Investigating the Effect of Chemical Gradient in Polymer Flooding.

Rawan Alkandari[1,+], *Mahmoud Ali*[1], *Meshal Algharaib*[1*], *Abdullah Alajmi*[1]

[1]Petroleum Engineering Department, Kuwait University, Kuwait
[+]Now with Kuwait Petroleum Corporation (KPC)

Abstract. Polymer flooding enhances oil recovery by integrating water-soluble polymers in water which improves sweep efficiency and reaching residual oil saturation more economically. Performance depends on polymer degradation (caused by biological, chemical, and mechanical factors) and retention (loss through adsorption, mechanical entrapment, and hydrodynamic retention in reservoir rocks). This study investigates the reversibility of polymer retention influenced by a chemically induced gradient, examining the effects of time, injection rates, and polymer concentrations through experiments with Berea sandstone cores initially flooded with either a 3000 ppm or 1500 ppm polymer solution at ambient temperature or 70°C, followed by a 5000 ppm NaCl brine injection. Subsequent water injections after varied shut-in periods showed that at certain shut-ins polymer release peaks regardless of injection rate, particularly evident in early times with increased polymer concentrations. Sensitivity analyses revealed significant influence of shut-in duration on polymer release, while injection rate had a lesser effect. Whereas higher temperatures led to a more pronounced polymer release. Moreover, low concentrations exhibited lower sensitivity to shut-in periods. The largest polymer release and reduction in retention occurred during the initial flooding stage, contributing to more than 50% of total release.

1 Introduction

The increasing global demand for energy has driven the petroleum industry to operate continuously, focusing on research, development, and innovation. This shift is essential as increased production has led to concerns about reservoir depletion. Enhancing reservoir lifespan across different stages of hydrocarbon recovery is a critical task for petroleum engineers.

During production, a reservoir typically experiences three main phases: Primary recovery, Secondary recovery, and Enhanced Oil Recovery (EOR). Primary recovery relies on natural mechanisms such as water influx, gas cap drive, solution gas drive, rock and fluid expansion, gravity drainage, and combination drives. These natural forces are sufficient to propel the hydrocarbons to the surface, overcoming gravitational resistance, and result in recovery factors ranging between 20-40%. Following this, secondary recovery employs techniques like water or immiscible gas injection to maintain pressure and displace oil, without altering the properties of the reservoir or the fluids involved, achieving up to an additional 20% recovery.

EOR represents a phase of keen interest within the industry due to its potential for further extending the operational life of oil reservoirs. EOR techniques aim to modify the reservoir or fluid properties to minimize trapping forces such as capillary, viscous, and gravitational forces. These techniques include thermal recovery, chemical EOR, and miscible gas injection. Thermal methods involve introducing heat to reduce oil viscosity and may include hot water flooding, steam flooding, or in-situ combustion. Miscible gas injection, particularly using CO_2 at pressures above the minimum miscibility pressure (MMP), helps to enhance oil flow by reducing capillary and viscous resistance. Chemical processes might involve the injection of surfactants, alkalis, or polymers to improve oil recovery by reducing interfacial tension or altering chemical interactions within the reservoir. One of the recent developments in EOR is the study of polymer flooding in chemical EOR.

1.1 Polymer Flooding Process and Mechanism

Polymer flooding is a recovery technique in the petroleum industry that involves introducing water-soluble macromolecule polymers into water at specific concentrations. This process is designed to enhance vertical and areal sweep efficiency, as well as overall oil recovery, by altering the mobility ratio—the ratio of the mobility of the polymer-injected water to that of the oil. Ideally, mobility ratios below unity are preferable as they indicate more efficient and favorable oil displacement conditions, reducing the severity of issues like viscous fingering and early breakthrough typical of higher ratios [1].

The application of polymer flooding is especially effective in high permeability reservoirs, and with oil viscosities in the range of 10-150 cP. These reservoir conditions are optimal as lower permeability scenarios often lead to complications with polymer injectivity and retention [1]. The process begins with an initial high-concentration polymer injection which gradually tapers off. This is followed by a subsequent water injection that pushes the polymer slug through the reservoir towards the production well, ensuring that the properties of the polymer are compatible with the reservoir conditions.

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[*] Corresponding author: m.algharaib@ku.edu.kw

Despite its efficacy in improving macroscopic sweep efficiency, polymer flooding does not significantly alter the interfacial tension between the water and oil phases, meaning it does not notably decrease residual oil saturation nor enhance microscopic sweep efficiency [2]. Nevertheless, it provides a rapid and cost-effective method to access residual oil. Some studies suggest that following extensive water injections, there is an observable improvement in microscopic sweep efficiency, although this is subject to ongoing debate [3].

Polymers used in this process can be divided into two categories: biopolymers like xanthan and synthetic polymers such as partially hydrolyzed polyacrylamide (HPAM). HPAM is preferred in industrial applications due to its cost-effectiveness, availability, viscosity-enhancing properties, and resistance to microbial degradation. Typical concentrations of these polymers in the injection mix range from 200 to 1500 parts per million, which helps to maintain the desired properties of the flood [4].

This study aims to investigate the interaction between the retained polymers and the injected water with respect to the chemically induced gradient and study the effect of time, injection rate, and concentration on the reversibility of the polymer adsorption process.

1.2 Literature Review

Polymers, defined as high molecular weight compounds consisting of repeating units called monomers linked by covalent bonds, play a crucial role in various industrial applications, including the petroleum sector [5]. The process of polymerization links monomers into chains or networks, with the degree of polymerization indicating the number of monomers in a chain and serving as a proxy for the polymer's molecular weight, which typically ranges from 2 to 35 millionDa. The properties of polymers depend on the type of monomer, chain length, architecture, and sequence, influencing their functionality in applications like polymer flooding in oil recovery.

There are two primary categories of polymers based on their structural composition: homopolymers and heteropolymers. Homopolymers consist of single types of monomers linked together, with their properties influenced by the monomer type, degree of polymerization, and chain architecture. In contrast, heteropolymers are composed of two or more different monomers, with the sequence of monomer placement within the chain significantly impacting their physical characteristics. Additionally, polymers can be classified as either biopolymers, produced naturally through microbial fermentation processes, or synthetic polymers, which are manufactured to meet specific industry demands. For instance, Xanthan gum is a widely used biopolymer in the petroleum industry, produced by the microbial action of Xanthomonas campestris. The focus on synthetic polymers like Polyacrylamide (PAM) and Hydrolyzed Polyacrylamide (HPAM) is due to their pivotal role in supporting the petroleum industry's needs.

Polyacrylamides are synthetic polymers formed from the polymerization of acrylamide monomers. They are notable for their water solubility and utility across various applications including wastewater treatment and soil stabilization. These polymers are characterized by a composition that includes a carbonyl group and an amine group, forming amides, which are crucial for their function as a viscosifier in polymer flooding. However, the effectiveness of PAM in polymer flooding can be compromised by its tendency to adsorb onto rock surfaces, due to negative charges on these surfaces [6].

To mitigate this adsorption, a fraction of the amide groups in PAM can be replaced with acrylate through a process called hydrolysis. This modification, known as partial hydrolysis, aims to maintain the balance between solution stability and the reduction of adsorption by achieving an optimal degree of hydrolysis, typically between 15-35%. However, excessive hydrolysis can lead to polymer instability and viscosity loss. Studies have shown that beyond a critical hydrolysis level, specifically around 40%, polymers begin to experience chain compression, distortion, and flocculation, leading to phase separation in environments rich in divalent metal ions [7].

The stability of polymers in various conditions is crucial for the success of polymer flooding. Polymer degradation, which can occur through biological, thermal, chemical, and mechanical means, significantly affects polymer flooding performance. For instance, biological degradation involves the consumption of polymers by bacteria, leading to a loss in solution viscosity [8]. Oxygen presence, particularly when combined with reducing agents found in polymer solutions, can initiate free-radical reactions that degrade polymers. Such degradation is especially detrimental in anaerobic reservoir conditions, where controlling oxygen levels becomes essential [9].

Thermal degradation also presents challenges, as high temperatures can accelerate degradation processes, particularly in oxygenated polymer solutions. Conversely, low-oxygen polymer solutions show more stability against thermal variations [9]. Salinity, another critical factor, can cause polymer chains to shrink in high salinity environments, further reducing the viscosity of polymer solutions and impacting the overall efficacy of polymer flooding [10]. Mechanical degradation, influenced by fluid stresses and flow rates, varies with polymer type and can significantly affect polymer molecular chains.

Chemical degradation of polymers involves mechanisms like hydrolyzation and oxidation, which are sensitive to environmental factors such as temperature, ion concentration, and pH. Elevated temperatures can catalyze hydrolysis, altering solution properties and leading to viscosity losses [7]. In contrast, oxidative degradation involves radical formation due to hydrogen abstraction or bond cleavage, processes that can be accelerated by the presence of oxidants and various ions in the solution [11].

Inaccessible Pore Volume (IAPV) plays a critical role in polymer flooding techniques used in enhanced oil recovery. IAPV refers to the portion of a reservoir's pore space through which polymer molecules cannot travel due to their relatively large size, making these pores inaccessible to the polymers. This concept is vital because it allows for faster propagation of polymer slug through porous media compared to water, which in turn can reduce overall retention levels [4]. Dawson (1972) highlighted that without retention, IAPV delays salt fronts since salt and water can access areas that polymers cannot, leading to slower movement of salt peaks relative to polymer peaks. The dynamics between accessible and inaccessible pore volumes involve processes like diffusion and possibly convection of salt, indicating complex interactions within the pore spaces of the reservoir [12].

Polymer retention has a significant impact on polymer propagation rate in porous media. Severe polymer retention can aggravate oil displacement and recovery during polymer flooding, resulting in both functional and economic failure of the project. Manichand and Seright (2014) found that low polymer retention values caused modest delays in polymer bank propagation through porous media. High polymer retention values may have a substantial impact on polymer flooding feasibility [13]. Polymer retention occurs through three mechanisms: adsorption, mechanical entrapment, and hydrodynamic retention [14, 15].

Adsorption is a common phenomenon observed during polymer flooding. It is the interaction between polymer molecules and solid surfaces that allows the polymer molecules to attach to the rock surface by physical processes such as van der Waals and hydrogen bonding. Mechanical entrapment occurs when polymer molecules enter pores with relatively small outlet sizes and become physically entrapped. The mechanism is triggered by the large polymer molecular size relative to pore size. As a result, polymer molecules confined and aggregated within pore throats. Hydrodynamic retention occurs when an increase in flow rate force polymer molecules to be retained inside the porous media due to hydrodynamic differences.

The factors influencing polymer retention include the type of polymer, molecular weight, concentration, rock mineralogy, salinity, hydrolysis degree, permeability, wettability, and temperature, each playing a distinct role in how polymers are adsorbed and retained within the reservoir rock. For instance, polymers like Xanthan show less sensitivity to salinity and lower adsorption compared to Hydrolyzed Polyacrylamide (HPAM), indicating that polymer type significantly affects adsorption characteristics [16]. Studies have shown that molecular weight impacts adsorption; higher molecular weight polymers tend to form thicker layers on rock surfaces, which increases adsorption but may also enhance retention to a point where it could block pore throats and reduce permeability [17].

Adsorption behavior is also influenced by polymer concentration. While higher concentrations generally increase retention, the relationship is not strictly linear and varies depending on other conditions like flow dynamics and rock properties. Dynamic measurements of adsorption, such as those done in studies by Seright et. al (2011), suggest that polymer adsorption can be independent of concentration in diluted solutions, but that concentration becomes a significant factor in semi-dilute to concentrated solutions [1].

Rock mineralogy also plays a crucial role as well. Rocks with higher contents of calcium carbonate tend to show significantly higher polymer retention than those composed mainly of silica, attributed to calcium bridging that enhances polymer adsorption [18]. Similarly, the presence of clays like Kaolinite can lead to higher retention rates due to their expansive surface areas and reactive nature, which promotes more extensive interactions with polymer molecules [19].

Salinity impacts polymer behavior by affecting the physical and chemical properties of the injected slug. Increased salinity enhances polymer adsorption due to higher ionic strength, which promotes more extensive interactions between the polymers and the charged rock surfaces. This effect is compounded by the presence of divalent cations, which can further increase polymer adsorption and retention [17].

Hydrolysis of polymers, particularly HPAM, plays a pivotal role in retention. As the degree of hydrolysis increases, polymers can become less retained until a specific threshold is reached, beyond which additional hydrolysis might reduce retention effectiveness. This relationship underscores the complex interaction between polymer chemistry and reservoir conditions, which can ultimately affect the efficacy of the polymer flooding process [20].

Permeability and wettability also affect how polymers are retained within the reservoir. Lower permeability often leads to higher retention due to mechanical entrapment [21], while the wettability of the rock can influence how polymers interact with the reservoir matrix. Oil-wet systems tend to show lower retention rates compared to water-wet systems, highlighting the importance of reservoir characteristics in determining the success of polymer flooding operations.

Temperature influences polymer retention mainly through its effect on the physical state and behavior of the polymers. Higher temperatures generally decrease polymer adsorption due to increased molecular motion, reducing interaction times between polymers and rock surfaces. However, for certain polymers, higher temperatures might slightly increase retention due to changes in polymer structure, such as increased coil size, which affects how polymers occupy rock surfaces [22].

Finally, the concept of adsorption reversibility is important in understanding long-term polymer behavior in reservoirs. Graiman and Myard (1981) emphasized the complex nature of adsorption and its irreversibility in many cases, suggesting that understanding these dynamics is crucial for optimizing polymer flooding techniques and improving recovery efficiency [23].

Huh et. al (1990) noticed that as polymer molecules accumulate in small pores, a chemical potential gradient is established, leading the polymer molecules to migrate out of the pores [8]. The chemical potential gradient refers to the presence of difference in polymer concentration between the adsorption and entrapment sites and the polymer concentration in the wash water following a polymer flood. If the adsorption energy is high, the chemical potential gradient decreases, reducing the likelihood of polymer outward release. However, when the adsorption energy is low and the flow resulting in polymer accumulation ceased, the chemical potential gradient causes the polymer to be released over time [8].

Despite the literature presented previously, the impact of chemical potential gradients in reducing overall polymer retention in porous media warrant further investigation. The purpose of this study is to investigate the interaction between the retained polymers and the injected water with respect to the chemically induced gradient as well as the effect of time, injection rate, temperature, and polymer concentration on the reversibility of the retained polymers due to the chemical potential gradient.

2 Methodology

2.1. Synthetic Brine

A 5000 ppm NaCl solution was prepared by adding 5 grams of NaCl salt to 1000 ml of distilled water. Furthermore, the solution was mixed via a magnetic stirrer for approximately 24 hours. Any dissolved gas, especially oxygen, was removed by Nitrogen purging.

2.2. Polymer Preparation

Polymer solutions were prepared using Flopaam 3630S, a polyacrylamide from SNF. A mother solution at 3,000 ppm concentration was prepared within a glovebox under a nitrogen atmosphere to avoid oxidation and moisture. The mixture was stirred vigorously to form a vortex and then at a slower rate overnight. The solution was subsequently diluted to 1,500 ppm for flooding experiments.

2.3 Core Samples

Gray Berea sandstone cores, measuring 2 inch in diameter and 1 foot in length, were utilized in core flooding experiments. Before each experiment, the core was kept in air dried oven at a temperature of 110 ℃ for 24 hours. The core was subjected to vacuuming for another 24 hours to ensure that no gas (air) was left inside. Then, water was allowed to flow into the core by opening the valve connected to a water accumulator and the core porosity was measured. After the water saturation step, the permeability of the core was measured by varying water injection rate and observing the pressure drop along the core sample. Table 1 shows the porosity, permeability and the weight of each core.

Table 1. Properties of core samples.

	Porosity (%)	Permeability (md)	Dry Weight (gm)
EXP1	17.0	45	1320
EXP 2	16.8	58	1305
EXP 3	17.1	62	1314

Figure 1 Shows the setup of the core flooding experiments.

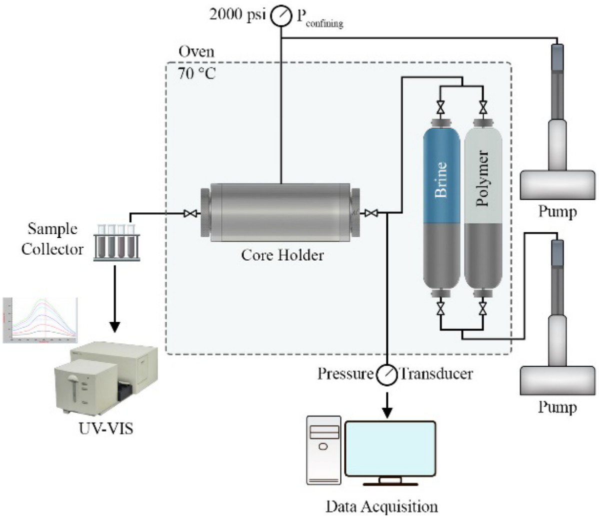

Fig. 1. Schematic diagram of the core flooding setup.

2.3 Polymer Rheology

Brookfield viscometer equipped with a UL spindle was used to measure the apparent viscosity of 3630 Flopaam polymer solutions at ambient conditions under different shear rates to check the non-Newtonian behavior of the prepared polymer sample.

2.4 Procedure of Flow Experiments

Initially, the polymer solution was injected into the core, which was fully saturated with water, at a rate of 0.3 cc/min (0.7 ft/day). The polymer flooding continued until the effluent matched the concentration of the injected solution. This occurred after approximately 3 pore volumes of polymer solution had been injected in each experiment. Upon reaching this concentration in the effluent, the injection was switched to a water flood, using synthetic brine at an increased rate of 1 cc/min (2.3 ft/day) to displace the unretained polymers in conditions resembling deep reservoir environment. Water injection proceeded until no traces of polymer were measured in the effluent solution. Subsequent to the water flooding, the core was isolated for varying periods to assess the impact of shut in time on the polymer's chemical gradient and desorption process. The study periods included shutdowns for 1 day, followed by another 7 days, followed by another 14 days, and lastly for 21 days. In total, each experiment ran for 43 days after the water washout stage except for experiment 1 where the 21 days shut in period was not implemented. Following each shut-in period, the core underwent water injections at two different rates. After shut-in periods of 1, 7, and 14 days, the injection started at 1 cc/min followed by 4 cc/min. However, for the shut-in period of 14 days, the injection rate started at 4 cc/min then reduced to 1 cc/min in experiments 1 and 2. The injection rate of 4 cc/min (9.3 ft/day) and 1 cc/min (2.3 ft/day) were selected to investigate the polymer release dynamics in situations near the wellbore and deep into reservoir. During each injection rate, around 1 pore volume of water was injected. Table 2 outlines the detailed injection schedule used throughout these experiments.

Table 2. Injection rates used and PVI in the flow experiments.

Injection	q (cc/min)	Approx. PVI
Polymer Injection	0.3	3
Water Flush	1	3
Water Injection 1 D	1 4	~1.0
Water Injection 7 Days	1 4	
Water Injection 14 Days	4 (1*) 1 (4*)	
Water Injection 21 Days**	1 4	

* Experiment 3
** Experiments 2 & 3

2.5 Polymer Concentration and Retention Measurements

The concentration of polymer in the produced effluent was measured using an ultraviolet (UV) spectrometer (Agilent 8453, Agilent technologies, CA, USA). Polymer concentration was determined using calibration curves of the absorbance created from known polymer concentrations. Polymer retention (R_p) was computed, in mg per 100 grams of rock, by means of mass balance using Equation (1):

$$R_p = \frac{C_o V_o - \sum_{i=1}^{n} C_e V_e}{w} \qquad (1)$$

where C_0 and V_0 represent polymer concentration in the injected solution (ppm) and total injected volume (mL) respectively; C_e and V_e stand for polymer concentration in the effluent (ppm) and the volume of taken sample (mL); W is the dry weight of rock sample (mg); n stands for the number of collection tubes where the produced effluent was collected.

3 Results and discussion

3.1 Experiment 1 – 3000 ppm at Ambient Temperature

The presence of a polymer release, from retention sites, induced by chemical gradient can be verified by analyzing the behavior of the effluent solution concentration curve. In Experiment 1, polymer solution with 3000 ppm concentration was injected. The experiment was conducted under ambient temperature. Figure 2 shows the profile of polymer concentration in the produced effluent versus pore volume injected (PVI) for the polymer injection and subsequent water injection periods after shut in periods of 1, 7, and 14 days.

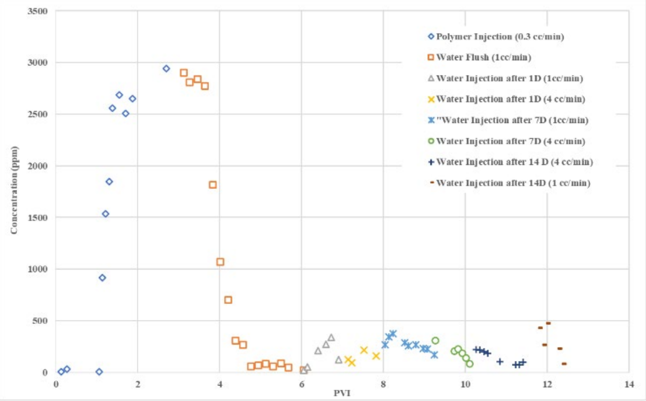

Fig. 2. Relationship between polymer concentration measured in effluent water versus PVI for experiment 1 after shut in periods of 1, 7, and 14 days.

Figure 2 shows that the produced polymer concentration reaches the injected polymer concentration of 3000 ppm around 3 PVi, after which 3 pore volumes of wash water are injected until the produced polymer concentration fades at around 6 pore volumes. After a one-day shut-in period, injection resumed, with 1 pore volume of water injected at a flow rate of 1 cc/min, followed by another 1 pore volume of water injected at a rate of 4 cc/min. A similar approach was followed following a 7- and 14-day shut in period. The cumulative pore volume injected into the core was around 12 pore volumes.

3.1.1 Effect of flow rate on the polymer released induced by the chemical gradient.

The effect of increasing the flow rate from 1 to 4 cc/min on the chemically induced released polymer is consistent with polymer retention by hydrodynamic imbalance. as illustrated in Figure 2, when the flow rate increased, the effluent polymer concentration peaked at lower levels. For example, after a one-day shut-in time, the maximum concentration of the released polymer was around 450 ppm for an injection rate of 1 cc/min and 300 ppm for 4 cc/min. This pattern is unrelated to whatever injection rate was initiated first following the shut-in time, as evidenced by the polymer concentration profile over the 14-day shut-in period, when we began with 4 cc/min and then 1 cc/min. This phenomenon is thought to occur as a result of the increased hydrodynamic retention.

3.1.2 Effect of shut-in period on the polymer released induced by chemical gradient.

Figure – 2 shows that longer shut-in periods resulted in an increase in the maximum polymer concentration observed in the effluent solution. This increase is due to the extended shut-in time enhancing the chemical gradient's ability to facilitate a greater exchange of polymer molecules between the rock and the solution within the core. Consequently, for the same injection rate, higher effluent polymer concentrations were recorded for longer shut in periods compared to the shorter shut-in periods. Additionally, with the increase in shut-in time, a more gradual decline in concentration values was noted. The temporal effect is believed to not only promote polymer desorption but also reduce the molecular attraction between polymer and rock. This combination of effects led to a gradual, rather than abrupt, decline in measured concentrations over time.

To further investigate the effect of the studied control variables (flow rate and shut-in duration) on chemically induced polymer desorption, the retention associated with the modifying/altering each of the previously mentioned parameters was calculated. Polymer retention in the core sample after each experimental step was calculated based on the mass balance equation (Equation – 1). Table 3 summarizes the retention values corresponding with implemented experimental procedures and modified parameters.

Table 3. Summary of polymer retention during experiment 1.

Rp (mg/100 g of rock)	
Polymer Flood	107.46
Initial Water Flood	97.53
Shut-in 1 Day, q = 1 cc/min	96.78
Shut-in 1 Day, q = 4 cc/min	96.46
Shut-in 7 Days, q = 1 cc/min	94.79
Shut-in 7 Days, q = 4 cc/min	94.08
Shut-in 14 Days, q = 4 cc/min	92.0
Shut-in 14 Days, q = 1 cc/min	92.0

Table 3 shows that as the experiments/injection proceeded, retention decreased. In other words, retention continued to decline as injection progressed regardless of the applied flow rate and shut-in period duration, with the most significant decline occurring during the initial waterflood. Table 3 shows that 92 mg of polymer were retained in each 100 gm of rock at the end of experiment 1 representing 85.6% of the total injected polymer.

In order to evaluate the influence of each parameter (flow rate and shut in period) on polymer desorption after having subjected the system to a chemical gradient, the percentage to which each parameter contributed to the final retention value was calculated. Figure 3 (pie chart) depicts the percentage of polymer release associated with each scenario relative to the total amount of polymer released at the end of the experimental work.

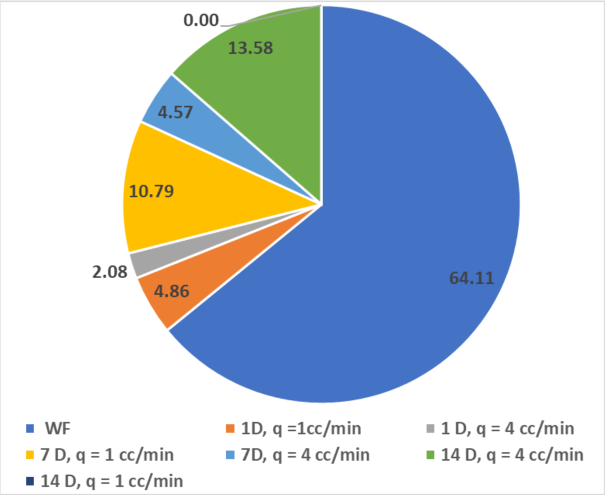

Fig. 1. Contribution of each water injection with respect to the overall polymer release after the shut-in periods for experiment 1.

The initial water flood caused the most polymer release and a decrease in polymer retention, accounting for approximately 64% of the total contribution. In fact, this proportion indicates the presence of a large amount of mobile polymer immediately following polymer injection, which can be displaced by water. The highest percentage was obtained with a 14-day shut-in time with a flow rate of 4 cc/min, resulting in a percentage of roughly 13.5%, which is thought to be mostly attributable to polymer desorption, as the subsequent injection rate of 1 cc/min released no polymer. The lowest percentages were associated with high flow rates that had been established in succession to low flow rates (q = 4 cc/min after 1 and 7 days).

The polymer release was highly influenced by the duration of the shut-in period where the observed effect of shut-in period on chemically induced polymer desorption was more pronounced after longer shut-in periods. Even in the presence of hydrodynamic retention, injecting 4 cc/s of water after having subjected the core to a shut-in period of 7 days resulted in polymer release approximately equal to the polymer release value when injecting 1 cc/s of water in core that has been shut in for 1 day.

After considering the previous discussion, it can be concluded that while extending the shut-in period is more effective in releasing the adsorbed polymer, reducing the injection rate is more effective in releasing the hydrodynamically trapped polymer.

3.2 Experiment 2 – 3000 ppm at 70°C

Experiment 2 involved repeating experiment 1 at an elevated temperature. The accumulators and the core holder were placed in an oven and the temperature was set to 70 °C. The following sections present the discussion of the experimental outcomes.

3.2.1 Effect of Elevated Temperatures on Chemically Induced Retention Values

Figure 4 shows the profile of polymer concentration in the produced effluent versus pore volume injected (PVI) during the polymer injection and subsequent water injection periods following shut in periods of 1, 7, 14 and 21 days.

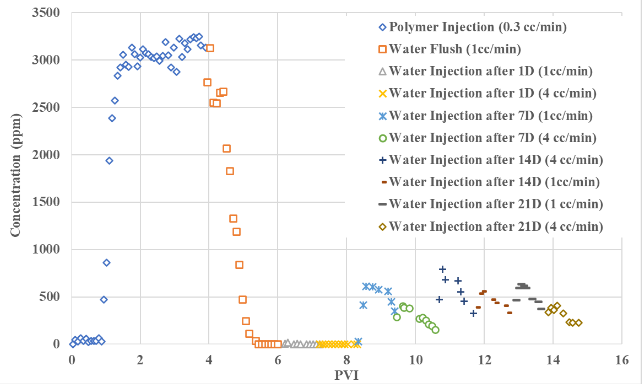

Fig. 2. Relationship between polymer concentration measured in effluent water versus PVI for experiment 2.

Figure 4 demonstrates that the effluent polymer concentration equaled the injection concentration after injecting approximately 1.6 pore volume. Furthermore, after injecting 2 pore volumes of chase water, the effluent polymer concentration was lowered to zero. After 1 day shut in period, a small trace of polymer was found in the effluent, but the amount was so small that effectively no polymer was released during this period. It was predicted that part of the hydrodynamically trapped polymer would be produced during this time. Comparing this to the results of the previous experiment, which was carried out at ambient temperature, one might conclude that temperature has an effect on the hydrodynamic entrapment of polymer molecules in porous media, with high temperature reducing the release of the hydrodynamically trapped polymers after a short time.

After 7, 14, and 21 days of shut-in, some polymers were released by introducing 2 pore volumes of water at rates of 1 and 4 cc/min after each shut in period. At elevated temperatures – despite facilitating higher polymer release therefore resulting in lower retention values – longer shut-in periods were required in order to stimulate chemical gradient. The reason is believed to be due to the requirement of longer periods for initiation and momentum of chemical diffusion to take place. Once chemical diffusion between the rock and effluent solution was stimulated, polymer concentrations were measured in the solutions exiting the core for the remaining shut-in periods of 7, 14, and 21 days.

The general trend in these cases suggests that high polymers release rate during the first imposed injection rate followed by a gradual decline. However, the effect of injection rate on the polymer production profile at elevated temperature and long shut in periods warrants further investigations.

Figure 4 shows that the polymer production did not stop during the injection cycles following shut in periods of 7, 14, and 21 days indicating that more polymers may be produced. However, we strictly followed the protocol of the previous experiment to make a fair comparison.

Various published experimental studies have established and proven that retention values at increased temperatures are lower than those at ambient temperatures [22, 23]. In this experiment, only 35% of the original polymer retained following polymer flood remained at the end of the experiment. Table 4 shows the progress of polymer retention in the core sample as the experimental procedure is executed.

Table 4. Summary of polymer retention during experiment 2.

Rp (mg/100g)	
Polymer Flood	47.84
Initial Water Flood	30.19
Shut-in 1 Day, q = 1 cc/min	30.17
Shut-in 1 Day, q = 4 cc/min	30.17
Shut-in 7 Days, q = 1 cc/min	27.50
Shut-in 7 Days, q = 4 cc/min	25.64
Shut-in 14 Days, q = 4 cc/min	22.81
Shut-in 14 Days, q = 1 cc/min	20.55
Shut-in 21 Days, q = 1 cc/min	18.3
Shut-in 21 Days, q = 4 cc/min	16.621

Table 4 shows that 47.84 mg of polymer were retained per 100 gm of rock just at the end of polymer flood. This represents 44% reduction in polymer retention compared to the value obtained in experiment 1 (107.46 mg/100gm). This is in line with the observation made by other researchers in which they noticed a strong reduction in polymer retention at elevated temperature [23]. A further reduction in polymer retention to 30.19 mg/100 gm was achieved after water washout injection. After 1 day shut in period, the retention was slightly reduced to 30.17 mg/100 gm indicating a negligible effect of short time shut in period on the polymer release. After the subsequent shut-in periods, it can be seen from Table 4 that polymer retention is reduced by 2 mg/100 mg after changing the injection rate. Figure 5 exhibits the polymer release contribution relative to the implemented experimental work.

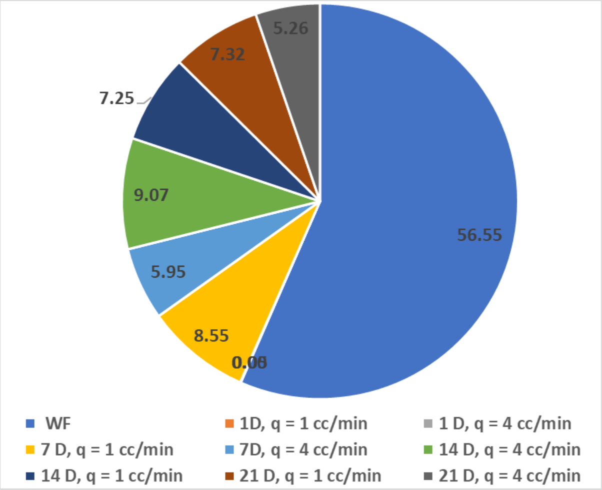

Fig. 3. Contribution of each water injection with respect to the overall polymer release after the shut-in periods for experiment 2.

The greatest contribution, ranked after the initial water flood, occurred after a shut-in duration of 14 days, at 4 cc/min with a contribution of approximately 9% as opposed to the low injection rate of 1 cc/min. During such experimental phase, the implementation of the high injection rate (4 cc/min) preceded the injection of brine at a low rate (1 cc/min). The deviation from conventional behavior observed in the previous and proceeding stages – that is, the association of low injection rates to increased polymer release quantities – may be explained by the fact that the combined effect of a long shut-in period as well as the persistence of an elevated temperature stimulated and augmented the de-adsorption of polymers from the rock surface, resulting in the release and re-absorption of polymer molecules into the effluent solution regardless of the injection rate applied. This raises uncertainties and provides prospect to further investigations regarding the sensitivity of polymer release after shut-in periods with respect to various injection rates.

3.3 Experiment 3 – 1500 ppm at Ambient Temperature

Following the methodical approach used in the previous experiments and as described in the sections above, a Berea Sandstone core was flooded with a 2.58 PVI polymer solution consisting of the same Flopaam 3630 S injected at a rate of 0.3 cc/min. The experiment was designed to investigate the effect of polymer concentration on the degree to which a chemical gradient occurs. The waterflood that preceded the polymer flood spanned another 2.07 PVI. After that, the core was shut in.

3.3.1 Effect of Concentration on Chemically Induced Retention Values

Experiment 3 investigated the effect of concentration reduction on overall retention values and polymer release at various stages of shut-in periods. The polymer flooding step was followed by an injection of chase water until no polymer was seen at the core outlet. The core then was shut in. After specific shut-in periods, water injection was resumed at injection rates of 1 cc/min followed by 4 cc/min as detailed in Table 2. Figure 6 shows the profile of polymer concentration in the effluent versus pore volume injected (PVI) during polymer injection and subsequent water injection periods following shut in periods of 1, 7, 14 and 21 days.

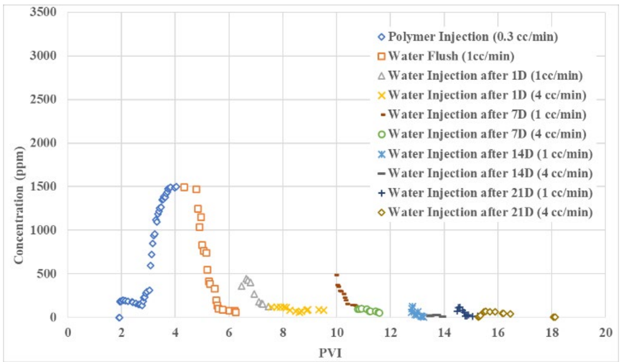

Fig. 4. Relation between polymer concentration measured in effluent water versus PVI for experiment 3.

At about 2 PVI, the polymer concentration equaled the effluent concentration and reached its lowest point after injecting 2.2 of chase water. After 1 and 7 days of shut in periods, the released polymer concentration peaked at 500 ppm during the 1 cc/min injection rate and declined gradually. The injection rate was increased to 4 cc/min, which extended the gradual decline further. Similar behavior was found after 14 and 21 days shut in periods, albeit at lower peaked polymer concentrations. Contrary to the results of experiment 1, variations in injection rate do not appear to have a significant impact on the released polymer concentration in polymer flooding cases having lower concentrations.

The peaked concentrations of released polymer after 1 and 7 days appear to be similar to those in experiment 1, indicating that polymer release after short shut in times is unrelated to polymer concentration. However, longer shut in periods results in less polymer released for the low polymer concentration case compared to experiment 1. It is thought that at low concentrations, the influence of longer shut-in periods on polymer diffusion into the affluent solution is greatly reduced and may be regarded minor.

Numerous scholars have investigated the impact of polymer concentration on polymer retention [24-26]. The prevailing consensus is that polymer retention tends to increase with increased polymer concentration. Zhang and Seright [24] proposed that the link between polymer retention and concentration varies according to the type of polymer solution: dilute, semi-dilute, and concentrated with the effect of polymer concentration being more prominent in semi-diluted solutions. According to their classification, the polymer solutions used in this study are considered semi-diluted solutions. As a result, lower polymer retention values are expected in experiment 3 than in experiment 1. Table 5 shows the polymer retained in the core sample following each experimental step.

Table 5: Summary of retention values during experiment 3.

Rp (mg/100g)	
Polymer Flood	49.94
Initial Water Flood	45.62
Shut-in 1 Day, q =1 cc/min	44.30
Shut-in 1 Day, q = 4 cc/min	43.92
Shut-in 7 Days, q = 1cc/min	42.56
Shut-in 7 Days, q = 4 cc/min	42.32
Shut-in 14 Days, q = 1 cc/min	42.2
Shut-in 14 Days, q = 4 cc/min	42.2
Shut-in 21 Days, q = 1 cc/min	41.99
Shut-in 21 Days, q = 4 cc/min	41.8

Table 5 reveals that 45.62 mg of polymer were retained in the core per 100 gm of the rock after water washout, as opposed to 97.53 mg in experiment 1. This represents a 53% reduction in polymer retention. The subsequent experimental actions show a slower decline in polymer release than experiment 1. As a result, one might conclude that the effect of changing injection rate and shut in periods has a greater impact on polymer retention for polymer flooding with high concentrations. Figure 7 shows how each experimental stage contributes to the release of retained polymers.

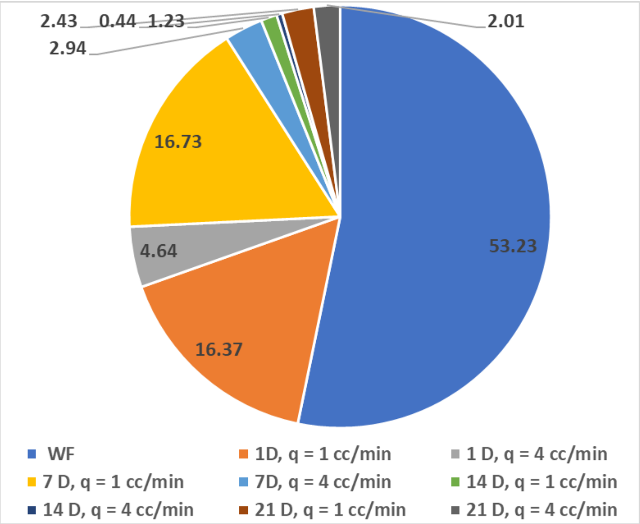

Fig. 5. Contribution of each water injection with respect to the overall polymer release after the shut-in periods for experiment 3.

Figure 7 shows that the majority of released polymers were obtained during the water washout stage (53.23%). Thus, it can be concluded that most of the retained polymer amenable to be released was collected during the washout water stage in experiments 1, 2, and 3 with a contribution ranging between 64 – 53%. Such observation is hypothesized to be the result of the presence of loose, weakly-bonded, de-adsorbable polymers in large quantities during the early stage of water washout injection. Figure 7 further indicates 16.37% of the released polymer was received with the injection rate of 1 cc/min and 4.64% with the injection rate of 4 cc/min after the shut in period of 1 day.

Furthermore, shutting in the core for an additional 7 days and then followed by the injection of 1 cc/min of water resulted in a contribution percentage of 16.73%. Polymer release dropped significantly after additional shut-in periods of 14 and 21 days. When compared to the other experimental phases, the effect of longer shut-in time on polymer diffusion from rock surface to the effluent solution is considerably minimal. Thus, over long shut in periods and for low polymer concentration floods, the effect of changing the injection rate has little influence on polymer release. The following section presents a comparison of polymer release trends across the three experiments.

3.4 Overall Retention Comparison

The amounts of polymer retained in core samples for experiments 1, 2, and 3 were compared to emphasize the effect of temperature, polymer concentration, injection rate, and shut in periods on the polymer release trend. To ensure a fair comparison, especially between experiments 1 and 3, the results are presented in terms of the normalized polymer retention following each experimental step. The normalized polymer retention is calculated as the ratio of the polymer retention after each experimental step to the initial retention after polymer flooding. Figure 8 depicts the trend profiles for normalized polymer retention in experiments 1, 2, and 3.

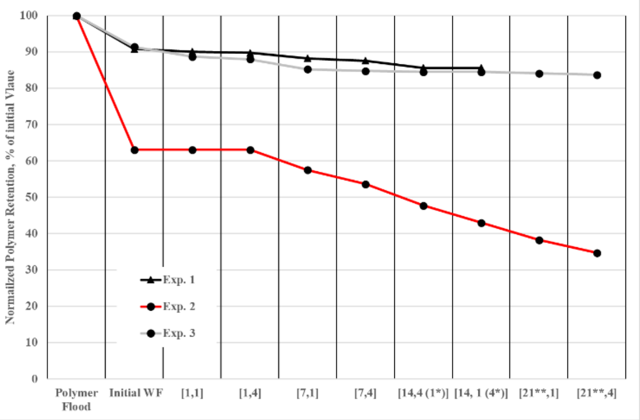

Fig. 6. Normalized retention values after each experimental step for experiments 1, 2, and 3 where x-axis represents [Shut in period, injection rate] (* Experiment 3, ** Experiments 2 and 3)

Figure 8 shows that temperature has the greatest effect on polymer retention with a reduction in polymer retention of more than 60%. Moreover, Figure 8 reveals that polymer concentration has a little effect on normalized polymer release as experiments 1 and 3 follow the same trend. Figure 8 clearly shows that the greatest reduction in normalized polymer retention in each experiment occurred after the initial water flood.

Figure 8 shows that polymer released ceased after 14 days in experiments 1 and 3. In contrast, polymer retention continues to decline after the designated 21 shut in days in experiment 2 where the temperature catalyzed polymer release from the core sample. It is worth noting that the release of polymer in experiment 2 ceased during the short time (1 day after initial water flood), which can be attributed to the necessity to establish a thermal equilibrium between the injected polymer solution and the core in order to initiate polymer release.

4 Conclusions and Recommendations

The purpose of this study was to investigate the effect of a chemical gradient on polymer retention in relation to injection rate, shut-in duration, polymer concentration, and temperature. Following polymer flooding, water washout establishes a chemical gradient between the polymer adsorbed to the rock surface and the hydrodynamically trapped polymer on one side and the polymer-free injected water on the other.

Published literature on rock fluid interactions are limited and have failed to address the rock fluid interactions instigated by the chemical gradient induced by the difference in concentration of the retained polymers and the injected water drive during polymer flooding projects. To further investigate such phenomenon/behavior, experimental work was conducted, which involved the implementation of water injection on Berea Sandstone cores that had previously been flooded with polymer. The retention values associated with different injection rates, shut in periods, polymer concentrations, and temperatures were measured, and the following observations were made:

- The presence of a chemically induced driven gradient can be verified by analyzing the effluent solution concentration curve after shutting in the core for different times.
- Polymer flooding at high polymer concentrations creates a higher chemical gradient between the adsorbed and the hydrodynamically trapped polymers on one side and the injected water on the other, promoting the release of retained polymers. In experiment 1 (3000-ppm), 15.46 mg of polymer were released per 100 gm of rock compared to 8.14 mg in experiment 3 (1500-ppm).
- The effect of shut in periods on polymer release is more pronounced in polymer flood with high polymer concentrations. However, this effect declines with prolonged shut-in periods.
- Polymer tracers were detected in the effluent solution of after a shut-in period of 14 days at ambient temperature for the experiments involving 3000 and 1500 ppm polymer floods, indicating that the maximum amount of retained polymers amenable to release was produced during the previous water injection phases.
- According to the experimental results, disturbing the hydrodynamic balance by changing the injection flow rate promotes more polymer released especially in high polymer concentration and high temperature cases.
- Following each shut in period, the polymer release trend peaks during the first implemented injection rate and gradually decreases and stabilizes afterwards. After stabilization, the combination of diluted effluent solution within the core as well as further shut-in periods causes an additional chemical gradient, which, while weak in intensity, yields an observable polymer release.
- Results pertaining to the effect of injection rate on polymer release after various shut-in periods remain ambiguous and inconclusive. As has been observed, after a given shut-in period, the preceding injection usually results in a higher contribution to the polymer release regardless of the rate applied.
- The effect of temperature on polymer release was more pronounced, resulting in low retention values and extended the time in which polymer release was measured in the effluent solution to the final stage of the experiment. In the high temperature case (experiment 2), approximately 31.2 mg of polymer were released per 100 gm of rock compared to 15.46 mg in the ambient conditions case (experiment 1).
- Due to the continuous release of polymer observed in the high temperature experiment (experiment 2), it is recommended to investigate the effect of temperature on the effectiveness of chemical gradients on polymer release over extended shut-in times.
- Given the significant influence of temperature on the polymer retention, dynamic polymer retention measurements should be performed in conditions simulating reservoir conditions.
- The initial water flood had the greatest impact on polymer release, with contribution to polymer discharge exceeding 50% across all experiments.
- It is recommended to investigate the contribution of modifying injection rates with respect to polymer discharge into the effluent solution after a given shut-in period, considering the variation of the sequence by which the rates are all altered.

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