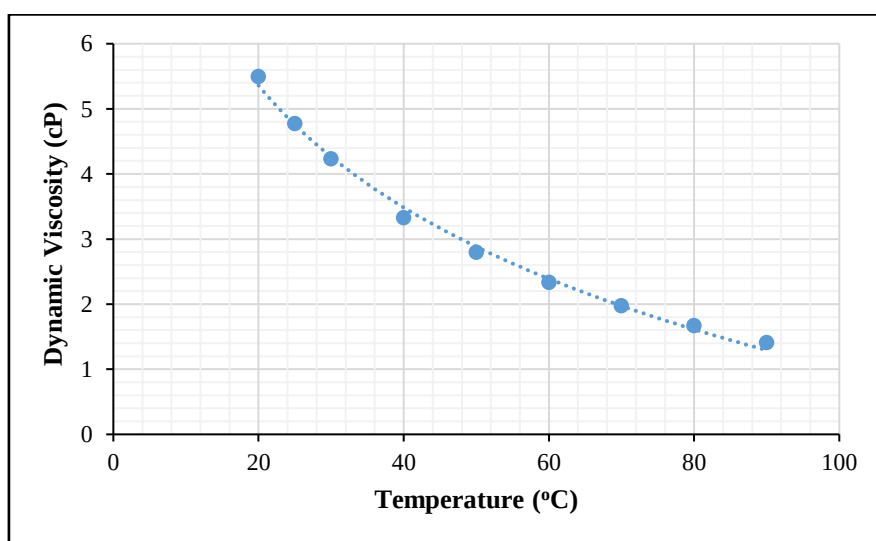


Figure 3.1: Viscosity of crude oil at different temperatures.

3.1.3 Polymer

SAV10, an ATBS-based polymer of molecular weight 4.3 – 6.8 MDa provided by SNF Floerger, was used in all tests. The polymer was received as white granular powders. SAV10

polymer is stable at high temperatures (up to 130 °C) and high salinity conditions (up to 300,000 ppm) in carbonate reservoirs (Jouenne, 2020).

3.1.4 Crushed Rock Samples

Indiana limestone outcrop samples were crushed to particle size in the range of 63-250 μm for static adsorption studies. The rock powder preparation is discussed later in **Section 3.2.5.1**.

3.1.5 Core Plug Samples

Indiana limestone outcrop samples provided by Kocurek Industries with permeabilities in the range of 200 mD were used for dynamic adsorption studies. The petrophysical properties for the core plugs used for this study are discussed later in **Chapter 5 (Tables 5.1 and 5.2)**, **Chapter 6 (Table 6.1)**, and **Chapter 7 (Table 7.1)**.

3.2 Experimental Methods

This section outlines the experimental framework and the methods employed for the research including fluid preparation and properties measurement, polymer hydrodynamic size and polydispersity index, polymer concentration determination, static adsorption studies, and dynamic retention studies.

3.2.1 Fluid Preparation

This section outlines the protocol for the preparation of fluid used in this study including brine, polymer solution, and glycerin-brine mixture.

3.2.1.1 Brine Preparation

The synthetic brine preparation involves dissolving specific quantities of high-quality salts, including potassium chloride, calcium chloride dihydrate, magnesium chloride hexahydrate, and sodium chloride in deionized water. Sodium sulfate was used to provide sulfate ions for seawater, diluted seawater, and brine recipes with varying ionic compositions. To ensure complete dissolution of the salts and to achieve a homogenous solution, the mixture was stirred continuously using a magnetic stirrer. Once the salts were fully dissolved, the brine was filtered using 0.45 μm nitrocellulose membrane to remove any undissolved particles, impurities, or potential contaminants. These brines were used for polymer solution preparation, brine

permeability measurements for different core plugs, as well as pre-flush and extended post-flush brine injections for the adsorption studies.

3.2.1.2 Polymer Preparation

Synthetic polymer powders were hygroscopic, and their moisture contents were determined to prepare the required concentrations accurately. For moisture content determination, 10 g of polymer powder was weighed nearest to 0.1 mg in three pre-weighed, clean, and dried glass bottles and was heated in an oven at 120 °C for 24 hours, cooled in a desiccator, and re-weighed to calculate the weight loss or moisture contents by taking the average of three samples. The active matter content in the SAV10 polymer was determined to be 89.5%.

The synthetic SAV10 polymer solution was prepared by adding a known amount of polymer powder to the respective brines using an overhead stirrer. The brine was kept stirring at a high speed of 550 rpm, and the polymer powder was gently added to the shoulder of the vortex to avoid fish-eye formation due to polymer aggregation. The mixture was then left for 30 minutes at a high rpm (550 rpm) to prevent agglomeration of the polymer. The speed was later reduced to 250 rpm and was left for 24 hours to achieve a homogeneous solution. The mouth of the beaker was covered using parafilm.

Different concentrations (500 - 2500 ppm) of SAV10 polymer solutions were prepared by diluting the mother solution with respective brine with a magnetic stirrer at 250 rpm for 2 hours. The amount of mother solution and brine required to achieve the desired concentration were calculated using **Equations 3.1** and **3.2**, respectively.

$$C_1V_1 = C_2V_2, \quad (3.1)$$

where C_1 is the mother solution concentration (ppm), C_2 is the diluted polymer solution concentration (ppm), V_1 is the volume of the mother solution required (ml), and V_2 is the volume of the diluted solution (ml).

$$V_{\text{Brine}} = V_2 - V_1, \quad (3.2)$$

where V_{Brine} is the volume of the brine required (ml), V_2 is the final volume of the diluted solution (ml), and V_1 is the volume of the mother solution required (ml).

Once the polymer solution was prepared, it was filtered using a 3 μm filter membrane under 15 psi pressure from a Nitrogen cylinder to achieve a filtration ratio lower than 1.2 and remove all microgels. The filtration ratio was calculated using **Equation 3.3**.

$$FR = \frac{t_{200} - t_{180}}{t_{80} - t_{60}}, \quad (3.3)$$

where t_{60} , t_{80} , t_{180} , t_{200} are the times taken to filter 60, 80, 180, and 200 grams of polymer, respectively.

To mitigate the risk of polymer oxidation at high temperatures, precautionary measures were implemented to control the oxygen content in the polymer solution. Sodium Thiourea, an oxygen scavenger, was introduced into the polymer solution at a concentration of 200 ppm. The solution was subjected to vacuum conditions to eliminate trapped gases before it was loaded into a vial specially designed for high-temperature applications. Lastly, to maintain an oxygen-free atmosphere, a process of N_2 purging and blanketing was employed. The sample was purged with nitrogen gas to displace any remaining traces of oxygen. Subsequently, a blanket of nitrogen gas was carefully maintained around the polymer solution during its loading into the high-temperature equipment. By implementing these measures, the risk of polymer oxidation was effectively minimized, ensuring the stability and integrity of the polymer solution throughout the high-temperature experiments.

3.2.1.3 Glycerol Brine Mixture

A mixture of glycerol and brine was employed for forced imbibition experiments. The viscosity of the glycerol brine mixture does not vary with shear rate (Segur and Oderstar, 1951). The glycerol brine solution was carefully formulated for various coreflooding experiments to ensure its viscosity was 25% greater than the respective polymer solution. The glycerol brine mixture was prepared by mixing the required amount of glycerol and brine in a beaker covered with paraffin film with a magnetic stirrer at 250 rpm for 2 hours. This mixture was used to assure achieving a representative true residual oil saturation during the coreflooding experiments; hence, subsequent polymer flooding does not mobilize the remaining oil, which might affect the analysis of polymer retention and other injectivity parameters.

3.2.2 Fluid Properties

This section describes the methodology adopted and equipment used to measure the properties including viscosity and density of the above-mentioned fluids.

3.2.2.1 Viscosity and Density Determination of Brine Solutions

Fluid properties such as viscosity and density of brine solutions were measured using a Cannon-Fenske viscometer and an Anton Paar density meter, respectively. A Cannon-Fenske viscometer of size 25 with a viscosity range of 0.5 to 2 cSt was used to measure the viscosity of the brines. The brine viscosity was assumed to be in the range of 1 cSt, and the best results were obtained by operating near the center of the viscometer's range. To measure the viscosity, the brine sample was inserted into the large bulb of the viscometer, placed in a constant temperature bath set at the required temperature, and the water bath's temperature was monitored using a digital thermometer. After 30 minutes for temperature equilibration, suction was applied to bring the brine sample into the bulb from the opposite side. The sample was allowed to flow freely until it reached the first mark in the tube, and the time required for the sample to reach the second mark was recorded using a stopwatch (**Figure 3.2**). The measurement was repeated three times, and the average time was calculated.

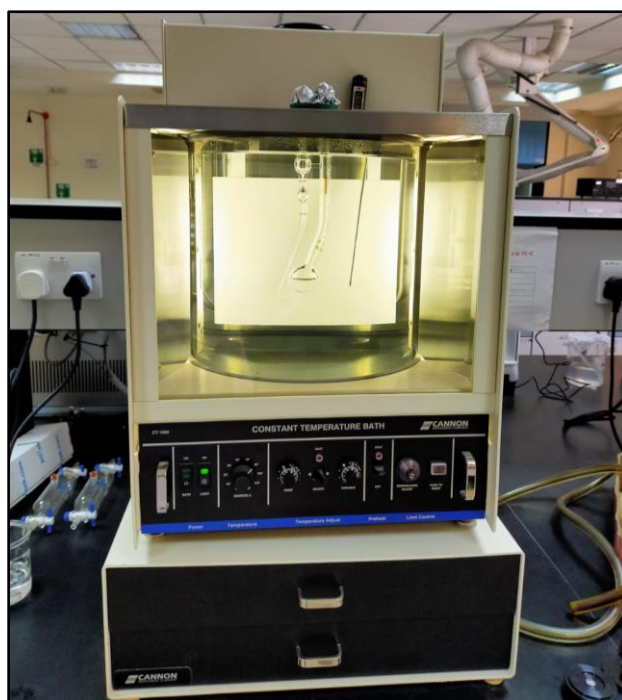


Figure 3.2: Cannon-Fenske routine viscometer for brine viscosity measurement.

The kinematic and dynamic viscosities were then calculated using **Equations 3.4** and **3.5**, respectively.

$$V = C \times t, \quad (3.4)$$

where V is the kinematic viscosity (cSt), C is the calibration constant of the viscometer (cSt/s), and t is the flow time (s).

$$\mu = V \times \rho, \quad (3.5)$$

where μ is the dynamic viscosity (cP), V is the kinematic viscosity (cSt), and ρ is the density (g/cc) measured at the same temperature.

The viscosity of the brine was measured at various temperatures below 70 °C, then extrapolated to 80 °C, and 90 °C.

The Anton Paar density meter was employed to measure the density of brine based on the oscillating U-tube method. Brine was introduced into the meter, ensuring no bubbles were present. Once inside the measuring chamber, the U-tube oscillated at a frequency that changed according to the brine's density. The meter was equipped with a temperature control system, as the density measurements are temperature dependent. The device then used the recorded oscillation frequency, in conjunction with the known temperature, to calculate the brine's density, which was displayed on its screen. After each measurement, the chamber was cleaned to avoid contamination, and the device was regularly calibrated using standards like distilled water to maintain its accuracy. The brine density was assessed at different temperatures below 70 °C, then extrapolated to 80 °C, and 90 °C.

3.2.2.2 Rheological Experiments

Once the polymer solution was prepared and filtered, rheological experiments were conducted on the polymer solution at different conditions using the Anton Paar MCR 302 rheometer. The rheometer was set up with the appropriate geometry (DG-42) and measuring system. The prepared polymer solution was carefully loaded onto the rheometer measuring system. Shear ramp-up tests with shear rates varying from 1 to 1000 s⁻¹ were conducted on SAV10 stock solutions and their dilutions in formation water and seawater at ambient conditions (25 °C). The viscosity of the polymer solution at varying concentrations were measured at a shear rate

of 10 s^{-1} . From the polymer concentration versus viscosity plot, the optimum concentration required to achieve the target viscosity was defined. A target viscosity of 4.5 cP at a shear rate of 10 s^{-1} was selected based on the optimum concentration analysis method (Gogarty *et al.*, 1967; Al-Shalabi, 2018). At this optimal concentration, total relative mobility of oil and water phases is minimum during the seawater (43,000 ppm) injection cycle for the reservoir conditions (Elhossary *et al.*, 2020).

This designed polymer viscosity was necessary to address the permeability contrast between the two zones in the representative Middle East carbonate reservoirs (Masalmeh *et al.*, 2011 and 2019). Subsequently, the selected polymer concentrations were kept constant for further rheological studies of SAV10 polymer in brines with varying salinities and ionic compositions. Temperature ramp-up tests were also conducted to investigate the temperature effect on the polymer solution. Pressure cell geometry of the Anton Paar MCR 302, was used for high temperature experiments. A 6 bar pressure was applied to prevent evaporation of the polymer samples.

3.2.3 Hydrodynamic Size and Polydispersity Index Determination

The hydrodynamic size and polydispersity index (PDI) of the polymer solution in the respective brine at varying temperatures were determined using a Malvern Zetasizer nano ZS (**Figure 3.3**), employing the principle of dynamic light scattering technique (Ruben-Hernán *et al.*, 2020; Sugar *et al.*, 2020; Agasty *et al.*, 2021). For high-temperature experiments, the cell area where cells were inserted to undertake measurements was completely self-enclosed and the sample temperature was controlled up to 90°C . Prior to the experiment, the equipment was calibrated using particles of known sizes and known polydispersity. The instrument was then set up with the appropriate settings for the polymer solution. The sample was carefully loaded into the cuvette or sample cell, ensuring the absence of air bubbles or contaminants. Glass cuvette was used to withstand the high temperature. The data acquisition software was started, and the measurement for hydrodynamic size and PDI was initiated. Dynamic Light Scattering (DLS) was used to gauge the size distribution of polymers in solution. When particles in a solution experience Brownian motion, scatter monochromatic laser light in various directions. This scattered light undergoes interference patterns, leading to intensity fluctuations over time because of the particle's random movement. These fluctuations are captured using a photodetector, producing a correlation function that describes the change in scattered light intensity with time. The rate of decay in this function provides insight into the diffusion

coefficient of the particles. The faster this decay, the smaller the particles and the higher their diffusion coefficient. Once this coefficient was determined, the Stokes-Einstein equation (**Equation 3.6**) was applied, connecting the diffusion coefficient to the particle's hydrodynamic size.

$$d_H = \frac{kT}{3\pi\eta D}, \quad (3.6)$$

where d_H is the hydrodynamic size (nm), k is the Boltzmann constant ($\text{kg.m}^2/\text{s}^2.\text{K}$), T is the Temperature (K), η is the solvent viscosity (kg/m.s), and D is the diffusion coefficient (m^2/s).

The polydispersity index (PDI) indicates the size distribution of particles in the sample as well as the uniformity and variation in the particle sizes. This was calculated from the width of the autocorrelation curve. A narrower curve corresponded to a more monodisperse sample, while a broader curve indicated a polydisperse sample.

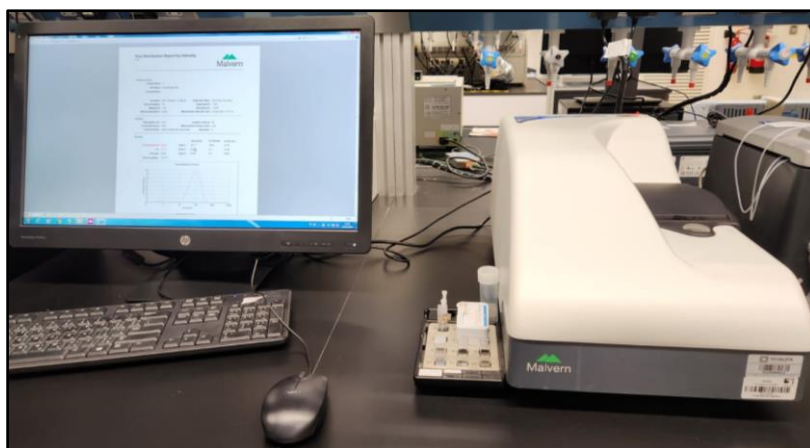


Figure 3.3: Malvern Zetasizer used for hydrodynamic size and polydispersity index measurement.

3.2.4 Polymer Concentration Determination

Three different analytical methods were utilized to determine the polymer concentration: UV-visible spectroscopy, viscosity measurements, and TOC-TN analysis. The details of these methods are discussed in the following subsections.

3.2.4.1 UV Method

For the SAV10 polymer being studied, a wavelength of 206 nm was chosen corresponding to the polymer's absorption peak obtained by wavelength scanning to ensure the highest sensitivity and specificity in the measurement. To enable accurate determination of polymer concentration, a calibration curve was developed. This was accomplished using standard solutions with predetermined polymer concentrations, which spanned the anticipated concentration range of the sample under analysis. These standard solutions were measured for absorbance at the chosen wavelength (206 nm) using the UV-Vis spectrophotometer. Also, the polymer concentration for the calibration curve was carefully selected so that the absorbance value falls between 0.5 – 2.5 for better results. It was critical to use clean, scratch-free cuvettes as even slight imperfections could influence the readings. The resulting absorbance values of these standard solutions were plotted against their respective known concentrations, forming the calibration curve. This is based on the Beer-Lambert Law that relates the attenuation of light to the properties of a material through which the light travels. It is a foundational principle used in spectrophotometry for concentration determinations of solutions. The law is mathematically expressed using **Equation 3.7** as follows:

$$A = \epsilon cl, \tag{3.7}$$

where A is the measured absorbance of the solution, ϵ is the molar absorptivity (or molar extinction coefficient) of the solute which is a constant with units of L/(mg·cm), c is the concentration of the solute in the solution and usually expressed in mg/L, and l is the path length through which the light passes and is usually expressed in centimeters.

The calibration curve plotted served as the reference for determining the concentration of unknown samples. Depending on the concentration of the unknown polymer solution, dilution has been conducted to bring its concentration within the range encompassed by the standard solutions. The absorbance of the unknown polymer solution was then measured at the chosen wavelength using the UV-Vis spectrophotometer. The absorbance value of this solution was subsequently compared to the calibration curve, allowing for the extrapolation of the polymer concentration in the unknown solution. For improved accuracy in the determination process, the measurement of the unknown polymer solution was performed multiple times, leading to the computation of an average concentration.

3.2.4.2 Viscosity Method

Viscosity measurement is a commonly used method to determine the concentration of polymers in a solution. The principle behind this method was that the viscosity of a solution was directly influenced by the presence of polymers and their concentration. In the viscosity-based determination of polymer concentration, the proRheo LS300 rheometer was employed to measure the viscosity of the polymer solution. A calibration curve was typically established to determine the polymer concentration using viscosity, relating the viscosity of standard solutions with known polymer concentrations. The standard solutions covered a range of concentrations that encompassed the expected concentration of the unknown sample. Next, the viscosity of the unknown polymer solution was measured using the same rheometer. The obtained viscosity value was then compared to the calibration curve, enabling the determination of the corresponding polymer concentration.

3.2.4.3 Total Organic Carbon-Total Nitrogen (TOC-TN)

The TOC-TN method is a prevalent approach for determining the concentration of polymers in a solution. This method relies on the principle that organic nitrogen content is directly related to the concentration of polymers. Shimadzu TOC-TN analyzer was utilized to determine the polymer concentration using the TOC-TN method. The TOC-TN analyzer measures the total organic nitrogen content in a sample. Accordingly, the samples undergo thermal decomposition to yield nitrogen monoxide (NO) when heated to 720 °C. This NO gas, after being thermally regulated and moisture-removed, is channeled through a chemiluminescence detection system. Here, it interacts with ozone, resulting in a mix of nitrous oxide (NO₂) and excited nitrous oxide (NO₂*). When the energized nitrous oxide (NO₂*) reverts to its fundamental state, it releases detectable radiation, which is quantified using a photodetector. This detected signal produces a representation indicative of the nitrogen concentration within the sample. This measured nitrogen content is correlated with the polymer concentration.

Based on the above principle a series of standard solutions with known polymer concentrations was prepared. These standard solutions covered a range of concentrations that included the expected concentration of the unknown sample. Once the calibration curve was established, the unknown polymer solution was analyzed using the TOC-TN analyzer. The measured Nitrogen content was then compared to the calibration curve to determine the corresponding polymer concentration in the unknown sample.

In each analytical method employed, appropriate steps were followed to ensure the accuracy and reliability of the results. This included maintaining the purity of the sample, carefully preparing it to ensure a complete and representative analysis, adhering to the operating parameters of the instruments, and utilizing a calibration curve with a high coefficient of determination (R^2) value of 0.999.

3.2.5 Static Adsorption Studies

This section describes the experimental procedure and conditions applied for static adsorption experiments.

3.2.5.1 Rock Powder Preparation

Rock powders with particle sizes between 63-250 μm were prepared as absorbents by crushing the Indiana limestone outcrop. The crushed rock powder was washed with distilled water to remove fine particles. The washed rock powder was then dried at 120 $^{\circ}\text{C}$ for 48 hours in an oven and sieved to the desired particle size range.

3.2.5.2 BET Surface Area Measurement of the Crushed Core Samples

The Brunauer–Emmett–Teller (BET) method was used to measure the surface area of the crushed core samples. Accordingly, the sample was degassed, under a vacuum at elevated temperatures (130 $^{\circ}\text{C}$) to remove any adsorbed substances, such as water, from the surface of the sample that might interfere with the measurement. Subsequently, the sample was cooled to liquid nitrogen temperatures (-196 $^{\circ}\text{C}$), which enabled the adsorption of the nitrogen gas onto the surface. The sample was then exposed to nitrogen gas at a series of increasing pressures. At each pressure point, the system was allowed to equilibrate, and the volume of gas adsorbed on the sample surface was measured. The pressure was then reduced stepwise, and the volume of gas desorbed from the sample was measured at each pressure point. Using this adsorption, desorption data, and based on BET equation as represented by **Equation 3.8**, a linear plot (BET plot) of $1/[W(P_0/P)-1]$ vs. P/P_0 was constructed. **Figure 3.4** represents the typical multipoint BET plot. The BET surface area could be determined from the slope and intercept of the linear portion of this plot based on **Equations 3.9** and **3.10**.

$$\frac{1}{W\left(\frac{P_0}{P}-1\right)} = \frac{1}{w_m C} + \frac{C-1}{w_m C} \left(\frac{P}{P_0}\right), \quad (3.8)$$

where W is the weight of gas adsorbed (g), P/P_o is the relative pressure, w_m weight of adsorbate as monolayer (g), and C is the BET constant.

$$w_m = \frac{1}{s+i}, \quad (3.9)$$

where s is the slope (1/g) and i is the intercept (1/g) of the linear plot respectively.

$$S_{BET} = \frac{(w_m * N * A)}{M * w}, \quad (3.10)$$

Where S_{BET} is the BET surface area (m^2/g), N is the Avogadro's number (6.023×10^{23}) (molecules/mol), A is the adsorbate cross sectional area ($1.62 \times 10^{-19} m^2/\text{molecules}$ for Nitrogen), M is the molecular weight (28.02 g/mol for Nitrogen), and w is the sample weight (g).

In **Figure 3.4**, from the slope, and intercept of the BET plot, and applying **Equations 3.9** and **3.10**, the bet surface area for this case was determined as $3.02 m^2/g$.

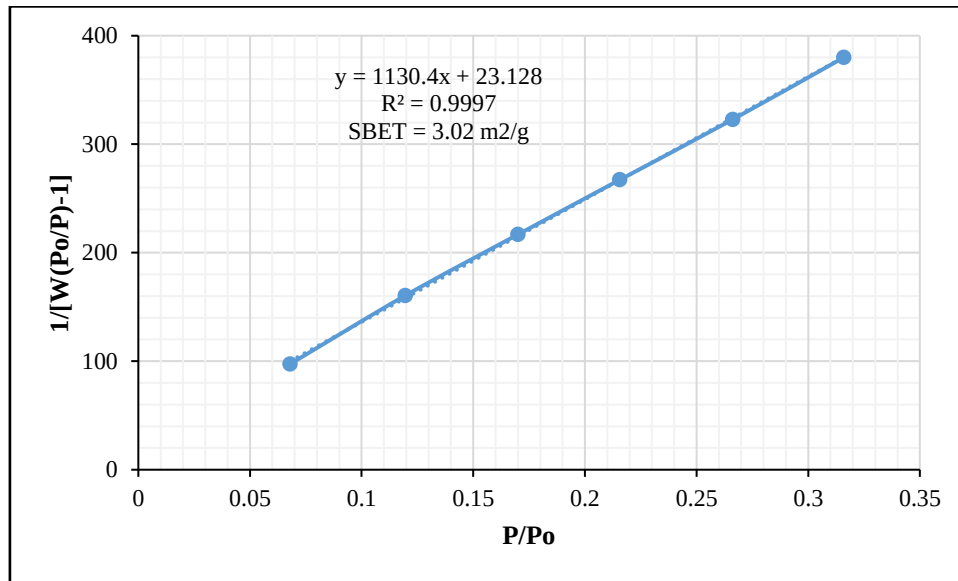


Figure 3.4: Typical multipoint BET plot.

3.2.5.3 Experimental Conditions

Static adsorption measurements were performed under specific conditions; the temperature varied from 25 - 90 °C, the liquid-to-solid ratio was set at a constant of 6, and a retention time of 6 hours was chosen. The liquid-to-solid ratio and the retention time were selected based on

previous static adsorption studies on the SAV10 polymer, where larger values did not impact adsorption (Thomas *et al.*, 2020).

3.2.5.4 Static Adsorption Measurement in Single-Phase Condition

A quantity of 5 grams of pulverized rock and 30 grams of a 1000 ppm polymer solution were mixed in a glass bottle. Glass bottles rated for high temperature were used for the experiments. The rock powder-polymer solution mixture was briskly stirred using a vortex mixer for a duration of two minutes to ensure an even initial mixture. These bottles, with their respective mixtures, were then transferred to a sample shaker outfitted with a water bath to uphold the target temperature. The oscillation speed of the sample shaker was set at a steady pace to promote consistent mixing of the polymer and rock particles. Following a period of 6 hours, these samples were removed from the shaker, and the liquid fraction was transferred into a separate centrifuge tube. Afterwards, the liquid fraction underwent a centrifugation process at an elevated speed of 4,000 rpm for a span of 20 minutes to fully separate the liquid segment from the rock particles. Further, the liquid fraction of the mixture was tested to identify the equilibrium polymer concentration that remained within the solution post-adsorption. The static adsorption on rock surface was determined using **Equation 3.11** (API RP 63, 1990) .

$$A_s = \frac{W_p(C_i - C_e)}{W_r}, \quad (3.11)$$

where A_s is the polymer adsorption in microgram per gram of rock ($\mu\text{g/g}$), W_p is the weight of the polymer solution used in gram (g), W_r is the weight of crushed rock used (g), C_i is the initial concentration of the polymer solution used in ppm, and C_e is the equilibrium concentration of the polymer solution after adsorption in ppm.

3.2.6 Dynamic Retention Studies

This section outlines the methods and conditions utilized for dynamic retention experiments.

3.2.6.1 Cleaning and Drying the Cores

The outcrop limestone samples were cleaned utilizing a Soxhlet distillation-extraction unit, to remove salts from the outcrop samples by vaporizing and condensing the solvent methanol. The methanol was continuously heated, vaporized, and subsequently condensed at the top,

flowing through the core samples placed in the extraction tube. This process effectively eliminates the salts present in the cores. Once deemed clean, the samples underwent a drying process at 90 °C for 48 hours. Post-drying, the sample dimensions and weight were accurately measured and documented. The gas porosity and permeability of these core plugs were analyzed using a Helium Porosimeter and a Gas Permeameter, respectively. Gas permeability evaluations were performed by applying a confining pressure of 400 psi without any back pressure.

3.2.6.2 Core Saturation

The core samples were placed in a pressure vessel, and a vacuum was applied for 4 hours to remove any remaining air within the core's pore spaces. Brine was then injected into the saturator vessel. The saturator was pressurized up to 2000 psi to facilitate the entry of the fluid into the pore spaces of the core. The pressure was maintained for 48 hours before taking out the samples. The pore volume was then determined based on the brine saturation, determined by weight difference.

3.2.6.3 Surface Area Measurement of the Core Samples

Mercury Injection Capillary Pressure (MICP) tests were conducted on Indiana limestone outcrop samples to investigate the pore throat size distribution and specific surface area. The core samples had been cleaned meticulously to remove any external debris or impurities. Post-cleaning, the samples were dried in an oven to eradicate any residual water or other liquids from the pore spaces. The dried core samples were then immersed in mercury, a non-reactive, non-wetting fluid, chosen for its inability to wet the rock surfaces. Subsequently, the core sample was placed in a high-pressure cell, sealed tightly to prevent any fluid leakage during the test. A vacuum pump was used to expel any air or gas present in the pore spaces of the rock, thus ensuring that only the mercury filled the void spaces. The pressure in the high-pressure cell gradually increased to inject the mercury into the core sample. Initially, the mercury entered the larger pores and subsequently filled the narrower pore throats as the pressure increased. The pressure at which mercury invaded the narrowest throats was defined as the “capillary pressure”. Throughout the injection process, the mercury pressure was monitored and recorded, and used to construct the capillary pressure curve. This curve represented the relationship between the pore throat size and the corresponding capillary pressure required to inject mercury into those pores. From the pressure data the amount of mercury entering the

sample as pressure rises can be determined, and the pore throat size distribution can be inferred using Washburn's equation (**Equation 3.12**). The specific surface area can be calculated from **Equation 3.13**.

$$\Delta P = -\frac{2\gamma\cos\theta}{r_{\text{pore}}}, \quad (3.12)$$

where ΔP is the incremental pressure (dynes/m²), γ is the surface tension of mercury (dynes/m), θ is the contact angle between the rock and mercury (140°), r_{pore} is the pore throat radius (m).

$$S_{\text{MICP}} = \frac{1}{W_s \gamma \cos\theta} \int_0^V P dV, \quad (3.13)$$

where S_{MICP} is the surface area in (m²), W_s is the dry weight of the sample (g), γ is the surface tension of mercury (dynes/m), P is the capillary pressure (dynes/m²), and dV is the incremental volume (m³).

3.2.6.4 Determination of IPV and Accessible Surface Area

The inaccessible pore volume was calculated from the pore throat distribution data gathered through MICP. This pore throat size distribution was compared against the polymer's hydrodynamic size measured using Dynamic Light Scattering (DLS) technique. It was inferred that pores bearing throat diameters smaller than the hydrodynamic size of the polymer would be inaccessible to the polymer. To determine the total volume of these inaccessible pores, the volumes of all pore throats that have a diameter smaller than the hydrodynamic size of the polymer were summed up. This combined volume represents the total pore space that the polymer cannot access. The accessible surface area for the polymer is obtained by deducing the area of pore space that is inaccessible to the polymer from the total surface area obtained from MICP by applying **Equation 3.13**.

3.2.6.5 Experimental Conditions

Dynamic adsorption measurements were conducted at various temperatures including 25, 40, 60, 80, and 90 °C, and a retention time of 6 hours. The retention time was selected based on previous static adsorption studies on the SAV10 polymer, where larger values did not impact adsorption (Thomas *et al.*, 2020).

3.2.6.6 Coreflooding Experiments to Determine Core Absolute Permeability

The core sample, fully saturated with brine, was mounted in the coreflooding apparatus (**Figure 3.5**). The rig was set to the respective experimental temperature, a confining pressure of 1200 psi, and a backpressure of 100 psi. Once the temperature was stabilized, the absolute permeability of the brine was determined by injecting the brine at varying flow rates and recording the stabilized differential pressure at each respective rate. Subsequently, the permeability of the brine was calculated using **Equation 3.14**.

$$K = \frac{Q * \mu * L}{A * \Delta P}, \quad (3.14)$$

where K is the absolute brine permeability (D), Q is the injection flow rate (cm³/sec), L is the length of the core sample (cm), A is the cross-sectional area of the core sample (cm²), μ is the brine viscosity (cP), and ΔP is pressure drop (atm).

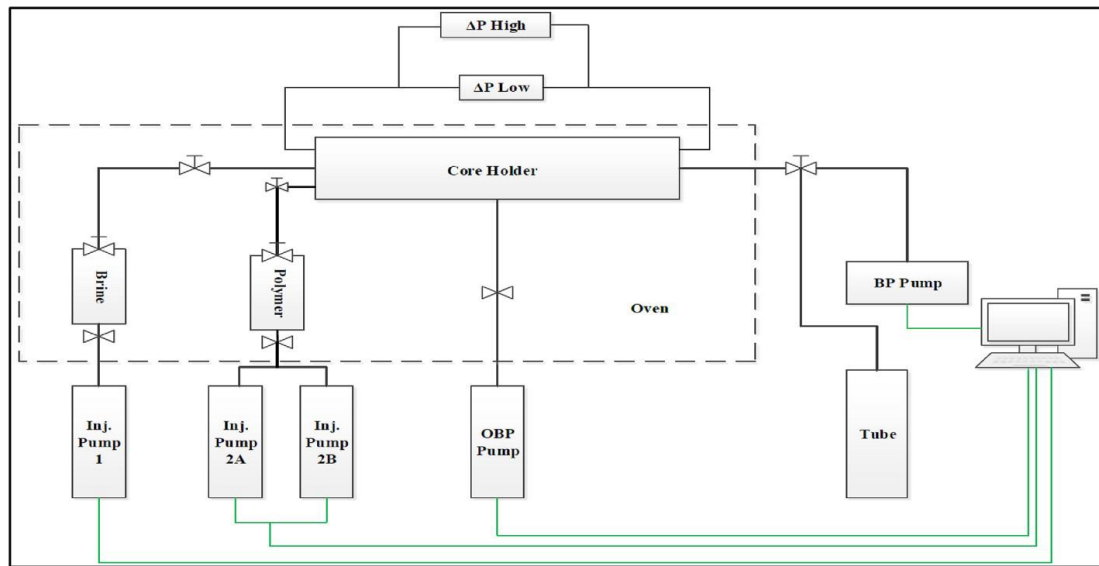


Figure 3.5: Schematic of the coreflooding equipment used for polymer adsorption experiments.

3.2.6.7 Drainage and Forced Imbibition

Drainage was conducted at the respective experimental temperature to achieve the initial water saturation (S_{wi}) in the core, where oil was injected at different flow rates. Following this, the core was aged for a period of 14 days at 90 °C. The aging process was vital in altering the

wettability of the core, ensuring that its surface properties were returned to an oil-wetting state that is representative of natural conditions.

Further, forced imbibition was conducted using two distinct protocols to reach residual oil saturation (S_{or}). Initially, protocol 1 was used, where brine was injected at various flow rates to attain S_{or} . However, this approach led to complications during the polymer injection stage, as oil was produced, resulting in changes to S_{or} , and subsequently impacting the interpretation of various findings. To mitigate this issue, protocol 2 was introduced for subsequent studies. Under this protocol, a mixture of glycerin and brine was injected at different flow rates to reach S_{or} . After achieving the desired saturation, the glycerin-brine mixture was completely flushed out using 100% brine; thus, avoiding the oil mobilization problem during the polymer injection phase experienced with the first protocol.

3.2.6.8 Dynamic Retention Experiments in Single-Phase and Two-Phase Conditions

Fully saturated core samples and core samples at S_{or} were utilized for polymer adsorption studies in the absence (single-phase) and presence of oil (two-phase), respectively. The coreflooding system was set to the desired temperature, and the brine was injected at a constant flow rate of 0.5 cc/min until the pressure was stabilized. Immediately after brine injection, a slug of the polymer solution of 1000 ppm was injected at a constant flow rate of 0.5 cc/min. The pore volumes to be injected was determined based on **Equation 3.15** (Afolabi *et al.*, 2021) considering a maximum retention time of 6 hours, beyond which polymer adsorption does not depend on the retention time.

$$PV_{inj} = \frac{Q \times t_{max}}{PV}, \quad (3.15)$$

where PV_{inj} is the total pore volume to be injected, Q is the injection flow rate, and t_{max} is the maximum retention time.

An extended post-flush brine injection at the same flow rate of 0.5 cc/min was conducted to remove all the mobile polymers within the core. The flow rate 0.5 cc/min, which is relatively higher than reservoir flow rate, was considered for brine-pre flush, polymer injection, and brine-post flush, since the primary focus of the study was on determining polymer adsorption and accordingly, this saves the time needed to achieve adsorption equilibrium in the conducted experiments. Moreover, polymer adsorption was found to be minimally dependent on the flow rate (Chen *et al.*, 2016). The effluent polymer solution was

analyzed for the polymer concentration and the normalized polymer concentration (C_e/C_i) versus pore volume was plotted, and the polymer adsorption was calculated by applying material balance (**Equation 3.16**).

$$A_d = \frac{(C_i V_i - \sum_{i=1}^n C_e V_e)}{W}, \quad (3.16)$$

where A_d is polymer adsorption ($\mu\text{g/g}$ of rock), C_i and V_i are initial concentration (mg/L) and volume (mL), respectively. C_e and V_e are the concentration (mg/L) and volume (mL) in each effluent collecting tube, respectively and W is the dry weight of the core sample (g). The dynamic polymer retention was also reported based on the specific surface area of the core as represented in **Equation 3.17**.

$$A_q = \frac{A_d}{SSA}, \quad (3.17)$$

where A_q is the polymer adsorption in ($\mu\text{g/m}^2$), A_d is polymer adsorption ($\mu\text{g/g}$ of rock), and SSA is the specific surface area of core sample in m^2/g .

3.2.6.9 Resistance Factor and Residual Resistance Factor

The Resistance factor (RF) is a dimensionless parameter that describes the increase in pressure drop caused by the increased viscosity of polymer solution achieved by adding polymer to the brine. The residual resistance factor (RRF) measures the resistance to flow by brine in porous media (permeability loss) after polymer flooding. Both RF and RRF were calculated using **Equations 3.18** and **3.19**, respectively:

$$\text{RF} = \frac{\Delta P_{\text{polymer-injection}}}{\Delta P_{\text{brine pre-flush}}}, \quad (3.18)$$

$$\text{RRF} = \frac{\Delta P_{\text{brine post-flush}}}{\Delta P_{\text{brine pre-flush}}}, \quad (3.19)$$

where $\Delta P_{\text{brine-preflush}}$, $\Delta P_{\text{polymer-injection}}$, $\Delta P_{\text{brine post-flush}}$ are the pressure drop data (psi) recorded during brine pre-flush, polymer injection, and brine post-flush, respectively.

3.2.6.10 In-situ Viscosity

In-situ polymer viscosity is the viscosity of the polymer solution within the reservoir during the polymer flooding process and can be calculated using **Equation 3.20** (Han *et al.*, 2012).

$$\mu_{insitu} = \frac{RF}{RRF} \mu_w , \quad (3.20)$$

where RF is the resistance factor, RRF is the residual resistance factor, μ_{insitu} is the polymer in situ viscosity (cP), and μ_w is the brine viscosity (cP).

3.2.6.11 Polymer Adsorbed Layer Thickness

Polymer adsorbed layer thickness refers to the thickness of the layer of polymer molecules that adheres to the rock surface (pores) in the reservoir during the polymer flooding process. It was determined by calculating the reduction in permeability under the assumption of Poiseuille fluid flow through a capillary constricted by a uniform layer of polymer (Han *et al.*, 2012) by applying **Equations 3.21** and **3.22**.

$$e = r_p \left(1 - \frac{1}{RRF^{\frac{1}{4}}} \right) , \quad (3.21)$$

$$r_p = \left(\frac{8 \cdot K}{\emptyset} \right)^{1/2} , \quad (3.22)$$

where e is the adsorbed polymer layer thickness (μm), r_p is the average pore throat radius for water flow (μm), K is the brine permeability (μm^2), and $\emptyset$ is the porosity (fraction).

3.2.6.12 Polymer Injectivity Loss

The polymer retention in porous spaces causes increased resistance to fluid flow. This results in reduced injectivity, which hinders the efficient injection of fluids and can limit the effectiveness of the polymer flooding process. **Equation 3.23** can be used to calculate the injectivity loss (I_r) during polymer injection based on brine injection (Han *et al.*, 2012).

$$I_r = 1 - \frac{I_p}{I_b} , \quad (3.23)$$

where I_p represents polymer injectivity and I_b represents brine injectivity. Injectivity (I) is the pressure gradient required to achieve a given injection flow rate. It can be described as the ratio of injection flow rate (superficial velocity, ft/d) to pressure gradient (psi/ft) as expressed in **Equation 3.24**.

$$I = \frac{\text{Injection flow rate}}{\text{Pressure Gradient}} \quad (3.24)$$

3.3 Uncertainty in Measurements

This section details different approaches considered to determine the uncertainties in the experimental results obtained.

3.3.1 Uncertainty in Experimental Values

For all experimental procedures, each measurement was conducted three-times to accurately assure the uncertainty associated with the results by measuring the standard deviation using **Equations 3.25** and **3.26**. The calculated standard deviation was represented as the length of the error bars.

$$\text{Mean} = \frac{(x_1 + x_2 + x_3)}{3}, \quad (3.25)$$

$$\text{Standard Deviation} = \sqrt{\frac{(x_1 - \text{Mean})^2 + (x_2 - \text{Mean})^2 + (x_3 - \text{Mean})^2}{3-1}}, \quad (3.26)$$

where x_1 , x_2 , and x_3 are the values obtained from the three experimental runs.

3.3.2 Uncertainty in Dynamic Retention Values

Dynamic polymer retention measurements using coreflooding experiments involved several sources of uncertainty that could affect the accuracy and reliability of the results. Some key uncertainties included measuring various parameters such as collected effluent volume and polymer concentration measurements. These errors could arise from instrument calibration issues, fluctuations in experimental conditions, or human error during data collection. Three readings were taken to obtain uncertainties in volume collection and polymer concentration measurements, and **Equation 3.27** was applied to calculate the corresponding uncertainty. This

process involved measuring the relevant parameters multiple times and using the equation to quantify the level of uncertainty associated with each measurement.

$$\Delta x = \frac{\text{Stdev}}{\sqrt{n}}, \quad (3.27)$$

where Δx is the uncertainty associated with the measured parameter, Stdev is the standard deviation, and n is the total number of repeated measurements of the individual parameter.

The Propagation of Error Theory provided a framework for quantifying the uncertainty or error in a calculated result that arose from uncertainties in the measured or input quantities. It enabled us to estimate the combined effect of these uncertainties on the results. Two fundamental rules were used in the Theory of Propagation of Error i.e., the addition rule and the quotient rule (John, 1982). The addition rule (**Equation 3.28**) states that if z is calculated by adding or subtracting $x_1, x_2, \dots, x_n$, the uncertainty associated with z was then simply the square root of the sum of squares of the uncertainties of $x_1, x_2, \dots, x_n$, i.e. $\Delta x_1, \Delta x_2, \dots, \Delta x_n$.

$$\Delta z = \sqrt{(\Delta x_1)^2 + (\Delta x_2)^2 + \dots + (\Delta x_n)^2}, \quad (3.28)$$

where Δz is the uncertainty associated with the measured parameter z , and $\Delta x_1, \Delta x_2, \dots, \Delta x_n$, are the uncertainties associated with $x_1, x_2, \dots, x_n$, respectively.

On the other hand, the quotient rule (**Equation 3.29**) states that if z is calculated by multiplying or dividing several quantities $x_1, x_2, \dots, x_n$ that have errors $\Delta x_1, \Delta x_2, \dots, \Delta x_n$, then the quotient rule was used to calculate the error in z . The quotient rule states that the fractional uncertainties add in quadrature.

$$\Delta z = |z| * \sqrt{\left(\frac{\Delta x_1}{|x_1|}\right)^2 + \left(\frac{\Delta x_2}{|x_2|}\right)^2 + \dots + \left(\frac{\Delta x_n}{|x_n|}\right)^2}. \quad (3.29)$$

By applying these rules, we were able to assess and quantify the impact of uncertainties in dynamic polymer retention values as well as provide a more comprehensive understanding of the overall uncertainty associated with the measurement or calculation process.

3.4 Developing Correlation to Predict Dynamic Retention from Various Parameters

This section delves into the methodology adopted to predict dynamic retention from various factors influencing it.

3.4.1 Parameters Influencing Dynamic Retention

Dynamic polymer retention occurs due to combination of mechanisms including polymer adsorption, mechanical entrapment, and hydrodynamic retention, ranked in order of their significance. Among these, adsorption stands out as the most significant, while hydrodynamic retention, influenced mainly by flow rates, is the least significant. The reversibility of hydrodynamic retention renders it often negligible.

The two primary contributors to dynamic retention are polymer adsorption and mechanical entrapment. The former is significantly influenced by factors such as polymer type, its hydrodynamic size, salinity and ionic compositions of the make-up water, temperature, rock mineralogy, and the available surface access for polymer interaction. This adsorption mechanism can typically be captured through static adsorption experiments. On the other hand, mechanical entrapment is predominantly determined by the core plug's pore structure and how the polymer solution behaves while flowing through the porous media. The flow behavior of the polymer solution within the porous media can be affected by different variables including salinity and ionic composition, temperature, and the presence of oil.

Given these considerations, the parameters chosen for predicting dynamic retention include static adsorption, average pore throat size, salinity, hardness, temperature, and residual oil saturation (S_{or}), as they encapsulate the different aspects affecting the polymer's retention behavior in a dynamic condition.

3.4.2 Experimental Conditions Considered for Developing the Correlation

To capture the adsorption phenomena representatively, the static adsorption and dynamic retention studies were conducted under the same experimental conditions including salinity, ionic compositions, temperature, retention time, solid-to-liquid ratio, and surface access. The surface access was kept same by considering the weight of the core, specific surface area of both the crushed core and the core sample, and accordingly determining the weight of the crushed rock sample (Al-Hajri *et al.*, 2020) as per **Equations 3.30, 3.31, and 3.32**. IPV and S_{or} were also considered in determining surface access.

$$SA = S_{MICP} * (1 - IPV) * W , \quad (3.30)$$

$$SA = S_{MICP} * (1 - IPV) * (1 - S_{or})W , \quad (3.31)$$

where SA is the surface access in m², S_{MICP} is the surface area of core sample obtained from MICP in m²/g, IPV is the inaccessible pore volume, S_{or} is the residual oil saturation, and W is the dry weight of core in g.

$$W_s = \frac{SA}{S_{BET}} , \quad (3.32)$$

where W_s is the weight of the crushed core in g, SA is the surface access in m², and S_{BET} is the crushed core surface area in m²/g.

3.4.3 Approach Used to Develop the Correlation

Machine learning approach was explored to determine a correlation between dynamic retention value based on different defined input parameters including static adsorption, average pore throat size, salinity, hardness, temperature, and residual oil saturation (S_{or}). Specifically, tree-based models were applied and implemented using a variety of Python tools. The details of the procedures and tasks followed are elaborated further in the sections below. In addition to these methods, symbolic regression using TuringBot software was employed to derive a specific and clear mathematical formula to better predict the dynamic retention value. All parameters considered are representative of Middle East reservoir conditions. **Figure 3.6** demonstrates the workflow applied for the study.

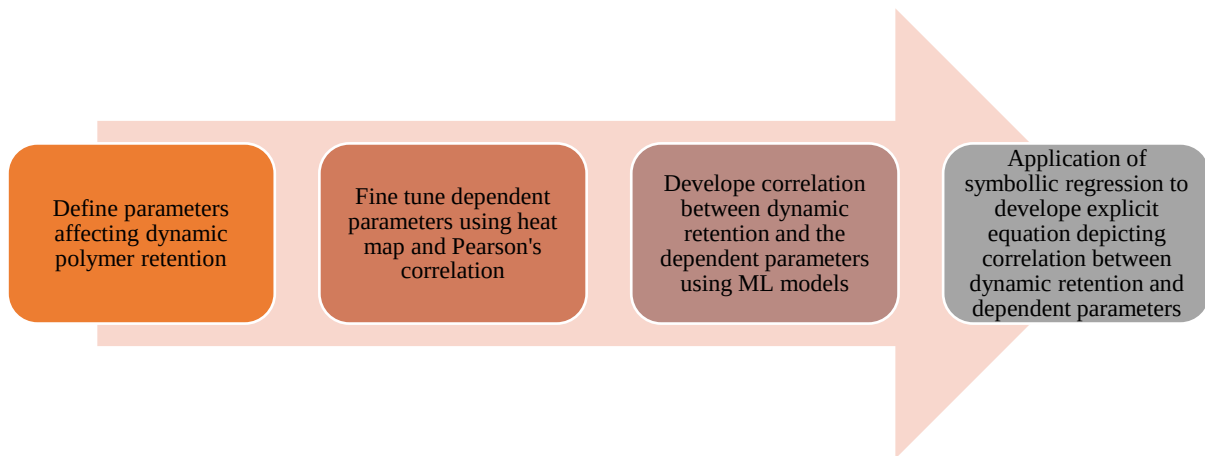


Figure 3.6: Workflow for developing correlation between dynamic retention and dependent parameters.

3.4.4 Applying Machine Learning to Estimate Dynamic Retention

Different tree-based Machine learning (ML) algorithms including decision tree, extra trees, random forest, adaptive boosting, gradient boosting, and extreme gradient boosting were applied to predict dynamic retention value based on input parameters. These regression models were performed using Python online libraries.

In this study, 36 representative experimental data for Middle Eastern reservoir conditions were considered. The dataset will be thoroughly discussed later in **Chapter 8**. **Figure 3.7** demonstrates the workflow of ML algorithms considered to achieve the objective. Data processing stage involves preparing the dataset for training the model. The model was trained on 80% of the samples and tested on the remaining 20%. In addition, K-fold cross validation technique was used in this research where a value of $k = 5$ was chosen.

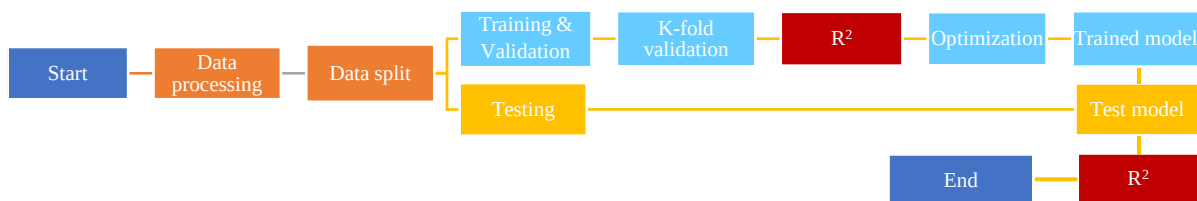


Figure 3.7: Schematic representation of the machine learning workflow.

Moreover, various hyperparameters were tuned to enhance the accuracy of machine learning models in forecasting dynamic retention. Additionally, the estimated values were compared against the actual dynamic retention values using different evaluation metrics including R^2 , RMSE, and MAE.

3.4.4.1 Random Forest Algorithm

Random Forest algorithm combines multiple decision trees to produce a more generalized and robust model. A random forest is a collection or “ensemble” of decision trees that are trained using different subsets of the training data and different subsets of features. When making predictions, the random forest aggregates the predictions of each individual tree to output a result. Random forest employs a technique called bootstrapping to create multiple datasets from the original training data. It randomly samples the original dataset with replacement to produce subsets of data. Each of these subsets is used to train an individual decision tree. Due to the

random sampling, each decision tree will have a slightly different perspective on the data. In random forest, at each split, only a random subset of features is considered for splitting. This introduces further diversity among the trees and reduces the chances of overfitting.

For regression tasks, the random forest averages the predictions of all the individual trees to produce the final prediction. Since each tree is trained on a bootstrap sample of the data, some observations may be left out during the training of a particular tree. These left-out observations are called “out-of-bag, OOB” observations. The OOB error is calculated by taking each observation, predicting its output using only the trees that did not have this observation in their bootstrap sample, and then averaging these errors. It provides an estimate of the generalization error without the need for a separate validation set. Combining multiple trees reduces the variance and generally produces a more robust and accurate model. Random forests can handle missing values and still provide accurate predictions. It offers a measure of feature importance, which can be beneficial in understanding the dataset and refining the model. Due to the diversity introduced by bootstrapping and feature randomness, random forests are less prone to overfitting compared to individual decision tree. **Figure 3.8** represents the flow chart for RF model.

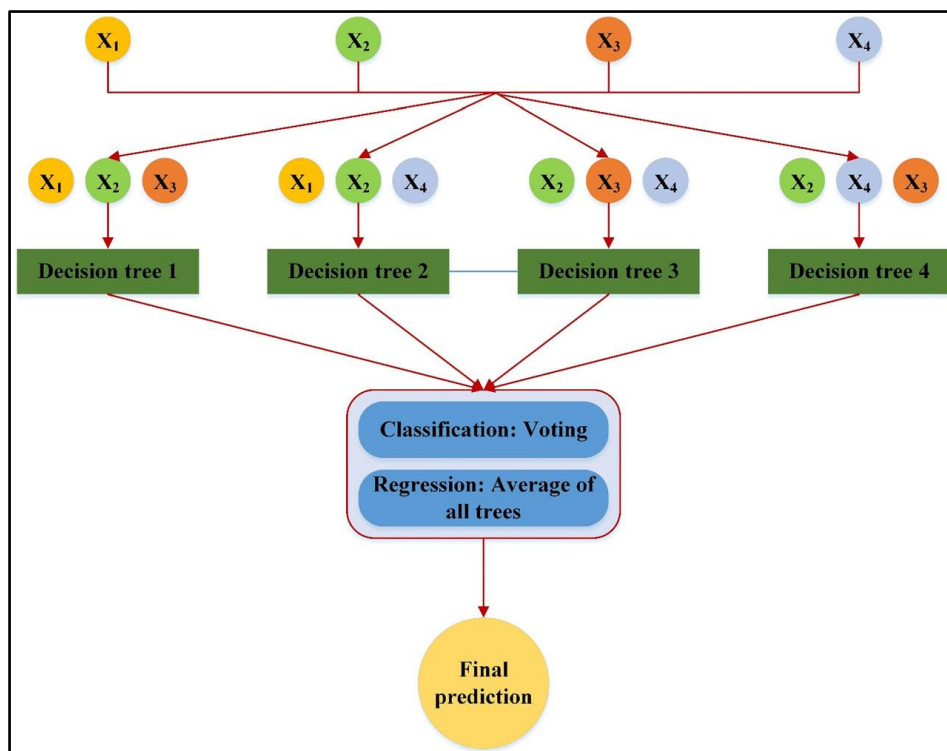


Figure 3.8: Flow chart illustrating RF algorithm (Han *et al.*, 2020).

3.4.4.2 Extra Trees Algorithm

Extra Trees is like the random forest algorithm, but with two main differences in the way the decision trees are constructed. When determining the best split for a feature, instead of searching for the most discriminative thresholds (like what is done in regular decision tree or the random forest), thresholds are drawn randomly for each candidate feature, and the best of these randomly generated thresholds is used as the splitting rule. This strategy reduces the variance of the model, at the cost of increasing its bias. Unlike random forest, which uses bootstrapping to create multiple datasets, extra trees use the whole original dataset to grow each tree. However, due to the randomness introduced in the splitting process, each tree is still diverse from the others. For each tree being built, at every node, a subset of features is randomly selected (just like in random forest). Nevertheless, instead of computing the best split among all possible values, a random value is chosen as the split threshold for each feature. The feature and threshold that give the best split (typically measured using variance reduction in case of regression) are then chosen to split the node. For a new input sample, predictions from all the individual trees in the ensemble are averaged to produce the final regression output. Since the splits are chosen randomly, there is no need for extensive threshold searching, rendering the extra trees algorithm often faster to train than random forest. The added randomness can act as a regularizing agent, and the model is less likely to overfit the training data. Just like random forest, extra trees can be used to compute feature importance, which can be beneficial for understanding the data and the impact of each feature on the prediction.

3.4.4.3 AdaBoost Algorithm

Adaptive Boosting is one of the first and most popular ensemble boosting algorithms. Boosting is a general ensemble method that aims to convert a set of weak learners into a single strong learner. The basic idea is to give more weight to misclassified instances, so subsequent learners focus on the harder-to-classify examples. Start with a training dataset of n instances, each with an equal weight of $1/n$. A weak learner (typically a decision tree with just one level, also known as a “decision stump”) is trained on the data. The algorithm iteratively trains weak learners, it highlights those instances which were misclassified in previous rounds by increasing their weights. The final prediction is a weighted combination of the predictions of all weak learners, where the weights are the weights assigned to the learners based on their accuracy. **Figure 3.9** depicts the flow diagram of the adaboost model.

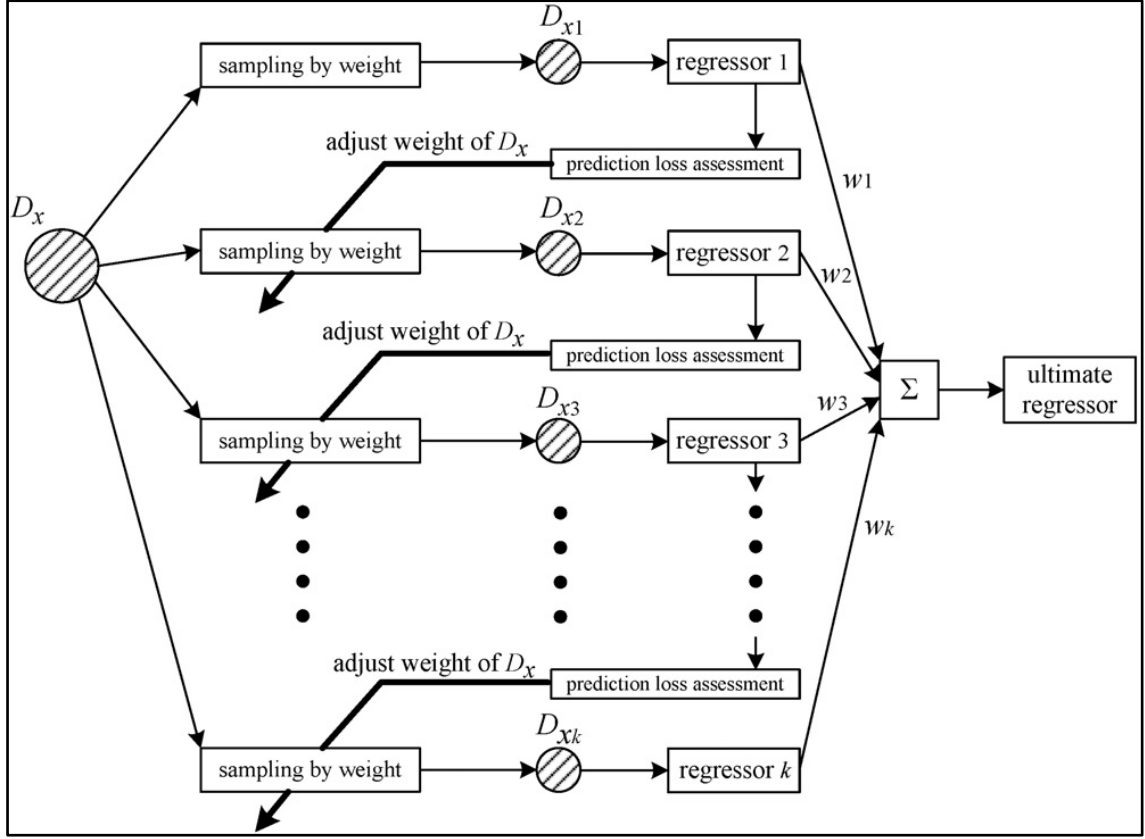


Figure 3.9: Flow chart illustrating AdaBoost model (Min and Luo, 2016).

The mathematics of the AdaBoost algorithm is as follows:

- Weight Initialization

Each training instance x_i initially is assigned a weight w_i , where $i = 1, 2, \dots, n$ and n is the number of instances. Typically, every instance is assigned an equal weight as depicted in **Equation 3.33**.

$$w_i = \frac{1}{n}. \quad (3.33)$$

- For each boosting iteration:

a. Training a weak learner

A weak learner (usually a decision stump, which is a decision tree with just one split) is trained using the weighted dataset. The goal of the weak learner is to minimize the weighted error.

$$\epsilon_j = \sum_{i: h_j(x_i) \neq y_i} w_i / \sum_{i=1}^n w_i, \quad (3.34)$$

where ϵ_j is the weighted error of the model, $h_j(x_i)$ is the prediction of the j^{th} weak learner for the i^{th} instance, y_i is the true label of the i^{th} instance.

b. Compute the weak learner weight: It was compute based on the **Equation 3.35**.

$$\alpha_j = \frac{1}{2} \ln\left(\frac{1-\epsilon_j}{\epsilon_j}\right), \quad (3.35)$$

where α_j is the weight of the j^{th} weak learner.

c. Update the Instance Weights:

The weight of each instance is updated by applying **Equation 3.36**.

$$w_{i(new)} = w_{i(old)} e^{\alpha_j}, \quad (3.36)$$

- Final model

The AdaBoost algorithm is comprehensively described by **Equation 3.37**.

$$F(x) = \text{sign}\left(\sum_{j=1}^w \alpha_j h_j(X)\right), \quad (3.37)$$

where $F(x)$ is the final prediction of the model and w is the total number of learners.

3.4.4.4 Gradient Boosting Algorithm

Gradient Boosting is an advanced ensemble machine-learning algorithm that builds on the principles of boosting, aiming to optimize a differentiable loss function. At its core, Gradient Boosting incrementally constructs an ensemble of weak learners, typically decision trees, to create a more powerful prediction model. Unlike AdaBoost, which adjusts instance weights, Gradient Boosting emphasizes the errors or residuals of the previous learners. In its iterative process, each new tree is trained to correct the errors made by the combined ensemble of all preceding trees. Essentially, it is as if the algorithm is navigating a landscape, adjusting its course by descending the gradient of the error surface, refining its predictions systematically.

One of its notable strengths is its capacity to handle various types of data (numerical, categorical, or a mix of both), and it can be employed for both regression and classification tasks. A salient feature of Gradient Boosting is its ability to optimize different loss functions, rendering it adaptable to various problem types. However, care must be taken in its application. Gradient Boosting requires careful tuning of parameters like tree depth, learning rate, and the

number of trees to prevent overfitting. Additionally, it can be computationally more demanding than other algorithms. Yet, its efficacy, particularly in predictive accuracy, has rendered it a preferred choice in numerous machine learning competitions and real-world applications, ranging from web search ranking to ecology. In summary, Gradient Boosting is a powerful ensemble technique that refines its predictions iteratively, focusing on the discrepancies of its preceding models, and stands as one of the paramount tools in the predictive modeling toolbox. **Figure 3.10** displays the workflow diagram for the gradient boosting model. The gradient boosting algorithm is represented mathematically by **Equation 3.38**.

$$F(X) = \sum_{m=1}^M v * h_m(X, w_m), \quad (3.38)$$

where $F(X)$ is the final ensemble prediction, M is the total number of boosting iterations, w_m is the weight, h_m represents each model indexed with m , X represents the features, and v is the learning rate, which is a hyperparameter that scales the contribution of each tree.

The model is updated at each iteration by adding the weighted weak learner's output to the previous model, given by **Equation 3.39**.

$$F_m(X) = F_{m-1}(X) + v * h_m(X, w_m), \quad (3.39)$$

Mean squared error is applied to determine the loss function at each tree, by applying **Equation 3.40**.

$$err_m = \frac{1}{2} (F_{true,m} - F_{predicted,m})^2. \quad (3.40)$$

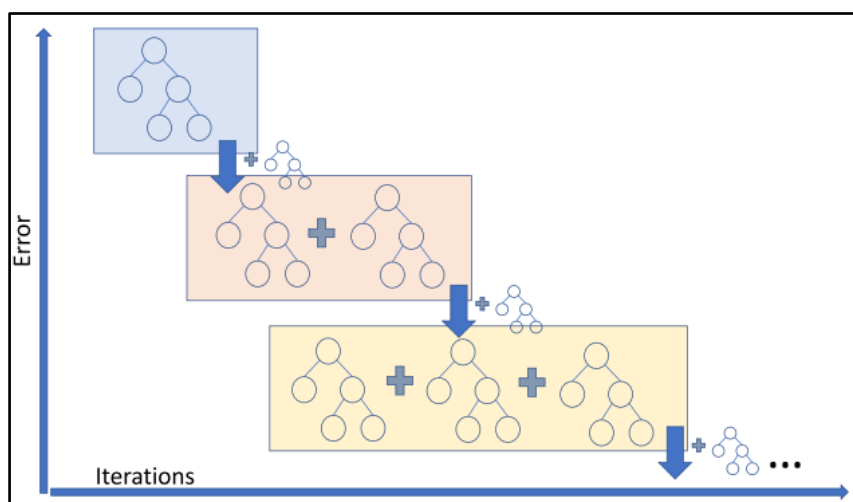


Figure 3.10: Flow chart illustrating gradient boosting model (Baturynska and Martinsen, 2021).

3.4.4.5 XGBoost Algorithm

Extreme Gradient Boosting (XGBoost) is an optimized and scalable machine learning system that builds upon the foundation of gradient boosting frameworks. XGBoost is meticulously engineered to maximize computational speed and model performance. Central to its design is the principle of gradient boosting, wherein the algorithm constructs a series of decision trees sequentially, with each tree aiming to rectify the errors or residuals of its predecessors. What sets XGBoost apart from traditional gradient boosting is a slew of enhancements and features. Notably, XGBoost implements regularization terms in its objective function, adding both L1 (Lasso regression) and L2 (Ridge regression) regularization. This incorporation inherently reduces model complexity and aids in preventing overfitting, leading to enhanced generalization on unseen data. XGBoost is also designed with computational efficiency in mind; it possesses parallel tree boosting, which allows for faster tree construction by leveraging all CPU cores. Additionally, the system handles missing data natively, using sparsity-aware algorithms, negating the need for elaborate preprocessing steps. XGBoost is not limited to just regression or classification. It is versatile, supporting ranking tasks and user-defined prediction tasks.

Furthermore, its cross-platform design, coupled with support for numerous programming languages, renders it an accessible and universally adoptable tool. Extensive documentation and community support amplify its usability. Given its robustness, accuracy, and speed, XGBoost has become a darling of the data science community, frequently being the algorithm of choice in machine learning competitions and a myriad of industry applications. In essence, XGBoost elevates the gradient boosting paradigm, combining computational rigor with advanced regularization to produce state-of-the-art predictive models. **Figure 3.11** showcases the schematic for the XGBoost model. The regularization term $\Omega(f)$ in XGBoost penalizes the complexity of the tree (this is what differentiates it from regular gradient boosting). The model is given by **Equation 3.41**.

$$\Omega(f_m) = \gamma T + \frac{1}{2} \lambda \|w\|^2, \quad (3.41)$$

where $\Omega(f_m)$ is the regularization term, λ is the regularization parameter that is used for reducing insensitivity of the prediction to individual observations, T is the number of leaves in the tree, w is the weight of each leaf, γ indicates penalty function that is used for pruning. After

adding the complexity function to the model, the general equation of XGBoost model is represented by **Equation 3.42**.

$$F^{(t)} = \sum_{i=1}^m f[y_i \hat{y}_i^{(t-1)} + f_t(x_i)] + \Omega(f_t). \quad (3.42)$$

It should be noted that the above equation represents XGBoost using L1 regularization. XGBoost also uses L2 regularization, which was already discussed along with L1 regularization in the previous subsection.

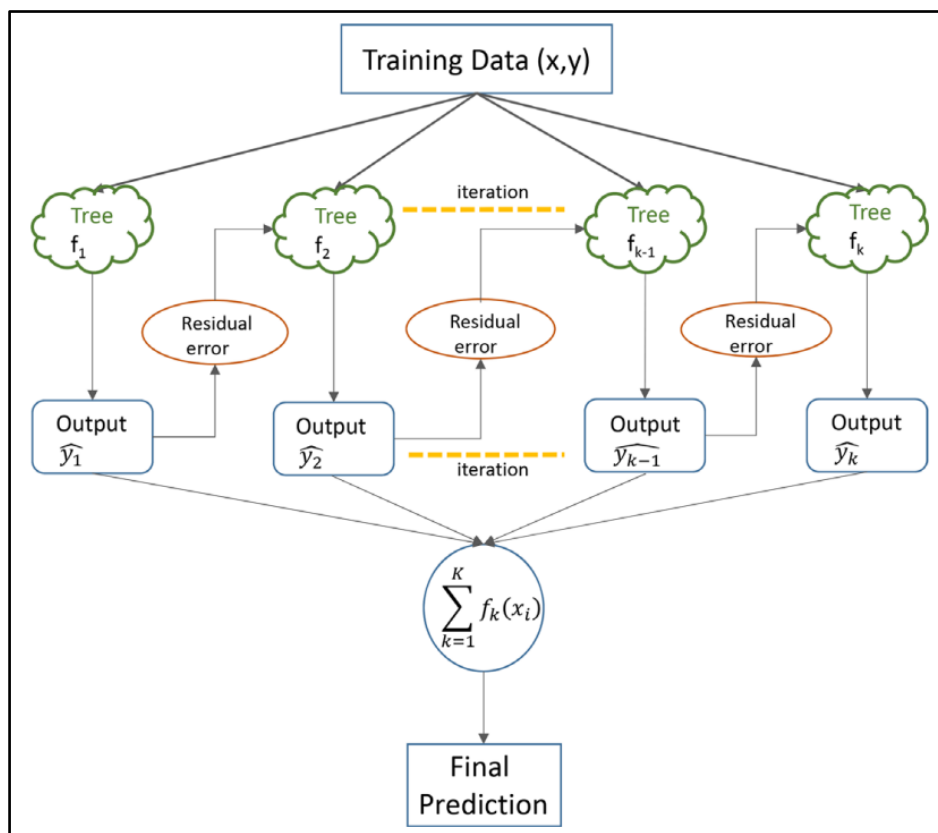


Figure 3.11: Flow chart illustrating XGBoost model (Mathew *et al.*, 2021).

3.4.4.6 Hyperparameters

Hyperparameters can be considered as the “knobs” or “dials” that are tuned to optimize the performance of machine learning algorithms. Unlike model parameters, which are learned directly from the data during training, hyperparameters are external configurations preset by practitioners before model training begins. They govern various aspects of the learning process, such as the learning rate in gradient-based optimization, the depth of a decision tree, or the

number of hidden layers in a neural network. The correct setting of hyperparameters can profoundly influence model performance, rendering the difference between a mediocre model and a highly performative one. However, identifying the optimal hyperparameters often demands systematic searching or experimentation, as the ideal configuration is typically problem specific. Techniques like grid search, random search, and more sophisticated methods such as Bayesian optimization are employed to navigate hyperparameter space. Given the significant impact of hyperparameters on model efficacy and the computational resources that can be consumed in their tuning, they remain a pivotal aspect of the machine learning workflow, necessitating careful consideration, and handling by data scientists and machine learning practitioners. Different hyperparameters used for the tree-based models are Minimum Samples to Split, Minimum Samples per Leaf, Maximum Depth, Maximum Features, Number of Estimators, Random State, Learning Rate (Kern *et al.*, 2019; Probst *et al.*, 2019; Zhu *et al.*, 2022b; Mansoori *et al.*, 2023). These hyperparameters are discussed below in detail.

In the realm of decision tree-based algorithms, the “Minimum Samples to Split” is a critical hyperparameter that governs the growth of the tree. Essentially, it designates the smallest number of data samples that a node must contain for a split to be even considered at that node. For instance, if this hyperparameter is set to 10, then any node containing fewer than 10 samples will not be split further and will consequently become a terminal or leaf node. The primary intention behind setting a threshold for this hyperparameter is twofold: to prevent overfitting and to control tree depth. If a tree is allowed to split on very few samples, it might capture noise or outliers in the data, leading to an over-complex model that performs well on training data but poorly on unseen data. By setting a higher threshold, we can ensure that the tree generalizes better to new data by avoiding extraneous splits based on inconsequential patterns. However, setting it too high can hinder the tree’s ability to capture genuine patterns, resulting in an overly simplistic and underfitting model. As with other hyperparameters, the ideal value for “Minimum Samples to Split” does not have a one-size-fits-all answer; it depends on the specific problem and the nature of the data. Therefore, it often requires experimentation or hyperparameter tuning to strike a balance between a tree that is too shallow (underfitting) and one that is too deep (overfitting).

The “Minimum Samples per Leaf” is an essential hyperparameter specific to decision tree-based algorithms, including their ensemble counterparts like random forests and Gradient Boosting Trees. As its name suggests, this hyperparameter determines the smallest number of samples that a leaf node can have in the decision tree. In essence, it sets a floor on the size of the terminal nodes, ensuring that no leaf node in the tree represents fewer than the stipulated

number of samples. This plays a pivotal role in the model's ability to generalize. By setting a higher "Minimum Samples per Leaf", one can prevent the tree from growing too deep and making decisions based on potentially noisy or outlier data, thereby curbing overfitting. Conversely, if set too low, the tree might capture minute idiosyncrasies in the training data, leading to a model that is overly tailored to the training set and possibly performing poorly on new, unseen data. In addition to its regularization effect, a practical benefit of this hyperparameter is that it can lead to faster training times, as having a higher threshold can result in fewer splits and therefore, a more concise tree. Finding the optimal value for "Minimum Samples per Leaf" is a balancing act. It is often discovered through a combination of domain knowledge, understanding the nature of the dataset, and systematic hyperparameter tuning. Ultimately, this hyperparameter serves as a valuable tool in the arsenal of a data scientist or machine-learning practitioner to ensure that the developed decision tree models are both accurate and generalizable.

The "Maximum Depth" hyperparameter, inherent to decision tree-based algorithms and their ensemble derivatives, signifies the maximum number of levels a decision tree can grow. This is considered as a constraint on the tree's height, where each level represents a possible decision boundary based on a feature. By setting this hyperparameter, practitioners can control the complexity and size of the tree. A deeper tree (i.e., one with more levels) can capture intricate relationships in the data, allowing for detailed partitioning of the feature space. However, this granularity comes at a cost. If the tree is allowed to grow without restraint, it might end up fitting not just the underlying patterns but also the noise or anomalies in the training data, leading to overfitting. An overfit model might boast impressive accuracy on the training data but falter when exposed to unseen data. On the other hand, if the "Maximum Depth" is set too shallow, the tree might not be sophisticated enough to capture essential patterns, resulting in underfitting. An underfit model tends to show mediocre performance across both training and test datasets. Consequently, the "Maximum Depth" hyperparameter acts as a regularization knob, balancing the bias-variance trade-off. The optimal value for this hyperparameter is often dataset-specific and is best identified through empirical means such as cross-validation. In the broader context of model interpretability, a tree with a limited depth also offers the advantage of being more comprehensible, making decision-making processes clearer to stakeholders. In summary, "Maximum Depth" plays a central role in the architecture and performance of decision tree-based models, and its judicious selection is crucial for achieving models that are both performative and interpretable.

“Maximum Features” is a pivotal hyperparameter commonly associated with tree-based algorithms, especially in ensemble methods like random forests. It defines the number of features to consider when looking for the best split at each node of a tree. By adjusting this hyperparameter, one can influence both the diversity of the trees in an ensemble and the overall algorithm’s computational efficiency. When the “Maximum Features” value is less than the total number of features available, the algorithm randomly samples the specified number of features at each split, introducing variability into the tree-building process. This random feature sampling acts as a form of inbuilt feature selection and serves a dual purpose: it reduces the risk of overfitting by ensuring that trees do not overly rely on a few dominant features, and it boosts model diversity within ensemble methods, leading to a more robust aggregate prediction. Furthermore, by considering fewer features for each split, the computational burden during tree construction is reduced, often speeding up training times. However, setting this hyperparameter too low might exclude relevant features from consideration, potentially weakening the model’s performance. Conversely, if set too high, the model might become more susceptible to overfitting, especially if there are features that are strongly predictive of the target variable. Identifying the optimal value for “Maximum Features” is more an art than an exact science, typically requiring iterative experimentation and validation. In essence, “Maximum Features” acts as a tuning lever, balancing model accuracy, diversity, and training efficiency, and its judicious setting is vital for harnessing the full potential of tree-based algorithms.

The “Number of Estimators” hyperparameter is prominently associated with ensemble methods such as random forests, Gradient Boosting Machines, and other bagging or boosting techniques. At its core, this hyperparameter denotes the number of individual models (often decision trees) in the ensemble. Each of these models, termed an “estimator” contributes its own prediction, and the ensemble aggregates these predictions to produce a final output. In bagging techniques, like random forests, the ensemble seeks to reduce variance by averaging the results of multiple, independently grown trees. In boosting methods, trees are grown sequentially to correct the errors of the preceding ones, and their predictions are combined, often in a weighted manner, to enhance accuracy. The “Number of Estimators” hyperparameter directly affects the ensemble’s performance and computational considerations. As one might intuit, increasing the number of estimators generally enhances the model’s robustness and reduces overfitting, given that it aggregates predictions across a more diverse set of models. However, there is a point of diminishing returns: after a certain threshold, adding more trees may offer minuscule, if any, improvement in performance, while significantly increasing

training time and memory usage. Conversely, a very low number of estimators might not capture the data's complexity adequately, resulting in an underfit model. It is also worth noting that while more trees might decrease variance in bagging methods, in boosting, one needs to be wary of adding too many trees as it might lead to overfitting. Finding the optimal "Number of Estimators" is a nuanced task, usually accomplished through a combination of cross-validation and domain expertise. In summation, the "Number of Estimators" hyperparameter is pivotal in ensemble algorithms, balancing predictive power, computational efficiency, and the risk of overfitting or underfitting. Proper tuning of this parameter is essential to realize the full potential of ensemble-based machine learning methods.

The "Random State" parameter, commonly encountered in many machine learning algorithms and functions, is crucial for ensuring reproducibility of results. At its heart, many machine-learning processes, from data splitting to model initialization, involve random procedures. This randomness can lead to variations in model performance and outcomes across different runs, even when using the same dataset and algorithm settings. To address this challenge, the "Random State" parameter is introduced. When a specific integer value is set for "Random State", it acts as a seed for the random number generator, ensuring that the same sequence of random numbers is produced every time. Consequently, any process or function relying on this generator will consistently produce the same results across multiple executions, given the same seed value. However, it is crucial to understand that while setting a "Random State" guarantees reproducibility, it does not imply that the chosen configuration is the optimal or most representative one. Sometimes, experimenting without a fixed random state can offer insights into the variability and stability of the model or process. In essence, the "Random State" parameter is a tool that offers control over randomness in machine learning, enabling researchers and practitioners to strike a balance between reproducibility and exploration.

The "Learning Rate" is a foundational hyperparameter in the domain of machine learning and deep learning, especially pertinent to optimization algorithms that iteratively adjust model parameters, such as gradient descent. Often symbolized by the Greek letter eta (η), the learning rate dictates the step size taken towards the direction of minimizing the cost or loss function. In simpler terms, when updating model parameters in response to the calculated gradient, the learning rate determines the magnitude of this update. A large learning rate might result in sizable steps, potentially speeding up the convergence process, but it runs the risk of overshooting the optimal point and causing oscillations. On the other hand, a small learning rate ensures more precise, incremental adjustments, but it may slow down convergence significantly and possibly get trapped in local minima. The choice of an

appropriate learning rate is pivotal for efficient training. Too high learning rate and the algorithm might never converge; too low rate and it might take impractically long or get stuck. Moreover, the ideal learning rate can vary depending on the specific dataset, model architecture, and optimization problem. Given its profound influence on model training dynamics, numerous strategies have been proposed to fine-tune it. Some techniques involve setting a decay for the learning rate, where it starts high and decreases over time, ensuring rapid initial progress but fine-tuning as training proceeds.

3.4.5 Symbolic Regression to Develop Dynamic Retention Correlation

Symbolic regression is a method used to find mathematical relationships between variables. Unlike traditional models that start with a specific formula, symbolic regression explores various mathematical equations to best fit the data. It uses mathematical functions like addition, multiplication, and sometimes even more advanced functions like trigonometry or logarithms. The goal is to develop an equation that accurately represents the data, but it should also be straightforward. Simple models are easier to understand and can prevent overfitting, where the equation fits the current data too precisely but might not work well with new data. One unique thing about symbolic regression is that it gives a clear formula, while some other methods are more like "black boxes" and harder to interpret. There are tools like TuringBot that develop symbolic regression equations. In this study, symbolic regression was performed using TuringBot to generate mathematical expressions to predict dynamic retention from the defined parameters affecting dynamic retention. TuringBot is a specialized software designed for symbolic regression tasks (Ashok *et al.*, 2021). The software employs advanced algorithms to search through the space of mathematical expressions, aiming to find the one that best fits the provided data.

CHAPTER 4: RHEOLOGICAL STUDIES

This chapter presents a rheological analysis of polymer solutions in various brine formulations, including shear ramp-up evaluations, temperature ramp-up studies, and experiments with varying polymer concentrations. The chapter further characterizes the polymer solution in various brine recipes by assessing both the hydrodynamic size and the polydispersity index. This chapter also discusses different analytical methods used for polymer concentration determination.

4.1 Bulk-Rheological Properties

Bulk rheological properties of polymer solutions relate to the flow behavior of the polymer solution. These properties provide valuable insights into the solution's viscosity, and other flow-related attributes. Rheological experiments were conducted using the Anton Paar MCR 302 rheometer as previously discussed in **Chapter 3**. This chapter details the comprehensive rheological characterization of polymer solutions within distinct brine formulations. This includes effects of varying shear rates (1 to 1000 s^{-1}), polymer concentrations ($500 - 3000$ ppm), and temperatures (25 to $90\text{ }^{\circ}\text{C}$).

4.1.1 Effect of Shear Rate on Polymer Solution Viscosity

The viscosity of polymer solutions is a fundamental property that reflects their resistance to flow. This section details the effect of varying shear rate on viscosity of polymer solutions, shedding light on their behavior under different flow conditions. The viscosity was measured by varying polymer concentrations (1000 to 3000 ppm) in both formation water (**Figure 4.1**) and seawater (**Figure 4.2**). The shear rate ramped up from 1 to 1000 s^{-1} . One can observe that all polymer solutions exhibited shear-thinning behavior (**Figures 4.1** and **4.2**); the viscosity decreases as the shear rate increases. This behavior is because the polymer solutions consist of long-chain polymer molecules dispersed in the brine. At low-shear conditions, they tend to be in a coiled or entangled state. This entanglement results in a high resistance to flow, leading to higher viscosity. When higher shear rates are applied, these coiled and entangled polymer chains begin to align in the direction of the shear. As the shear rate increases, the alignment becomes more pronounced, and the chains stretch out along the flow direction. Hence, there is less internal resistance to flow. Consequently, the solution becomes less viscous with increasing shear. It is important to note that the alignment and disentanglement are not

permanent. Once the shear force is removed, the polymer chains will, over time, return to their coiled and entangled state, and the viscosity will rise back to its original value. The degree of shear-thinning is more noticeable in solutions with higher polymer concentrations (3000, 2500, and 2000 ppm) compared to those with lower polymer concentrations (1500 and 1000 ppm). This is because high polymer concentrations tend to result in stronger entanglements and higher viscosity. Accordingly, the induced alignments of molecules show significantly decreased viscosity, leading to a more pronounced shear-thinning behavior (Xin *et al.*, 2018; Navaie *et al.*, 2022). Furthermore, one can note that higher polymer viscosities are achieved in seawater as makeup brine as opposed to formation water, which was also reflected in more pronounced shear-thinning behavior accordingly.

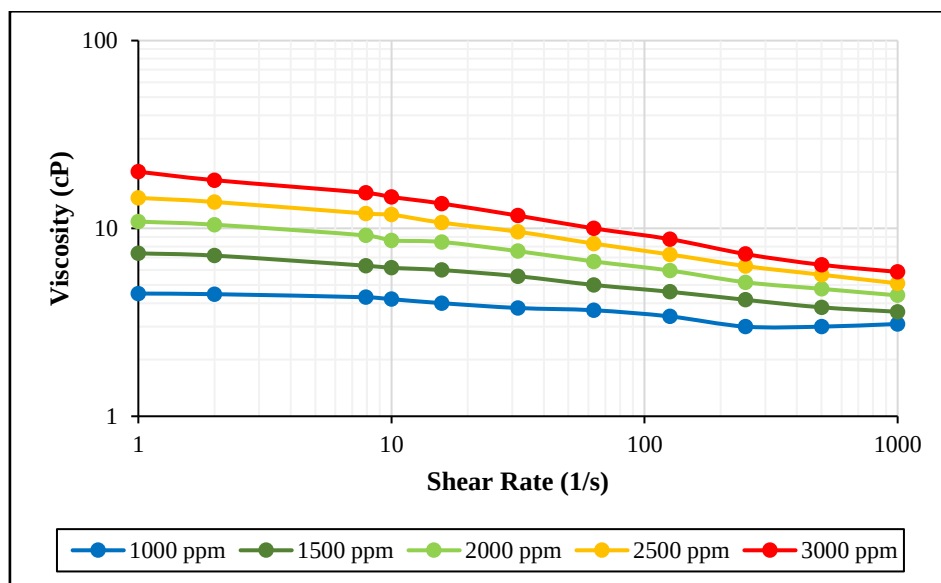


Figure 4.1: Bulk-rheology of SAV10 in FW (167,114 ppm) at 25 °C.

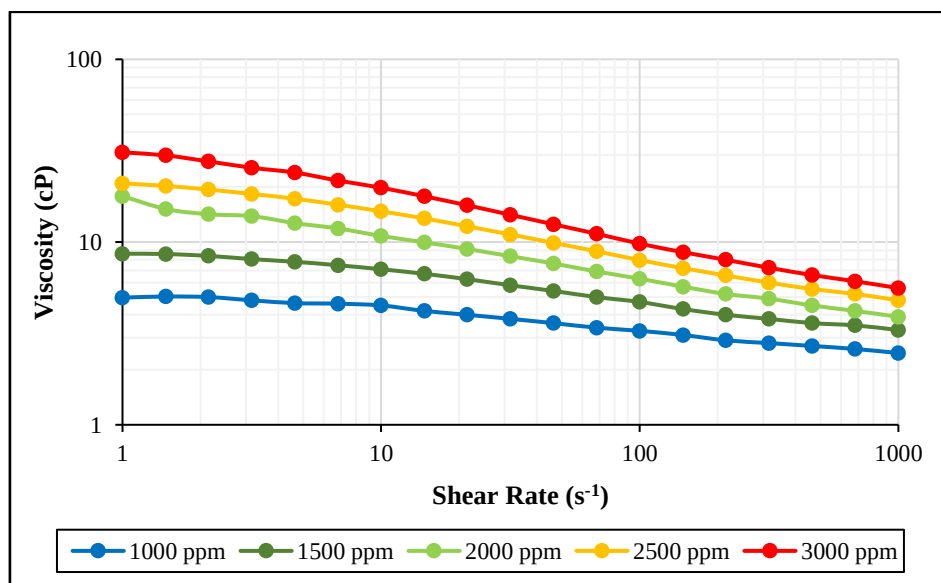


Figure 4.2: Bulk-rheology of SAV10 in SW (42, 507 ppm) at 25 °C.

4.1.2 Optimum Polymer Concentration

This section discusses the determination of the optimum polymer concentration required to achieve the designed target viscosity of 4.5 cP at a shear rate of 10 s^{-1} based on the optimum concentration analysis method (Gogarty *et al.*, 1967; Al-Shalabi, 2018; Elhossary *et al.*, 2020). The latter is based on achieving the minimum total relative mobility of oil and water phases during the seawater (43,000 ppm) injection cycle for the reservoir conditions. This designed polymer viscosity is needed to tackle the permeability contrast between the two zones in the representative Middle East carbonate reservoirs (Masalmeh *et al.*, 2011 and 2019). Accordingly, the viscosities of six arbitrary concentrations (3,000, 2,500, 2,000, 1,500, 1,000, and 500 ppm) of polymer prepared in both seawater and formation water were measured at a temperature of $25 \text{ }^{\circ}\text{C}$ and a shear rate of 10 s^{-1} . **Figure 4.3** shows the effect of polymer concentration on polymer solution viscosity in seawater and formation water. An optimum polymer concentration of 1,000 ppm was selected for further studies. One should note that the same 1,000 ppm of polymer solution in formation water will also result in the required target viscosity of 4.5 cP.

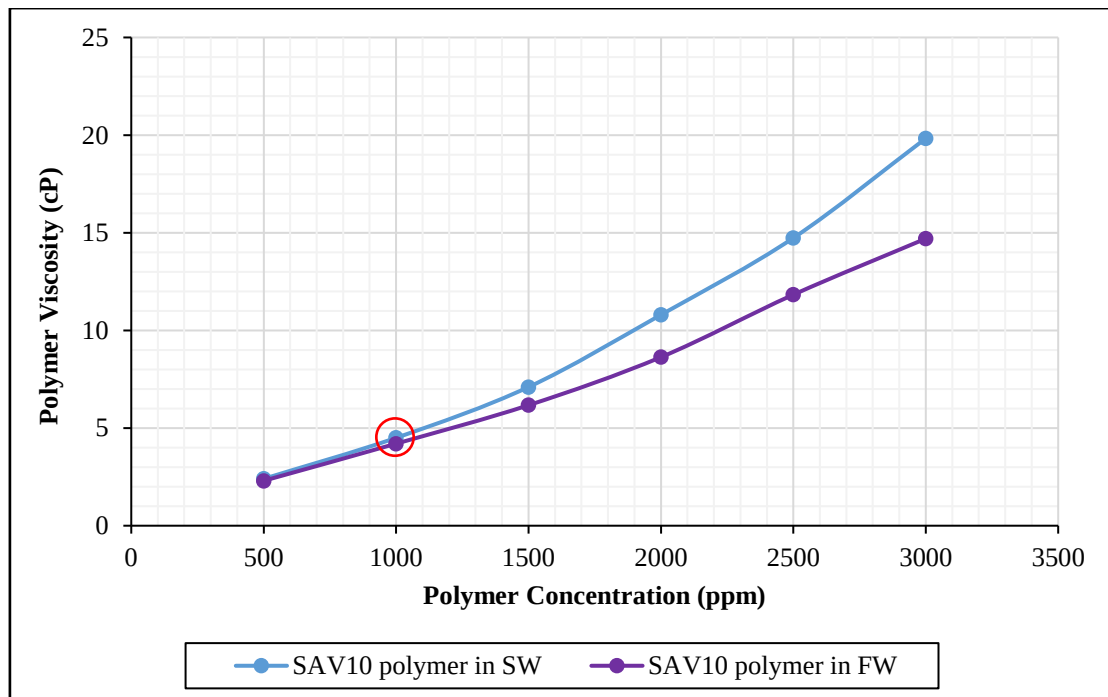


Figure 4.3: SAV10 polymer viscosity vs. concentration in SW (42, 507 ppm) and FW (167,114 ppm) at a shear rate of 10 s^{-1} and a temperature of $25 \text{ }^{\circ}\text{C}$.

4.1.3 Effect of Diluting Makeup Water on Polymer Viscosity

The influence of makeup water salinity on the viscosity of polymer solutions was comprehensively examined. The investigation utilized formation water (FW) with salinity of 167,114 ppm, and its subsequent dilutions: 33,423 ppm (FW-1), 16,711 ppm (FW-2), and 8,356 ppm (FW-3). Seawater (SW) with a salinity of 42,507 ppm and its respective dilutions of 8,502 ppm (SW-1), 1,701 ppm (SW-2), and 425 ppm (SW-3) were also utilized for comparison. The details of the brine compositions mentioned above were previously given in **Chapter 3 (Tables 3.1 and 3.2)**. **Figure 4.4** graphically demonstrates the relationship between makeup water salinity and the bulk viscosity of polymer solutions in the distinct brines.

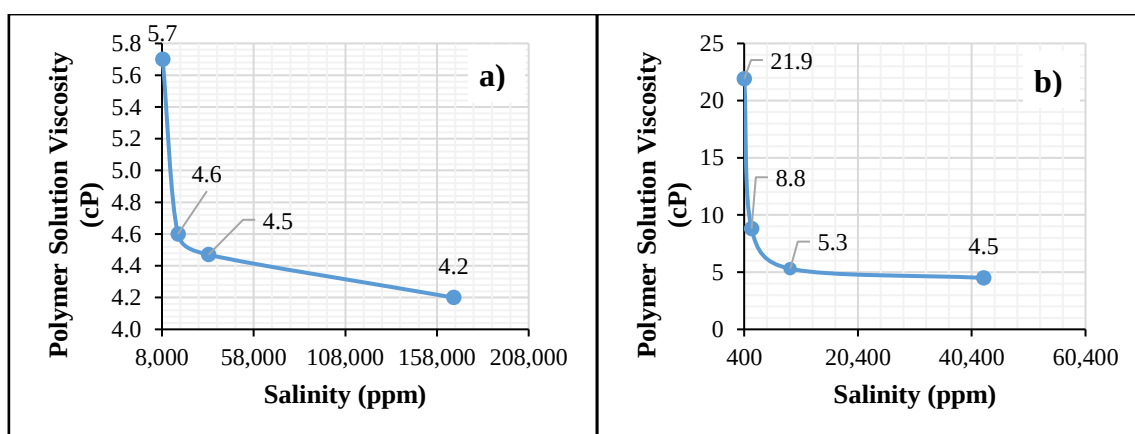


Figure 4.4: Effect of makeup water dilution using a) FW and b) SW on polymer viscosity using 1,000 ppm polymer concentration at a shear rate of 10 s⁻¹ and 25 °C.

For the formation water with a salinity of 167,114 ppm, the viscosity achieved was 4.2 cP. Subsequent dilutions, FW-1 and FW-2, recorded viscosities of 4.5 cP and 4.6 cP, respectively, showcasing marginal increase in polymer solution viscosity. Nevertheless, a notable increase in viscosity to 5.7 cP was observed for the FW-3 (**Figure 4.4a**). In the context of seawater, the base polymer solution presented a viscosity of 4.5 cP. Notably, dilutions SW-1, SW-2, and SW-3 exhibited significantly higher viscosities of 5.3 cP, 8.8 cP, and 21.9 cP, respectively (**Figure 4.4b**).

In conclusion, the findings indicate that the increase in viscosity of polymer solutions is minimal with salinities above 10,000 ppm. However, there is a notable increase in viscosity when these polymer solutions are mixed with brines with lower salinities. This increase in polymer solution viscosity is due to the pronounced repulsive intermolecular forces between the anionic backbone chain of the polymer molecules at low salinity levels (less ionic species)

that expand the molecular chains, resulting in high viscosities (Vermolen *et al.*, 2011; Sun *et al.*, 2018; Kakati *et al.*, 2020).

Furthermore, the observed increase in viscosities at reduced salinity levels advocates for a reduction in the requisite polymer concentration to attain the targeted viscosity (Vermolen *et al.*, 2014; Nascimento *et al.*, 2023). **Figure 4.5** shows the polymer concentrations necessary to attain the desired viscosity of 4.5 cP at a temperature of 25 °C and a shear rate of 10 s⁻¹ for polymer solution in different brines (FW and SW dilutions). The findings show that when the salinity level is at 8,502 (SW-1), 8,356 (FW-3), 1,701 (SW-2), and 425 ppm (SW-3), the amount of polymer required to achieve the desired viscosity decreases significantly by 23%, 25%, 55%, and 73%, respectively.

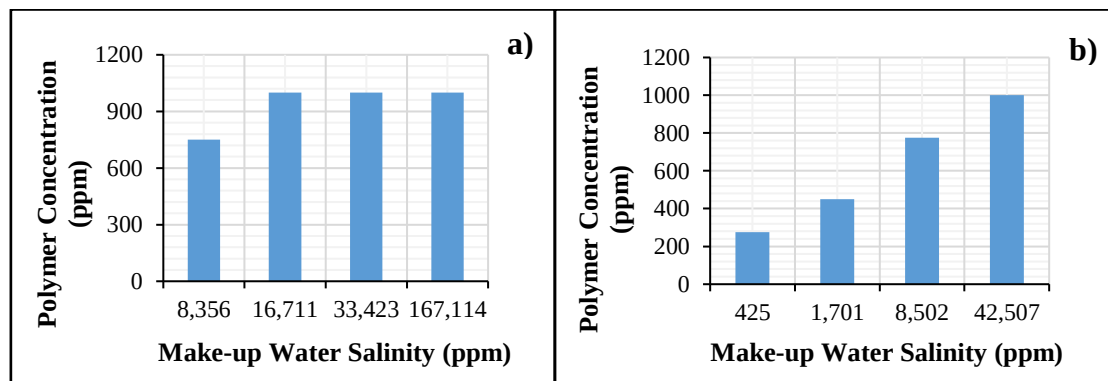


Figure 4.5: Polymer concentration for the brine recipes a) FW dilutions and b) SW dilutions needed to achieve desired viscosity of 4.5 cP at 10 s⁻¹ and 25 °C.

4.1.4 Effect of Varying Ionic Composition of Makeup Water on Polymer Viscosity

The impact of changing ionic composition on the polymer solution was investigated using a series of five brines, namely SW-1, SW-1A, SW-1B, SW1-C, and SW-1D, all having the same total dissolved salt content (8,502 ppm) as that of 5-times diluted seawater (SW-1) but differing in their ionic composition. The ionic compositions of these brines were previously reported in **Chapter 3 (Table 3.3)**. **Figure 4.6** shows the effect of varying ionic compositions on polymer solution viscosity using above-mentioned brines.

The polymer solution viscosity is 4.5 cP in seawater (SW) brine, which can be considered a baseline where other seawater-derived brines are concerned. As the salinity is maintained at 8,502 ppm in all five compositions, the only difference in the other four compositions apart from the SW-1 is the changes in Ca²⁺, Mg²⁺, and SO₄²⁻ ionic concentrations. SW-1 has shown an enhancement in viscosity from 4.5 cP (SW) to 5.3 cP. The same salinity

as in SW-1 was maintained in SW-1A, SW-1B, and SW-1C (8,502 ppm), and the hardness level was varied and it was achieved by the partial or complete removal of divalent cations. In SW-1D, sulfate was spiked two times compared to SW-1. The highest increment in viscosity to 7.5 cP compared with the 4.5 cP of SW is obtained in the case of complete softening of the brine (SW-1C), demonstrating the significant impact of the divalent cations on the polymer solution viscosity.

Furthermore, it is interesting to note the relative effects of Ca^{2+} versus Mg^{2+} ions on the polymer solution viscosity. A higher polymer solution viscosity is observed in the SW-1B brine in comparison with the SW-1A brine (6.8 cP vs. 6.0 cP), which can be explained by the significant difference in the concentration of hardness ions; 108 ppm of Ca^{2+} in SW-1B versus 317 ppm of Mg^{2+} in SW-1A. The latter is justified by the fact that there is a relatively three times lower concentration of Ca^{2+} ion (108 ppm) compared to Mg^{2+} ion (317 ppm) in the SW-1B composition. Another factor is the smaller ionic radius of Mg^{2+} compared to that of Ca^{2+} , though both cations possess the same electric charge. This exhibits a higher charge density and stronger effect of the Mg^{2+} ion compared to the Ca^{2+} ion (Ren *et al.*, 2015). The dependency of polymer solution viscosity on salinity and hardness is due to the polyelectrolyte (ionic) nature of the polymer molecules, which interact strongly with the dissolved ions in the brine solution (Eiroboyi *et al.*, 2019). Studies have shown that divalent cations (Ca^{2+} and Mg^{2+}) have a more significant impact than monovalent ions (Na^+ and K^+) on polymer solution viscosity since their higher positive charges are more effective in screening the negative charges on the polymer backbone chain. Hence, polymer solution swelling and straightening of polymer chains are greater in the presence of monovalent cations than divalent cations, resulting in higher viscosities (Jouenne, 2020; Kakati *et al.*, 2020).

Further, the sulfate spiked brine recipe (SW-1D) showed an increase in viscosity compared to SW-1 (6.0 vs. 5.3 cP). This is mainly because the high sulfate content reduces the hardness effect caused by the divalent cations. Hence, the shielding of the anionic backbone of the polymer is reduced and thus, enhancing the viscosity (Tahir *et al.*, 2020). The error bars depicted in **Figure 4.6** were derived from the standard deviation of three experimental repetitions.

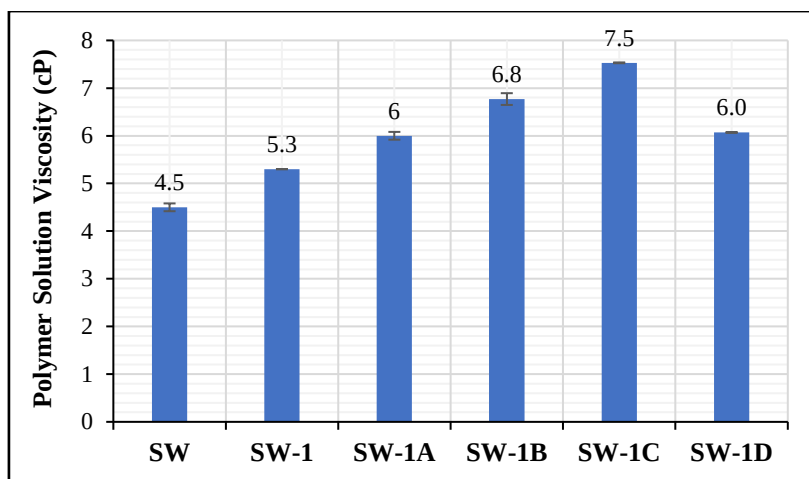


Figure 4.6: Effect of varying ionic compositions of make-up water on polymer solution viscosity using 1,000 ppm polymer concentration at shear rate of 10 s^{-1} and temperature of 25°C .

Rheological studies of polymer solution in all these brines have shown that the enhancement in viscosity resulted in a remarkable reduction in polymer concentration to achieve a viscosity of 4.5 cP with the highest reduction of 50% in the case of completely softened brine (SW-1C) (**Figure 4.7**). Therefore, by formulating polymer solutions using softened brine compositions, the consumption of these chemicals can be reduced, providing an advantage when considering polymer flooding projects at the field scale that necessitate significant polymer quantities (Ferreira and Moreno, 2019). Moreover, the reduction in polymer concentration achieved by spiking the sulfate was not attractive enough considering the negative aspects with sulfate resulting in chances of scale formation and production of sour gas (Ghosh *et al.*, 2020; Khurshid *et al.*, 2020).

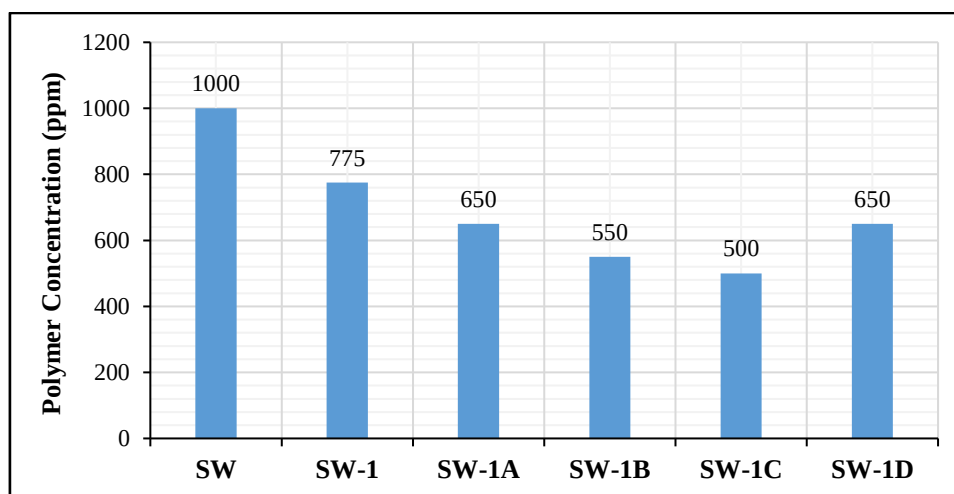


Figure 4.7: Polymer concentration for brine recipes with varying ionic composition needed to achieve the desired viscosity of 4.5 cP at 10 s^{-1} and 25°C .

4.1.5 Effect of Temperature on Polymer Viscosity

The influence of temperature on the viscosity of polymer solutions was systematically examined over a range spanning 25 to 90 °C. These experimental evaluations were conducted utilizing the pressure cell geometry of the Anton Paar MCR 302. A pressure of 6 bars was applied to prevent evaporation of the polymer samples. **Figure 4.8** shows the exponential decay trend of polymer solution viscosity with temperature.

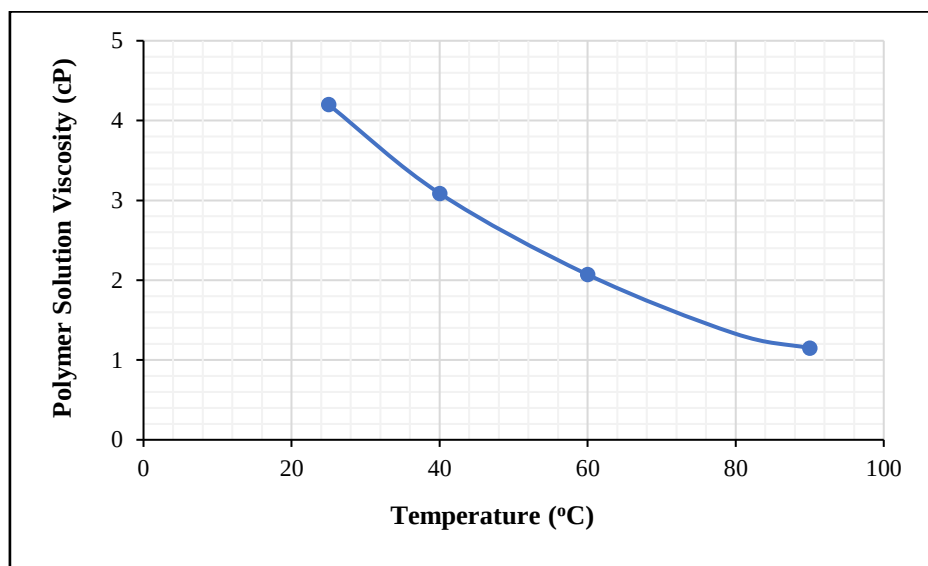


Figure 4.8: Polymer solution viscosity in FW at varying temperatures and shear rate 10 s^{-1} .

The comparison of polymer solution viscosity with respective brine viscosity across varying temperatures is illustrated in **Figures 4.9 – 4.11** (logarithmic scale was used for better comparison). These figures demonstrate a consistent decrease in the viscosity of both the polymer solution and the brine as the temperature rises.

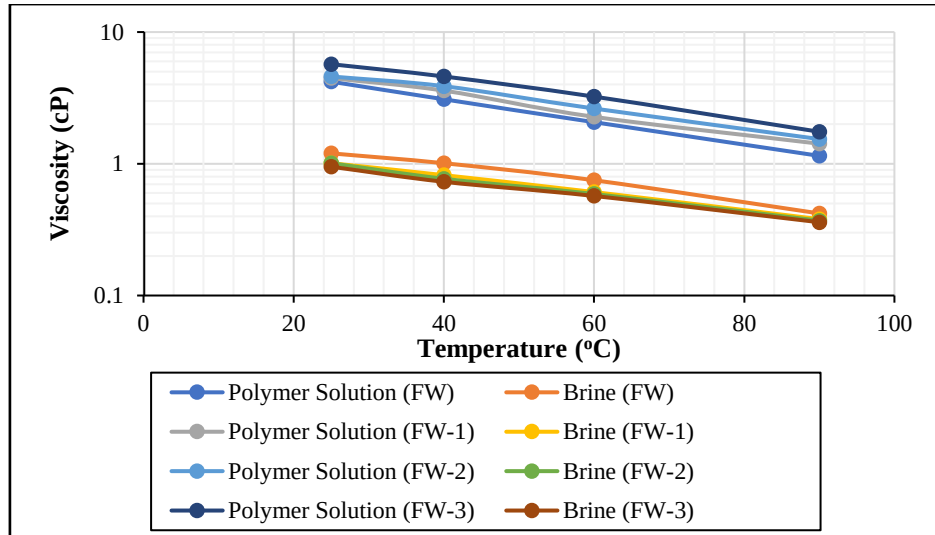


Figure 4.9: Polymer solution and brine viscosities of FW and its dilutions at varying temperatures and shear rate 10 s^{-1} .

Moreover, the results show that both the polymer solution and the brine exhibit similar trends in viscosity as the temperature is increased, as depicted in **Figures 4.9 – 4.11**. This parallel behavior indicates that at elevated temperatures, the polymer was stable, avoiding significant degradation and maintaining the structural and functional integrity at these challenging thermal conditions (Vermolen *et al.*, 2011). The stability of the polymer was further evidenced by its viscosity reverting to its initial state upon cooling to ambient conditions. This highlights the potential of this polymer for high-temperature applications (Audibert and Argillier, 1995; Salih *et al.*, 2016; Navaie *et al.*, 2022). Further, the noticed reduction in polymer viscosity was due to the reduction of the solvent (brine) viscosity.

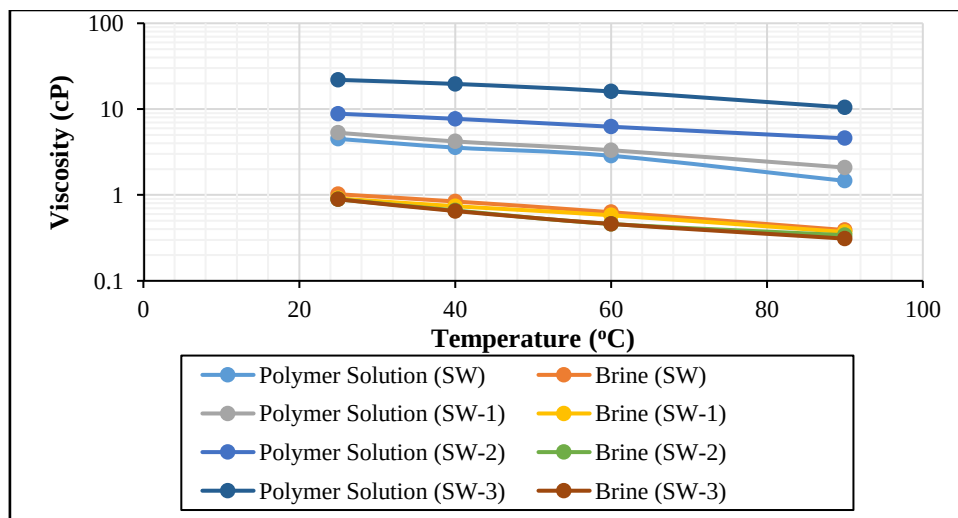


Figure 4.10 Polymer solution and brine viscosities of SW and its dilutions at varying temperatures and shear rate 10 s^{-1} .

The decreasing brine viscosity with increasing temperature can be explained by molecular dynamics of the brine solution. At a lower temperature, molecules have less kinetic energy, which results in them moving slower and interacting more strongly with their neighboring molecules. These interactions contribute to a higher resistance to flow, resulting in higher viscosity. As the temperature increases, the kinetic energy of the molecules increases, causing them to move faster. This reduces the intermolecular interactions, leading to a reduction in the resistance to flow. Consequently, the viscosity of the brine solution decreases (Rogers and Pitzer, 1982; Francke and Thorade, 2010).

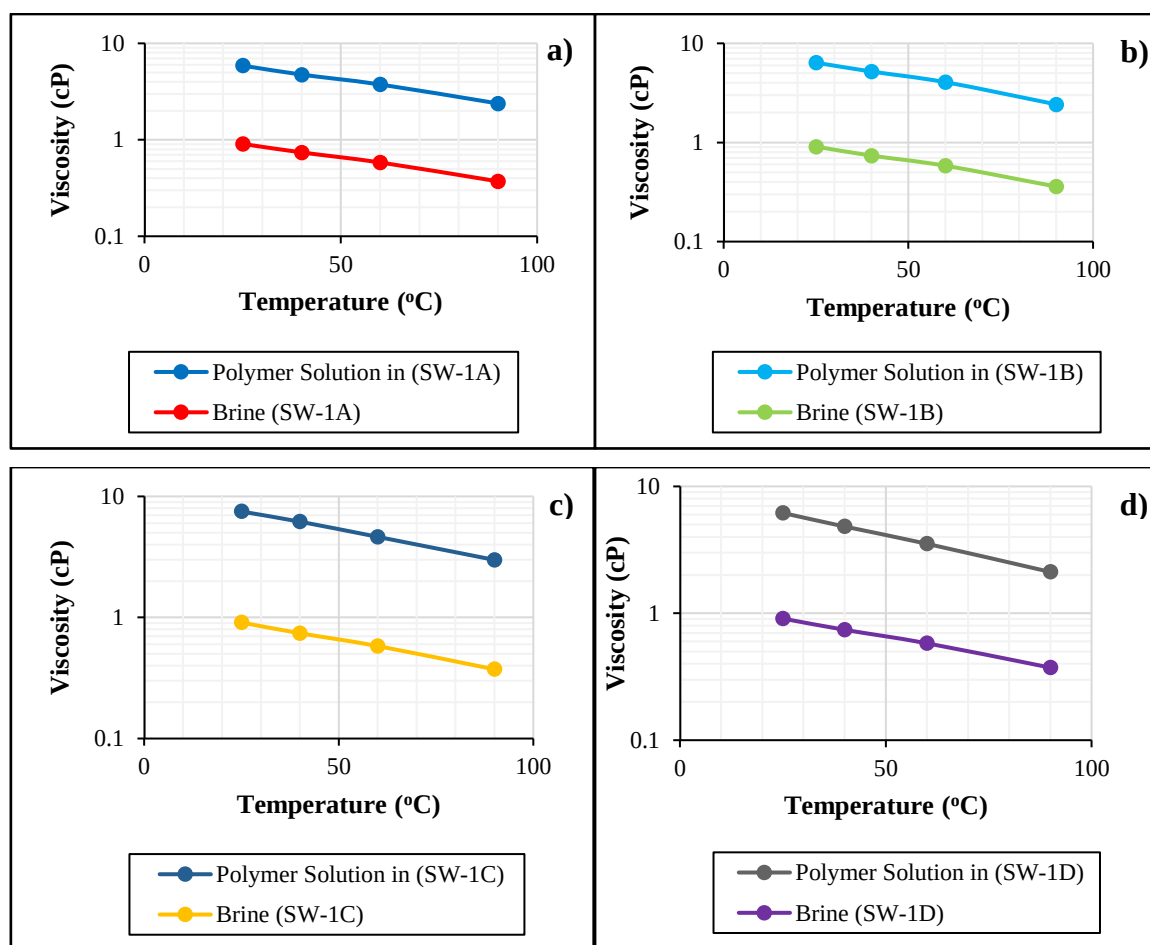


Figure 4.11: Polymer solution and brine viscosities with varying ionic composition a) SW-1A, b) SW-1B, c) SW-1C, d) SW-1D at different temperatures and shear rate 10 s^{-1} .

4.2 Hydrodynamic Size and Polydispersity Index of Polymer solutions

The hydrodynamic size of a polymer depicts the effective diameter of a polymer in a solvent, reflecting its conformation. In contrast, the polydispersity index (PDI) indicates the size distribution within a polymer sample, with values near 0 representing uniform sizes and higher

values indicating a broader distribution. Both provide vital insights into a polymer's behavior in the solution. This section describes the hydrodynamic size and polydispersity of polymer in different brine compositions and temperature conditions used in this study.

4.2.1 Effect of Makeup Water Salinity (FW and SW dilutions) on Hydrodynamic Size

In this section, a detailed examination of the polymer's hydrodynamic size was carried out across the full range of salinities considered in this research, including formation water (FW), seawater (SW), and their dilutions. The ionic compositions of these brines were previously reported in **Chapter 3 (Tables 3.1 and 3.2)**. **Figure 4.12** illustrates the hydrodynamic size of the polymer solution as determined using the dynamic light scattering technique discussed in **Chapter 3**.

Notably, the polymer's hydrodynamic size is influenced by the salinity of the makeup water. For high salinities, FW (167,114 ppm) and SW (42,507 ppm), the hydrodynamic size was 102 nm and 103 nm, respectively. Further, for FW-1 (33,423 ppm), FW-2 (16,711 ppm), SW-1 (8,502 ppm), and FW-3 (8,356 ppm), the hydrodynamic size increased further and remained relatively consistent, ranging between 108-115 nm. This variation falls within the error margins indicated by the error bars (**Figure 4.12**). However, more pronounced changes were observed at lower salinities, 119 nm and 146 nm for 1,701 ppm (SW-2) and 425 ppm (SW-3), respectively.

At low salinities, the electrostatic repulsion between the anionic sulfonyl groups on the polymer chains prevents aggregation. This repulsion ensures that the polymer chains remain dispersed and extended in the solution, contributing to the larger hydrodynamic size of the polymer (Li *et al.*, 2014). However, at high salinities, the increased ionic strength of the solution reduces the electrostatic repulsion between the polymer chains, and the polymer chains undergo coiling. Consequently, the polymers tend to aggregate, leading to a decline in the average size of individual polymer chains in solution (Fang *et al.*, 2015; Silva *et al.*, 2018; Ruben-Hernán *et al.*, 2020).

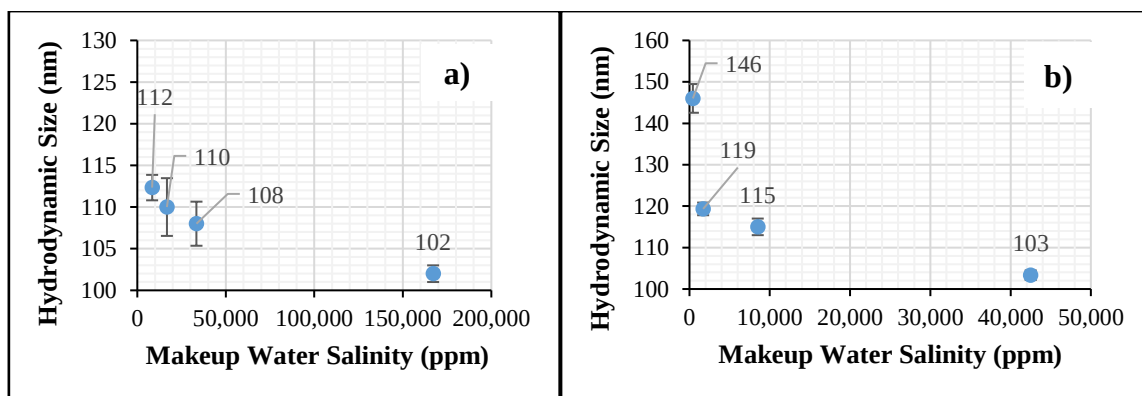


Figure 4.12: Effect of makeup water dilution on SAV10 polymer hydrodynamic size for 1,000 ppm polymer concentration at a temperature of 25 °C a) FW and its dilutions, b) SW and its dilutions.

4.2.2 Effect of Varying Ionic Compositions of Makeup Water on Hydrodynamic Size

In this section, the hydrodynamic size of the polymer was investigated across brines with distinct ionic compositions: SW-1, SW-1A, SW-1B, SW1-C, and SW-1D, all having the same total dissolved salt content (8,502 ppm) but differing in their ionic composition. **Table 3.3** in **Chapter 3** details the ionic compositions of these brines. **Figure 4.13** illustrates how varying concentrations of ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) influence the hydrodynamic size of the polymer.

The SW brine showed a polymer hydrodynamic size of 103 nm, serving as a baseline for comparisons with other seawater-derived brines. The most notable increase in hydrodynamic size was observed in SW-1C (zero hardness) at 120 nm. Meanwhile, the hydrodynamic sizes of SW-1, SW-1A, SW-1B, and SW-1D were measured to be 115 nm, 112 nm, 110 nm, and 111 nm respectively. As depicted in **Figure 4.13**, these values fall within the error limits indicated by the error bars. Although the viscosities of the polymer solutions varied, being 5.3, 6.0, 6.8, and 6.0 for SW-1, SW-1A, SW-1B, and SW-1D respectively, these differences did not significantly influence the hydrodynamic sizes as the hydrodynamic sizes mentioned represent the peak values in the particle size distribution.

For the brine recipes with high hardness ions (SW-1, SW-1A, SW-1B, and SW-1D), the ions present (Ca^{2+} , Mg^{2+}) can screen the charges on the polymer, reducing repulsions between similarly charged segments or molecules. This can lead to reduced expansion of the polymer chain, lowering its hydrodynamic size. Softened brine (SW-1C) typically has reduced ionic strength due to the removal of divalent ions. This decreased ionic strength can enhance electrostatic repulsions between charged segments of the polymer, causing the polymer to adopt a more expanded conformation. Also, the absence of hardness ions in softened water can

lead to improved solvation of the polymer chains, causing them to expand further and increase their hydrodynamic size (Wever *et al.*, 2011; Al-Hajri *et al.*, 2019; Gbadamosi *et al.*, 2022).

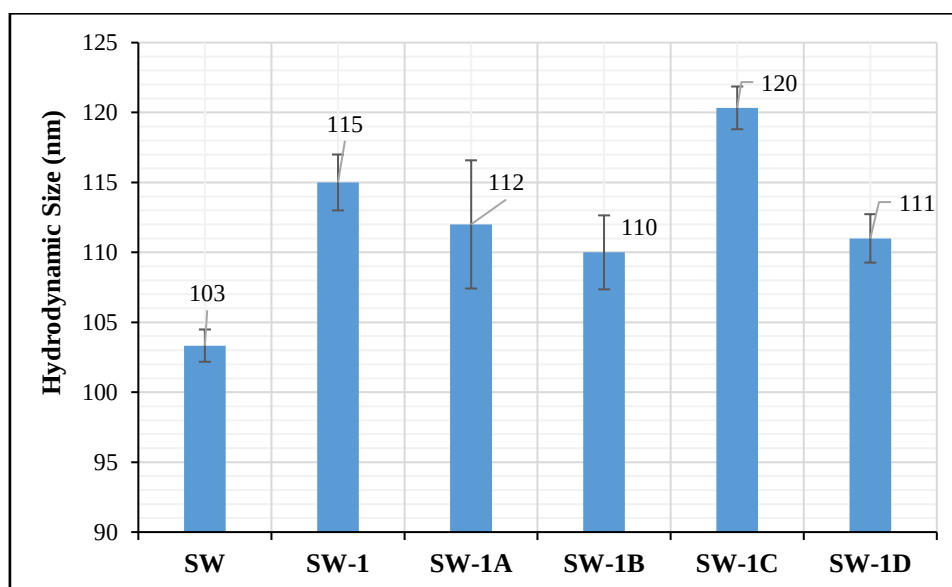


Figure 4.13: Effect of varying ion composition in makeup water on SAV10 polymer hydrodynamic size for 1,000 ppm polymer concentration at a temperature of 25 °C.

4.2.3 Effect of Temperature on Hydrodynamic Size

The hydrodynamic size of the polymer in high salinity brine (167,114 ppm) and low salinity brine (425 ppm) was determined at various temperatures (25, 40, 60, 80, and 90 °C) as shown in **Figure 4.14**. The hydrodynamic size of the polymer decreased with increasing temperature in both the salinities. This is because at higher temperatures, polymer chains tend to contract due to the increased thermal motion of individual polymer segments. This increased movement can lead to reduced chain expansion and therefore, a decrease in the hydrodynamic size (Samanta *et al.*, 2010; Sandengen *et al.*, 2017).

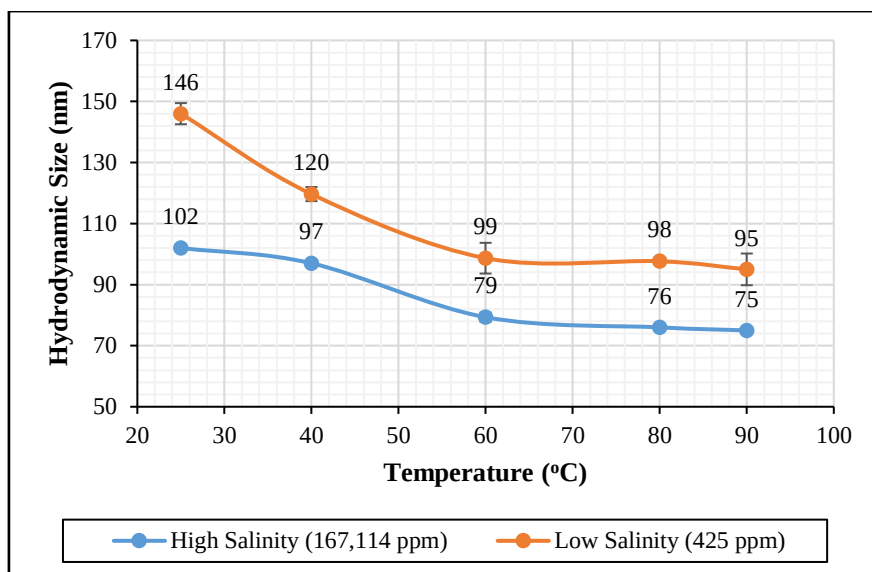


Figure 4.14: Effect of temperature on hydrodynamic size of the polymer.

4.2.4 Polydispersity Index

The Polydispersity Index (PDI) measures the size distribution of particles in a sample. A polydispersity index value of 0 would indicate a monodisperse sample, where all particles are of the same size. As the polydispersity index value increases, it signifies a broader size distribution (Ghosh and Mohanty, 2020; Agasty *et al.*, 2021; Al-Jaber *et al.*, 2023).

For the highest salinities, the polymer solution displayed a PDI between 0.3 and 0.4. The observed polydispersity index for the samples suggests that the sample has a relatively narrow distribution of particle size. The narrower size distribution suggests that most of the polymer chains responded similarly to the high salt environment, coiling up uniformly.

Nevertheless, an exception was observed for the polymer solution at the lowest salinity of 425 ppm under ambient conditions. In this case, a polydispersity index of 0.6 was observed indicating a moderate heterogeneity in particle sizes. The larger polydispersity index in the low salinity environment suggests a more heterogeneous response of the polymer chains to the brine. While many chains would have expanded due to the reduced ionic strength, some might not have expanded as much. This varied response leads to a broader size distribution, reflected in the higher PDI value. **Figure 4.15** shows a typical particle size distribution curve with a PDI value of 0.4.

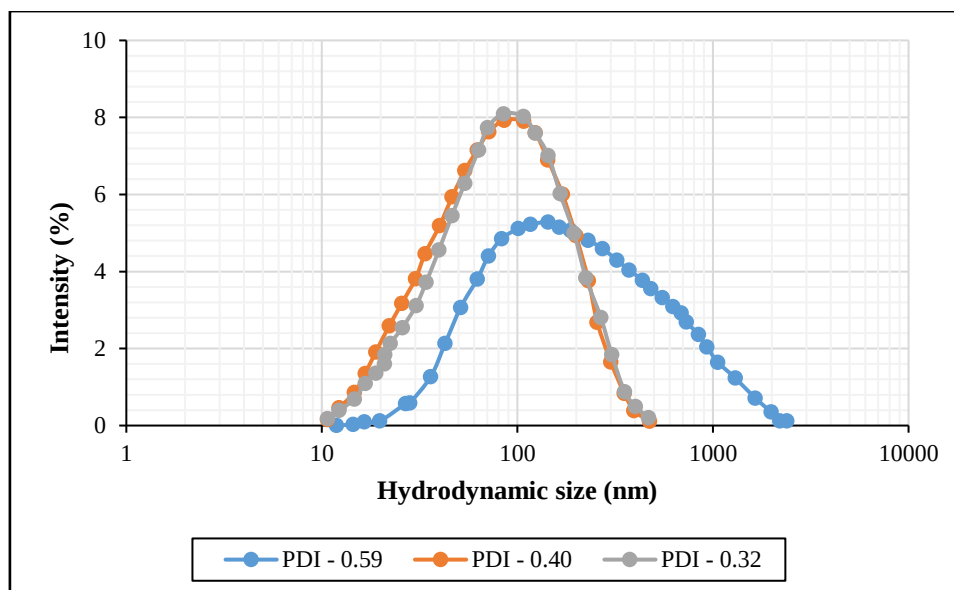


Figure 4.15: Particle size distribution curve with different PDI values.

4.3 Polymer Concentration Measurements using Different Analytical Methods

The polymer concentration measurements as part of the research were conducted using different analytical methods including UV, viscosity, and TOC-TN methods.

4.3.1 UV Method

A calibration curve was constructed using a UV spectrophotometer from standard solutions with known concentrations (**Figure 4.16**). Based on this calibration curve, the concentration of the collected samples was determined.

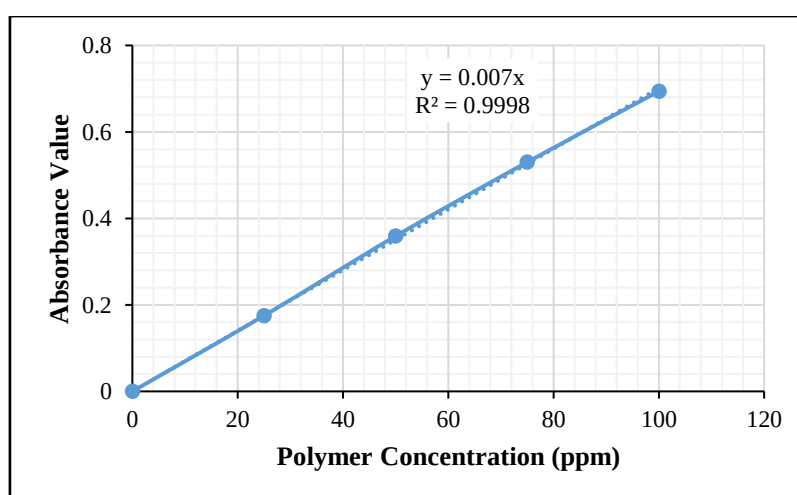


Figure 4.16: Calibration curve using UV spectrophotometer.

4.3.2 Viscosity Method

Figure 4.17 illustrates the calibration curve obtained from the viscosity method, depicting the relationship between viscosity and polymer concentration. To obtain polymer concentration of unknown samples using this calibration curve, the viscosity of these samples were measured.

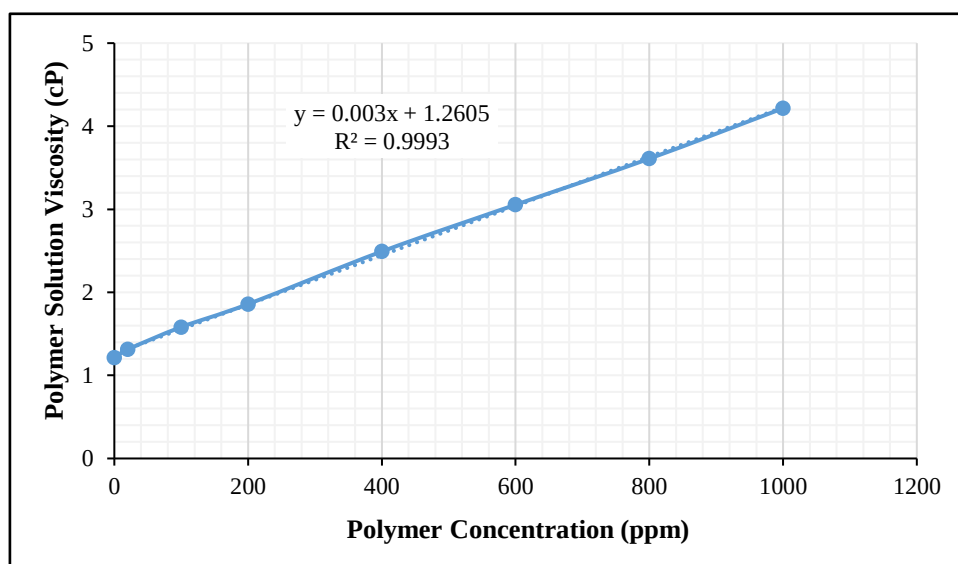


Figure 4.17: Calibration curve using the viscosity method.

4.3.3 TOC-TN Method

Figure 4.18 presents the calibration curve derived using the TOC-TN method, establishing a relationship between the known polymer concentration and the total nitrogen content in the sample. By assessing the total nitrogen content in the unknown samples, we can subsequently determine the polymer concentration within those samples.

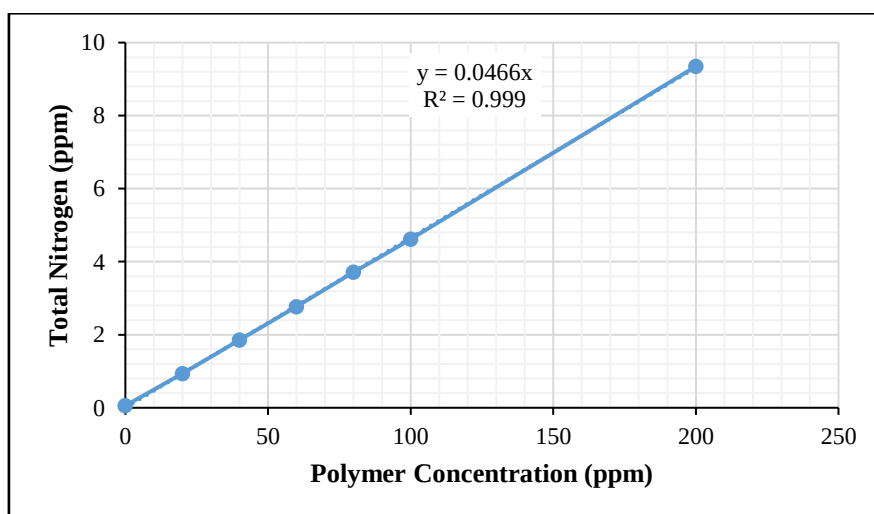


Figure 4.18: Calibration curve using the TOC-TN method.

4.3.4 Comparison of Different Analytical Methods for Polymer Concentration Measurements

The analysis of the calibration curves derived from all three methods (**Figures 4.16 – 4.18**) clearly demonstrates their efficacy in measuring the concentration of polymer in effluent samples. **Table 4.1** represents the polymer concentration measurements using all the three methods. Notably, the consistency across these methods is further substantiated by the narrow error bars (**Figure 4.19**), which represent the standard deviation based on three separate runs. The proximity of these error bars indicates minimal discrepancies in the results obtained from each method, thereby highlighting their comparability. Therefore, given their demonstrable accuracy and consistency, any of the three methods can be confidently employed for quantifying polymer concentrations.

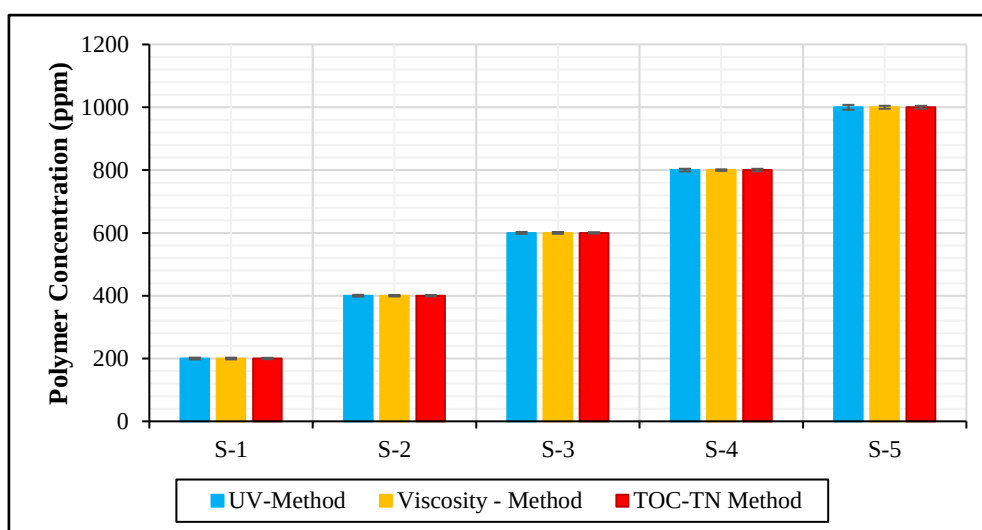


Figure 4.19: Uncertainty in polymer concentration measurements using different analytical methods.

Table 4.1: Polymer concentration measurements using different analytical methods

	Polymer Concentration (ppm)				
UV- Method	R1	R2	R3	Average	Standard Deviation
	197	198	206	200	5
	397	396	407	400	6
	596	594	610	600	9
	796	792	811	800	10
	992	997	1010	1000	9
Viscosity- Method	R1	R2	R3	Average	Standard Deviation
	204	197	199	200	3

	402	405	394	400	5
	602	597	602	600	3
	792	799	808	800	8
	1004	994	1001	1000	5
TOC-TN- Method	R1	R2	R3	Average	Standard Deviation
	199	200	202	200	1
	398	399	403	400	3
	597	599	605	600	4
	796	799	806	800	5
	995	998	1008	1000	7

4.4 Highlights of the Chapter

This chapter explored the influence of makeup water salinity, brine ionic composition, and temperature on the viscosity of polymers. Additionally, the hydrodynamic size and polydispersity index of the polymer under different conditions were determined. Various analytical methods were also evaluated for measuring polymer concentrations. The investigation yielded several significant findings, which are summarized as follows:

- The diluted and softened brines increased the viscosity favorably compared to high salinity injection waters. This could lead to a reduction in polymer flood operating costs by allowing for a lower polymer dosage.
- The polymer's hydrodynamic size was higher at low salinity and low temperature conditions. The hydrodynamic size of polymer was in the range of 75 - 146 nm for varying conditions. Typically, the polymer solution exhibited a PDI ranging from 0.3 to 0.4, indicating a relatively consistent size distribution. However, an exception was noted at 425 ppm salinity under ambient conditions, showing a PDI of 0.6.
- All the three analytical methods evaluated including UV-Vis, Viscosity, and TOC-TN, were effective in determining unknown polymer concentration.

CHAPTER 5: EFFECT OF SALINITY ON POLYMER ADSORPTION IN STATIC AND DYNAMIC CONDITIONS

Chapter 5 examines the influence of salinity on polymer adsorption, using representative samples of Middle Eastern formation water, seawater, and their respective dilutions. Initially, static adsorption studies in single-phase were conducted. Further to investigate representative retention values, dynamic retention studies were performed in the absence and presence of oil. Moreover, the impact of salinity on in-situ rheology is highlighted.

5.1 Experimental Overview

The effect of salinity on polymer adsorption was studied using seven brine compositions, which includes formation water (FW), seawater (SW), and their dilutions. The overall salinities of the brines used are reported in Tables 5.1 and 5.2.

The crushed rock powder, core plugs, and polymer solutions were characterized and prepared using the methods described in **Chapter 3**. Static adsorption experiments were conducted in single-phase conditions at ambient temperature, with polymer solutions prepared in the proposed brine compositions. To ensure precise polymer retention measurements, 15 dynamic retention experiments were conducted: 7 without oil (single-phase) and 8 with oil present (two-phase).

In the single-phase experiments, the adsorption tests were conducted by first injecting brine, then polymer, and finally flushing with brine at a rate of 0.5 cc/min. In the brine post-flush stage, approximately 60 - 70 pore volumes of brine were injected to ensure complete flushing out of the polymer. During the polymer injection and brine post-flush, effluents were collected every 0.2 PV for the first 5 PVs. Once the differential pressure stabilized, the collection interval was increased to 1 PV.

On the other hand, for the two-phase experiments, two protocols were used. Initially, for CF-8 protocol 1 was used for forced imbibition; the oil was injected first to bring the core to S_{wi} condition, then aged at 90 °C for 14 days to alter wettability to oil wet. This was followed by injecting formation brine at different flow rates to reach residual oil saturation (S_{or}). Further, polymer adsorption study was initiated with a brine preflush, polymer injection, and brine-post flush at a flow rate of 0.5 cc/min. In the polymer injection stage oil was produced, which altered the S_{or} . Hence, representative RF and RRF were not obtained. To avoid oil mobilization during the polymer injection phase, protocol 2 was employed for further studies (CF- 9 to CF- 15). In

the latter protocol, a mixture of glycerin and brine was injected at varying flow rates to reach residual oil saturation (S_{or}), followed by flushing the mixture using 100% brine for at least 20 PVs. The effluents were tested for glycerin absence before proceeding with polymer injection phase. This helped in removing the maximum amount of mobile oil from the sample and preventing any oil mobilization during polymer injection and allowed for better characterization of polymer retention. Further, the polymer concentration was analyzed in the collected effluent samples at regular intervals. **Tables 5.1** and **5.2** show the properties of the outcrops and experimental conditions considered for this study.

Table 5.1: Petrophysical properties of core samples and experimental conditions applied for single-phase coreflooding experiments

Core ID (Single-phase Tests)	CF-1	CF-2	CF-3	CF-4	CF-5	CF-6	CF-7
Connate Water/ Injection Water Salinity, TDS (ppm)	167,114 FW	33,423 FW-1	16,711 FW-2	8,356 FW-3	42,507 SW	1,700 SW-2	425 SW-3
Polymer Concentration (ppm)	1000						
Length (cm)	6.85	7.50	7.30	7.95	7.71	7.22	7.70
Diameter (cm)	3.80	3.80	3.81	3.72	3.81	3.80	3.80
Porosity (%)	17	15	15	15	16	16	17
Absolute Brine Permeability (mD)	265	265	286	283	244	231	225
Temperature (°C)	25						
Confining Pressure (psi)	1200						
Backpressure (psi)	100						

Table 5.2: Petrophysical properties of core samples and experimental conditions applied for two-phase coreflooding experiments

Core ID (Two-phase Tests)	CF-8	CF-9	CF-10	CF-11	CF-12	CF-13	CF-14	CF-15
Connate Water/ Injection Water Salinity, TDS (ppm)	167,114 FW	167,114 FW	33,423 FW-1	16,711 FW-2	8,356 FW-3	42,507 SW	1,700 SW-2	425 SW-3
Polymer Concentration (ppm)	1000							
Length (cm)	7.61	6.32	6.20	7.10	7.30	7.34	7.56	7.20
Diameter (cm)	3.80	3.76	3.80	3.80	3.80	3.78	3.8	3.8
Porosity (%)	15	15	15	15	15	15	19	15
Absolute Brine Permeability (mD)	234	200	224	284	263	218	260	223
S_{wi} (%)	34	32	33	32	34	36	32	34
S_{or} (%)	37	35	34	35	35	38	31	39
Temperature (°C)	25							
Confining Pressure (psi)	1200							
Backpressure (psi)	100							

5.2 Static Adsorption Studies

Static adsorption experiments were performed as per the methodology explained in **Chapter 3** to determine the effect of salinity on polymer adsorption.

5.2.1 Effect of Salinity on Static Polymer Adsorption

BET surface area of crushed samples used for the static adsorption experiments was obtained from BET measurements as discussed in **Chapter 3, Section 3.2.5.2**. BET surface area of crushed core samples based on the BET plot (**Figure 5.1**) was $0.73 \text{ m}^2/\text{g}$.

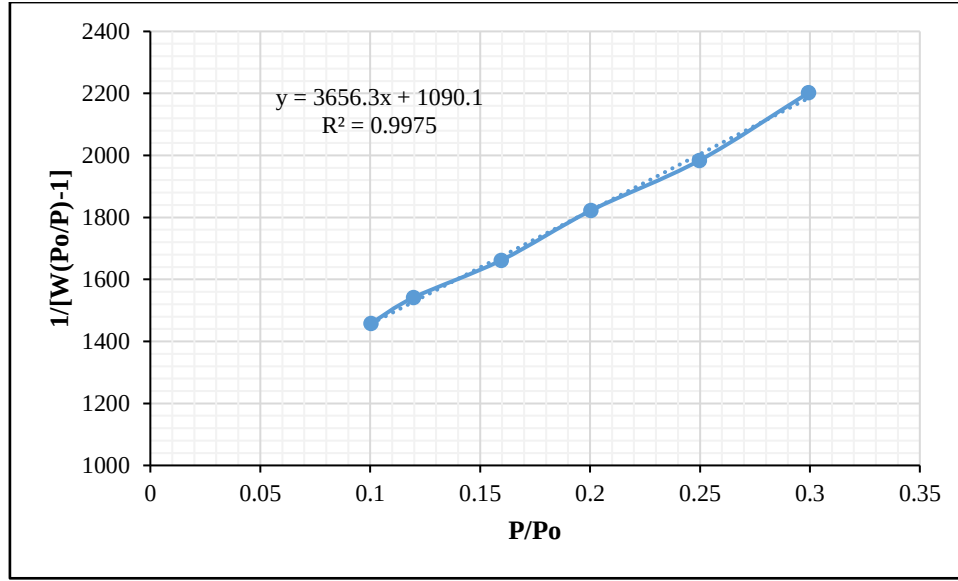


Figure 5.1: BET plot for the crushed rock sample used for static adsorption studies.

Figures 5.2 and **5.3** show the effects of make-up water dilution on polymer adsorption in static single-phase tests at 25 °C for formation water, seawater, and their dilutions, respectively. The static polymer adsorptions were 252 µg/g-rock and 212 µg/g-rock when formation water and seawater were used as the make-up brine for polymer solution, respectively. For polymer solution prepared in formation water dilutions FW-1 (33,423 ppm), FW-2 (16,711 ppm), FW-3 (8,356 ppm), the static polymer adsorptions were 203, 103, and 94 µg/g-rock, respectively (**Figure 5.2**). Similarly, for polymer solution prepared in seawater dilutions SW-2 (1,701 ppm), and SW-3 (425 ppm), the static polymer adsorptions were 47, and 25 µg/g-rock, respectively (**Figure 5.3**). This indicates a strong decreasing trend of polymer adsorption with lowering makeup water salinity. This reduction in polymer adsorption is due to the expansion of polymer molecules at reduced salinities, which results in fewer expanded polymer molecules required to fill the adsorption sites (Sorbie, 1991; AlSofi *et al.*, 2018). It is worth noting that the static adsorption tests usually result in inflated polymer adsorption levels due to the high surface access area to polymer provided by the crushed powder (Thomas *et al.*, 2020).

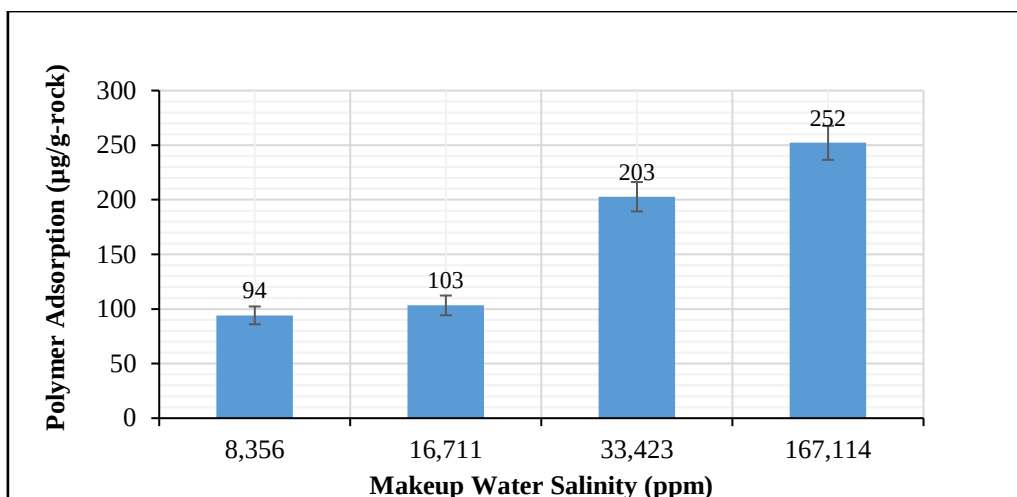


Figure 5.2: Effect of FW and its dilutions on SAV10 polymer adsorption in static single-phase tests at 25 °C.

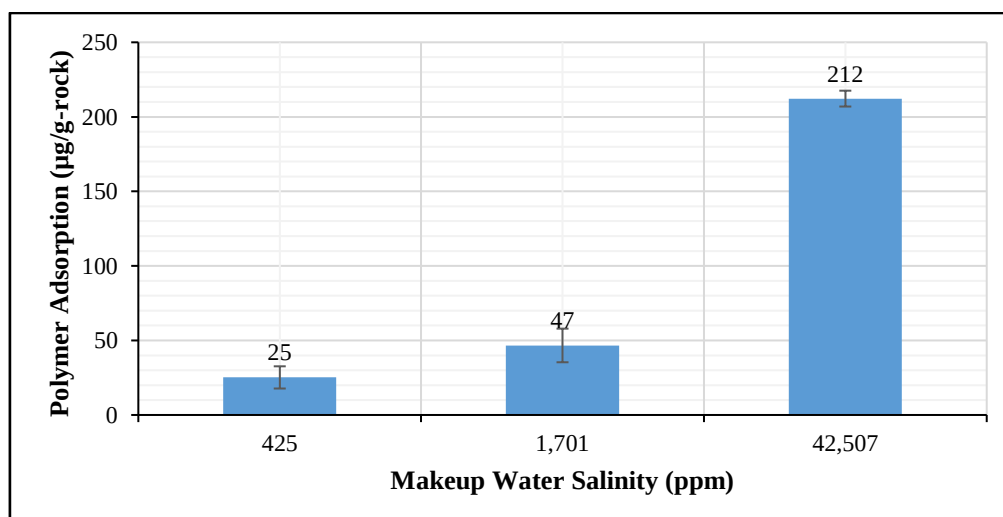


Figure 5.3: Effect of SW and its dilutions on SAV10 polymer adsorption in static single-phase tests at 25 °C.

To ascertain the reliability of the static polymer adsorption measurements, a series of three distinct experiments were meticulously conducted. By deriving the standard deviation from the results of these trials, the degree of uncertainty in the measurements were captured. This derived uncertainty is visually represented using error bars, which are prominently displayed in **Figures 5.2 and 5.3.**

5.3 Dynamic Retention Studies

5.3.1 Dynamic Polymer Retention Measurements in the Absence of Oil

For dynamic polymer retention measurements, the effluent polymer samples collected at every 0.2 pore volumes and later every 1 pore volume during polymer injection and post-flush stage, were analyzed for the effluent polymer concentration using UV-Vis spectrophotometer. In **Chapter 4**, three methods for measuring effluent polymer concentration in single-phase experiments were discussed. Among them, the UV-Vis spectrophotometer was frequently mentioned in the literature, often used alongside TOC-TN. However, since TOC-TN was unavailable during our single-phase experiments, and because the viscosity method demanded prolonged testing to assess viscosity losses from degradation to determine exact effluent concentration, we opted to utilize the UV-Vis spectrophotometer. The polymer concentration of each effluent sample was then normalized by dividing the polymer concentration in the effluent by the initial polymer concentration in the solution that was injected. The normalized concentration was then plotted against the pore volumes (**Figure 5.4**).

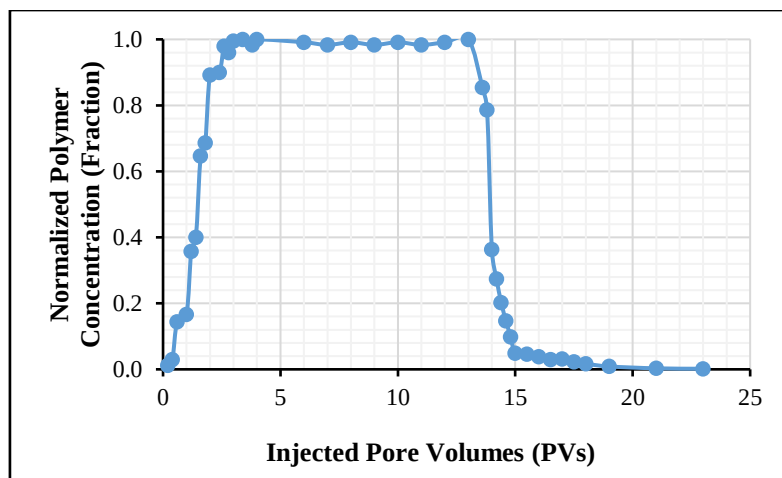


Figure 5.4: Polymer concentration profile of CF-1 during polymer injection and brine post-flush cycles at 25 °C.

5.3.1.1 Uncertainty in the Dynamic Polymer Retention Measurements

The uncertainty associated with dynamic polymer retention measurements primarily stemmed from the uncertainties in two key factors: the volume of effluent collected at various intervals (V_e) and the measurement of effluent polymer concentration (C_e). These uncertainties significantly impacted the final polymer retention value (A_d) (**Equation 3.16**) (Manichand and Seright, 2014). **Table 5.3** presents a comprehensive overview of the uncertainties encountered

during these measurements obtained by taking readings for each parameter and applying **Equation 3.27**. To determine the overall uncertainty in the final polymer retention value, the theory of error propagation (**Equations 3.28 and 3.29**) was employed in **Equation 3.16**. This theory allowed for the systematic evaluation and quantification of how uncertainties in the measured volume and polymer concentration propagated and affected the final retention value. The final uncertainty in dynamic polymer retention value with UV-Vis Spectrophotometer is presented in **Table 5.3**.

Table 5.3: Summary of uncertainties in parameters observed using UV Spectrophotometer method for CF-1

Analytical Method	UV Spectrophotometer Method
Parameter	Uncertainty (Δx)
C_i (ppm)	996 ± 4.45
V_i (cc)	$187.2 \pm 1.73 \times 10^{-3}$
$C_i V_i$ (μg)	186451.2 ± 833.28
$\Sigma C_e V_e$ (μg)	176501.4 ± 159.84
W_d (g)	$174.8 \pm 5.77 \times 10^{-4}$
A_d ($\mu\text{g/g-rock}$)	56 ± 5

5.3.1.2 Effect of Salinity on Dynamic Polymer Retention in the Absence of Oil

In the single-phase experiments, the material balance method yielded dynamic polymer retention values. For CF-1 where polymer solution was prepared in high salinity formation water (167,114 ppm), the dynamic polymer retention was observed to be $56 \mu\text{g/g-rock}$ (**Figure 5.5**). The amount of polymer retention varied when different formation water dilutions were used. The dynamic polymer retention values were $50 \mu\text{g/g-rock}$ for FW-1 (33,423 ppm), $46 \mu\text{g/g-rock}$ for FW-2 (16,711 ppm), and $25 \mu\text{g/g-rock}$ for FW-3 (8,356 ppm) (**Figure 5.5**). The first two dilutions of FW-1 and FW-2 did not show a pronounced difference in polymer retention, but the third dilution of FW-3 showed a significant reduction. This suggests that reducing salinity below 10,000 ppm is necessary to achieve a notable reduction in polymer retention.

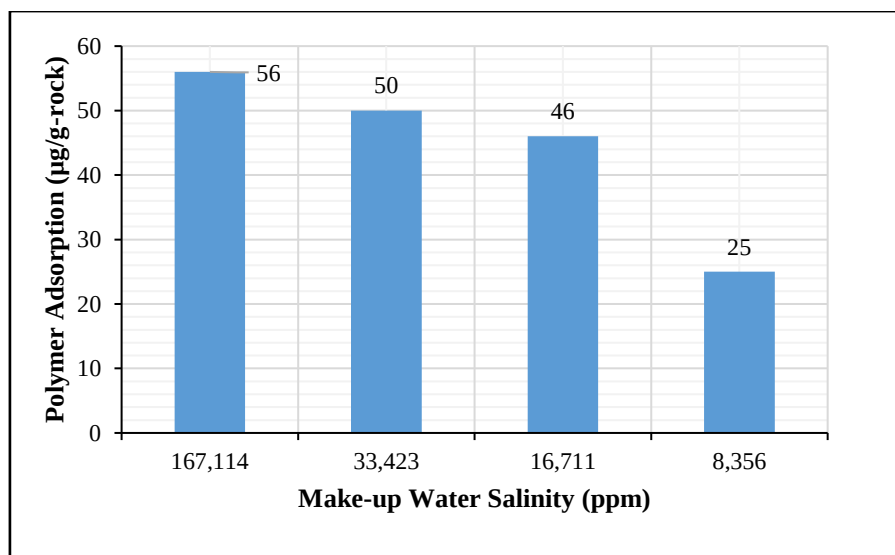


Figure 5.5: Dynamic polymer retention for formation water and its dilutions in the absence of oil.

Further, in the case of polymer solution in seawater, a dynamic polymer retention of 47 µg/g-rock was observed (**Figure 5.6**). In addition, significant reduction in polymer retention was observed when SW-2 (1,701 ppm) and SW-3 (425 ppm) were used with values of 38 and 24 µg/g-rock, respectively (**Figure 5.6**). It is interesting to highlight that both salinities were below 10,000 ppm, which confirms the previous observation that there were notable reductions in polymer retention at salinities below 10,000 ppm.

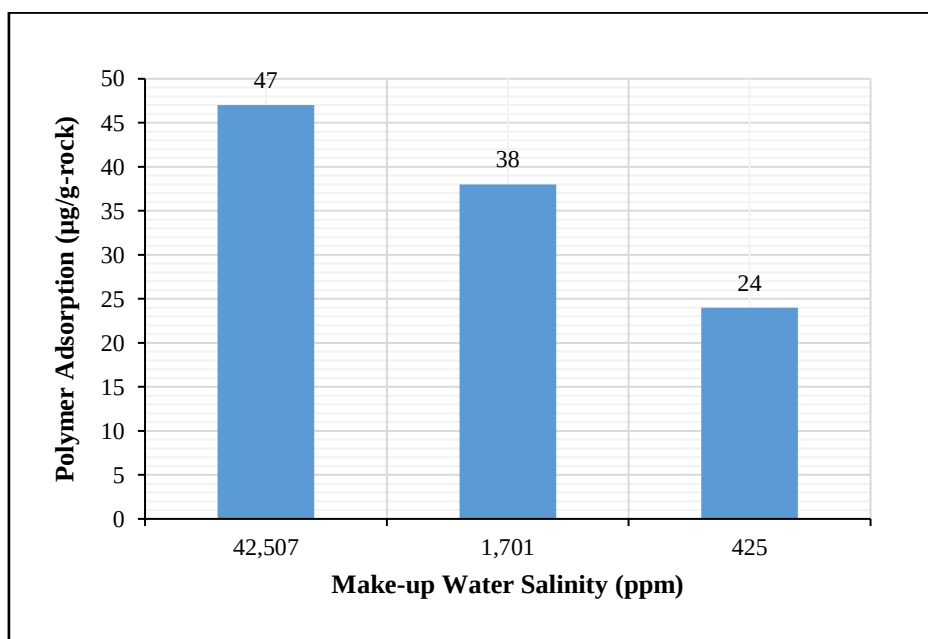


Figure 5.6: Dynamic polymer retention for seawater and its dilutions in the absence of oil.

The reduction in polymer retention with decreasing brine salinity could also be justified by the high solvency of low salinity brine for the polymer, which reduces the interactions between the polymer and the rock. Additionally, the larger hydrodynamic size of the polymer molecules at reduced salinities, the fewer polymer molecules needed to fill the adsorption sites. Furthermore, the polymer chains expand in low-salinity brine, resulting in unfavorable conformations for adsorption and high conformational entropy loss during adsorption (Sorbie, 1991; AlSofi *et al.*, 2018).

5.3.1.3 Effect of Salinity on In-Situ Rheology in the Absence of Oil

The ability of a polymer solution to exhibit its viscosity as it flows through a porous medium is measured by the resistance factor. **Figure 5.7** provides a summary of the RF values for formation water and its dilutions in the absence of oil. In single-phase experiments, the RF values for the base cases FW (**Figure 5.7**) and SW (**Figure 5.8**), with salinities of 167,114 and 42,507 ppm, respectively, were relatively similar (9.00). However, higher RF values were observed for diluted brine recipes of both FW and SW. For FW-1, FW-2, and FW-3, with salinities of 33,423, 16,711, and 8,356 ppm, respectively, the RF values were 14.70, 15.64, and 12.54, respectively. Similarly, for SW-2 and SW-3, with salinities of 1,701 and 425 ppm, respectively, the corresponding RF values were 19.56 and 43.02.

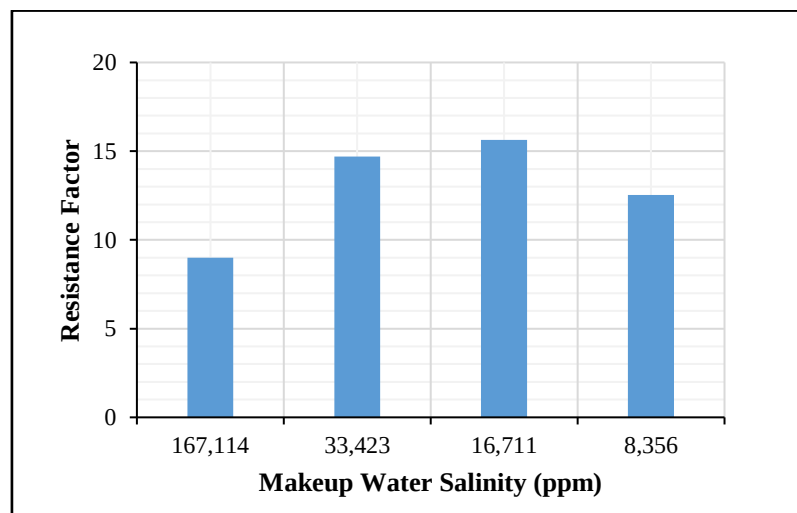


Figure 5.7: Effect of formation water and its dilutions on RF in the absence of oil.

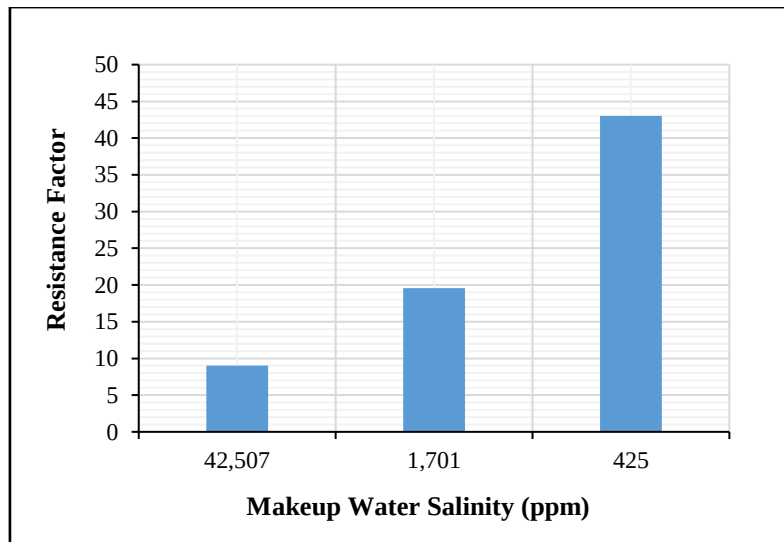


Figure 5.8: Effect of seawater and its dilutions on RF in the absence of oil.

As was previously mentioned, the resistance factor refers to the increase in flow resistance experienced by a polymer solution as it flows through the porous reservoir rock. The resistance factor is influenced by several factors, including polymer injection rate, polymer concentration, molecular weight, polymer structure, in-situ polymer viscosity, makeup water salinity, rock properties (porosity, permeability, pore size distribution, presence of oil, and wettability), and the interactions between the polymer solution and the reservoir rock (polymer adsorption) (Zamani *et al.*, 2015).

In single-phase experiments, salinity and polymer adsorption seem to be the main factors influencing the RF, as the same polymer and core samples with similar petrophysical properties were used. In the experiments using formation water and its dilutions, the resistance factor (RF) showed an increasing trend as the salinity decreased, reaching a peak at 16,711 ppm, then it decreased at 8,356 ppm. This observed trend is due to the shear thickening behavior and effect of salinity on shear thickening behavior of the polymer solution while flowing through the porous media.

Shear thickening is a phenomenon where the viscosity of a fluid increases with an increase in the shear rate. This behavior is due to the interaction between polymer chains and the flow field. When polymer solutions are in high salinity brine, the high salinities usually reduce coil gyration and hydrodynamic size. Consequently, higher shear rates are required to uncoil the polymers, and the onset of shear thickening is delayed for high salinity compared to low salinity (Rock *et al.*, 2020). The shear thickening behavior can be explained by the in-situ viscosity illustrated in **Figures 5.9** and **5.10**. The in-situ viscosity of FW and its dilutions were increasing with decreasing salinity. However, it is important to note that the bulk viscosity of

FW and its dilutions remains constant at around 3.6 cP, except for 8,356 ppm, which is slightly higher about 4.4 cP (**Figure 5.9**). The bulk viscosity and in-situ viscosity data suggest that low salinity may not affect the bulk viscosity of the polymer, but it affects the in-situ viscosity (at constant flow rates) and increases it.

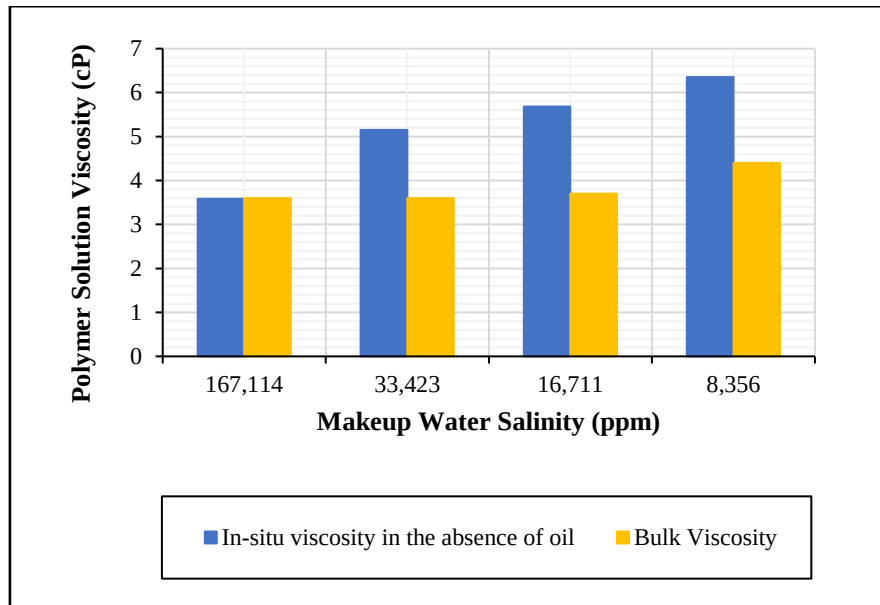


Figure 5.9: Effect of salinity on in-situ viscosity and bulk viscosity at 0.5 cc/min (~ 10 ft/d) and 25 °C for formation water and its dilutions in the absence of oil.

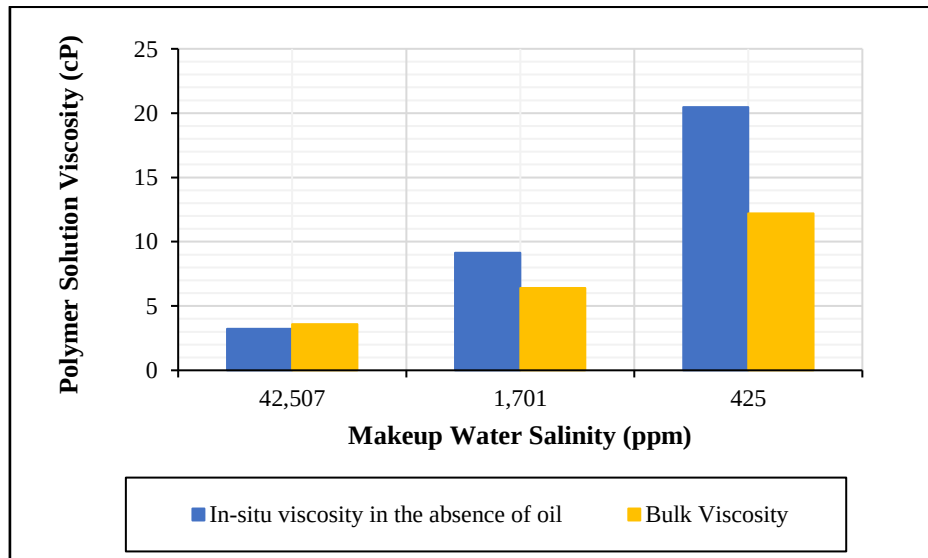


Figure 5.10: Effect of salinity on in-situ viscosity and bulk viscosity at 0.5 cc/min (~ 10 ft/d) and 25 °C for seawater and its dilutions in the absence of oil.

The RF values (**Figure 5.7**) vary and follow the trend of in-situ viscosity (**Figure 5.9**) up to 16,711 ppm. Further, the in situ-viscosity increases and RF decreases for FWI-3; RF for FW-3 (8,356 ppm) was slightly less than FW-1 (33,423 ppm) and FW-2 (16,711 ppm). This is due to low polymer adsorption (**Figure 5.5**) seen in 8,356 ppm which has overcome the salinity effect. The low RRF value for the polymer solution at this salinity supports this observation, which will be discussed further in the coming section.

Furthermore, the experiments using seawater and its dilutions also exhibited almost a similar behavior, with the RF increasing as the salinity decreased to 425 ppm (**Figure 5.8**). However, the impact is more prominent than FW and its dilutions, mainly due to the relatively lower salinity of SW dilutions than FW dilutions. In this case, the bulk viscosity has shown a steady increase from 3.6 cP to 12.2 cP, while the in-situ viscosity increased from 3.2 cP to 20.5 cP (**Figure 5.10**). The bulk viscosity and in-situ viscosity are almost similar at high salinity SW (42,507 ppm), showing that no shear thickening was observed at the flow rate of 0.5 cc/min. However, in-situ viscosity takes the lead at dilutions and becomes highest for the lowest salinity (425 ppm). This observation further supports the fact that the shear thickening for polymers directly depends on the salinity, and the lower the salinity, the higher the shear thickening values observed at the same flow rate of 0.5 cc/min (Rock *et al.*, 2020). Overall, the interplay between makeup water salinity, polymer adsorption, and the resultant shear-thickening behavior contributes to the observed variations in RF values in the 100% brine saturated cores (Han *et al.*, 2012).

The resistance factor impact on the polymer flooding process can be both beneficial and detrimental. On the positive side, a higher resistance factor can enhance the polymer sweep efficiency. However, it can also result in a rise in pressure drop, reducing injectivity, and rendering it more difficult to inject the polymer solution into the reservoir. Furthermore, a high resistance factor indicates a high in-situ viscosity indicating a larger hydrodynamic size resulting in trapping of these polymers on to the narrow pore throats, thereby reducing the polymer flooding process's efficacy over time (Glasbergen *et al.*, 2015; Skauge *et al.*, 2018). The injectivity reduction for all coreflooding experiments were calculated and summarized in **Table 5.4**, which includes primary brine injectivity, polymer injectivity, and the loss of injectivity during polymer injection. Injectivity refers to the ease with which fluids can be injected into a reservoir. As polymers are introduced into the reservoir, they can lead to a reduction in the permeability of the formation, thus reducing injectivity. The findings indicate that the injectivity loss for polymer flooding with formation water and seawater was within the acceptable range of 0.5 to 0.9 (Han *et al.*, 2012).

Table 5.4: Summary of injectivity during polymer injection with different makeup water salinities in the absence of oil

Brine Type	Makeup Water Salinity (ppm)	Polymer Injectivity Behaviour			
		Single-Phase Experiments			
		I_b (ft/d)/ (psi/ft)	I_p (ft/d)/ (psi/ft)	I_p/I_b	Injectivity loss
FW and its dilutions	167,114	8.49	0.95	0.11	0.89
	42,507	9.85	1.09	0.11	0.89
	33,423	10.85	0.74	0.07	0.93
	16,711	12.83	0.82	0.06	0.94
SW and its dilutions	8,356	13.56	0.77	0.06	0.94
	1,701	9.17	0.47	0.05	0.95
	425	8.34	0.19	0.02	0.98

Nonetheless, when injecting polymer with low salinity (33,423, 16,711, 8,356, 1,701 and 425 ppm), a significant injectivity loss (> 0.9) is observed due to the elevated in-situ viscosity of the polymer. This is mainly attributed to the relatively high viscosity of polymer solution due to low salinity. The uniform concentration of 1,000-ppm polymer was used for all salinities, to study the effect of salinity on polymer performance, which contributed to resultant viscosities at different salinities. Despite this high viscosity and inferior injectivity, the differential pressure was stable during polymer injection (**Figure 5.11**) at low salinity, indicating no plugging due to increased viscosity. **Figure 5.11** illustrates the pressure drop profiles for the brine preflush, polymer injection, and brine postflush stages across all coreflooding experiments. Although 60 to 70 pore volumes were injected during the brine postflush, the differential pressure readings were only displayed up to 10 pore volumes because the pressure stabilized within 5 to 7 pore volumes in all cases.

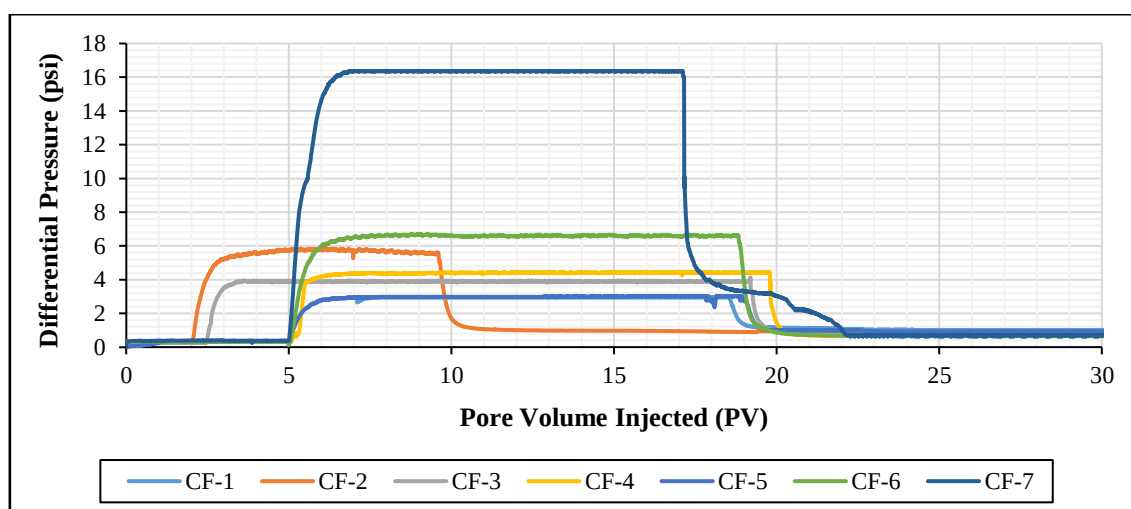


Figure 5.11: Pressure drop profile during brine pre-flush, polymer injection, and brine post-flush at a flow rate of 0.5 cc/min for CF-1 to CF-7.

5.3.1.4 Effect of Salinity on Residual Resistance Factor, Permeability Reduction, and Adsorbed Layer Thickness in the Absence of Oil

From **Figure 5.10**, it is evident that the differential pressure of post-flush brine injection at a flow rate of 0.5 cc/min is higher than that of pre-flush brine injection. This indicates a reduction in permeability, mainly due to the polymer adsorption onto the pore walls. The decrease in permeability can be inferred from the residual resistance factor (RRF). **Figures 5.12** and **5.13** summarize the RRF values calculated at an injection rate of 0.5 cc/min (approximately 10 ft/d). According to **Figures 5.12** and **5.13**, in the absence of oil, the RRF values range from 2.76 to 3.00 for high salinities (ranging from 16,711 to 167,114 ppm), whereas RRF ranges from 1.87 to 1.91 for low salinities (ranging from 425 to 8,356 ppm). These findings indicate that high salinity brines exhibit greater polymer retention compared to low salinity brines (**Figures 5.5** and **5.6**) (Lee *et al.*, 2019).

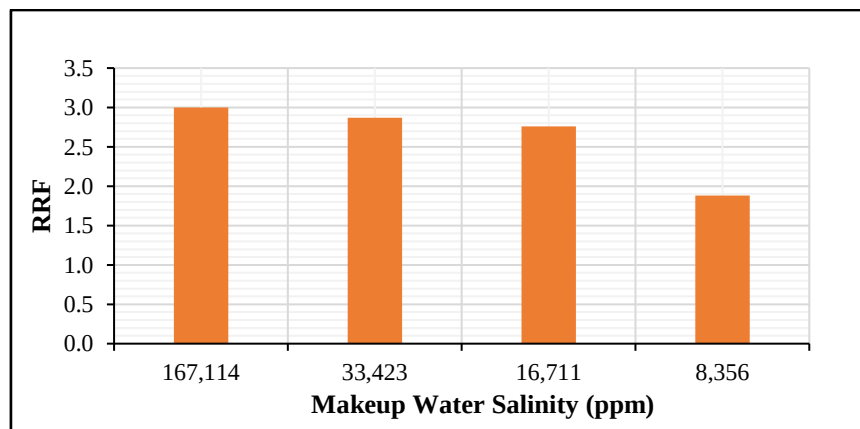


Figure 5.12: Summary of RRF values for coreflooding experiments with formation water and its dilutions in the absence of oil.

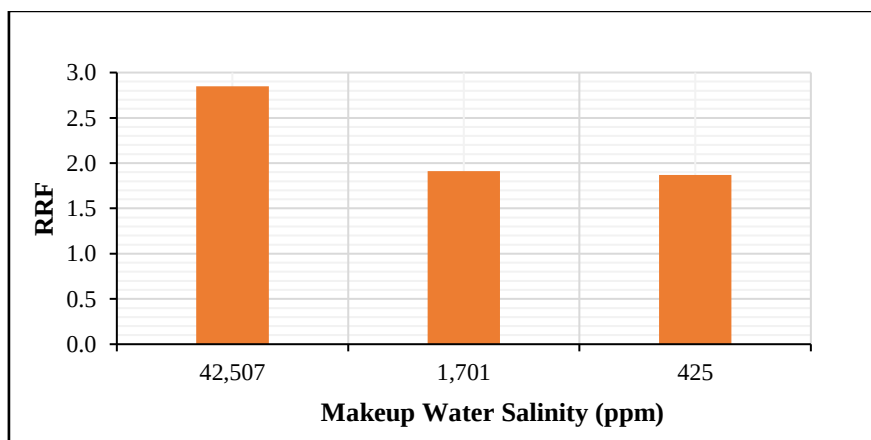


Figure 5.13: Summary of RRF values for coreflooding experiments with seawater and its dilutions in the absence of oil.

The adsorption layer thickness is thicker in the case of high salinity brines, compared to low salinity brines (**Figures 5.14** and **5.15**). This is due to a greater number of adsorbed polymer molecules with the high salinity makeup brines as opposed to that with the low salinity makeup brines.

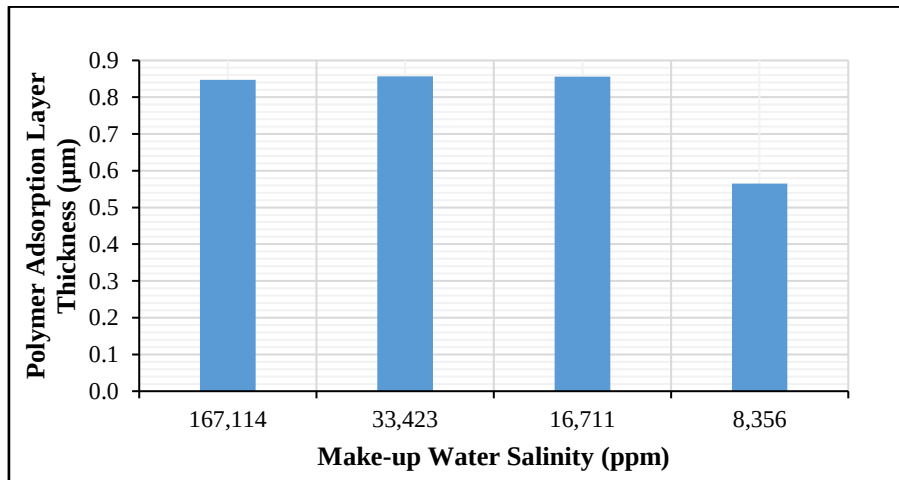


Figure 5.14: Summary of polymer adsorption thickness due to polymer retention for formation water and its dilutions in the absence of oil.

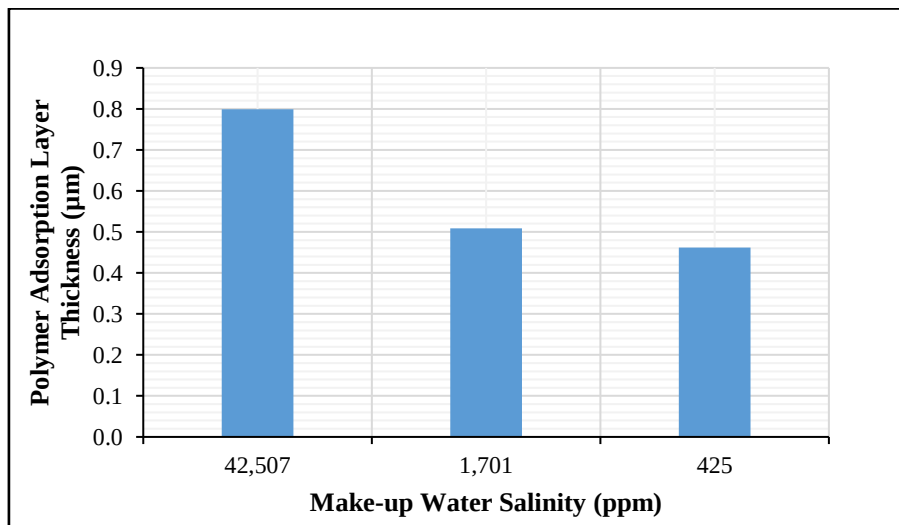


Figure 5.15: Summary of polymer adsorption thickness due to polymer retention for seawater and its dilutions in the absence of oil.

5.3.2 Dynamic Polymer Retention Measurements in the Presence of Oil

For two-phase dynamic polymer flooding experiments two protocols were used as previously discussed in **Chapter 3**. Initially, protocol 1 was used for forced imbibition (CF-8), and later protocol 2 was utilized for (CF-9 to CF-15).

The UV-Vis spectrophotometer method was chosen to determine the effluent polymer concentration for CF-8 initially. However, this method encountered challenges due to the interference of trace amounts of oil in the effluent polymer solution. Specifically, these oil traces skewed the UV absorbance measurements, preventing obtaining accurate dynamic retention values. In search of an alternative method, the viscosity method was explored. Yet again, the trace amounts of oil posed a problem, interrupting the viscosity measurements. Nevertheless, a solution was found by utilizing the TOC-TN method. Despite the presence of traces of oil in the effluent samples from the CF-8 experiment, the TOC-TN method successfully determined the polymer concentration and yielded a representative dynamic polymer retention value of 24 $\mu\text{g/g-rock}$. Later, the normalized concentration vs. pore volumes was plotted (**Figure 5.16**). For CF-9 to CF-15, TOC-TN was employed for effluent polymer concentration measurements.

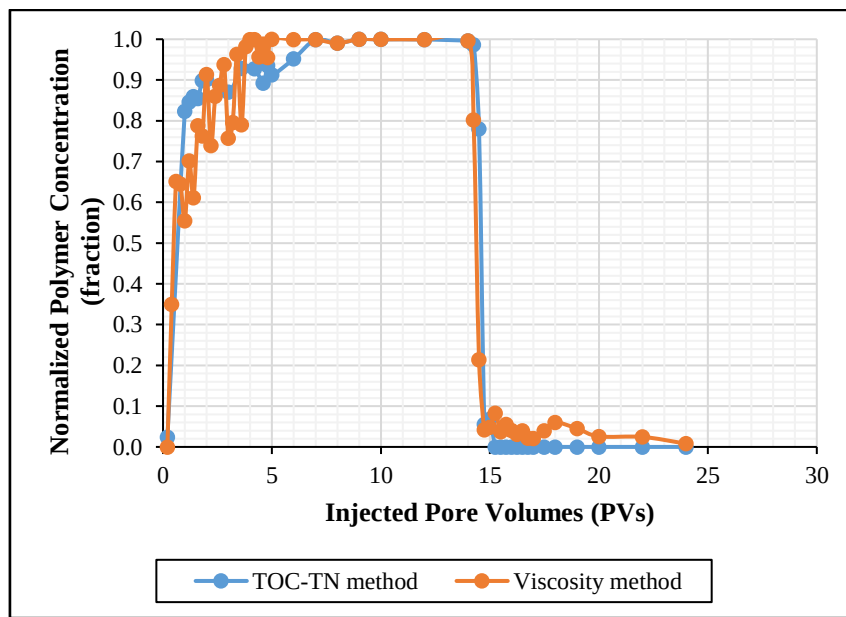


Figure 5.16: Polymer concentration profile of CF-8 during polymer injection and brine post-flush cycles at 25 °C using viscosity and TOC-TN method.

5.3.2.1 Uncertainty in Dynamic Polymer Retention Measurements

The uncertainty associated with dynamic polymer retention measurements in presence of oil was also determined and presented in **Table 5.5**.

Table 5.5: Summary of uncertainties in parameters observed using TOC-TN method for CF-9

Analytical Method	UV Spectrophotometer Method
Parameter	Uncertainty (Δx)
C_i (ppm)	1000 ± 2.69
V_i (cc)	$185.5 \pm 1.73 \times 10^{-3}$
$C_i V_i$ (μg)	185648.4 ± 494.77
$\Sigma C_e V_e$ (μg)	181705.6615 ± 154.16
W_d (g)	$151.77 \pm 5.77 \times 10^{-4}$
A_d ($\mu\text{g/g-rock}$)	26 ± 3

5.3.2.2 Effect of Salinity on Dynamic Polymer Retention in the Presence of Oil

For the two-phase experiments, significantly lower polymer retention values were observed for CF-9 to CF-15 compared to those in the single-phase experiments (CF-1 to CF-7). The retention values for CF-9 to CF-15 were 26, 26, 23, 19, 28, 20, and 14 $\mu\text{g/g-rock}$, respectively as opposed to the values in the single-phase experiments (CF-1 to CF-7) of 56, 50, 46, 25, 47, 38, and 24 $\mu\text{g/g-rock}$, for the respective brines of FW, FW-1, FW-2, FW-3, SW, SW-2, and SW-3. The reason for these low polymer adsorption values is due to the presence of oil and the relatively more oil-wet cores, which resulted in significantly reduced available rock surface area for polymer molecules adsorption (Hughes *et al.*, 1990; Broseta *et al.*, 1995; Hatzignatiou *et al.*, 2015; Wang *et al.*, 2020).

The impact of salinity on the polymer adsorption onto the cores in the presence of oil was also noted. When low salinity brines (8,356, 1,701, and 425 ppm) were used, polymer retention values were lower (19, 20, and 14 $\mu\text{g/g-rock}$) compared to the values observed with formation water (167,114 ppm) and seawater (42,507 ppm), which resulted in higher retention values of 26 and 28 $\mu\text{g/g-rock}$, respectively. **Figures 5.17** and **5.18** present the dynamic polymer retention results for all coreflooding experiments.

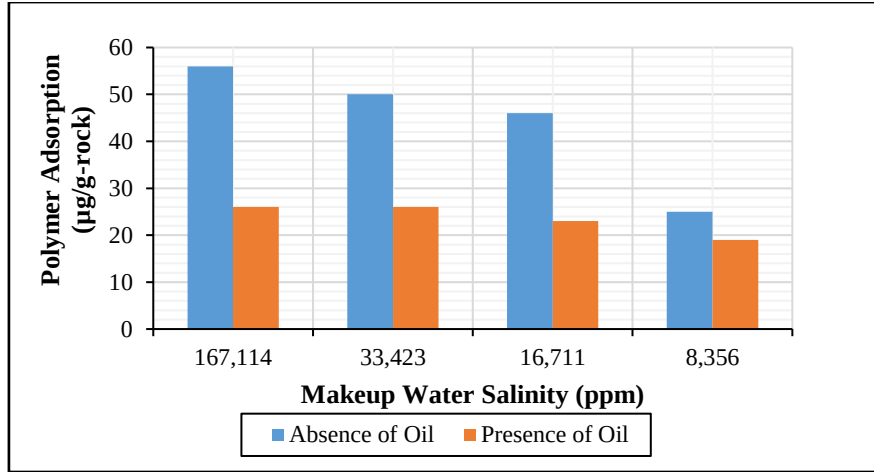


Figure 5.17: Dynamic polymer retention for formation water and its dilutions in the absence and presence of oil.

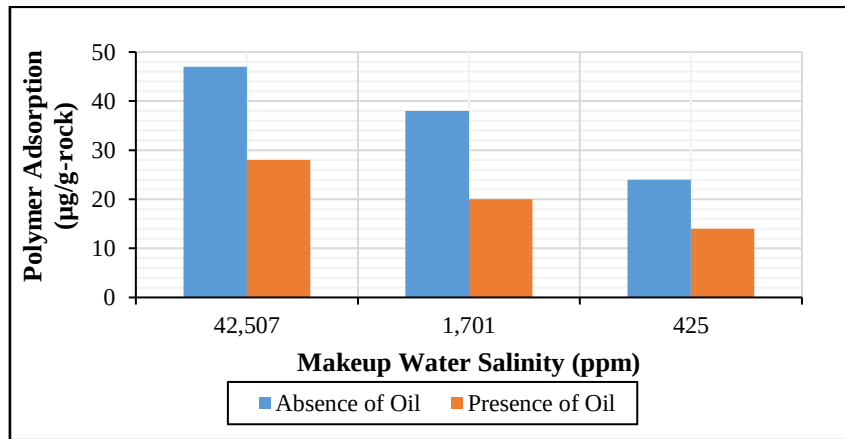


Figure 5.18: Dynamic polymer retention for seawater and its dilutions in the absence and presence of oil.

5.3.2.3 Effect of Salinity on In-situ Rheology in the Presence of Oil

In two-phase experiments, one can note from **Figure 5.19** that the RF values for FW with salinity of 167,114 was 8.31 and for FW-1, FW-2, and FW-3, with salinities of 33,423, 16,711, and 8,356 ppm, respectively, the RF values were 9.23, 7.98, and 7.83, respectively. On the other hand, **Figure 5.20** shows the RF values for seawater and its dilutions. Polymer flooding experiment with SW salinity of 42,507 ppm indicates an RF of 10.16, and for seawater dilutions SW-2 and SW-3, with salinities of 1,701 and 425 ppm, respectively, the corresponding RF values were 16.73 and 20.22.

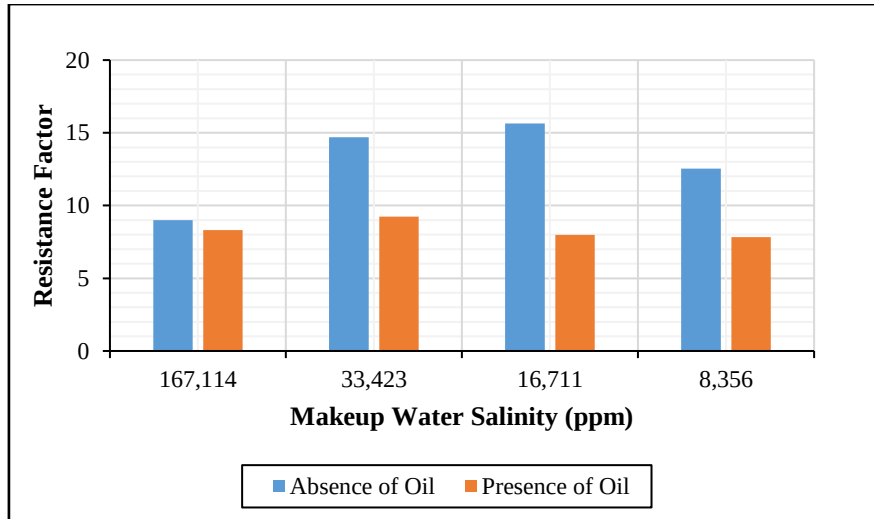


Figure 5.19: Effect of salinity on RF using formation water and its dilutions in the absence and presence of oil.

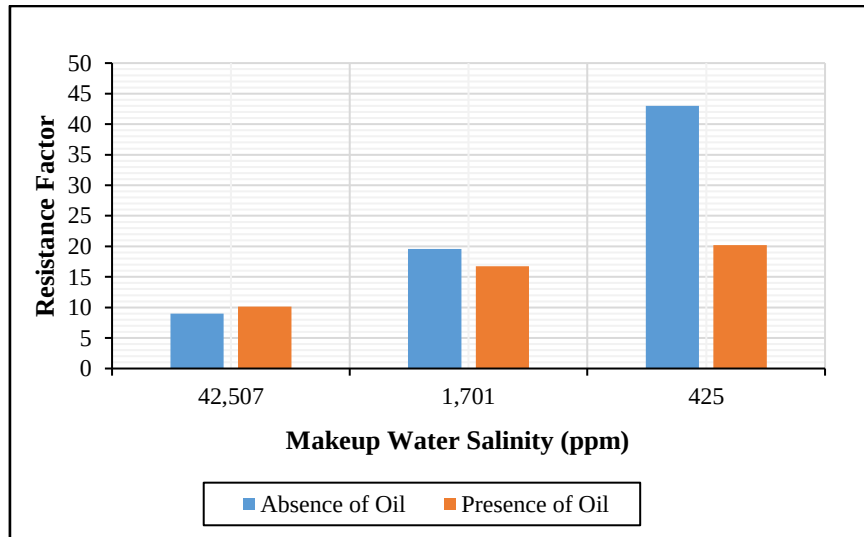


Figure 5.20: Effect of salinity on RF using seawater and its dilutions in the absence and presence of oil.

In two-phase experiments, the key influencing factors affecting RF values were attributed to the presence of oil and the rock wettability (Al-Shakry *et al.*, 2018; Masalmeh *et al.*, 2019). In the presence of oil in oil-wet cores, there are notable changes in RF and in-situ viscosity values. Specifically, RF values drop significantly compared to cores 100% saturated with brine. As depicted in **Figures 5.21** and **5.22**, the presence of oil leads to lowered in-situ viscosity compared to the absence of oil. The in-situ viscosity values for FW and its dilutions are very similar to bulk viscosity values. This behavior indicates that shear thickening in the presence of oil is less. Further, in the case of SW and SW-2, the in-situ viscosity was slightly

higher than the bulk viscosity indicating a mild shear thickening behavior. Overall, the presence of oil has lowered the shear thickening behavior. This is because the presence of oil in the porous rock leads to a smoother flow of the polymer solution through the porous media due to several factors. Firstly, the oil reduces the effective pore volume, resulting in a shorter propagation path for the polymer. Additionally, the slipping effect of oil-wet surfaces aids in facilitating a smoother flow of the polymer. This lowers in-situ viscosity of the polymer solution, as represented in **Figures 5.21** and **5.22** (Masalmeh *et al.*, 2019; Alfazazi *et al.*, 2021).

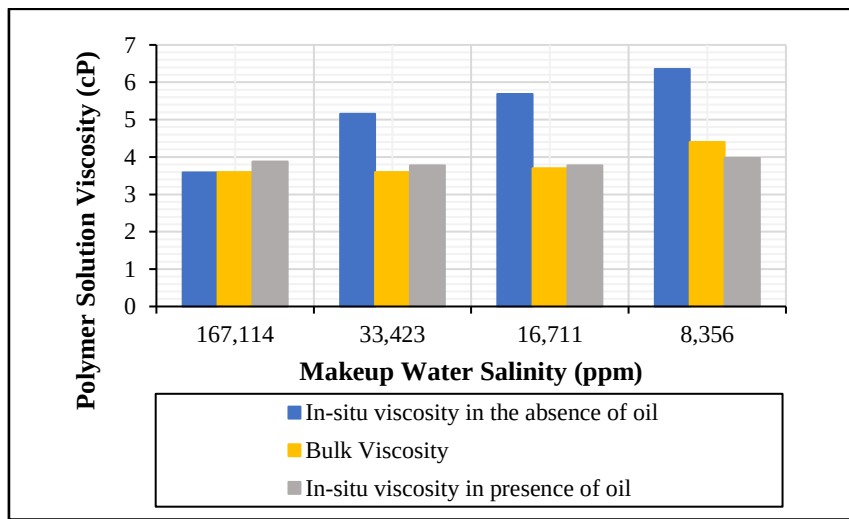


Figure 5.21: Effect of salinity on in-situ viscosity and bulk viscosity at 0.5 cc/min (~ 10 ft/d) and 25 °C for formation water and its dilutions.

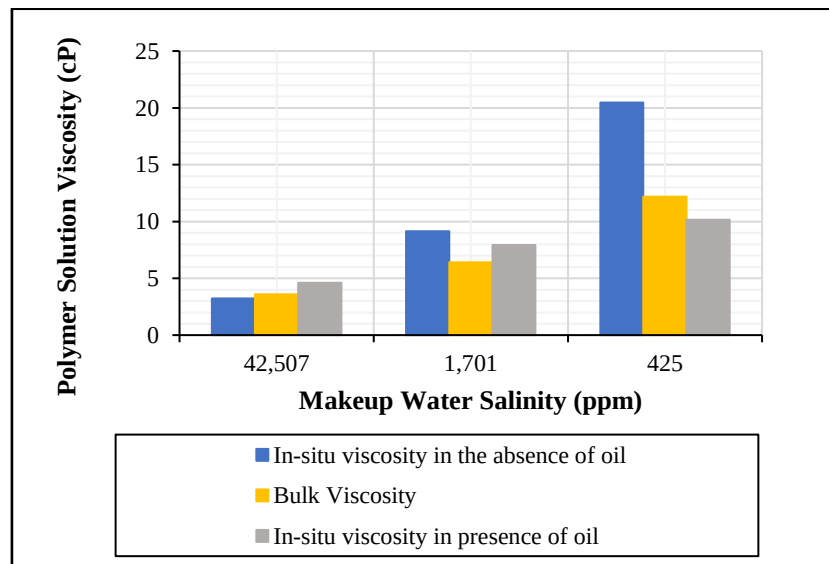


Figure 5.22: Effect of salinity on in-situ viscosity and bulk viscosity at 0.5 cc/min (~ 10 ft/d) and 25 °C for seawater and its dilutions.

The reduced injectivity loss observed in aged cores at S_{or} compared to 100% saturated cores (**Table 5.6**), can be predominantly attributed to the weakened dilatant behavior of the polymer solution in the oil-wet cores. The inherent presence of oil, due to its nature, minimizes friction, facilitating the smoother flow of the polymer solution through the porous media. These factors reduce the magnitude of shear thickening, ultimately enhancing the polymer solution's injectivity through the porous medium (Masalmeh *et al.*, 2019).

Table 5.6: Summary of injectivity during polymer injection with different makeup water salinities

Makeup Water Salinity (ppm)	Polymer Injectivity Behaviour							
	Single-Phase Experiments				Two-Phase Experiments			
	I_b (ft/d)/ (psi/ft)	I_p (ft/d)/ (psi/ft)	I_p/I_b	Injectivity loss	I_b (ft/d)/ (psi/ft)	I_p (ft/d)/ (psi/ft)	I_p/I_b	Injectivity loss
167,114	8.49	0.95	0.11	0.89	4.81	0.58	0.12	0.88
42,507	9.85	1.09	0.11	0.89	5.33	0.52	0.10	0.90
33,423	10.85	0.74	0.07	0.93	5.25	0.57	0.11	0.89
16,711	12.83	0.82	0.06	0.94	5.45	0.68	0.13	0.87
8,356	13.56	0.77	0.06	0.94	5.50	0.70	0.13	0.87
1,701	9.17	0.47	0.05	0.95	5.47	0.33	0.06	0.94
425	8.34	0.19	0.02	0.98	5.90	0.29	0.05	0.95

In addition, it is worth mentioning that in all the cases (CF-9 - CF-15), there was no unsteady pressure build-up, indicating that the observed retention was mainly due to adsorption. The latter is supported by **Figure 5.23**, which shows the pressure drop profiles for CF-9 to CF-15.

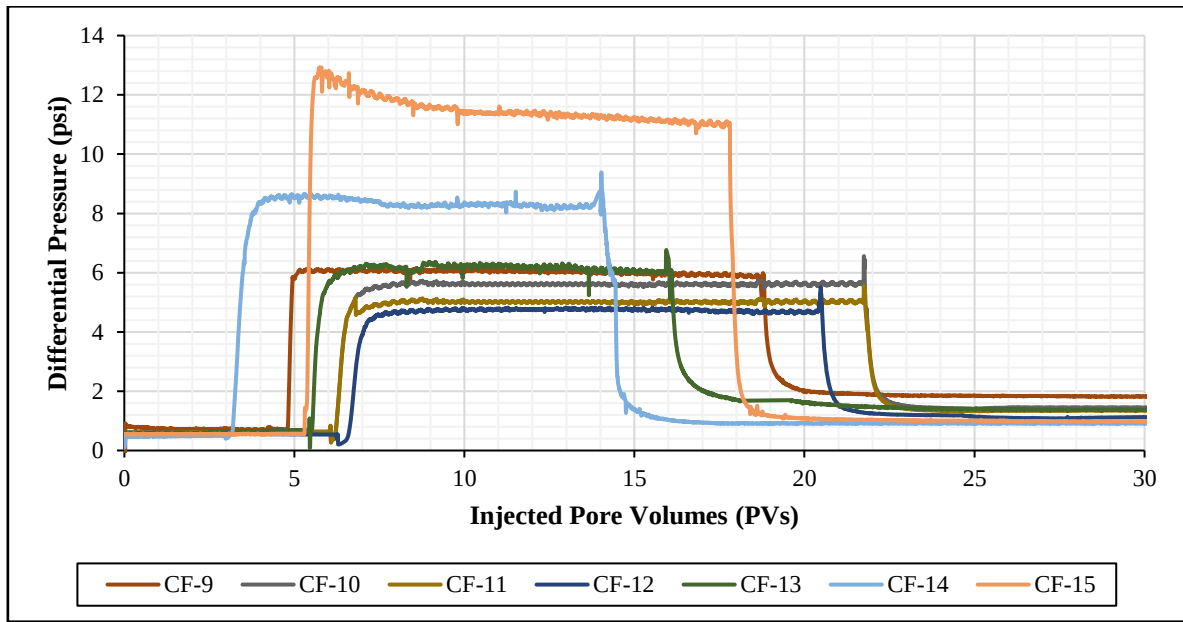


Figure 5.23: Pressure drop profile during brine pre-flush, polymer injection, and brine post-flush at a flow rate of 0.5 cc/min for CF-9 to CF-15.

5.3.2.4 Effect of Salinity on Residual Resistance Factor, Permeability Reduction, and Adsorbed Layer Thickness in the Presence of Oil

In the presence of oil, the RRF varies between 2.12 and 2.56 for high salinity brines, while it reduces and ranges from 1.77 to 1.88 for lower salinities. The RRF values for high salinity brines (16,711 to 167,114 ppm) without oil (2.76 to 3.00) and with oil (2.12 to 2.56) showed a decreasing trend, indicating lower dynamic polymer retention in the cores at S_{or} conditions (**Figures 5.17 and 5.18**), similar observation was noted in the literature (Alfazazi *et al.*, 2021). Similarly, for low salinity brines (425 to 8,356 ppm), the RRF values for the two-phase condition (1.77 to 1.88) were also lower than those for the single-phase condition (1.87 to 1.91). The findings are further supported by the calculated adsorption layer thickness for all cases as depicted in **Figures 5.24 and 5.25**. It is worth noting that the polymer adsorption layer thickness is reduced in the oil-wet cores due to lower polymer retention observed in these cores.

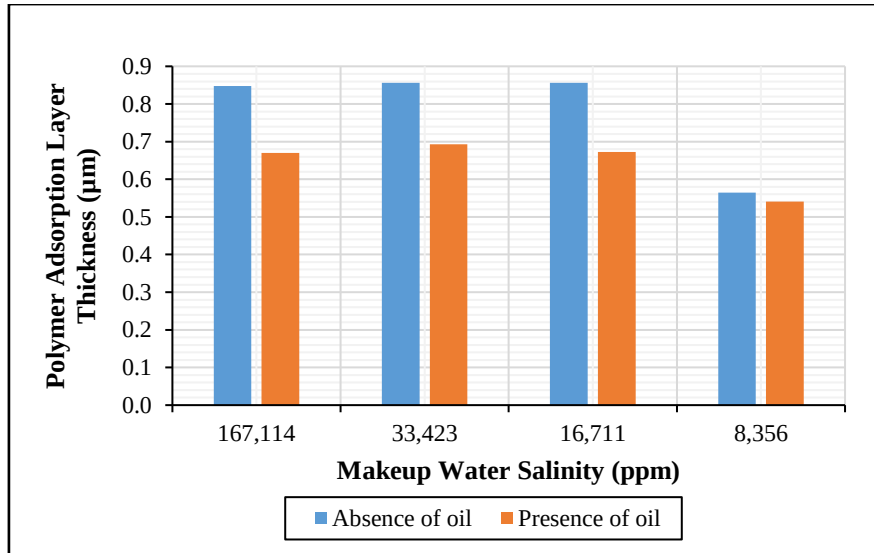


Figure 5.24: Summary of polymer adsorption thickness due to polymer retention in formation water and its dilutions.

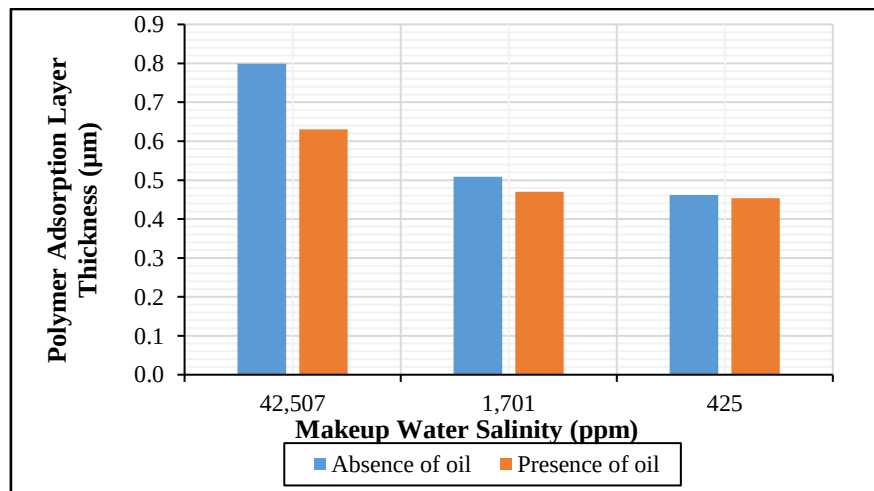


Figure 5.25: Summary of polymer adsorption thickness due to polymer retention in seawater and its dilutions.

5.3.3 Proposed Desalination Methods for Targeted Dilutions

The study conclusively determined that a salinity level below 10,000 ppm is crucial for achieving a marked decrease in dynamic polymer retention. Among the various brine recipes tested, SW-3 emerged as the most effective, which is the 100 times diluted seawater. To attain this specific dilution, one can employ the reverse osmosis method, a pressure-driven membrane process. Reverse osmosis filter out both monovalent and divalent ions and yields fresh water that can be utilized to dilute seawater to achieve the targeted degree of dilution (Nair *et al.*, 2016).

5.4 Highlights of the Chapter

In this study, the effects of low salinity on polymer in-situ viscosity and retention were investigated in the presence and absence of oil thoroughly using a set of 15 coreflooding experiments. The study included both single-phase and two-phase experiments, leading to several significant findings as follows:

- The study found that polymer retention levels were significantly reduced when diluted brines were used, as opposed to high salinity formation water or seawater. While working on polymer injection in the presence of oil, it was noted that the presence of oil in aged cores further reduced polymer retention, emphasizing the importance of using wettability-restored cores to obtain accurate retention values.
- The study also observed that the polymer retention was mainly due to adsorption of polymer for all types of brines used since the residual resistance factor (RRF) was less than 3, and there were no undesired pressure peaks during and after polymer injection.
- An important benefit of using makeup brine dilution is the increase in the resistance factor, which is due to the polymer's higher viscosity; however, the resultant loss in injectivity needs to be carefully monitored. This study shows that low-salinity brine is beneficial for polymer flooding and can effectively be used in carbonate reservoirs.

CHAPTER 6: EFFECT OF VARYING IONIC COMPOSITIONS ON POLYMER ADSORPTION IN STATIC AND DYNAMIC CONDITIONS

Chapter 6 delves into the effects of different ionic compositions on polymer adsorption, specifically focusing on Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions. This chapter explores brines of varying hardness levels. Additionally, a sulfate-spiked brine composition was analyzed to determine the impact of sulfate on polymer adsorption. Initial experiments involved static adsorption studies in a single phase. Later, to obtain a comprehensive understanding of retention values, dynamic retention experiments were conducted in both the presence and absence of oil. The chapter also assesses how varying ionic compositions influence the in-situ rheology

6.1 Experimental Overview

The core plugs and polymer solutions were characterized and prepared using the methods described in **Chapter 3**. Diluted and softened brines of representative seawater of Middle East fields were investigated in this chapter. The compositions of the five brines used were previously listed in **Table 3.3**. The first brine is SW-1, which was 5-times diluted seawater (8,502 ppm). This brine was considered as the base case due to the promising results obtained from initial screening (**Figure 4.4**); hence, it was decided to further improve its performance through varying the ionic composition. Four additional brines were used with the same total dissolved salt level of SW-1 (8,502 ppm), but they differ in their ionic compositions (**Table 3.3**).

Initially, static adsorption experiments were conducted on crushed rock powder to study the adsorption behavior of polymer prepared in brines of varying ionic compositions. Further, dynamic retention experiments including five single-phase, and five two-phase coreflooding experiments were performed to get more representative polymer retention values. The core plugs were saturated with respective brines, and experiments were performed at a temperature of 25 °C for the single-phase retention studies. For two-phase experiments, the core samples saturated with respective brine were flooded by oil to initial water saturation (S_{wi}) condition and aged at 90 °C for 14 days to institute wettability. After aging, glycerol brine mixture was injected into the core samples to displace oil and achieve the true residual oil saturation. Then, glycerol was flushed thoroughly with respective brine before the polymer injection. Using glycerol during the forced imbibition phase prevents oil mobilization during polymer injection,

resulting in more precise and accurate measurements of polymer retention. The polymer retention studies include brine pre-flush, polymer injection, and brine post-flush at a constant flow rate of 0.5 cc/min. **Tables 6.1** and **6.2** provide an overview of the outcrop properties and experimental conditions.

Table 6.1: Petrophysical properties of core samples and experimental conditions applied for single-phase coreflooding experiments

Core ID (Single-phase Tests)	CF-16	CF-17	CF-18	CF-19	CF-20
Connate Water/ Injection Water Salinity, TDS (ppm)	8,502 SW-1	8,502 SW-1A	8,502 SW-1B	8,502 SW-1C	8,502 SW-1D
Polymer Concentration (ppm)	1000				
Length (cm)	7.45	7.50	7.50	7.60	7.60
Diameter (cm)	3.80	3.80	3.80	3.80	3.75
Porosity (%)	15	21	18	22	20
Absolute Brine Permeability (mD)	225	203	226	205	202
Temperature (°C)	25				
Confining Pressure (psi)	1200				
Backpressure (psi)	100				

Table 6.2: Petrophysical properties of core samples and experimental conditions applied for two-phase coreflooding experiments

Core ID (Two-phase Tests)	CF-21	CF-22	CF-23	CF-24	CF-25
Connate Water/ Injection Water	8,502	8,502	8,502	8,502	8,502
Salinity, TDS (ppm)	SW-1	SW-1A	SW-1B	SW-1C	SW-1D
Polymer Concentration (ppm)	1000				
Length (cm)	7.58	7.47	7.62	7.30	7.47
Diameter (cm)	3.8	3.8	3.8	3.8	3.8
Porosity (%)	20	20	20	19	20
Absolute Brine Permeability (mD)	280	277	239	248	281
S_{wi} (%)	32	33	32	33	32
S_{or} (%)	37	37	37	36	34
Temperature (°C)	25				
Confining Pressure (psi)	1200				
Backpressure (psi)	100				

6.2 Static Adsorption Studies

This section investigates the effects of brines with varying ionic compositions on static polymer adsorption at ambient (25 °C) conditions following the protocol discussed in **Chapter 3**.

6.2.1 Effect of Varying Ionic Compositions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) on Static Polymer Adsorption

Static polymer adsorption values in varied brine composition in single-phase conditions are reported in **Figure 6.1**. The highest polymer adsorption was observed in SW-1 (425 ppm of Ca^{2+} + Mg^{2+} and 660 ppm of SO_4^{2-}) with an adsorption value of 102 $\mu\text{g/g-rock}$. Further, the polymer adsorption values for SW-1A (317 ppm of Mg^{2+} and 660 ppm of SO_4^{2-}), SW-1B (108 ppm of Ca^{2+} and 660 ppm of SO_4^{2-}), SW-1C (0 ppm of Ca^{2+} + Mg^{2+} and 660 ppm of SO_4^{2-}), and SW-1D (425 ppm of Ca^{2+} + Mg^{2+} and 1,320 ppm of SO_4^{2-}) were 62, 51, 37, and 66 $\mu\text{g/g-rock}$, respectively. It is evident that the brines SW-1A, SW-1B, SW-1C, with lower concentration of hardness (Ca^{2+} and Mg^{2+}) exhibited reduced polymer adsorption compared to SW-1 with highest amount of hardness (Ca^{2+} and Mg^{2+}). Notably, SW-1C, which is completely devoid of hardness, recorded the lowest adsorption at 37 $\mu\text{g/g-rock}$, a significant decrease from the 102 $\mu\text{g/g-rock}$ observed in SW-1. This decrease in polymer adsorption for softened brines is likely due to the polymer molecular chain expanding in the absence of divalent ions.

Consequently, fewer polymer molecules are needed to occupy the available adsorption sites (AlSofi *et al.*, 2018). **Figure 6.1** depicts the inverse relationship between adsorption and polymer solution viscosity.

Additionally, the SW-1D composition spiked with sulfate, demonstrated a decline in polymer adsorption (66 $\mu\text{g/g-rock}$) when compared with SW-1 (102 $\mu\text{g/g-rock}$). Yet, its adsorption value was comparable to that of SW-1A (62 $\mu\text{g/g-rock}$). This reduction can be due to the slight swelling of the polymer molecular chain, mainly because of the high sulfate content that reduces the hardness effect caused by the divalent cations and lowers the shielding of the anionic backbone of the polymer chain (Tahir *et al.*, 2020). The error bars depicted in **Figure 6.1** for polymer adsorption values were derived from the standard deviation of three experimental repetitions.

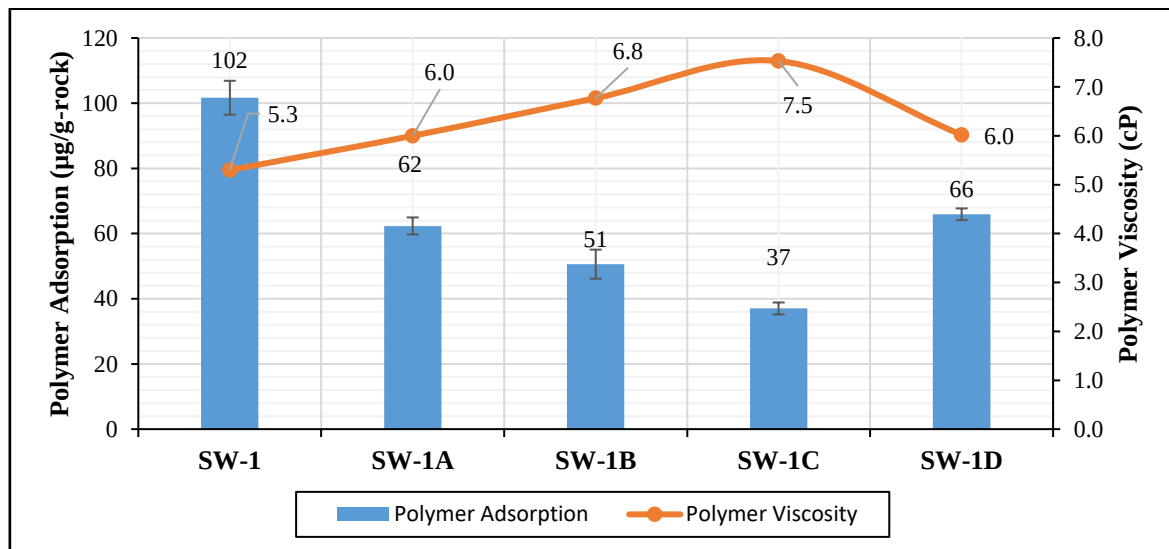


Figure 6.1: Effect of varying ion compositions on polymer adsorption in static single-phase condition at 25 °C.

6.3 Dynamic Retention Studies

This section discusses the results obtained for polymer dynamic retention experiments as a result of injecting brines with varying ionic composition. The experiments include five single-phase and five two-phase coreflooding experiments to get more representative polymer retention values.

6.3.1 Effect of Varying Ionic Compositions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) on Dynamic Polymer Retention in the Absence and Presence of Oil

The dynamic polymer retention in single-phase was studied with five polymer flooding experiments. The dynamic retention values obtained were 42, 44, 34, 33, and 44 $\mu\text{g/g-rock}$ for CF-16, CF-17, CF-18, CF-19, and CF-20, respectively (**Figure 6.2**). The retention values indicate that the polymer retention was the lowest in CF-18 and CF-19 tests (34 and 33 $\mu\text{g/g-rock}$). These tests were performed in low hardness (Ca^{2+} and Mg^{2+}) brines, i.e., SW-1B (108 ppm Ca^{2+}) and SW-1C (0 ppm Ca^{2+} and Mg^{2+}). On the other hand, the adsorption values for CF-16 and CF-17 were found to be higher of 42 and 44 $\mu\text{g/g-rock}$, respectively. The latter tests were conducted in SW-1 and SW-1A brines with higher respective hardness values (Ca^{2+} and Mg^{2+}) of 425 and 317 ppm, respectively. These adsorption results show a significant reduction in polymer adsorption with reducing the hardness values (Ca^{2+} and Mg^{2+}) in brine to approximately 100 ppm. At low hardness levels, polymer molecular chain expands, which is substantiated by higher viscosities of polymer solution in these brines (SW-1B, and SW-1C) (**Figure 6.2**). This results in fewer molecules required for satisfying the adsorption sites. Moreover, in CF-20 with SW-1D brine, the polymer adsorption value was 44 $\mu\text{g/g-rock}$, which was comparable to CF-16 (42 $\mu\text{g/g-rock}$) and CF-17 (44 $\mu\text{g/g-rock}$) indicating that spiking of sulfate did not reduce polymer adsorption.

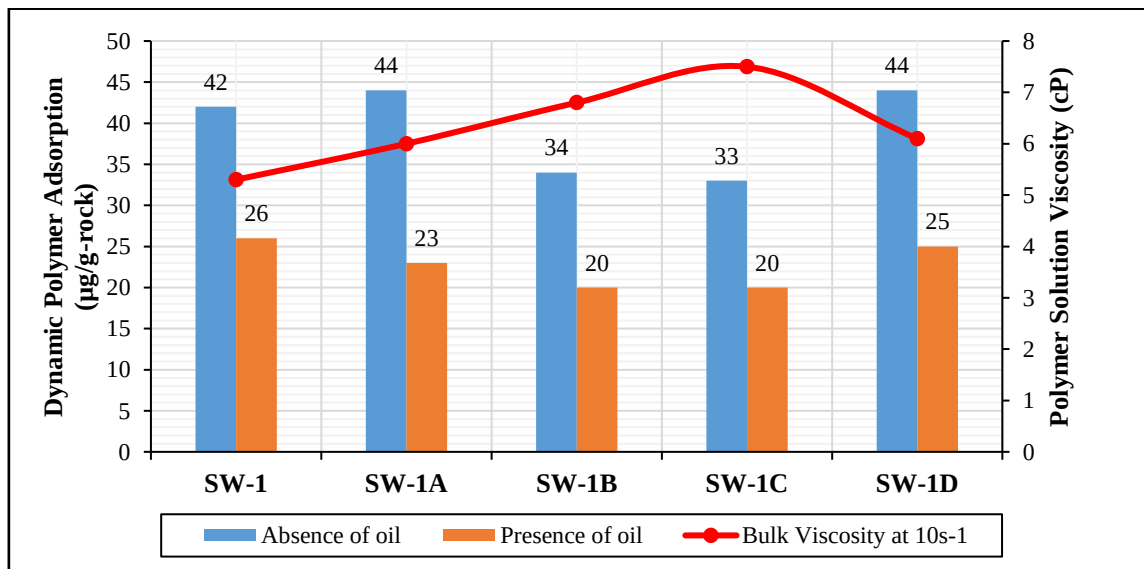


Figure 6.2: Effect of varying ion compositions on dynamic polymer retention in the presence and absence of oil at 25 °C.

In two-phase studies, the polymer retention values measured for the CF-21 to CF-25 were 26, 23, 20, 20, and 25 $\mu\text{g/g-rock}$, respectively (**Figure 6.2**). The polymer retention in the

presence of oil was less compared to retention values in the absence of oil (42, 44, 34, 33, and 44 $\mu\text{g/g-rock}$, respectively). The cause of these low adsorption values is due to the oil-wet nature of the core (2 weeks of aging) and the presence of oil, which significantly reduced the surface area available for the polymer molecules to get adsorbed (Skauge *et al.*, 2020; Alfazazi *et al.*, 2021; Wang *et al.*, 2021).

It is important to mention that the concentration of the polymer was measured differently for single-phase and two-phase experiments. UV-vis spectroscopy was used for single-phase experiments, where the concentration was determined by correlating it to the absorbance value. Also, by applying the theory of propagation of error an uncertainty of ± 5 $\mu\text{g/g-rock}$ was observed (Table 5.3). For two-phase experiments, the TOC-TN method was used, and a calibration curve of total nitrogen versus concentration was plotted to determine the effluent polymer concentration by measuring the total nitrogen in the effluent. In this case, an uncertainty of ± 3 $\mu\text{g/g-rock}$ was determined (Table 5.5). Figure 6.3 shows a typical normalized effluent polymer concentration profile.

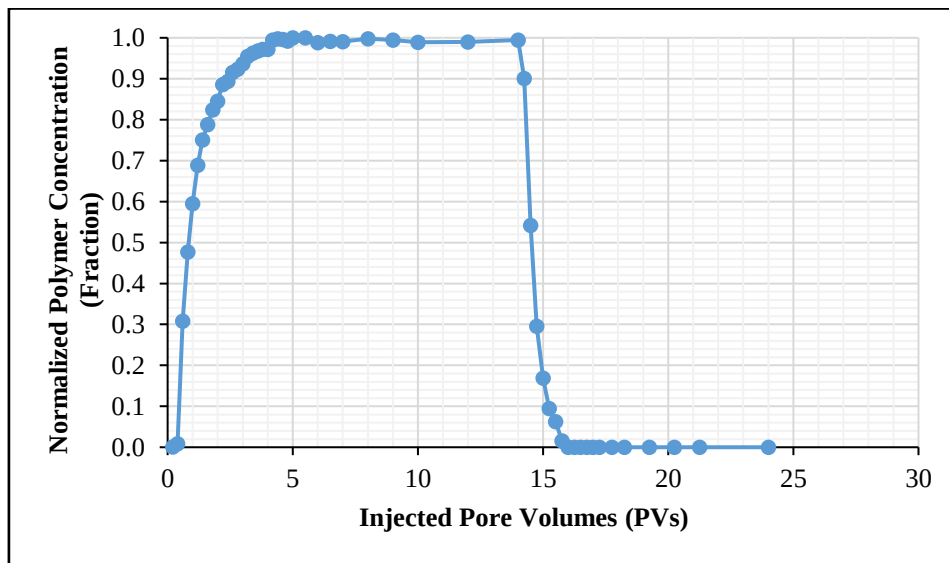


Figure 6.3: Typical normalized effluent polymer concentration profile (CF-16) at 25 °C.

6.3.2 Effect of Varying Ionic Compositions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) on In-Situ Rheology in the Absence and Presence of Oil

The resistance and residual resistance factors were calculated at a flow rate of 0.5 cc/min in both single-phase and two-phase experiments for brines with varying ionic composition. The resistance factor directly depends on the apparent viscosity of polymer solution in the porous media in case of 100% brine saturated cores (Figures 6.4 and 6.5). Figure 6.5 presents the

bulk viscosity, alongside the in-situ viscosity in both the absence and presence of oil, for the polymer solution across all examined brine compositions at a flow velocity of ~ 10 ft/d (0.5 cc/min). The observed in-situ viscosity in the absence of oil surpassed the bulk viscosity, indicating a pronounced shear thickening behavior. Also, the flow rate (0.5 cc/min) considered in the study was expected to fall within the flow regime associated with shear thickening behavior (Alfazazi *et al.*, 2021). Notably, the shear thickening behavior is more pronounced in SW-1B and SW-1C. This can be attributed to the observation that a reduction in brine hardness prompts a high shear thickening at a flow rate of 0.5 cc/min, resulting in elevated in-situ viscosities under these conditions (**Figure 6.5**) and consequently high RF (**Figure 6.4**).

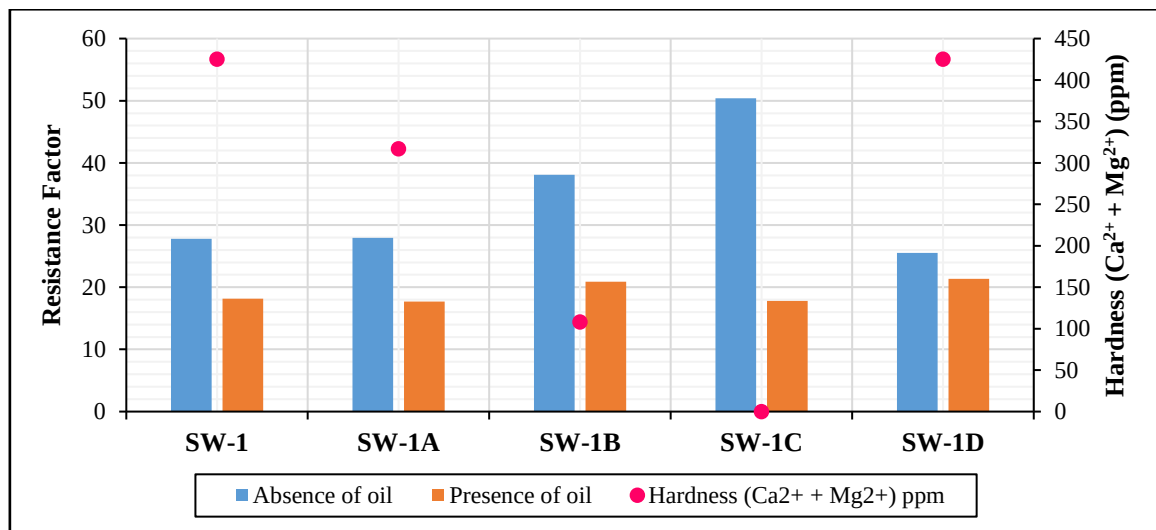


Figure 6.4: Effect of varying ion compositions on RF in the absence and presence of oil.

In addition, in the two-phase experiments, the in-situ viscosity consistently surpassed the bulk viscosity across all scenarios (**Figure 6.5**), pointing to a distinct shear thickening behavior. However, in-situ viscosity in the presence of oil for SW-1, SW-1A, SW-1B, SW-1C, and SW-1D were 7.48, 7.59, 8.94, 9.19, and 9.04, respectively, indicating less variation. This was reflected in the RF values 18.15, 17.69, 20.91, 17.78, and 21.36, respectively (**Figure 6.4**). RF and in-situ viscosity values imply that in the presence of oil even though the shear thickening behavior is observed, the magnitude of shear thickening is less, and hence, it results in lower RF compared to that of a single-phase experiments (Skauge *et al.*, 2018; Song *et al.*, 2022).

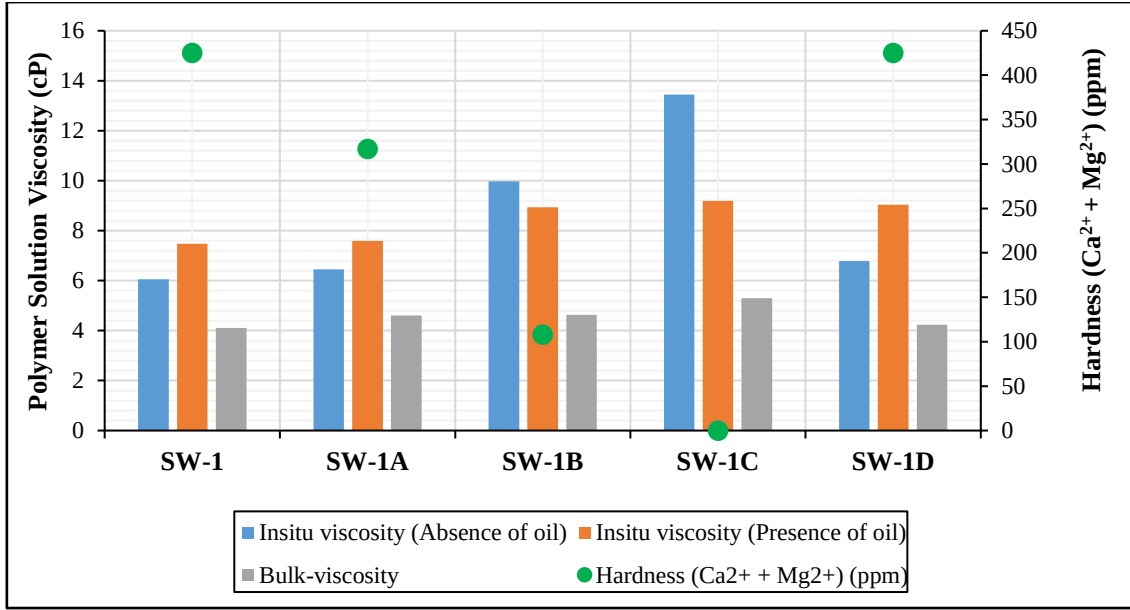


Figure 6.5: Effect of varying ion compositions on in-situ viscosity and bulk viscosity at 0.5 cc/min (~ 10 ft/d) and 25 °C.

As was previously mentioned, injectivity loss in polymer flooding refers to an increased resistance to flow of polymer solutions in the reservoir. This is due to the polymer molecules blocking the pore spaces because of interactions between the polymer and the reservoir rock. Such a loss can affect the efficiency of enhanced oil recovery operations using polymer flooding. **Table 6.3** details the injectivity loss in single-phase and two-phase coreflooding experiments using the brines with varying ionic compositions. In single-phase experiments, the polymer injectivity loss exceeded the acceptable range of 0.5-0.9 (Han *et al.*, 2012). This elevated injectivity loss is primarily attributed to the high in-situ viscosity observed consistently across tests. A notable factor in this regard is the consistent use of a 1,000-ppm polymer concentration for all brine compositions. This was chosen to investigate the impact of varying ionic compositions on polymer performance, but in turn, influenced the resulting viscosities for each brine composition. However, it is worth noting that even with this increased viscosity and reduced injectivity, **Figure 6.6** shows a steady differential pressure during polymer injection, suggesting no pore plugging arise from the viscosity increment. The latter figure describes the pressure differential profiles for the stages of brine preflush, polymer injection, and brine post-flush for all experiments with varying brine composition under both presence and absence of oil.

In two-phase experiments injectivity loss was slightly reduced compared to the single-phase experiments, but still exceeding the acceptable range of 0.5-0.9. The injectivity loss in

two-phase conditions is less than in single-phase, primarily due to the smoother flow of the polymer solution through porous media. For polymer flooding with SW-1, SW-1A, and SW-1D, the in-situ viscosity is greater in the presence of oil compared to its absence. This would typically suggest a greater injectivity loss in the presence of oil, but observations indicated otherwise. A key factor behind the smoother flow of the polymer solution is its reduced polymer retention when oil was present (**Figure 6.2**). Conversely, for SW-1B and SW-1C, the in-situ viscosity is lower in the presence of oil compared to its absence. Coupled with decreased polymer retention when oil is present, this leads to reduced injectivity loss in the absence of oil for both scenarios (Masalmeh *et al.*, 2019).

Table 6.3: Summary of injectivity loss during polymer injection for brines with varying ionic composition in the absence and presence of oil

Brine Type	Polymer Injectivity Loss	Polymer Injectivity Loss
	Single-Phase	Two-Phase
SW-1	0.96	0.94
SW-1A	0.96	0.94
SW-1B	0.97	0.95
SW-1C	0.98	0.94
SW-1D	0.96	0.95

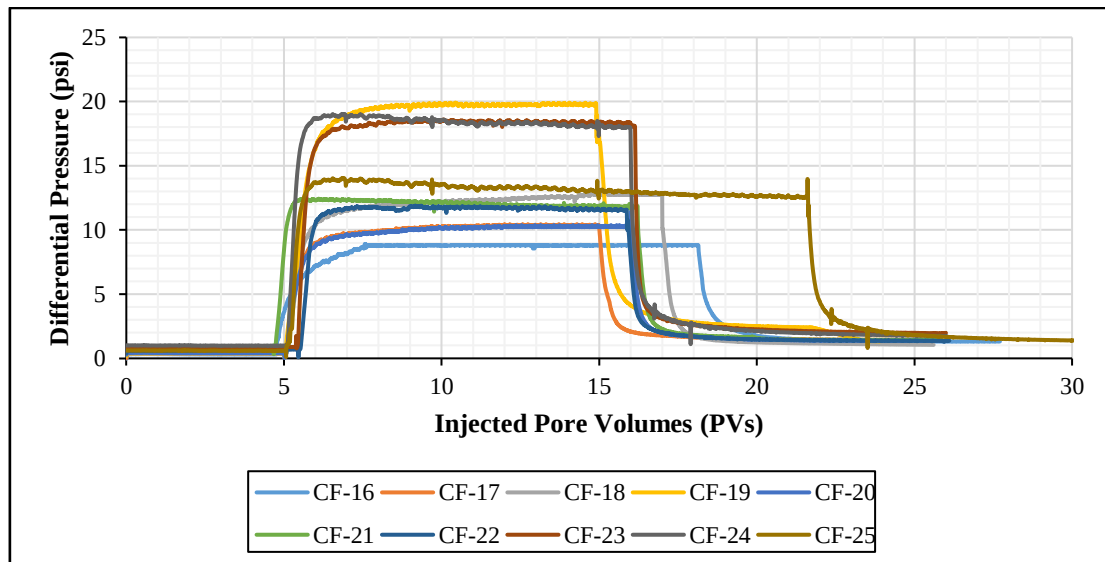


Figure 6.6: Pressure drop profile during brine pre-flush, polymer injection, and brine post-flush at a flow rate of 0.5 cc/min for CF-16 to CF-25.

6.3.3 Effect of Varying Ionic Compositions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) on Residual Resistance Factor and Polymer Adsorption Layer Thickness in the Absence and Presence of Oil

The residual resistance factor (RRF) indicates the permeability reduction due to the adsorbed layer of polymer onto the pore walls. **Figure 6.7** shows adsorbed polymer layer thickness for all coreflooding experiments with varying brine ionic composition in the absence and presence of oil. In the absence of oil, the adsorbed polymer layer thickness was less for coreflooding experiment with SW-1C brine (0 ppm of Ca^{2+} + Mg^{2+}) indicating less permeability reduction happened. This is also reflected by the low RRF (3.35) for SW-1C. Also, in two-phase coreflooding experiments, the adsorbed polymer layer thickness is less compared to the single-phase experiments, indicating low permeability reduction in oil-wet cores. Consequently, this implies low polymer adsorption. Therefore, the permeability reduction indicated by low RRF are in agreement with adsorption values observed in **Figure 6.2** for all cases.

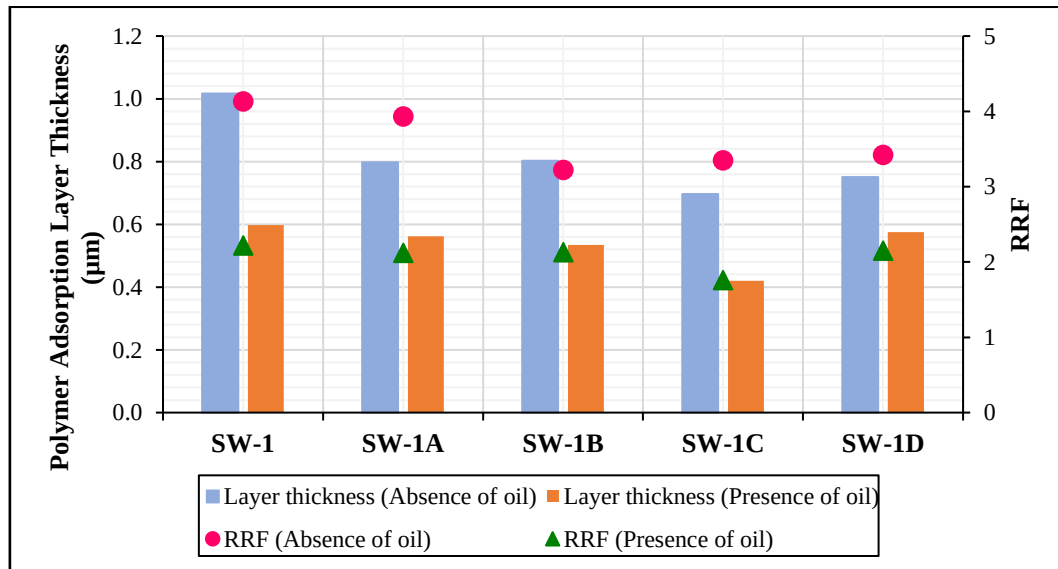


Figure 6.7: Summary of Residual Resistance Factor (RRF) and polymer adsorption layer thickness for all experiments with varying brine ionic composition.

6.3.4 Possible Desalination Methods for the Proposed Brine Compositions

Among the various brine compositions analyzed, SW-1B and SW-1C outperformed the other brine recipes. Both brines showed a reduced dynamic retention of 34 and 33 $\mu\text{g/g-rock}$ without oil, respectively and 20 $\mu\text{g/g-rock}$ with oil for each. A recommended desalination approach is to first dilute seawater five-times using the fresh water from reverse osmosis permeate. Subsequently, this diluted seawater should be processed through a nanofiltration unit to remove

Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions. The resulting nanofiltration permeates can then be supplemented with precise amounts of required ions to reach the desired brine composition.

Nevertheless, producing these specific compositions on a field-scale poses substantial challenges compared to simpler dilutions. Additionally, **Chapter 5** highlighted that a brine composition resulting from diluting seawater 100-times (SW-3), resulting in a salinity of 425 ppm, demonstrated even lower dynamic retention values of 24 $\mu\text{g/g-rock}$ without oil and 14 $\mu\text{g/g-rock}$ with oil. Given its practicality for larger-scale applications, brine composition with 100-times diluted seawater (SW-3) seems more favorable. Therefore, further research using this brine composition is recommended.

6.4 Highlights of the Chapter

- The ATBS-based polymer showed a positive result with the softened brines in terms of viscosity increase (by 1.5 times) and retention decrease (33 $\mu\text{g/g-rock}$ in the absence of oil and 20 $\mu\text{g/g-rock}$ in the presence of oil), which can significantly reduce polymer consumption.
- Lower polymer retention was observed in the presence of oil in aged cores compared to 100% water-saturated cores, concluding that a better representation of polymer adsorption was obtained in wettability-altered cores.
- Experiments using softened brine showed a lower residual resistance factor (RRF), which confirmed the lower polymer retention and indicated less permeability reduction.
- The highest resistance factor was observed in the brine with zero hardness. This is due to the direct proportionality of the resistance factor to the polymer's apparent viscosity.
- The resistance factor was lower in the presence of oil due to the improved polymer injectivity in the wettability-altered cores.

CHAPTER 7: EFFECT OF TEMPERATURE ON POLYMER ADSORPTION IN STATIC AND DYNAMIC CONDITIONS

Chapter 7 examines the influence of temperature on polymer adsorption, using formation water representative of middle eastern reservoirs, and 100-times diluted seawater (SW-3), which showed promising results in terms of enhanced polymer solution viscosity and reduced dynamic polymer retention. Initially, static adsorption studies in single-phase were conducted. Further, dynamic retention studies were performed in the absence and presence of oil to investigate more representative retention values. Moreover, the impact of temperature on in-situ rheology was studied.

7.1 Experimental Overview

Using the methodologies outlined in **Chapter 3**, the core plugs and polymer solutions were prepared and characterized. Static adsorption tests were conducted at various temperatures (25, 40, 60, 80, and 90 °C) under single-phase conditions. To accurately measure polymer retention, 12 dynamic retention experiments were executed: 8 in single-phase (without oil) across two salinity levels (167,114 ppm and 425 ppm) and at temperatures of 40, 60, 80, and 90 °C, and 4 in two-phase conditions (with oil) across the same two salinities, but only at 60 and 90 °C.

These findings were then compared with the data from ambient temperature studies (25 °C) reported in **Chapter 5**. The properties and experimental parameters of the utilized outcrops are detailed in **Tables 7.1** and **7.2**. Due to high temperature conditions, oxygen control measures were taken for the polymer solutions. These polymer solutions underwent vacuuming and bubbled with nitrogen to remove air; subsequently, filled into accumulator that was pre-flushed with nitrogen to remove oxygen. Oxygen scavenger (200-ppm Sodium Thiourea) was added to remove any remaining oxygen and act as a buffer for residual oxygen from other sources.

Table 7.1: Petrophysical properties of core samples and experimental conditions applied for elevated temperatures in single-phase coreflooding experiments

Core ID (Single-phase Tests)	CF-26	CF-27	CF-28	CF-29	CF-30	CF-31	CF-32	CF-33
Connate Water/ Injection Water Salinity, TDS (ppm)	167,114 FW				425 SW-3			
Polymer Concentration (ppm)	1000							
Length (cm)	7.34	7.23	7.30	6.97	6.20	6.10	6.30	7.70
Diameter (cm)	3.80	3.80	3.80	3.76	3.80	3.81	3.80	3.80
Porosity (%)	17	18	17	18	18	19	18	19
Absolute Brine Permeability (mD)	250	238	216	208	205	207	223	210
Temperature (°C)	40	60	80	90	40	60	80	90
Confining Pressure (psi)	1200							
Backpressure (psi)	100							

Table 7.2: Petrophysical properties of core samples and experimental conditions applied for elevated temperatures in two-phase coreflooding experiments

Core ID (Two-phase Tests)	CF-34	CF-35	CF-36	CF-37
Connate Water/ Injection Water Salinity, TDS (ppm)	167,114 FW		425 SW-3	
Polymer Concentration (ppm)	1000			
Length (cm)	6.46	6.23	6.93	6.38
Diameter (cm)	3.80	3.80	3.80	3.80
Porosity (%)	17	17	18	19
Absolute Brine Permeability (mD)	290	287	272	271
S _{wi} (%)	35	36	36	39
S _{or} (%)	38	38	37	36
Temperature (°C)	60	90	60	90
Confining Pressure (psi)	1200			
Backpressure (psi)	100			

7.2 Static Adsorption Studies

Following the procedure outlined in **Chapter 3**, static adsorption experiments were conducted in single-phase to assess the impact of temperature on polymer adsorption.

7.2.1 Effect of Temperature on Static Polymer Adsorption

BET surface area of crushed core samples used was $0.73 \text{ m}^2/\text{g}$ for experiments conducted at varying temperatures (25, 40, 60, 80, and 90°C) with high salinity formation water (167,114 ppm). Nevertheless, for low salinity brine (425 ppm), the experiments were carried out at the same range of temperatures, but with samples BET surface area of $1.33 \text{ m}^2/\text{g}$.

Figure 7.1 provides a clear insight into the influence of temperature on the static adsorption of the polymer solutions, when analyzing the polymer solutions in both high and low salinity brines. For the polymer solution with high salinity (167,114 ppm), there is a noticeable decrease in static polymer adsorption with the increase in temperature. At 25°C , the adsorption stands at $250 \text{ }\mu\text{g/g-rock}$, which drops down to $100 \text{ }\mu\text{g/g-rock}$ by the time the temperature reaches 90°C . This represents a substantial reduction of approximately 60% in adsorption values from the starting temperature. Similarly, for the polymer solution in low salinity (425 ppm), the decline trend continues, though the starting value is lower at $54 \text{ }\mu\text{g/g-rock}$ at 25°C and concludes at $25 \text{ }\mu\text{g/g-rock}$ at 90°C .

The underlying reason for this observed trend can be attributed to two mechanism one is the reduced hydrodynamic size of the polymer solution (Samanta *et al.*, 2010; Sandengen *et al.*, 2017) at high temperature due to decreased brine viscosity, which increases the polymer adsorption as a greater number of polymer molecules are required to satisfy the adsorption sites. And the second phenomena is the changes in kinetic energy of polymer molecules with temperature. As temperature increases, the kinetic energy of polymer molecules increases. This enhanced kinetic energy causes the polymer molecules to move at a faster pace. With increased movement, the average distance between the polymer molecules widens. As a result, the electrostatic force of attraction, which is crucial in adhering polymers to rock surfaces, becomes weaker due to the increased distance. The weakening of this force translates to reduced polymer adsorption onto the rock surfaces. In principle, the increased kinetic energy at elevated temperatures results in the polymer molecules moving more swiftly and energetically, thereby diminishing their binding or adsorption potential on the rocks (Sabhapondit *et al.*, 2004; Wiśniewska, 2012; Mansoori *et al.*, 2023). Considering the above two-phenomena, it seems that in static adsorption the reduced adsorption due to weaker intermolecular forces is

prominent resulting in a decreasing trend of polymer adsorption with increasing temperature. This behavior is consistent for both high and low salinity polymer solutions. The adsorption values for low salinity polymer were less compared to the high salinity polymer despite having higher BET surface area for the crushed rock sample used for low salinity polymer adsorption studies ($1.33 \text{ m}^2/\text{g}$). This suggests that while salinity can affect polymer adsorption, the trend of decreasing adsorption with increasing temperature remains consistent.

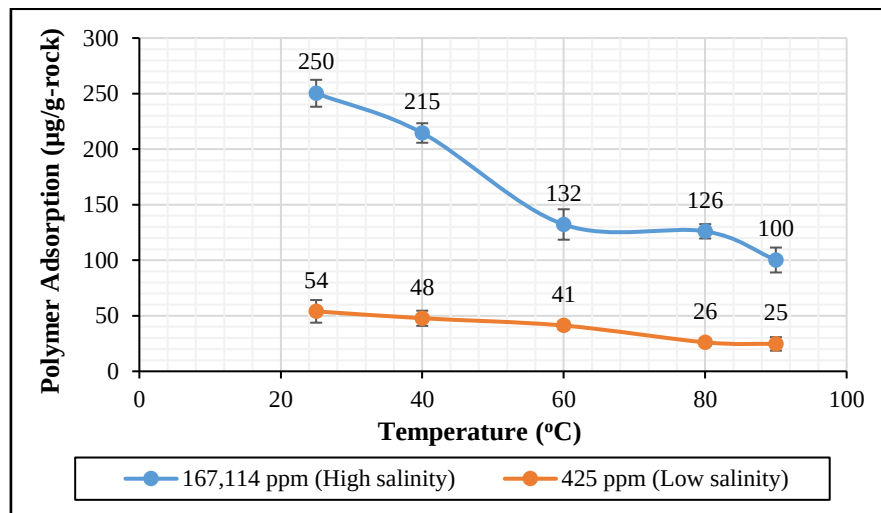


Figure 7.1: Effect of temperature on static polymer adsorption in high salinity and low salinity brine conditions.

7.3 Dynamic Retention Studies

Following the procedure outlined in **Chapter 3**, dynamic retention studies were conducted in both the absence and presence of oil at varying temperatures to determine representative retention values. Additionally, the effects of temperature on the resistance factor and residual resistance factor were examined. The results were then compared with the retention value at 25°C presented in **Chapter 5**.

7.3.1 Effect of Temperature on Dynamic Polymer Retention in the Absence and Presence of Oil

The dynamic polymer retention observed in polymer solutions of high (167,114 ppm) and low salinities (425 ppm), across different temperatures (25, 40, 60, 80, and 90°C) in the absence and presence of oil are presented in **Figures 7.2** and **7.3**, respectively. In the absence of oil (**Figure 7.2**), the retention rates for the high salinity solution were 56, 53, 45, 45, and 46 µg/g-rock at 25, 40, 60, 80, and 90°C , respectively. Similarly, for the low salinity solution without

oil, the dynamic retention values were 24 $\mu\text{g/g-rock}$ for both 25°C and 40°C, 20 $\mu\text{g/g-rock}$ at 60°C, and 19 and 20 $\mu\text{g/g-rock}$ at 80°C and 90°C, respectively. Furthermore, using the error propagation theory, an uncertainty of ± 5 $\mu\text{g/g-rock}$ was noted (**Table 5.3**). This suggests a relatively similar retention values in oil-free conditions for both salinities.

On the other hand, when oil was introduced (**Figure 7.3**), the high salinity solution showed retention levels of 26, 21, and 23 $\mu\text{g/g-rock}$ at 25, 60, and 90 °C, respectively. While the low salinity solution in the presence of oil yielded 14, 13, and 12 $\mu\text{g/g-rock}$ at the aforementioned temperatures, respectively. In this case, an uncertainty of ± 3 $\mu\text{g/g-rock}$ was identified (**Table 5.5**). Notably, the trend also indicates that dynamic retention remains largely unaffected by temperature variations (Rashidi *et al.*, 2011), which is consistent with the results presented in single-phase conditions.

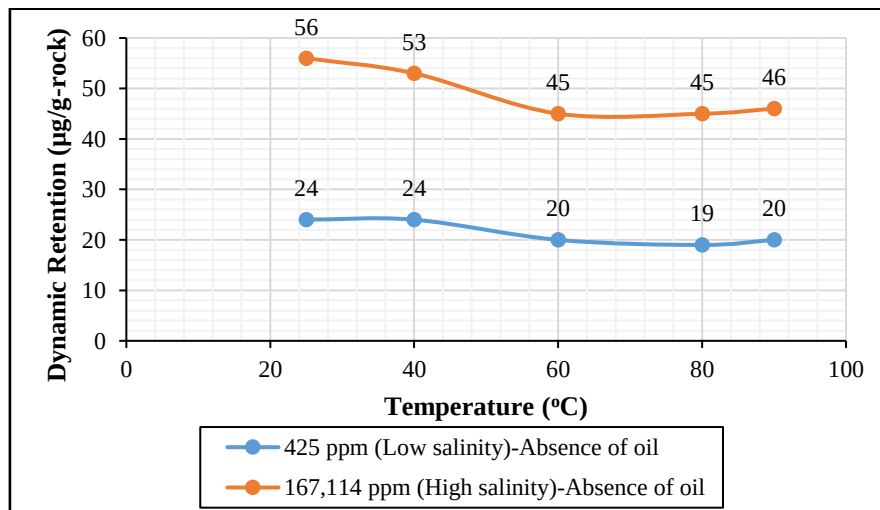


Figure 7.2: Effect of temperature on dynamic polymer retention in the absence of oil.

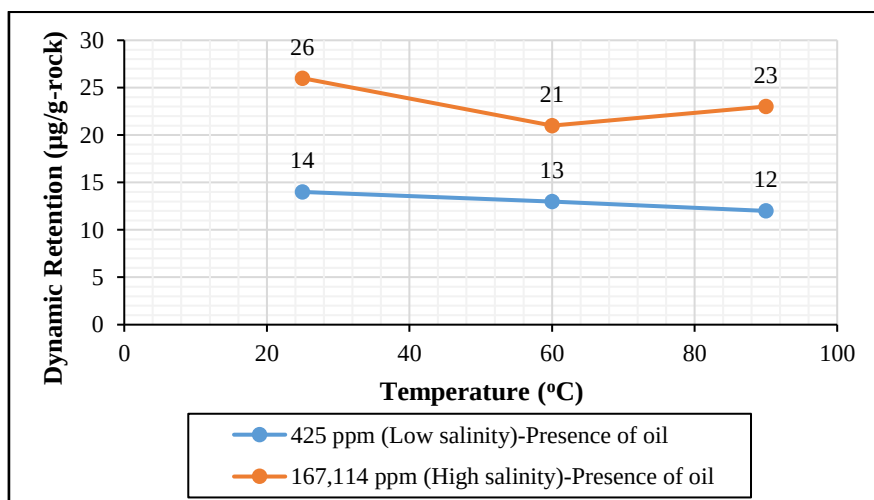


Figure 7.3: Effect of temperature on dynamic polymer retention in the presence of oil.

The ATBS-based polymer under consideration shows commendable stability at elevated temperatures. This stability prevents the occurrence of precipitation, ensuring that retention levels remain relatively consistent as the temperature escalates (Dupuis *et al.*, 2017; Alfazazi *et al.*, 2018; Jouenne, 2020). However, it is noteworthy that despite the absence of chain degradation, there is a distinct reduction in viscosity as temperature increases. This is due to a conformational alteration in the polymer which results in a more coiled structure, reducing its hydrodynamic size (Samanta *et al.*, 2010; Sandengen *et al.*, 2017). This newly adopted configuration requires larger polymer molecules to satisfy the adsorption sites, potentially amplifying retention. Conversely, the elevation in temperature weakens the intermolecular forces binding the polymer to the adsorbent, which could lead to a decline in retention (Sabhaponnit *et al.*, 2004; Sazali *et al.*, 2019). This contrast, i.e., a change in the polymer's conformation and the weakening of binding forces, poses opposing effects. In dynamic coreflooding experiments, which are characterized by a relatively smaller surface area compared to static studies, these competing factors seem to counterbalance each other. As a result, the experiments do not reflect a drastic influence of temperature on polymer retention.

7.3.2 Effect of Temperature on In-Situ Rheology in the Absence and Presence of Oil

The resistance factor (RF) across various salinities and temperatures for all coreflooding experiments (CF-26 – CF-37), both in the presence and absence of oil are illustrated in **Figure 7.4**. In single-phase coreflooding experiments conducted with polymer solution in high salinity, the resistance factor (RF) exhibited values of 9.00, 8.59, 6.92, 6.67, and 6.69 at temperatures of 25, 40, 60, 80, and 90 °C, respectively. This suggests that temperature had a less influence on the resistance factor under high salinity conditions. Conversely, during low salinity polymer flooding experiments, a clear temperature-dependent trend emerged; RF values decreased as temperature increased, yielding values of 43.02, 35.38, 30.82, 29.91, and 24.80 for temperatures of 25, 40, 60, 80, and 90°C, respectively.

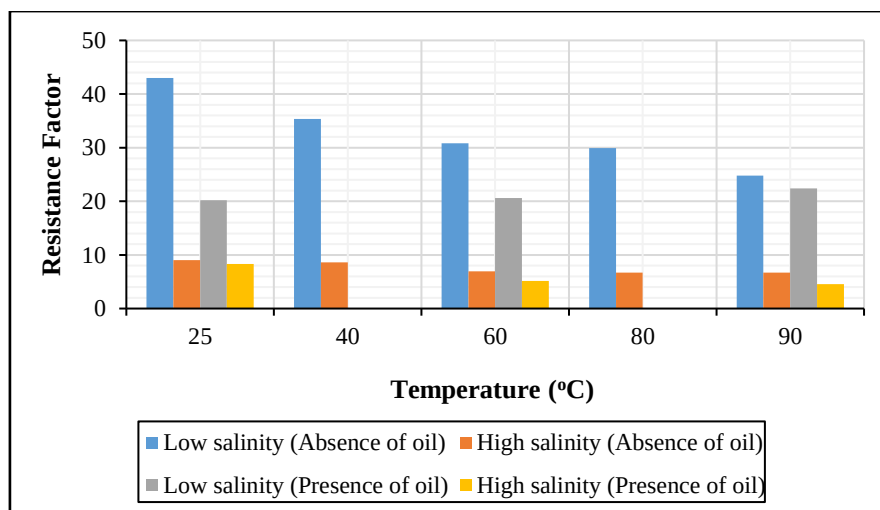


Figure 7.4: Effect of temperature on RF across various salinities in the absence and presence of oil.

Figures 4.8 and 4.9 from Chapter 4 illustrate a congruent temperature-driven change in the viscosities of both the polymer solution and the brine. Given this parallel behavior, one might expect RF to remain consistent across varying temperatures. However, a reduction in RF values at higher temperatures, particularly for the low salinity polymer flooding was observed. This can be attributed to the variances in bulk and in-situ viscosity, given that the resistance factor is dependent on in-situ viscosity. **Figure 7.5** underscores that the in-situ viscosity of the polymer solution in low salinity (425 ppm) brine reduces with increasing temperatures, a trend mirrored in its RF during single-phase experiments. The underlying mechanism for this behavior is that no shear thickening was observed at elevated temperatures at flow rate of 0.5 cc/min (Heemskerk *et al.*, 1984; Qi *et al.*, 2018). Interestingly, this pattern was absent in high salinity experiments indicating that shear thickening phenomena was not observed for high salinity conditions across the varying temperatures at a flow rate of 0.5 cc/min (Skauge *et al.*, 2018). This results in negligible alterations between bulk and in-situ viscosity across the temperatures (Al-Shakry *et al.*, 2018), which is supported in **Figure 7.5**.

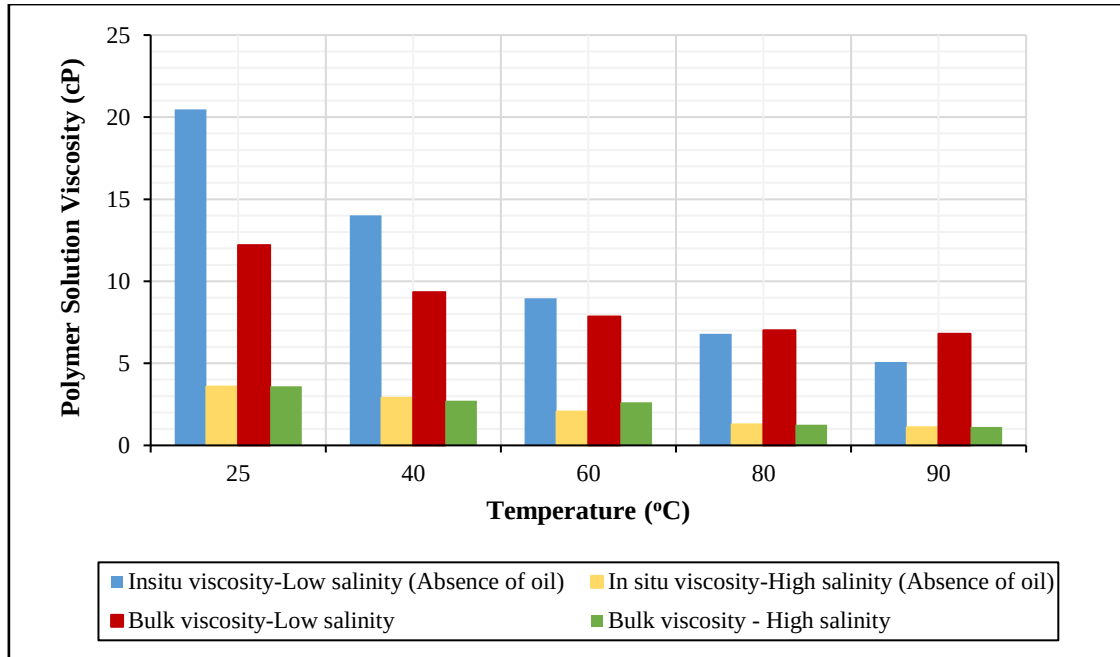


Figure 7.5: Effect of temperature on in-situ viscosity across various salinities in the absence of oil.

In two-phase coreflooding experiments, high salinity conditions at temperatures of 25, 60, and 90 °C yielded resistance factor (RF) values of 8.31, 5.12, and 4.56, respectively. Meanwhile, under low salinity polymer flooding conditions (425 ppm), the RF values were 20.22, 20.63, and 22.40 for the same respective temperatures. Notably, temperature exhibited a minimal influence on the RF. This is because in-situ viscosity was almost similar to the bulk viscosity in both salinity scenarios (**Figure 7.6**) as shear thickening behavior was less due to the oil presence. In addition, it was already discussed in **Chapter 4 (Figures 4.8 and 4.9)** that as temperature increases, the reduction in viscosities of both the polymer solution and brine parallels, leading to a consistent RF across varying temperatures in the absence of shear thickening behavior.

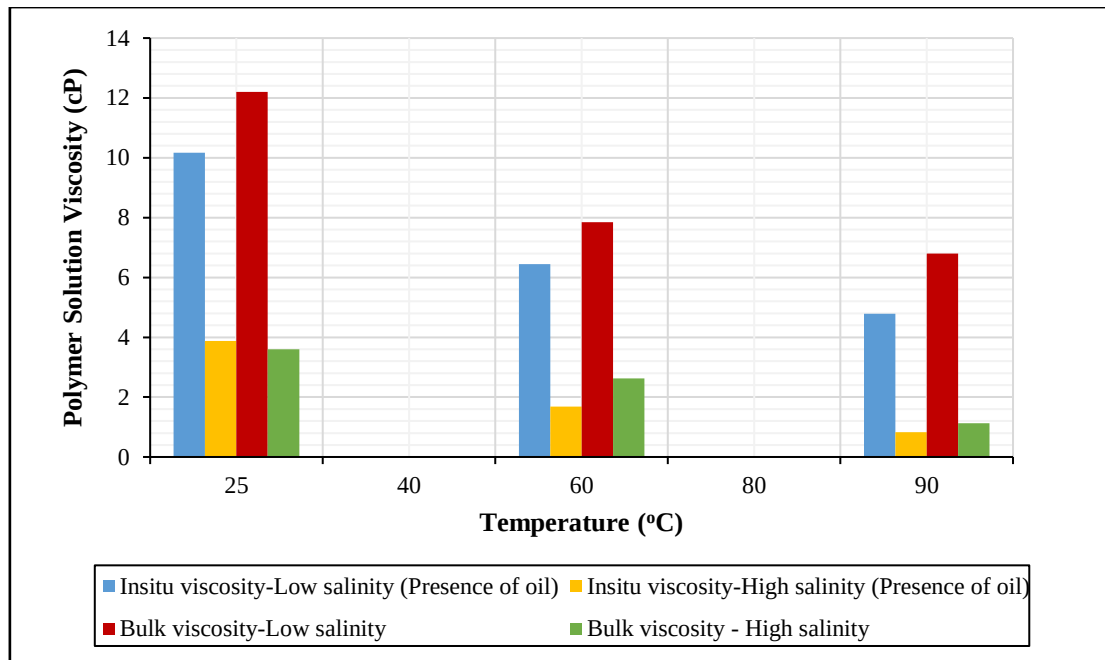


Figure 7.6: Effect of temperature on in-situ viscosity across various salinities in the presence of oil.

From **Table 7.3**, it is evident that injectivity loss is within the acceptable limit of 0.5 - 0.9 for polymer flooding with high salinity brine (167,114 ppm) across various temperatures and in the presence and absence of oil. However, high injectivity loss was observed for polymer flooding with low salinity (425 ppm) (> 0.9), particularly in the single-phase experiments. This is due to the use of same polymer concentration (1,000 ppm) for both salinity ranges, for studying the effect of various other parameters on dynamic polymer retention. However, from the pressure drop profiles (**Figure 7.7**), it is evident that there is no injectivity issues encountered with low salinity polymer flooding. One can also observe the improvement in polymer injectivity with increasing temperature in general, particularly for the high salinity water and in the presence of oil, which is mainly due to the lubrication effect of oil on the polymer solution as well as the less pronounced shear-thickening effect.

Table 7.3: Summary of injectivity loss during polymer injection across various temperatures

Brine Salinity (ppm)	Temperature (°C)	Polymer Injectivity Loss	Polymer Injectivity Loss
		Single-Phase	Two-Phase
167,114	25	0.89	0.88
	40	0.88	-
	60	0.86	0.80
	80	0.85	-
	90	0.85	0.78
425	25	0.98	0.95
	40	0.97	-
	60	0.97	0.95
	80	0.97	-
	90	0.96	0.96

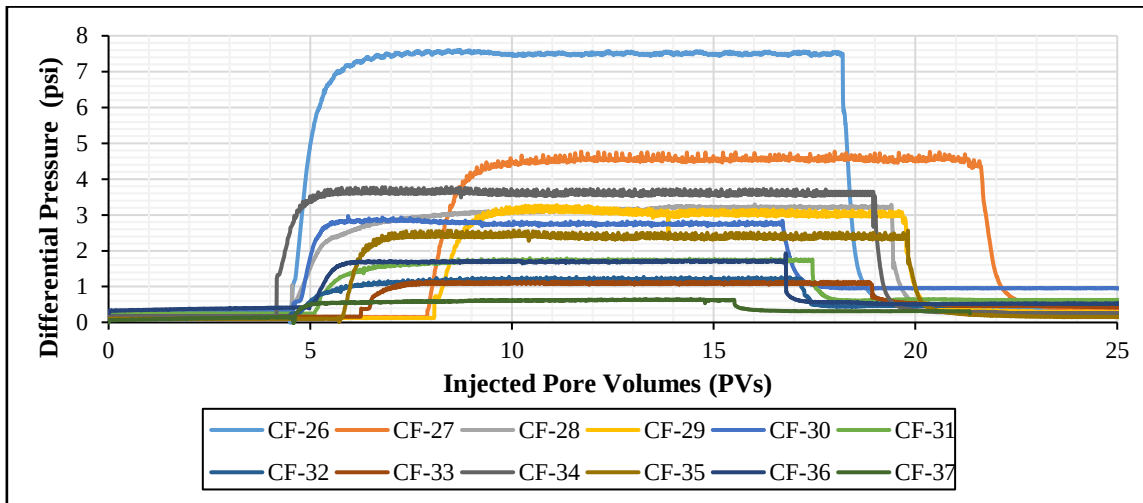


Figure 7.7: Differential pressure drop profiles for CF-26 – CF-37.

7.3.3 Effect of Temperature on Residual Resistance Factor and Polymer Adsorption Layer Thickness in the Absence and Presence of Oil

Residual Resistance Factor is a measure of the change in permeability of the reservoir due to polymer retention during polymer flooding operations. **Figures 7.8 and 7.9** illustrate consistent RRF values and polymer adsorption layer thickness across different temperatures for both salinity levels. In single-phase coreflooding experiments, RRF for high salinity polymer flooding for various temperature 25, 40, 60, 80, and 90 °C were 3, 3, 2.52, 2.56, and 2.56, respectively (**Figure 7.8**). Moreover, for low salinity polymer flooding, the RRF values for the same temperature range were 1.87, 1.64, 1.58, 1.54, and 1.51, respectively (**Figure 7.8**). Furthermore, the polymer adsorption layer thickness ranged between 0.85 - 0.63 μm and 0.46

- 0.29 μm for high salinity and low salinity polymer flooding, respectively across the aforementioned temperatures.

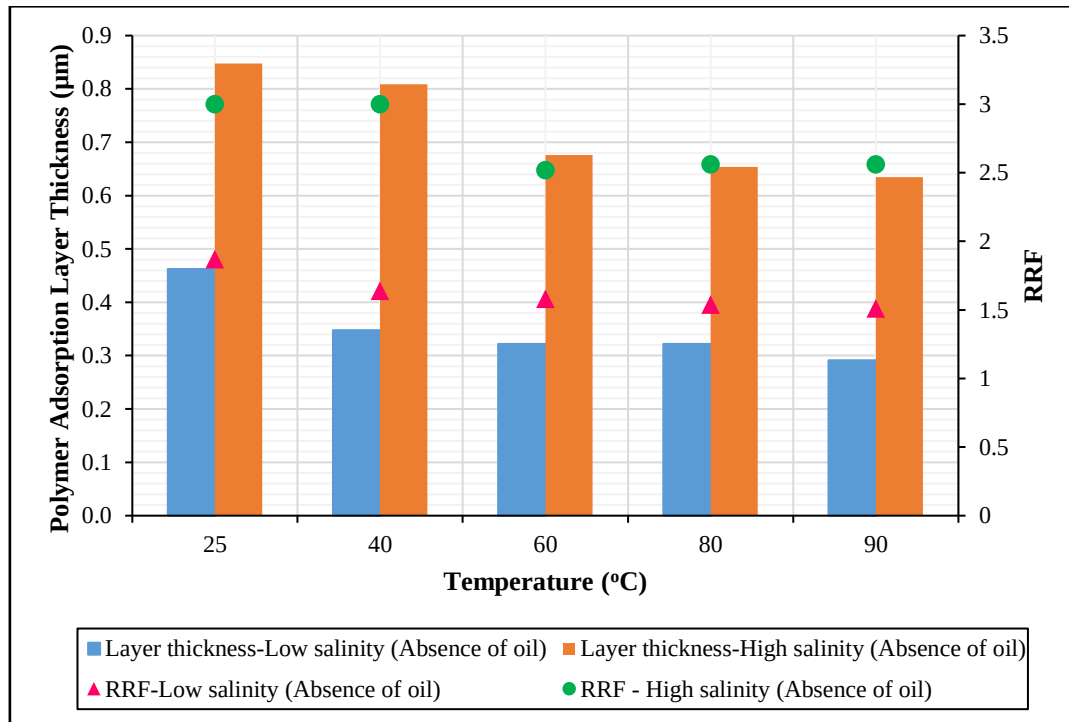


Figure 7.8: Summary of RRF and polymer adsorption layer thickness across various temperature in the absence of oil.

In two-phase coreflooding experiments, the RRF for high salinity polymer flooding were 2.56, 2.28, and 2.32, for temperatures 25, 60, and 90 °C, respectively. Moreover, for low salinity polymer flooding, the RRF were 1.77, 1.47, and 1.45, respectively for the above-mentioned temperatures. The polymer adsorption layer thickness was 0.67, 0.69, and 0.69 μm for high salinity polymer flooding, and 0.45, 0.32, and 0.30 μm for low salinity polymer flooding at temperature conditions for 25, 60, and 90 °C, respectively.

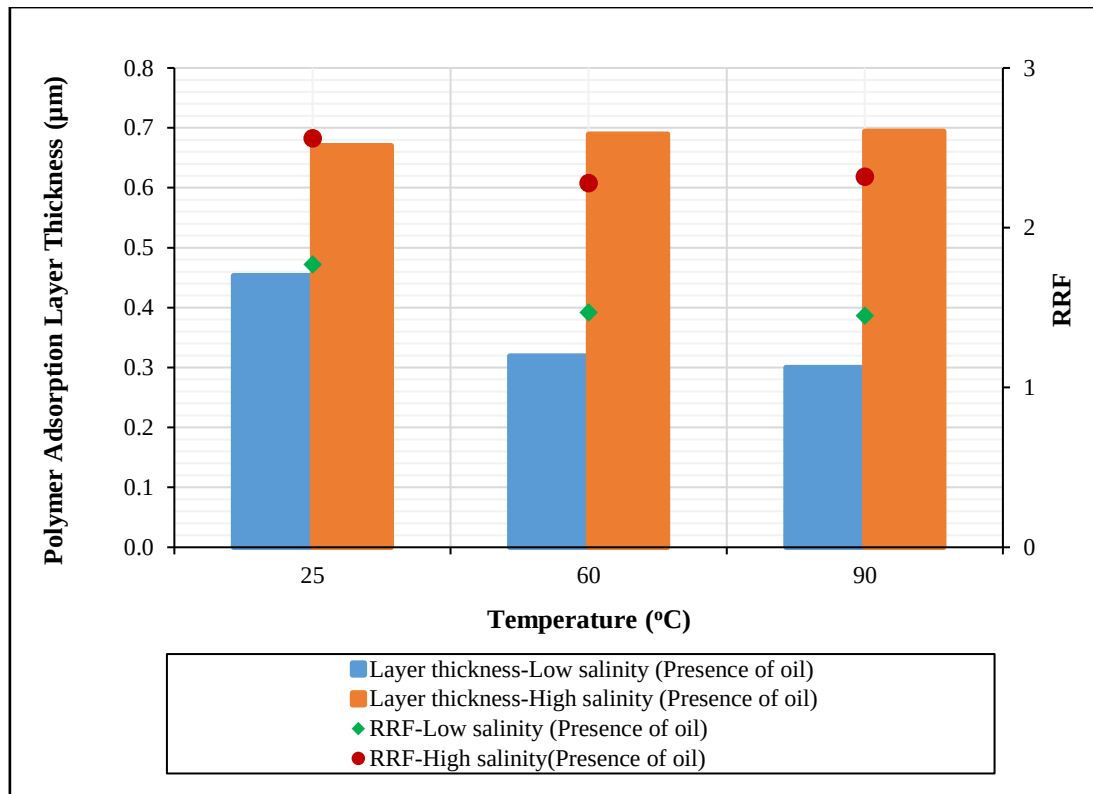


Figure 7.9: Summary of RRF and polymer adsorption layer thickness across various temperatures in the presence of oil.

In general, the findings show a consistent RRF and polymer adsorption layer thickness across different temperatures in the absence and presence of oil. This suggests that the polymer's impact on the reservoir's permeability remains relatively uniform throughout the temperature range studied. This consistency supports the observation that dynamic retention remained largely unchanged throughout the studied temperature range.

7.4 Highlights of the Chapter

This chapter investigated the proposed low salinity polymer flooding in representative reservoir conditions of high temperature along with the effect of temperature variation on polymer retention. The main findings can be summarized as follows:

- Static polymer adsorption showed a decreasing trend with increasing temperature. However, dynamic polymer retention was consistent across the considered temperature range (25 – 90 °C) for both single- and two-phase studies.
- The findings regarding dynamic polymer retention results were substantiated by comparable residual resistance factors across varying temperatures.

- Higher temperatures have shown less polymer shear thickening behavior, especially in the presence of oil, which further improved polymer injectivity.
- Overall, the study concludes that low salinity polymer flooding can reduce polymer retention to as low as 12 $\mu\text{g/g}$ -rock in the oil-wet conditions at representative reservoir conditions.

CHAPTER 8: DEVELOPMENT OF CORRELATION FOR DYNAMIC RETENTION USING MACHINE LEARNING

Chapter 8 focuses on establishing a correlation to predict dynamic retention based on static adsorption experimental data. Static adsorption experiments were conducted, maintaining identical experimental conditions to those of dynamic retention. A subsequent analysis was then undertaken to understand the relationship between static adsorption and dynamic retention. For a more accurate prediction of dynamic retention, additional influencing parameters, such as average pore throat size, total salinity, hardness, residual oil saturation, and temperature, were also considered. The prediction of dynamic retention from static adsorption and these influencing factors was achieved using various tree-based machine-learning algorithms. Ultimately, symbolic regression was employed to derive an explicit correlation equation, which captures the relationship between dynamic retention and its influencing parameters.

8.1 Experimental Materials

The crushed rock powder and polymer solutions were characterized and prepared using the methods described in **Chapter 3**. All the brines with varying salinities (**Tables 3.1** and **3.2**) discussed in **Chapter 5** and brines with varying ionic compositions (**Table 3.3**) discussed in **Chapter 6** were used for preparing polymer solution and conducting static adsorption studies. A total of 36 static adsorption experiments were conducted by varying salinities, ionic compositions, and temperatures. These static adsorption experiments have similar experimental conditions to that of dynamic retention experiments discussed in **Chapters 5, 6, and 7**. The crushed rock powder utilized in each experiment was derived from the same core used for dynamic retention studies. Before the experiments, a thin section of this core was taken and crushed to the desired particle size. The weight of the rock powder used in static studies was determined based on the consideration of keeping same surface access for both dynamic retention experiments and static adsorption experiments. This was achieved by considering surface area of core and crushed rock powder, inaccessible pore volume, and additionally residual oil saturation in the case of dynamic retention experiments in the presence of oil. The amount of polymer solution was also honored based on the liquid-to-solid ratio in the corresponding dynamic retention experiments.

8.2 Specific Surface Area of Crushed Core and Core Plugs

The specific surface area of crushed rock and core plug was obtained from BET and MICP experiments, respectively. BET and MICP experiments were conducted for the crushed rock powder of particle size 63 -250 microns and the end trims representative of the rock powder and core plugs used for static adsorption and dynamic retention studies respectively. BET and MICP results of crushed rock (CR-36) and core plug (CF-36) respectively will be discussed in the upcoming sections.

8.2.1 BET Results

The BET surface area of the crushed rock (CR-36) was obtained as $0.98 \text{ m}^2/\text{g}$ from BET plot (Figure 8.1), and following the approach described in **Chapter 3, Section 3.2.5.2**.

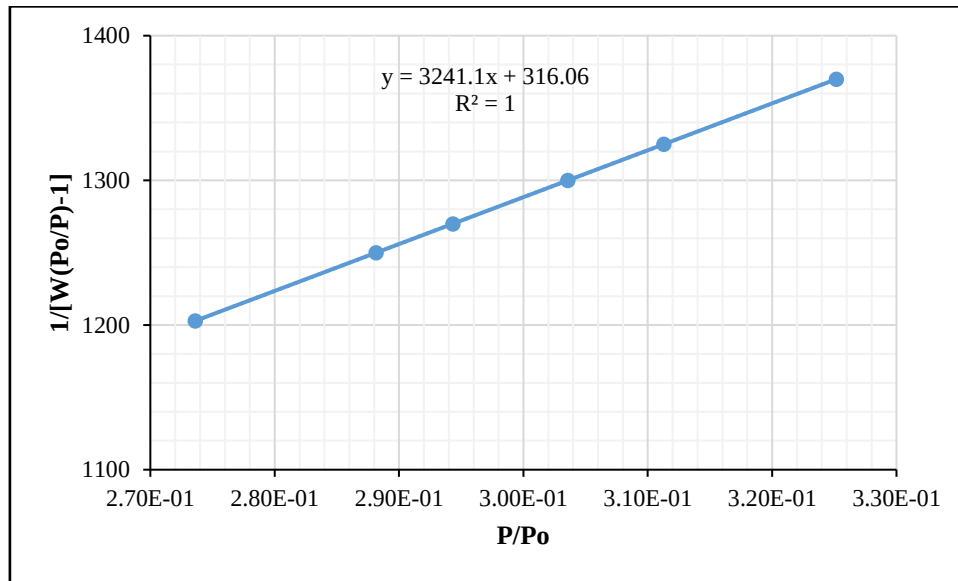


Figure 8.1: BET plot for CR-36.

8.2.2 MICP Results

The specific surface area of the core plug CF-36 was determined as $0.47 \text{ m}^2/\text{g}$ from pore throat distribution data, and following the approach described in **Chapter 3, Sections 3.2.6.3, 3.2.6.4, and 3.4.2** and utilizing the hydrodynamic size of the polymer depicted in **Chapter 4 (Figures 4.11, 4.12, and 4.13)**. The mercury intrusion curve for Indiana limestone outcrop (CF-36) is illustrated in **Figure 8.2**. This curve provides insight into the distribution of pore throat sizes and pore structure of the rock sample. The curve starts from 1 (or 100% saturation) and

decreases to 0, representing the process of mercury progressively saturating the rock's pores as pressure increases. The pressure varies across multiple orders of magnitude, from 1 psi to 100,000 psi. This wide range indicates the rock has a varied pore throat size distribution, with mercury intruding into larger pores at lower pressures and smaller pores at higher pressures.

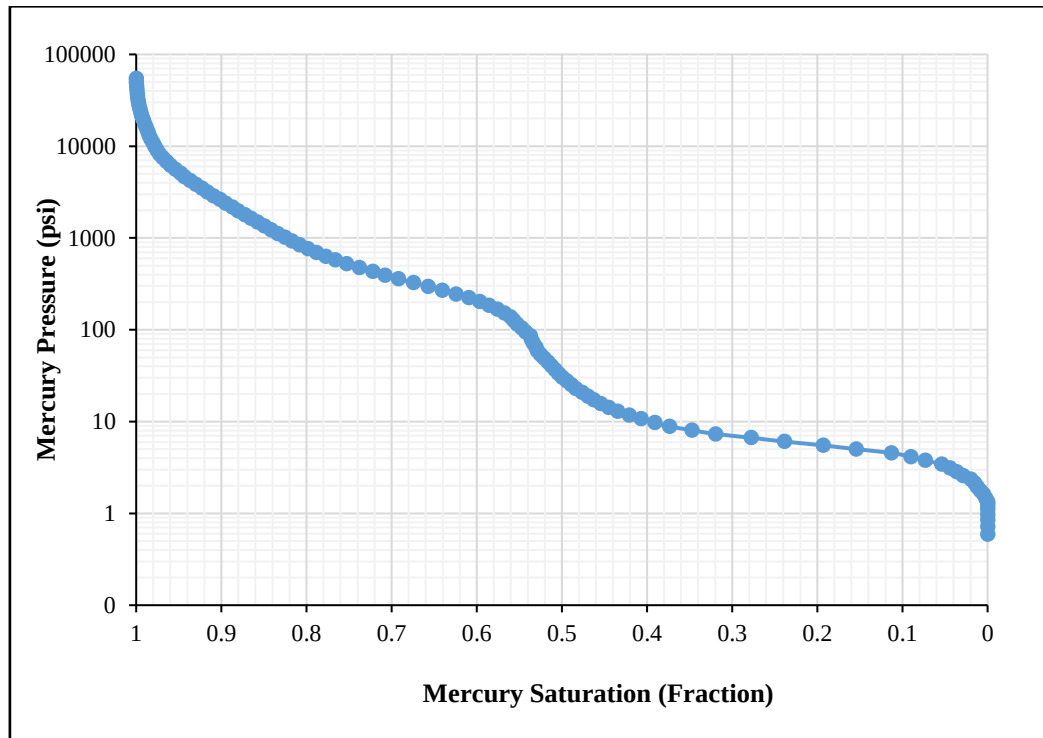


Figure 8.2: Mercury intrusion curve for Indiana limestone outcrop (CF-36).

Pore throat size distribution for the sample was deduced from the mercury intrusion capillary pressure (MICP) metrics, as illustrated in **Figure 8.3**. The graph displays three categories of pores: micropores, mesopores, and macropores. Micropores are the smallest pores and are seen at the far left of the graph between 0.001 and 0.01 microns. Mesopores lie in the intermediate range and can be observed between roughly 0.01 to 10 microns. This region displays a slight peak, suggesting a moderate concentration of meso-pores. Macropores are the largest pores and are represented between 10 to 100 microns. This region exhibits the most significant peak, indicating that the sample has a substantial proportion of macro-pores. The highest peak in the macro region suggests that the rock has a dominant macro-pore network indicating good permeability. The continuous nature of the curve without any sharp drops or flat regions suggests good pore connectivity in the rock. Moreover, the rock sample appears to be heterogeneous with a wide range of pore sizes.

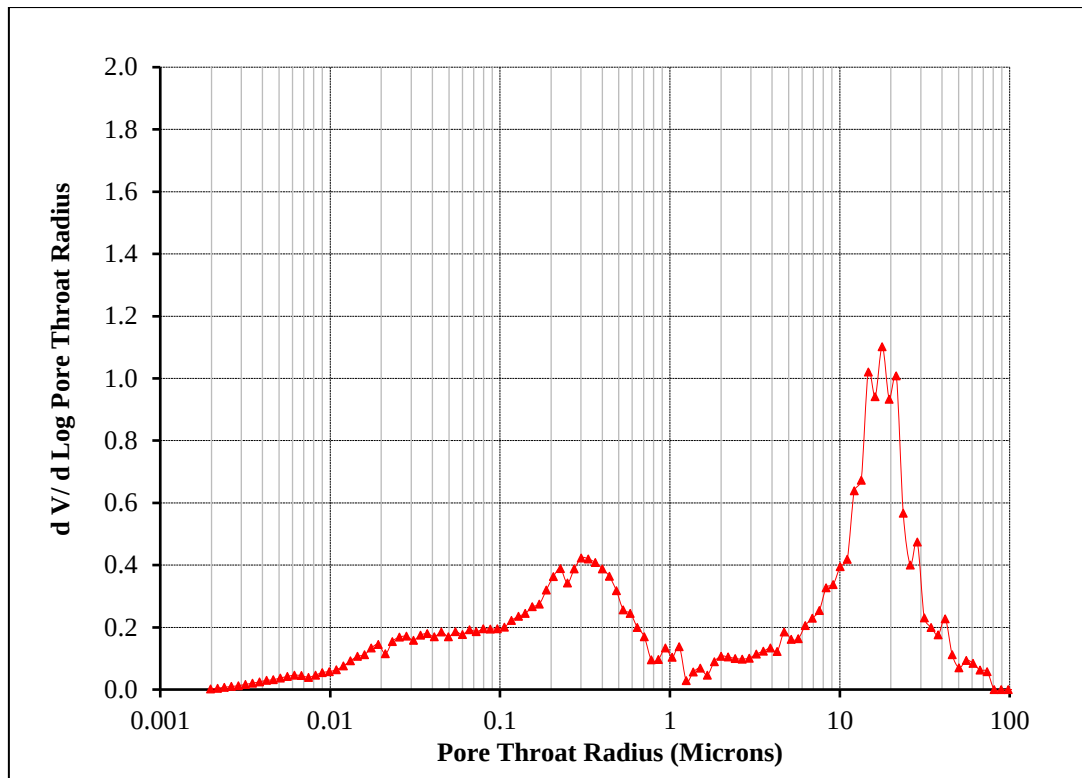


Figure 8.3: Pore throat size distribution plot from MICP for outcrop (CF-36).

The ascertained surface area of both crushed rock and core plug was used for determining the quantity of crushed rock powder needed for static adsorption experiments. **Table 8.1** represents the total surface area for the core samples, S_{MICP} (m^2/g), inaccessible pore volume, IPV (%), residual oil saturation, S_{or} (%), and accessible surface area (m^2/g) (by deducing IPV and S_{or} from total surface area).

Table 8.1: Summary of inaccessible pore volume and accessible surface area of the core plugs

Core No.	Core-ID	S_{MCP} (m ² /g)	IPV (%)	S_{or} (%)	Accessible Surface Area (m ² /g)
1	CF-1	0.49	22	0	0.38
2	CF-2	0.50	16	0	0.41
3	CF-3	0.50	16	0	0.41
4	CF-4	0.50	16	0	0.42
5	CF-5	0.51	20	0	0.41
6	CF-6	0.58	17	0	0.48
7	CF-7	0.58	17	0	0.49
8	CF-9	0.60	13	35	0.34
9	CF-10	0.63	15	34	0.35
10	CF-11	0.70	19	35	0.37
11	CF-12	0.75	15	35	0.41
12	CF-13	0.75	15	38	0.39
13	CF-14	0.78	15	31	0.46
14	CF-15	0.90	18	39	0.45
15	CF-16	0.53	13	0	0.46
16	CF-17	0.58	20	0	0.47
17	CF-18	0.63	25	0	0.47
18	CF-19	0.56	14	0	0.48
19	CF-20	0.52	11	0	0.46
20	CF-21	0.67	18	37	0.34
21	CF-22	0.69	16	37	0.36
22	CF-23	0.68	14	37	0.37
23	CF-24	0.81	19	36	0.42
24	CF-25	0.70	18	34	0.38
25	CF-26	0.49	21	0	0.39
26	CF-27	0.48	16	0	0.40
27	CF-28	0.48	16	0	0.40
28	CF-29	0.48	16	0	0.40
29	CF-30	0.60	18	0	0.50
30	CF-31	0.59	16	0	0.49
31	CF-32	0.61	18	0	0.50
32	CF-33	0.61	17	0	0.50
33	CF-34	0.64	20	38	0.32
34	CF-35	0.60	16	38	0.32
35	CF-36	0.90	18	37	0.47
36	CF-37	0.90	18	36	0.47

Table 8.2 displays the surface access, SA (m²), BET surface area of the crushed rock powder, S_{BET} (m²/g) and the weight of the crushed core utilized in the static adsorption experiments (g).

Table 8.2: Summary of surface access and weight of the rock powder

Sample No.	Sample-ID	SA (m ²)	S _{BET} (m ² /g)	Weight of Rock Powder (g)
1	CR-1	67.16	2.23	30
2	CR-2	79.51	2.23	36
3	CR-3	76.47	2.23	34
4	CR-4	79.27	2.00	40
5	CR-5	80.53	2.00	40
6	CR-6	88.41	3.02	29
7	CR-7	89.30	1.77	50
8	CR-9	51.68	1.51	34
9	CR-10	62.83	1.29	49
10	CR-11	65.31	1.29	51
11	CR-12	77.42	1.29	60
12	CR-13	72.19	1.32	55
13	CR-14	83.51	1.30	64
14	CR-15	82.82	1.80	46
15	CR-16	86.76	2.23	39
16	CR-17	83.51	2.10	40
17	CR-18	89.13	3.00	30
18	CR-19	84.73	1.74	49
19	CR-20	84.85	2.10	40
20	CR-21	63.29	1.76	36
21	CR-22	65.13	1.76	37
22	CR-23	64.33	1.30	49
23	CR-24	73.57	1.30	56
24	CR-25	68.03	1.76	39
25	CR-26	71.76	1.94	37
26	CR-27	73.09	2.02	36
27	CR-28	74.34	1.94	38
28	CR-29	70.22	2.00	35
29	CR-30	76.47	1.87	41
30	CR-31	74.32	1.86	40
31	CR-32	78.91	1.86	43
32	CR-33	75.05	1.63	46
33	CR-34	52.03	1.53	34
34	CR-35	55.09	1.56	35
35	CR-36	80.83	0.98	83
36	CR-37	75.27	1.24	61

8.3 Application of Machine Learning to Predict Dynamic Retention

Static adsorption values were obtained and reported in $\mu\text{g}/\text{m}^2$. A comparison between these static adsorption values and the dynamic retention values both reported in $\mu\text{g}/\text{m}^2$, revealed a noteworthy observation that the dynamic retention values consistently exceeded the corresponding static adsorption values (**Table 8.3**). This difference emphasizes that dynamic retention not only represents the adsorption mechanism, but also accounts for the mechanical entrapment phenomenon.

To predict dynamic retention, a series of machine learning algorithms were employed. These algorithms include Decision Tree (DT), Random Forest (RF), Extra Trees (ET), Gradient Boosting (GB), AdaBoost, and XGBoost. From the total dataset of 36 samples, 80% of the data was designated for training and validation, while the remaining 20% was reserved for testing. To enhance the accuracy and robustness of the predictive models, the K-cross validation method was incorporated, with the K-fold value 5.

For the predictive modeling of dynamic retention, two distinct approaches were adopted. In the first approach, the above discussed machine learning models were applied to predict dynamic retention from only the static adsorption values. In the second approach, besides the static adsorption values, several other critical parameters known to influence dynamic retention were integrated into the modeling process. These parameters comprise total salinity, hardness, residual oil saturation, and temperature, as these parameters influence the flow behavior of the polymer while flowing through the porous media. Additionally, the pore throat size of the core (obtained using **Equation 3.22**) was considered, as it is a significant parameter influencing mechanical entrapment. **Table 8.3** represents the static adsorption values, total salinity, hardness, residual oil saturation, temperature, average pore throat size, and dynamic retention for all the 36 samples.

Table 8.3: Summary of parameters used for machine learning

Residual Oil Saturation (%)	TDS (mg/l)	Temperature (° C)	Pore Throat Size (nm)	Static Adsorption (µg/m²)	Dynamic Retention (µg/m²)
0	167,114	25	3529	141	146
0	33,423	25	3697	115	121
0	16,711	25	3819	103	111
0	8,356	25	3867	54	60
0	42,507	25	3469	109	114
0	8,502	25	3407	83	92
0	1,701	25	3405	55	79
0	425	25	3191	25	49
0	8,502	25	2752	82	94
0	8,502	25	3165	54	72
0	8,502	25	2670	43	69
0	8,502	25	2835	85	95
0	167,114	40	3368	129	136
0	167,114	60	3277	107	112
0	167,114	80	3035	108	112
0	167,114	90	2979	107	114
0	425	40	3055	25	48
0	425	60	3002	22	41
0	425	80	3017	22	38
0	425	90	2908	23	40
0.35	167,114	25	3219	70	76
0.34	33,423	25	3441	68	74
0.35	16,711	25	3928	61	63
0.35	8,356	25	3706	43	46
0.38	42,507	25	3395	70	71
0.37	8,502	25	3325	50	75
0.31	1,701	25	3245	41	44
0.39	425	25	3407	14	31
0.37	8,502	25	3280	48	63
0.37	8,502	25	3104	47	55
0.36	8,502	25	3184	31	48
0.34	8,502	25	3304	49	66
0.38	167,114	60	3702	65	66
0.38	167,114	90	3658	70	73
0.37	425	60	3475	28	28
0.36	425	90	3382	20	25

8.3.1 Prediction of Dynamic Retention from Static Adsorption

In this section, we have applied the first approach i.e., predicting dynamic retention from static adsorption alone using machine learning. This approach involves creating models that can analyze static adsorption values to forecast the corresponding dynamic retention values. In this context, static adsorption serves as the input feature for the model, while dynamic retention is the target variable that the model aims to predict. Different machine learning algorithms were employed including Decision Tree (DT), Random Forest (RF), Extra Trees (ET), AdaBoost, Gradient Boosting (GB), and XGBoost. These algorithms aim to analyze the complex relationships and patterns between static adsorption and dynamic retention, which further provide a robust model to understand and predict dynamic retention in scenarios where only static adsorption data is available. **Table 8.4** shows the evaluation metrics of different algorithms used to predict dynamic retention from static adsorption alone. It is evident from the table that all the machine-learning models performed well with R^2 values above 0.9 in both testing and training.

Table 8.4: Dynamic retention prediction from static adsorption alone using different machine learning algorithms

ML Algorithm	Evaluation Metrics			
	Training	Testing		
	R^2	R^2	MAE	RMS
AdaBoost	0.96	0.92	8.17	9.83
DT	0.95	0.94	6.94	8.43
ET	0.95	0.95	6.38	8.10
RF	0.98	0.94	6.13	8.44
GB	0.98	0.93	7.43	9.74
XGB	0.96	0.93	7.17	9.32

The evaluation metrics presented for predicting dynamic retention from static adsorption using various machine-learning algorithms emphasize that all the models have exhibited commendable performance. For Training, every algorithm displays an R^2 score of 0.95 or above, signifying a very high proportion of variance in the dependent variable that is

predictable from the independent variable. For unseen data and testing stage, all models maintain an impressive R^2 score above 0.9. This consistency between training and testing scores across models underlines their robustness and generalizability. The range of MAE across models were 6.13 (Random Forest) to 8.17 (AdaBoost), suggesting that the predictions from all models are, on average, reasonably close to actual values. No algorithm exhibits an excessively high MAE, further solidifying the observation of universally good performance. With RMS scores oscillating between 8.10 (ET) and 9.83 (AdaBoost), all models demonstrate consistent and reliable predictions, reinforcing the notion of overall competence. In conclusion, all models have performed well in predicting dynamic retention from static adsorption. **Figure 8.4** demonstrates the Extra Trees (ET) algorithm that offered the most balanced performance across the metrics, showcasing both effective fitting of the training data and excellent generalization to the testing data.

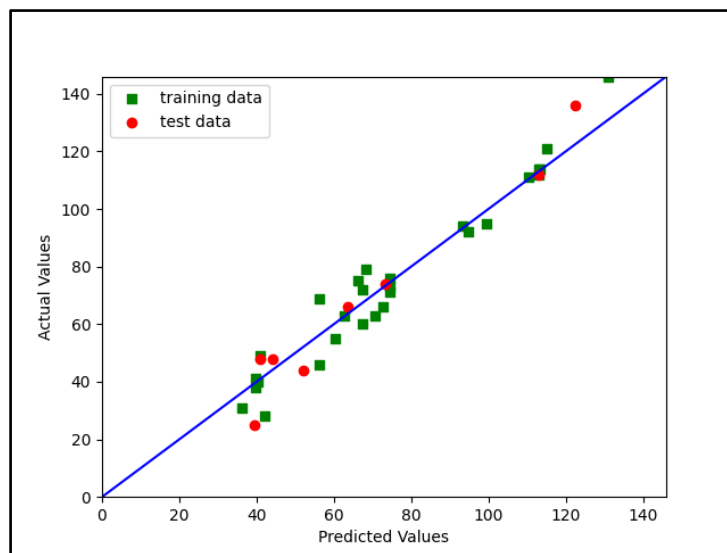


Figure 8.4: Dynamic retention prediction from static adsorption value alone based on ET algorithm.

8.3.2 Prediction of Dynamic Retention from Static Adsorption and Various Influencing Parameters

In this section, the second approach to estimate dynamic retention is discussed where the same machine learning algorithms were applied including Decision Tree (DT), Random Forest (RF), Extra Trees (ET), AdaBoost, Gradient Boosting (GB), and XGBoost. This prediction was derived not just from static adsorption, but also by considering specific parameters that play a significant role in the mechanical entrapment process within porous media. Mechanical

entrapment, in the context of flow through porous structures, is significantly influenced by several parameters including pore throat size, salinity, hardness that is characterized by the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, temperature, and residual oil saturation.

To gauge the relationships and dependencies between these input parameters, a heat map was constructed. This visualization method allows for the easy identification of linear relationships between variables by showcasing correlation coefficients. As presented in **Figure 8.5**, an important observation emerged regarding the relationship between total dissolved salts (TDS) and hardness (measured as the combined concentration of Ca^{2+} and Mg^{2+} ions). The high correlation between these two parameters suggests a strong linear positive relationship, indicating that they convey redundant or overlapping information. To avoid multicollinearity, which can potentially distort the performance and interpretability of some machine learning models, one of these correlated parameters, specifically hardness, was excluded from subsequent analyses.

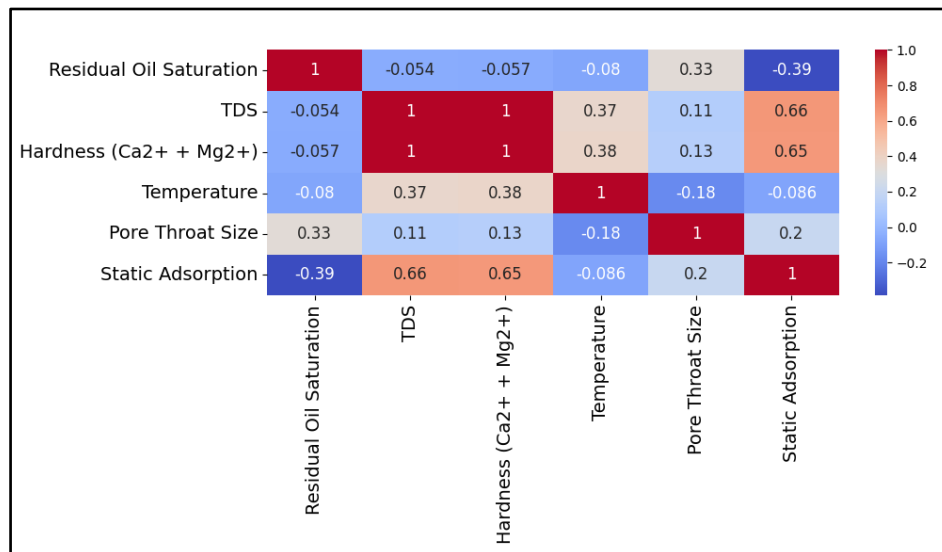


Figure 8.5: Heatmap to examine the interdependencies between input parameters to predict dynamic retention.

Subsequently, a heat map was constructed for the tuned parameters including static adsorption, average pore throat size, total dissolved salts (TDS), temperature, and the residual oil saturation as presented in **Figure 8.6**. Notably, the heat map underscores the fact that all the chosen input parameters appear to be independent, exhibiting minimal to no linear correlation

with one another. Such independence of features is crucial, as it ensures that each variable contributes unique information to the model, enhancing its predictive capability and reliability.

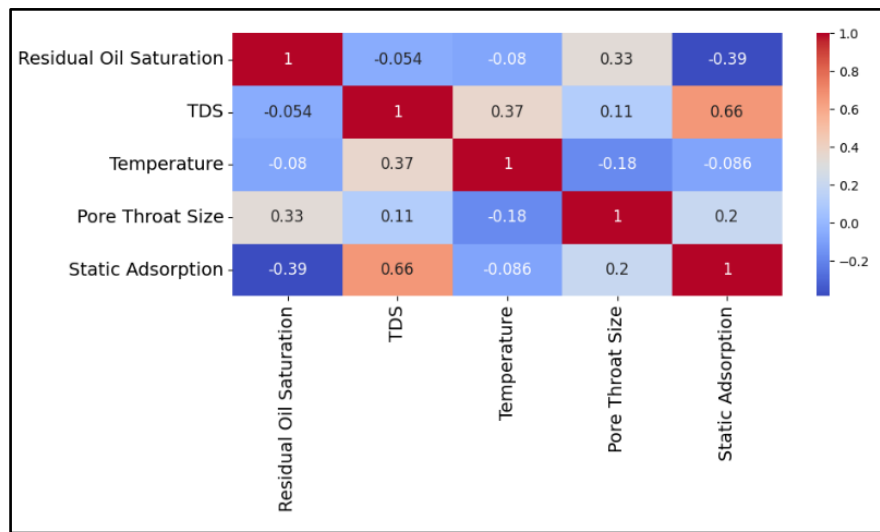


Figure 8.6: Heatmap to examine the interdependencies between the tuned input parameters to predict dynamic retention.

Following the correlation analysis, feature importance evaluation was also conducted. This is a critical step in machine learning as it determines which parameter has the most influence on the model's performance and outcomes. As illustrated in **Figure 8.7**, static adsorption is clearly a dominant factor in the model formulation. Specifically, it commands a considerable weight, as evidenced by its high importance coefficient of 0.91. This signifies that static adsorption substantially influences the predictive accuracy and the overall efficacy of the model. In contrast, the remaining parameters including total dissolved salts (TDS), average pore throat size, residual oil saturation, and temperature demonstrate markedly lower feature importance values of 0.04, 0.02, 0.01, and 0.01, respectively.

The relatively low significance of these parameters could be attributed to low contribution of mechanical entrapment into the dynamic retention. This could also be related to a constrained dataset that is unable to capture the comprehensive impact of all parameters. The breadth and depth of a dataset play a crucial role in discerning the weightage of each parameter. In addition, the reduced variability of the dataset may lead to those parameters appearing less influential when, in different circumstances, they might be more significant. In summary, while the feature importance clearly highlights static adsorption as the pivotal element in this model, it is crucial to recognize that the contribution of other parameters may become more apparent with a more diverse and extensive dataset.

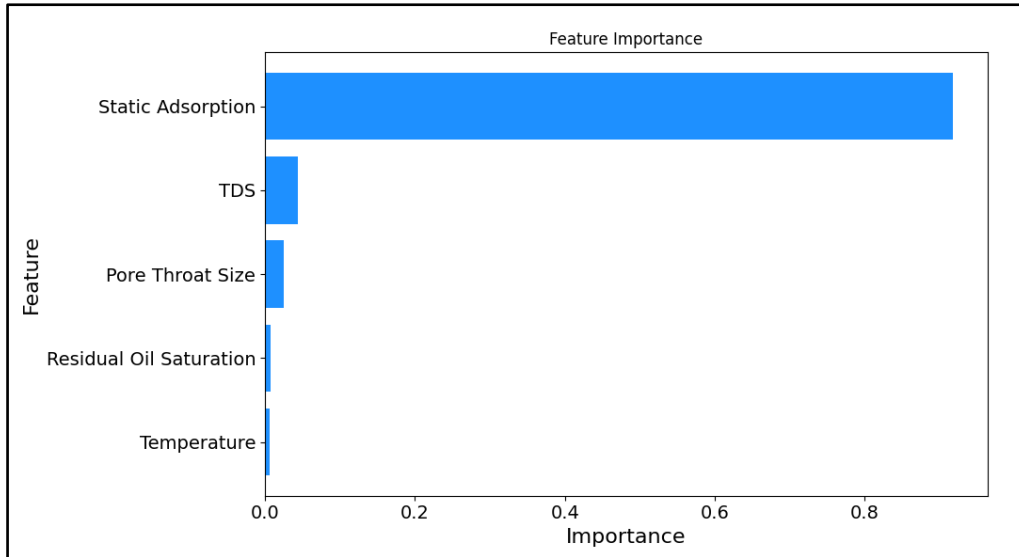


Figure 8.7: Feature importance for dynamic retention prediction.

Table 8.5 summarizes the evaluation metrics of different machine learning algorithms including AdaBoost, Decision Tree (DT), Extra Trees (ET), Random Forest (RF), Gradient Boosting (GB), and XGBoost (XGB) used to predict dynamic retention from static adsorption, TDS, average pore throat size, residual oil saturation, and temperature. The evaluation metrics indicate that AdaBoost shows excellent training and testing R^2 scores of 0.98 and 0.97, respectively. This indicates that the model fits the data well and generalizes well on unseen (blind) data (**Figure 8.8**). Also, its MAE and RMS errors are relatively low, suggesting precise predictions.

Table 8.5: Dynamic retention prediction from various influencing parameters using different machine learning algorithms

ML Algorithm	Evaluation Metrics			
	Training	Testing		
	R^2	R^2	MAE	RMS
AdaBoost	0.98	0.97	4.26	5.17
DT	0.87	0.87	10.57	12.61
ET	1.00	0.98	2.97	3.71
RF	0.99	0.98	3.28	4.95
GB	0.99	0.98	3.44	5.31
XGB	0.99	0.97	4.91	5.74

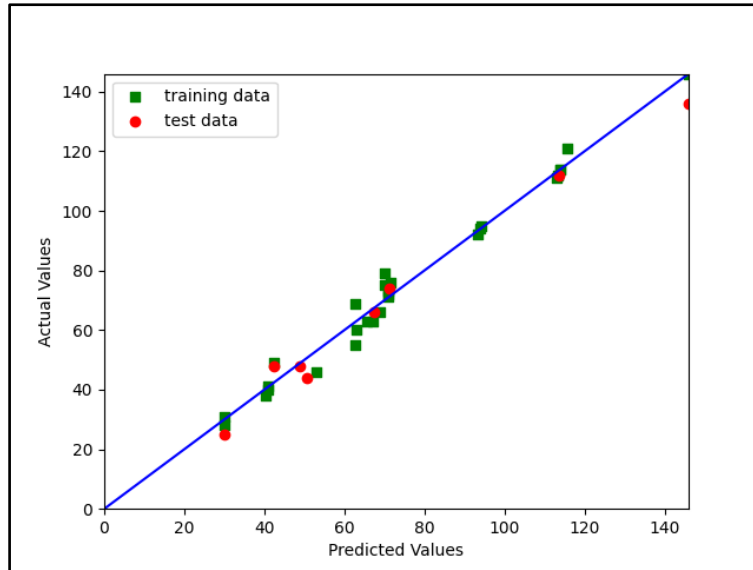


Figure 8.8: AdaBoost ML algorithm for dynamic retention prediction based on several influential parameters.

Decision Tree (DT) (**Figure 8.9**) presents a modest R^2 score of 0.87 for both training and testing sets. The relatively higher MAE and RMS values compared to other models hint at less accuracy in the predictions. This is expected since DT is the simplest ML tree-based algorithms in terms of building structure.

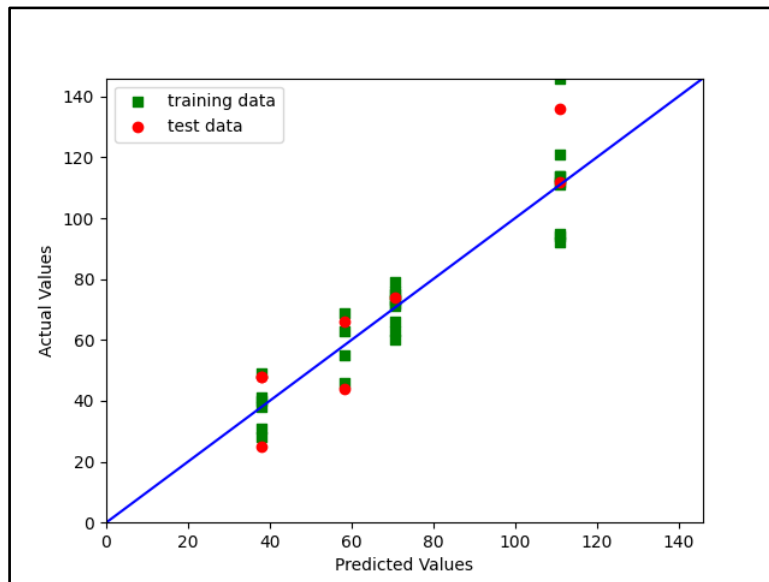


Figure 8.9: Decision tree algorithm for dynamic retention prediction based on several influential parameters.

Extra Trees (ET) achieves a perfect R^2 score on the training set and a high score on the testing set, rendering it one of the top-performing algorithms (**Figure 8.10**). Its low MAE and RMS values reinforce this observation. Similarly, Random Forest displays strong performance with R^2 values of 0.99 (training) and 0.98 (testing) (**Figure 8.11**). Its MAE and RMS errors are also among the lower ranges, highlighting its robustness and precision.

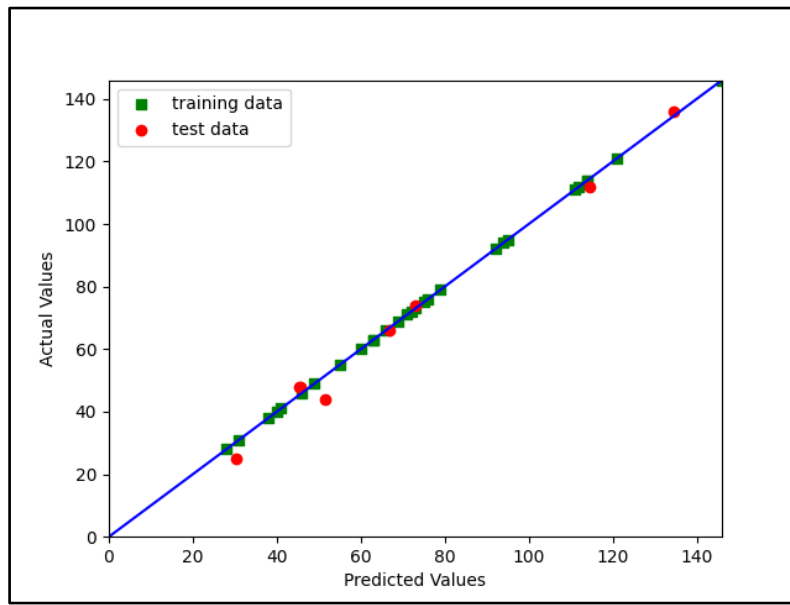


Figure 8.10: Extra tree algorithm for dynamic retention prediction based on several influential parameters.

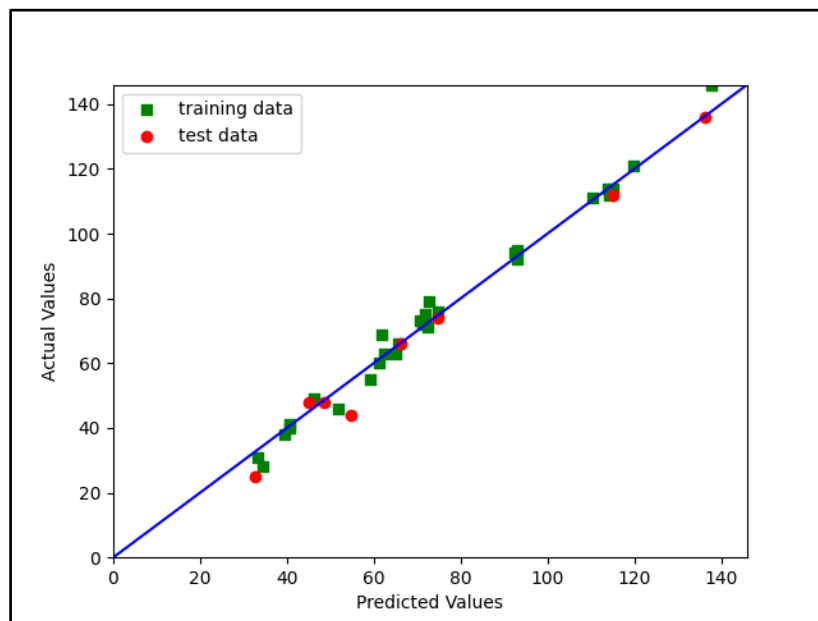


Figure 8.11: Random Forest algorithm for dynamic retention prediction based on several influential parameters.

Furthermore, Gradient Boosting (GB) mirrors the RF in R^2 scores, but has slightly higher MAE and RMS errors, though they are still competitive (**Figure 8.12**). For XGBoost or XGB, it exhibits a strong fit to the data with R^2 scores nearing 1, but its MAE and RMS errors are a bit higher than those of RF and GB, though still lower than DT (**Figure 8.13**).

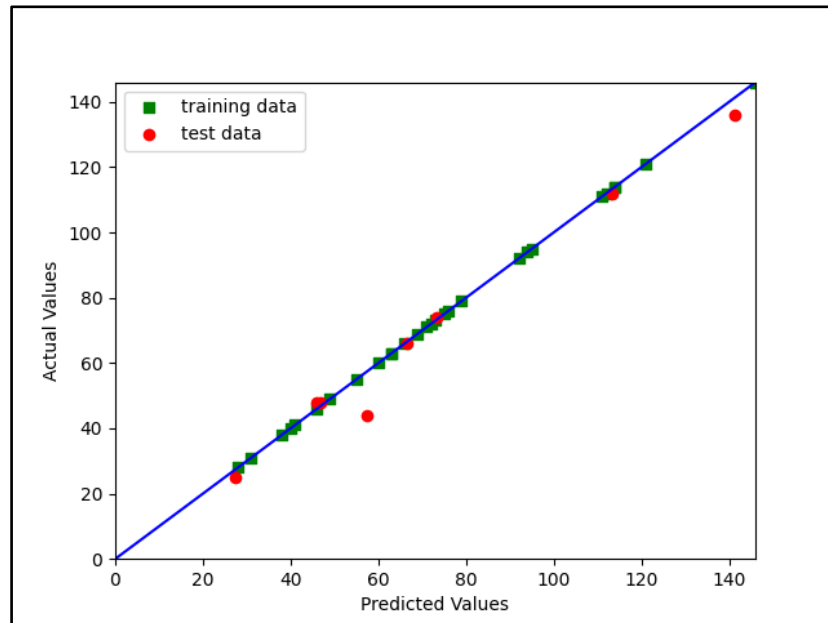


Figure 8.12: Gradient Boosting algorithm for dynamic retention prediction based on several influential parameters.

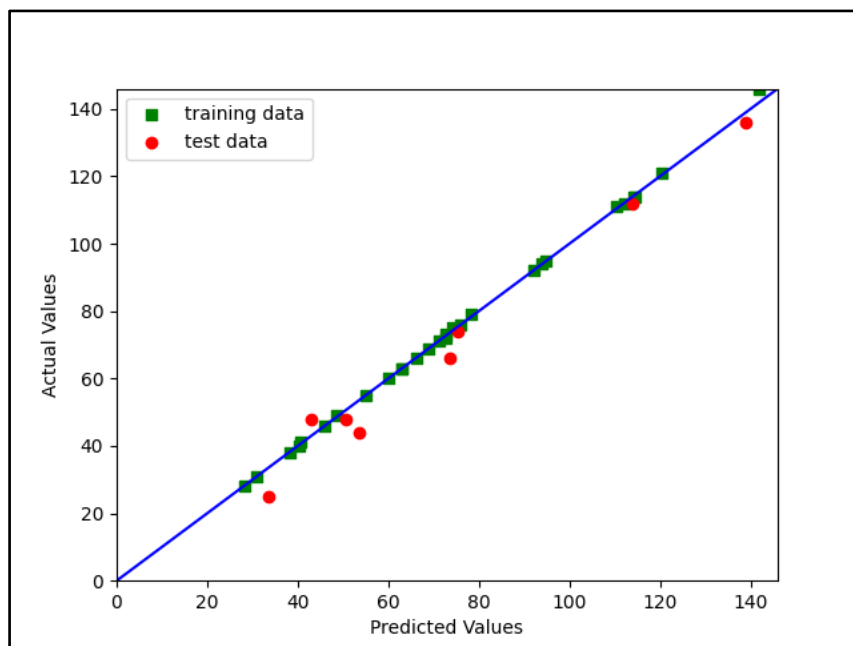


Figure 8.13: XG Boosting algorithm for dynamic retention prediction based on several influential parameters.

Based on the analysis, ET and RF are the best predictive models in terms of both R^2 scores and error metrics (MAE and RMS). These algorithms seem particularly well-suited for this dataset and problem. DT, while still delivering decent results, lags behind compared to the other models in terms of both fit and error metrics. This suggests that tree ensemble methods, which combine multiple decision trees, provide a more accurate model for this data. Despite their slightly higher error rates, boosting algorithms (AdaBoost, GB, and XGBoost) have shown strong performance.

8.3.3 Comparison of the Two Approaches

The first approach, while providing an initial understanding, only considered static adsorption. On the other hand, the second approach was more holistic in its methodology. By factoring in multiple parameters, it did not only capture the effects of static adsorption, but also considered other important parameters that could influence dynamic retention. This comprehensive nature renders the second approach more representative of the real-world complexities inherent in the process of dynamic retention.

The analysis of the performance metrics (**Tables 8.4** and **8.5**), specifically the Mean Absolute Error (MAE) and the Root Mean Square (RMS), provides an objective comparison between the two approaches. Lower values in these metrics indicate a better performing model. The second approach demonstrated superior performance, as evidenced by its reduced MAE and RMS values compared to the first approach. This quantitatively supports the assertion that the second approach is more accurate in its predictions.

The increased accuracy of the second approach can likely be attributed to its inclusiveness of all potential influencing factors that capture mechanical entrapment components added to that of static adsorption. Every parameter, even those with minor influence, can collectively contribute to a more refined and accurate prediction. Overlooking even a single influential parameter might lead to significant deviations in certain scenarios. Thus, the comprehensive nature of the second approach ensures that the model is robust across a wider range of conditions.

8.3.4 Application of Symbolic Regression to Develop Dynamic Retention Correlation

Symbolic regression differs from traditional regression methods in its approach to model the data fitting. Symbolic regression searches for the best functional form of the model itself,

instead of fitting to a predetermined functional form (like linear or polynomial). This enables it to capture intricate and potentially non-linear relationships between variables, delivering models that are both interpretable and accurate.

In this section, symbolic regression was chosen to derive explicit mathematical formulas that describe the relationship between the influencing parameters and dynamic retention. The goal was to unearth a mathematical representation that can illuminate how changes in these parameters might influence dynamic retention. Such an equation could be valuable for theoretical understanding, and prediction of dynamic retention values. TuringBot software was used to derive these symbolic regression equations. The equations derived through symbolic regression, accompanied by their respective evaluation metrics, are presented in **Table 8.6**. One should note that in the presented correlations, A_q is the dynamic retention ($\mu\text{g}/\text{m}^2$), A is the static adsorption ($\mu\text{g}/\text{m}^2$), TDS is the total salinity (mg/l), r_p is the average pore throat size (nm), S_{or} is the residual oil saturation in (fraction), and T is the temperature ($^{\circ}\text{C}$).

Considering both correlations. The first one predicts dynamic retention from only static adsorption values. Whereas the second one predicts the dynamic retention value from all defined parameters influencing dynamic retention including static adsorption, TDS, average pore throat size, residual oil saturation, and temperature. While the first equation is simpler and uses only static adsorption to predict dynamic retention with good accuracy, the second equation considers a broader set of parameters and provides an even better fit (as indicated by the higher r^2). However, the increased RMSE for the second equation suggests that this enhanced fit comes with larger individual prediction errors. This could be a trade-off between model simplicity and comprehensiveness. Moreover, the second equation can capture a broader set of influencing factors, which will be essential considering the practical applications.

Table 8.6: Correlation developed using symbolic regression to predict dynamic retention

Correlation	R^2	RMSE
$A_q = 17.19 + (0.89 * A)$	0.95	6.84
$A_q = 53.35 + (0.83 * A) + (-0.007 * r_p) + (1.98 * 10^{-5} * TDS) + (-0.13 * T) + (-21.00 * S_{or})$	0.98	19.82

8.3.5 Application Envelope of the Developed Model

The current model's applicability is framed within specific parameters and conditions, which outline its operational boundaries. Firstly, the dataset primarily leans on Indiana limestone as

its core source of mineralogical data. This refers to the model's specific calibration to this limestone's characteristics. Secondly, in terms of polymer choices, the model predominantly accounts for sulfonated polymers, specifically ATBS-based polymer. This preference stems from their renowned stability, especially under the challenges posed by harsh reservoir conditions. Thirdly, the model's predictions and findings are tailored to scenarios involving high permeability core samples. Moreover, the model is versatile in terms of salinity and temperature variations. Specifically, it can operate within a broad salinity range, from as low as 425 ppm to an elevated 167,114 ppm. In terms of temperature adaptability, the model is designed to function effectively across a spectrum from 25 °C to a high of 90 °C. Collectively, these parameters define the model's application envelope, underlining its strengths and potential areas of expansion in future developments.

8.3.6 Limitations of the Developed Model

One of the intrinsic limitations of the machine-learning model that predicts dynamic retention solely based on static adsorption revolves around the characterization of wettability in oil-wet cores. Currently, the representation of surface area in static adsorption studies accounts only for residual oil saturation. Hence, might not precisely mimic the dynamic retention conditions.

The second shortcoming of the predicted model is determination of residual oil saturation. Residual oil saturation for a particular core is reached after the process of drainage and imbibition, which is a time-consuming process. Hence, its value must be sourced from an existing database. This approach is essential to maximize the model's applicability, especially as its main goal is to eliminate the need for time-intensive and expensive coreflooding experiments.

8.4 Highlights of the Chapter

This chapter explored the application of machine learning and symbolic regression approaches to predict dynamic retention. The main findings of this study are highlighted below:

- Two approaches were considered for predicting dynamic retention using ML. The first approach was to predict dynamic retention from static adsorption alone. While the second approach considered other influential parameters including average pore throat size, TDS, residual oil saturation, and temperature along with static adsorption values to predict dynamic retention. Both approaches were able to predict dynamic retention

with machine learning models. However, the second approach stood out due to its broader scope and better performance metrics. By including all relevant factors, this model captures dynamic retention more accurately, rendering it a reliable tool for analysis and forecasting.

- In the second approach, while all the employed algorithms provide valuable insights into the prediction of dynamic retention, tree-ensemble algorithms (RF, ET) and boosting algorithms seem especially promising.
- Symbolic regression equations were obtained for both approaches with a good fit and robust predictability of polymer retention.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

This study aimed to determine how water chemistry (salinity and ionic composition) affects the retention of synthetic polymer (SAV10) in carbonates under high temperature and salinity conditions. It also examined the impact of oil presence on polymer retention through dynamic adsorption tests. A comprehensive study was undertaken to investigate the behavior of bulk polymer solutions under different conditions. The experimentation included variations in shear rates from 1 to 1000 s⁻¹, polymer concentrations between 500 to 3000 ppm, salinity levels from 425 to 167,114 ppm, different ionic compositions, and temperatures ranging from 25 to 90 °C. This extensive analysis demonstrated the influence of make-up water salinity, the varying ionic composition of brine, and temperature on the polymer solution viscosity. Furthermore, a correlation was developed to predict dynamic retention values from static adsorption values. The research revealed several key findings that can guide future research and practical applications related to polymer retention in carbonate reservoirs. The main findings of this research can be summarized as follows:

- It was noted that polymer solutions with diluted makeup water with salinity less than 10,000 ppm, exhibited enhanced viscosity. This notable observation has practical implications, indicating a potential reduction in the operational costs of polymer flood projects by facilitating the use of a lower polymer dosage, thereby optimizing resource utilization.
- Also, the reduction in polymer solution viscosity parallels the reduction of the viscosity of respective brine, which signifies the stability of these polymers under high temperature.
- Further, the study showed that the hydrodynamic size of the polymer was prominently higher at conditions marked by low salinity and temperature. The polymers generally demonstrated a polydispersity index (PDI) between 0.3 and 0.4, illustrating a relatively uniform size distribution, barring certain exceptions observed at 425 ppm salinity under ambient conditions, where a PDI of 0.6 was recorded.
- Moreover, different analytical methods were also examined for polymer concentration measurements, including UV-Vis, Viscosity, and TOC-TN, and polymer concentration was measured effectively with all the three methods.

- For the impact of salinity on polymer adsorption, the study showed that utilizing diluted brines with salinity less than 10,000 ppm salinity yielded lower retention levels of polymers compared to using solutions in high salinity formation water or seawater.
- Furthermore, polymer adsorption in the presence of oil in aged cores was further reduced, emphasizing the necessity of employing wettability-restored cores to ascertain precise retention values. The lowest polymer retention was 14 $\mu\text{g/g-rock}$ in oil-wet cores for seawater dilution of salinity 425 ppm compared to 26 $\mu\text{g/g-rock}$ for polymer solution in formation water with salinity 167,114 ppm.
- For the impact of brines with varying ionic composition (Ca^{2+} , Mg^{2+} , and SO_4^{2-}), a significant reduction in retention values was achieved with softened brine. However, the polymer solution in sulfate-spiked brine did not show any significant reduction in polymer retention.
- Softened brine yielded a retention of 20 $\mu\text{g/g-rock}$ in aged cores. This was still higher compared to the dynamic retention value of 14 $\mu\text{g/g-rock}$ observed for seawater diluted to a salinity of 425 ppm. When considering the practical aspects of larger-scale applications, dilutions are more feasible than modifying ionic compositions. Therefore, diluted seawater is proposed as the most effective brine composition for minimizing polymer retention due to its efficiency and feasibility.
- For the effect of temperature on polymer adsorption, the results indicated that dynamic polymer retention in all salinity conditions did not vary due to the temperature changes from 25 – 90 °C. The stable retention values across the varied temperatures highlighted the polymer's stability and efficiency at high temperature conditions.
- The findings from the temperature experiments suggest that employing low-salinity polymer flooding can effectively minimize polymer retention, achieving values as low as 12 $\mu\text{g/g-rock}$ at representative reservoir conditions without being affected by temperature variations.
- For developing a correlation to predict dynamic retention, the study showed that the second approach is superior to the first approach. While the former has holistic consideration of multiple influencing variables (average pore throat size, total dissolved solids (TDS), residual oil saturation, temperature, and static adsorption values), the latter relies on static adsorption alone.

- In terms of machine learning techniques, tree ensemble methods such as Random Forest (RF) and Extra Trees (ET) as well as boosting algorithms were found to be particularly effective.
- To make the findings more relatable and understandable, symbolic regression was applied, resulting in an explicit equation for both approaches, and the fit was good.

9.2 Recommendations for Future Work

Based on the outcomes and shortcomings of the research, future works are recommended.

9.2.1 Experimental Work

In this study, the incorporation of sulfate ions did not show any impact on polymer adsorption at ambient conditions. However, sulfate ions have been widely reported to be effective in wettability alterations. Accordingly, the effect of sulfate on polymer adsorption will be further investigated in the presence of oil and at high temperatures as a wettability alteration agent. In addition to the potential effect in polymer adsorption reduction, other potential drawbacks of scale formation need to be investigated. Further, an optimum sulfate concentration can be recommended for reducing polymer retention while avoiding any formation damage and scale formation.

9.2.2 Enhancing Polymer Retention Model's Applicability

Although the current polymer retention prediction model serves as a robust starting point, the following recommendations offer a roadmap for future studies aimed at expanding its accuracy and scope across a more diverse set of reservoir conditions:

- The dataset used in our current model is largely based on Indiana limestone. To better capture the intricate influences of mineralogy on retention, it is recommended to include data from different rock types, including actual reservoir core samples.
- The model predominantly focuses on sulfonated ATBS-based polymers, chosen for their stability in harsh reservoir conditions. To expand the model's relevance, future work should explore and integrate data from other polymer types.
- Permeability is crucial in determining fluid flow dynamics in porous media. By including core samples with a wider range of permeabilities, the model can be optimized to offer predictions across varied reservoir characteristics.

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