



## Enhancing Water Flooding Efficiency in Carbonate Oil Reservoirs through Controlled Imbibition and Mobility using a Combination of Smart Water and Polymer Flooding

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### ABSTRACT

To enhance the efficiency of oil recovery, a combination of multiple methods or materials can be utilized. This study aimed to investigate a hybrid method of using smart water and polymers to improve water flooding. Moreover, in this paper the influence of sulfate on the performance of polymers for increasing the efficiency of this method is investigated. To this end, we examine mechanisms, including changes in viscosity and interfacial tension (IFT), affecting oil recovery. To assess the impact of the injected fluid on oil recovery, a micro-model consisting of sand packs prepared from carbonate rock grains was employed as a two-dimensional simulated porous medium. The Response Surface Methodology (RSM) and Central Composite Design (CCD) were used as the most precise methods to design the experiments. The design was based on five levels and three variables including three parameters of the concentration of polymers ranging from 1000 to 3000 ppm, the concentration of the ions of smart water ranging from 12210 to 54180 ppm, and the temperature of 25–75°C. Considering the defined conditions, the effects of the prepared compositions on viscosity, IFT, and oil recovery were evaluated. The highest final oil recovery obtained, for the polymer-smart water without the NaCl (Sw-NaCl) solution, was reported about 60.32% of oil originally in place (OOIP), while the lowest one was reported to be about 50.67% of OOIP.

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### 1. Introduction

Global heavy oil reserves are estimated to be approximately 3,396 billion barrels. With the

decline in light oil reserves, production from heavy oil reservoirs faces technical and economic challenges. Due to the high viscosity

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of heavy oils, the recovery factor in heavy oil reservoirs is typically less than 20%, or even as low as 10% [1]. Despite the challenges and limitations associated with water flooding for secondary oil recovery in heavy oil reservoirs, water flooding remains one of the fundamental technologies for enhancing oil production. However, early water breakthrough can lead to issues such as reduced efficiency in oil recovery. To improve oil recovery in heavy oil reservoirs, polymer flooding has been selected as a process option with higher potential compared to water flooding [2]. The control of the fluid flow during microscopic displacement enhances its efficiency, as confirmed by numerous studies, including those conducted by Pitts et al. [3]. Adding polymers to the displacement phase increases the viscosity of the water phase and reduces phenomena such as fingering or channel blockage. Furthermore, in the polymer flooding process, the polymer retention in the porous medium leads to a reduction in the permeability of the displacement phase. This behavior enables polymer flooding to be effective in improving the volumetric displacement efficiency of oil recovery [3]. Significant progress has been made in studying the microscopic mechanisms of oil displacement for this method. A study by Wang et al. 2007 demonstrated that the residual oil saturation ( $S_{or}$ ) decreases during polymer injection, a reduction attributed to the flexibility and viscoelastic properties of the polymer solution [4]. By increasing the concentration of the polymer solution, and the molecular weight or molecular structure of the polymer the viscosity of the polymer solution enhances, thereby its ability to control movement during the flooding process is improved. However, increasing the viscosity of the polymer solution may also lead to higher flow resistance in the porous medium. This, in turn, creates additional challenges for the

development of polymer technology for EOR applications and increases costs. Moreover, the higher viscosity of the polymer solution also imposes greater operational constraints on the flooding system. As the polymer solution passes through pores, high-pressure zones, and regions near the wellbore, shear effects can significantly reduce the viscosity and other properties of the polymer solution. Moreover, thermal degradation and the mineralization of the injected water by ions such as  $Ca^{2+}$  and  $Mg^{2+}$  can prevent the polymer solution from achieving the desired viscosity and reservoir requirements. Therefore, promoting the effectiveness of polymerization by creating an effective residual resistance factor in the flow zone of oil reservoirs, alongside improving the displacement efficiency and mitigating polymer molecular flow issues, remains the most efficient and reliable strategy [5].

Al-Soofi et al. (2022) investigated the synergistic effects of smart water as a potential optimization strategy to achieve more efficient and economic enhanced oil recovery (EOR) applications. The results of their investigation demonstrated that diluted polymer in smart water at the concentrations ranging from 250 to 500 ppm increased the viscosity of the injected water by 2 to 4 times, enabling better mobility control for recovering light oils. Furthermore, the use of smart water reduced chemical consumption by up to one-third and improved oil recovery by 5–7% [6]. Wang et al. (2024) examined the beneficial synergy between smart water flooding and surfactant-polymer flooding for carbonate reservoirs. Their findings revealed that injecting surfactant-polymers along with smart water achieved approximately 10% higher oil recovery compared to conventional surfactant-polymer flooding, with reduced chemical consumption [7]. Kakati et al. (2020) explored the synergistic effects of low-salinity water flooding and polymer flooding by focusing on

the impact of low salinity on polymer rheology, polymer solution injection, polymer retention in reservoir rocks, and the oil recovery efficiency of low-salinity polymer flooding. The results of this study show that low-salinity water significantly increases polymer rheology, which can substantially improve the overall oil recovery efficiency in the process [8].

Sarvestani et al. (2021) experimentally demonstrated that reinforcing low-salinity brine with a small amount of polymer, as a viscosifying agent and mobility control factor, can significantly suppress salt dispersion. They showed that adding 200 ppm of partially hydrolyzed polyacrylamide (HPAM) to the injected brine reduced dispersion by more than 70%. Furthermore, the analysis of variance revealed that the concentration of the polymer and brine salinity are the primary factors influencing dispersion [9].

Wang et al. (2023) investigated the mechanisms of enhanced oil recovery (EOR) through polymer flooding in high-porosity and high-permeability reservoirs. They analyzed the characteristics of oil-water relative permeability curves, mobility control capabilities, and microscopic features during polymer flooding in these reservoirs. Based on this analysis, they examined the effects of mobility ratio and the mechanisms for improving oil recovery. The results demonstrated that polymers could effectively enhance the mobility control of the displacing fluid. This improvement significantly increases the profile control and plugging capability of the polymer, thereby expanding the displacement volume in larger pores and improving the displacement efficiency in smaller pores [10].

Due to the low viscosity and high mobility of water compared to those of oils, the mobility of water is greater, leading to inefficient oil recovery. Therefore, to improve the effect of

water flooding in hydrocarbon reservoirs, polymers can be used to increase the viscosity of the injected solution and control mobility.

Prior studies on smart water-polymer flooding have predominantly focused on sandstone reservoirs or have not systematically investigated the synergistic effects of the concentration of sulfates and polymer mobility control in carbonate systems. Studies have demonstrated the benefits of combining low-salinity water and polymer flooding, but the role of sulfate ions as a wettability modifier in hybrid smart water-polymer systems, particularly at the micro-bed scale, remains underexplored. Our study addresses this gap by providing a comprehensive experimental investigation that (1) evaluates the individual and combined effects of sulfate-rich smart water and xanthan polymer on oil recovery in carbonate porous media, (2) quantifies the changes in wettability, IFT, and viscosity under controlled conditions, and (3) employs Response Surface Methodology/Central Composite Design to optimize the process and identify key interactions. Therefore, it is aimed in this paper to investigate the combined effect of smart water with polymer and smart water alone on oil production. In this study, xanthan polymer was used to increase viscosity for controlling imbibition and mobility. The choice of xanthan is due to its reasonable resistance to temperature and its ability to enhance viscosity and modify rheology. Additionally, the effects of increasing the concentration of sulfates in smart water on the properties of the polymer were examined. The goal of using smart water is to alter wettability, most likely to change interfacial tension (IFT), and to develop a cost-effective, accessible, and efficient method for enhanced oil recovery (EOR) in carbonate reservoirs. Moreover, in addition to improving the effect of water flooding, the polymer may influence the mobility ratio and IFT between the injected

fluid and oil, the mechanisms behind these effects will be explored. The contribution of each of these methods to EOR will also be determined.

## 2. Materials and methods

Xanthan gum, a heteropolysaccharide with a basic structure consisting of repeating Penta saccharide units, is composed of two glucose units, two mannose units, and one glucuronic acid unit. This polymer generally has a very high molecular weight and extremely stiff polymer chains. The xanthan gum used in this study is a product from Sigma, manufactured in Germany. It is a natural polysaccharide and a vital biopolymer in the industry, with a purity

of 99.5%. Smart water was considered as the injection fluid for oil recovery in this study. Additionally, for preparing brine, salts including sodium chloride, magnesium chloride, calcium chloride, sodium sulfate, and sodium bicarbonate from Merck with 99% purity were used. The oil from the southwestern region of Iran, specifically from Gachsaran, was utilized for the experiments. The molecular weight of this oil is 254 grams per mole, and its specific gravity at 60°F is reported to be 0.834. The characteristics of production water, formation water and crude oil are given in Table 1 and 2.

**Table 1.**

Concentration of salts in formation water and injection fluid

| Salts                                | Formation water(ppm) | Injection fluid(ppm) |                     |                     |              |
|--------------------------------------|----------------------|----------------------|---------------------|---------------------|--------------|
|                                      |                      | Sw                   | Sw+2SO <sub>4</sub> | Sw+4SO <sub>4</sub> | Sw-NaCl      |
| NaCl                                 | 70000                | 23157                | 23157               | 23157               | -            |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O | 1425                 | 5169                 | 5169                | 5169                | 5169         |
| CaCl <sub>2</sub> ·2H <sub>2</sub> O | 20100                | 1125                 | 1125                | 1125                | 1125         |
| Na <sub>2</sub> SO <sub>4</sub>      | 1290                 | 3663                 | 14155.5             | 24648               | 5935         |
| NaHCO <sub>3</sub>                   | 1000                 | 81                   | 81                  | 81                  | 81           |
| <b>Total dissolved salt (TDS)</b>    | <b>93815</b>         | <b>33195</b>         | <b>43687.5</b>      | <b>54180</b>        | <b>12310</b> |

**Table 2.**

Components of crude oil

| Components                  | Mole % |
|-----------------------------|--------|
| H <sub>2</sub> S            | 0.722  |
| C <sub>3</sub>              | 9.356  |
| IC <sub>4</sub>             | 1.905  |
| NC <sub>4</sub>             | 5.555  |
| IC <sub>5</sub>             | 2.494  |
| NC <sub>5</sub>             | 3.213  |
| NC <sub>6</sub>             | 5.156  |
| C <sub>7</sub> <sup>+</sup> | 71.599 |

A stirrer was used to homogenize the polymer solution and to dissolve the salts in distilled water. A syringe pump (SP1000),

manufactured at the nanoscale, was used to inject fluids onto the surface of the micro-rock bed. To determine the viscosity of the solutions, a DV3TLVTJ0 rheometer, produced by Brookfield, was utilized. The IFT measuring device enables the measurement of the surface tension between liquids using both the ring and the immersed plate methods. To evaluate the performance of fluids in a porous medium for improving the effect of water injection, a micro-rock bed with a transparent polymethyl methacrylate (PMMA, Plexiglass) body was constructed. This micro-bed was designed using carbonate rocks with different mesh sizes to reduce porosity and was fully

sealed using O-rings. The specifications of the micro-rock bed and its structural

representation are provided in Table 3 and Figure 1 respectively.

**Table 3.**

Specifications of the Simulated Two-dimensional micro-Bed composed of Rock Grains

| Porosity (%) | Pore Volume (cm <sup>3</sup> ) | Depth (μm) | Width (cm) | Length (cm) |
|--------------|--------------------------------|------------|------------|-------------|
| 33.3         | 7.128                          | 0.3        | 3          | 26          |



**Figure 1.** Schematic of the simulated two-dimensional micro-bed composed of carbonate rock grains

To prepare the viscosifying agent solution, first the polymer and deionized water were weighed, then, the polymers were added to a beaker containing deionized water. The beaker containing the polymer solution was placed on a stirrer for 60 minutes. Afterward, the prepared polymer solution in the specified amount was added to the brine solutions in each section of the experimental design and mixed on a stirrer for 10 minutes to ensure uniformity. A specific amount of each solution was then used for the designated analyses.

### 3. Injection of fluids into the micro-bed of rock

After creating a vacuum space, every hour, 1 milliliter of water was injected into the micro-bed at a rate of three times the pore volume to saturate it with brine. Then, the oil was injected at a rate of 1 milliliter per hour, three times the pore volume, to displace the formation water and create an initial oil saturation. Subsequently, to make the rocks oil-wet, the micro-bed was placed in an oven at 75°C for 14 days to oil-wet the rocks within the micro-

bed. Next, to enhance the performance of water flooding in the micro-bed, the prepared smart water was used as the injection fluid for secondary flooding. It was injected at a rate of 1 milliliter per hour at a ratio of 1.5 times the pore volume, and the recovery for each concentration of smart water and under its respective conditions was measured. Then, a polymer-smart water solution was used as the injection fluid for tertiary flooding, also at a rate of 1 milli-liter per hour at a ratio of 1.5 times the pore volume, and the recovery for the third injection was measured again. Finally, the ultimate oil recovery was measured. The initial oil saturation ( $S_{oi}$ ) was determined by the material balance method: the volume of the oil injected into the dry micro-bed minus the volume of oil produced during the initial oil injection stage. Residual oil saturation ( $S_{or}$ ) was calculated from the volume of the oil produced during the water flooding stages. The pore volume of the micro-bed was determined by weighing the dry and fully brine-saturated pack. Also to make sure about the results, saturations have been calculated by the image analysis and processing several photos taken at different steps of flooding.

## 4. Results

### 4.1. Results of Viscosity Testing

#### 4.1.1. Effect of the concentration of polymers on viscosity

As shown in Figure 2, increasing the concentration of the polymer leads to an

increase in the viscosity of the polymer-smart water solution. The increase in the concentration of the polymer causes molecular interactions between the polymer molecules, known as hydrodynamic interactions, which have a long-range effect. As a result, real network structures are formed [11]. At low concentrations, xanthan exhibits thermal sensitivity, which is partly associated with a decrease in the chain strength at high temperatures [12]. The presence of salt in the xanthan solution leads to a decrease in its viscosity, which is related to changes in the structure of the side chains and the main chain. When electrostatic interactions are influenced

by the electrolyte, xanthan adopts a regular helical structural state, where the side chains interact with the main chain through strong hydrogen bonding interactions. In the absence of an electrolyte, the side chains move away from the main chain, and due to intra-molecular electrostatic repulsive forces, the main chain is stretched and remains in that state. The expansion of the side chains and the random arrangement of the structure, in the absence of salts, effectively increases the hydrodynamic volume of the biopolymer, which results in the increased entanglement and viscosity of the solution [12].

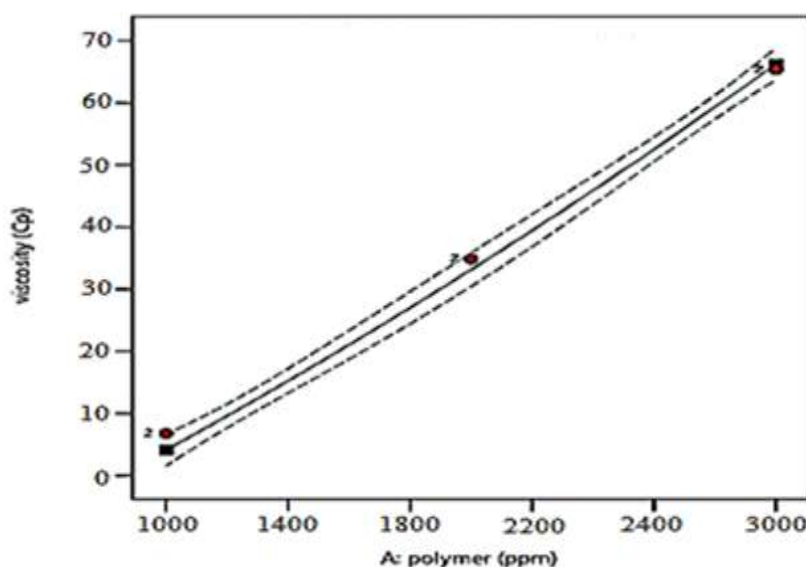


**Figure 2.** Effect of the concentration of polymers on the viscosity of the polymer-smart water solution. Increasing the concentration of xanthan indicated an increase in viscosity.

#### 4.1.2. Effect of temperature on viscosity

As shown in Figure 3, increasing temperature leads to a decrease in the viscosity of polymer-smart water solutions. This effect occurs because by rising temperature, the strength of polymer molecules decreases, and in other words, the polymeric structure in the solution changes, resulting in reduced viscosity. However, it is important to note that very high temperatures may cause the degradation of polymers. For example, it has been observed

that at temperatures between 120 and 150°C, polymers may lose their viscosity [13]. This highlights the necessity of precise temperature control in processes involving polymer-smart water solutions to prevent polymer degradation and maintain the desirable characteristics of these solutions. Additionally, high temperatures accelerate the oxygen free radical reactions, which in turn accelerate the polymer degradation process. The rate of polymer degradation was also investigated at

three different temperatures (140, 120, and 73°F), and the results indicate that at higher temperatures, polymer degradation occurs more rapidly. However, the total loss of polymer viscosity is found to be similar at all three temperatures. Upon observing the effect

of high temperatures on the flow behavior of the xanthan solution, it is evident that this polymer begins to exhibit behavior similar to that of a Newtonian fluid at 80°C under low shear rates [13].

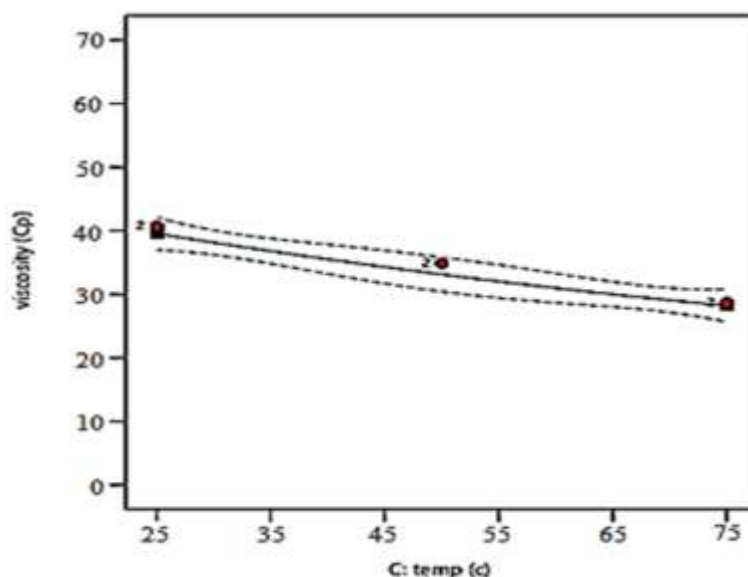


**Figure 3.** Effect of temperature on the viscosity of the polymer-smart water solution. Increasing temperature reduces the viscosity of the xanthan and smart water solution.

#### 4.1.3. Effect of the Concentration of Smart Water on Viscosity

As shown in Figure 4, increasing salinity can lead to a decrease in the viscosity of polymers. This is due to the effect of water in absorbing or releasing water molecules around the polymer chains. This phenomenon is known as the "water effect." When a polymer solution dissolves in water, water attaches variably to the polymer chains. The attachment of water to the chains increases the distance between the chains, and consequently, the volume of the solution increases. As salinity increases, more water attaches to the salt molecules. This results in less water attaching to the polymer chains, causing the distance between the chains to increase. This increase in distance

reduces the interaction between the chains and increases the free movement of the polymer molecules. In other words, increasing salinity decreases the attraction of water to the polymer chains, leading to less water attaching to the polymer, which results in increased movement and greater freedom of polymer molecules, thereby reducing viscosity [14]. However, here, with the increase in the concentration of the  $\text{SO}_4$  ions in seawater, the viscosity of the polymer increases slightly compared to the same under other experimental conditions. This is due to the intermolecular interactions between the polymer and sulfate ions, as well as the formation of viscosity layers and bubbles in the solution [14].

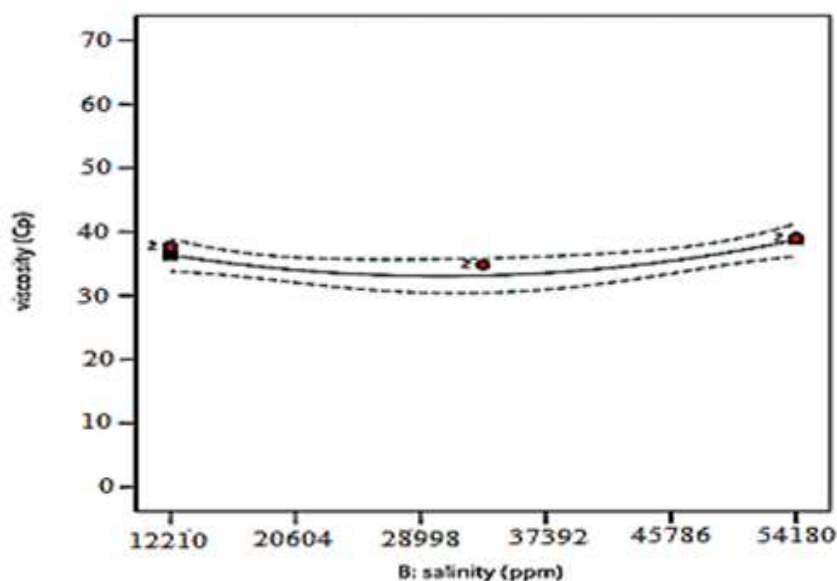


**Figure 4.** Effect of the concentration of the salt on the viscosity of the polymer-smart water solution. The effect of the sulfate and its impact on viscosity are examined in this graph.

## 4.2. Surface tension study

### 4.2.1. Effect of the concentration of polymers on surface tension

As shown in Figure 5, generally, with an increase in the concentration of the polymer in the polymer-smart water solution, and according to laboratory test results, the IFT between the oil and the polymer-smart water solution decreases. This reduction occurs because adding polymer increases the viscosity of the aqueous phase, thus lengthening the time for molecules to spread

from the aqueous phase to the interface [15]. However, this effect is less pronounced compared to the impact of surfactants on IFT, likely because polymers typically remain in the aqueous phase, and their properties differ from those of surfactants that can exist in various phases [15]. In the graphs, the closer the dashed lines around the solid line are to it, the more accurate the model is. The red points on the graph represent the experimental design points.

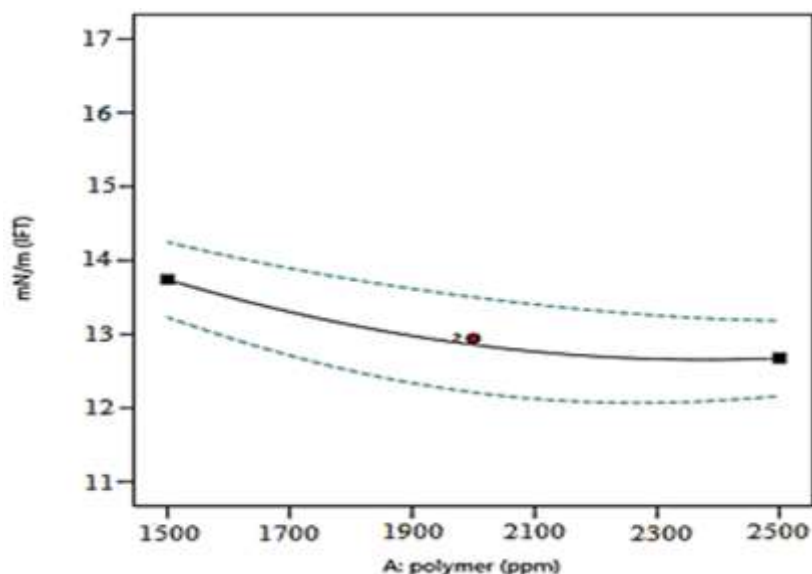


**Figure 5.** Effect of the concentration of polymers on the IFT between the oil and polymer-smart water solution. Increasing the concentration of xanthan polymer reduces the surface tension.

#### 4.2.2. Effect of temperature on surface tension

As shown in Figure 6, during the use of the polymer, an increase in temperature leads to a decrease in the IFT between the oil and the experimental solution. This effect may be due to the reduced water content in the polymer molecules at higher temperatures. In other words, as temperature increases, hydrophobic interactions between polymer molecules are strengthened, which facilitate the adsorption of polymer molecules onto the oil phase [15]. The effect of temperature on the properties of

materials is due to its direct impact on molecular energy, molecular movement, and molecular expansion. Although it is generally accepted that temperature changes inversely affect surface tension [16], an increase in temperature may result in increased entropy, reduced molecular attraction, and a decrease in IFT. It may also reduce the possibility of molecular aggregation at the oil-water interface, as the increased molecular energy reduces the chances of molecular clustering at this surface [16].

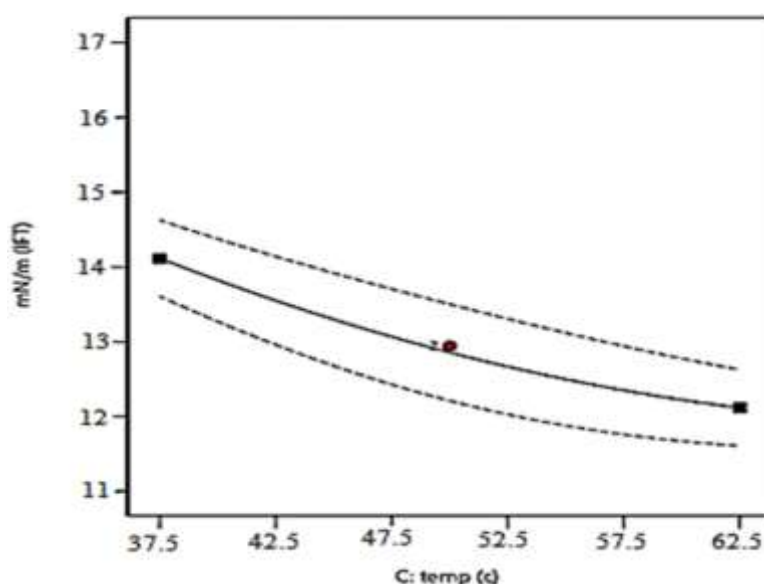


**Figure 6.** Effect of temperature on the IFT between the oil and the polymer-smart water solution. Elevating temperature leads to a decrease in surface tension.

#### 4.2.3. Effect of smart water on IFT

As shown in Figure 7, an increase in salinity generally leads to an increase in surface tension. However, due to the presence of xanthan polymer and the application of temperature to the solution, the addition of key ions such as magnesium, calcium, and sulfates to the xanthan structure results in a decrease in surface tension. The primary role of xanthan is to increase the viscosity of the injected fluid,

improving the mobility ratio and sweep efficiency. This is its main function, consistent with established polymer flooding mechanisms. Any observed reduction in IFT is likely minor and could be due to the presence of the polymer at the interface or to the interactions with other components in the system, but it is not indicative of true surfactant behavior. Additionally, in the  $Sw+2SO_4$  solution, an increase in IFT is

observed due to the elevated concentration of sulfate ions in seawater (compared to regular seawater). The molecular interactions between sulfate ions and the polar components of the oil form a hard viscoelastic layer. This elastic layer promotes continuous oil flow and also resists phase breakdown in the oil. Moreover,

the re-increase of sulfate ions in the  $Sw+4SO_4$  solution compared to seawater may reduce the efficiency of xanthan as a surface tension reducing agent, either through interference with xanthan functionality or competition for the interface, thereby leading to an increase in the surface tension of the solution [17].

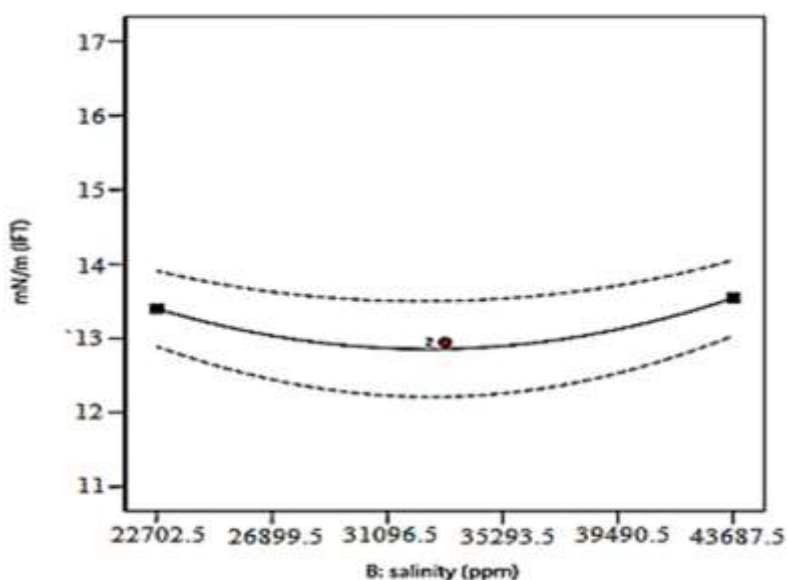


**Figure 7.** Effect of the concentration of smart water on the IFT of the oil and polymer-smart water solution.

#### 4.3. Results of flooding tests with sand pack

The main focus of this project is to enhance the effect of water flooding through smart water and polymer flooding. Polymer flooding refers to introducing an aqueous solution containing polymers into the reservoir via an injection well to displace the oil towards the production well. Adding polymers to the injected water increases the viscosity of the injected phase. This increase in viscosity improves the oil recovery process and creates favorable mobility between the injected water and the oil. This leads to better efficiency and effectiveness in the injection and oil recovery process.

As shown in Figure 8, the highest oil recovery is observed with the injected water  $Sw+4SO_4$ ,

at 41.47%. The increase in the sulfate content in the injection water  $Sw+4SO_4$  and formation water influences IFT and viscosity forces. Additionally, the recovery rate for  $Sw-NaCl$  is 44.39%, which can be attributed to potential-determining ions (PDI) such as  $Mg^{+2}$ ,  $Ca^{+2}$ , and non-PDI ions like  $Na^{+}$ . Another factor contributing to this recovery rate is the reduction in the hardness of smart water, meaning the decrease in salinity of the water plays a crucial role in the oil recovery rate. Based on the reasons discussed previously, the recovery rates for the injected water  $Sw+2SO_4$  and  $Sw$  are 41.37% and 38% respectively. Moreover, the breakthrough time for all cases is after 0.4 times the pore volume [17].

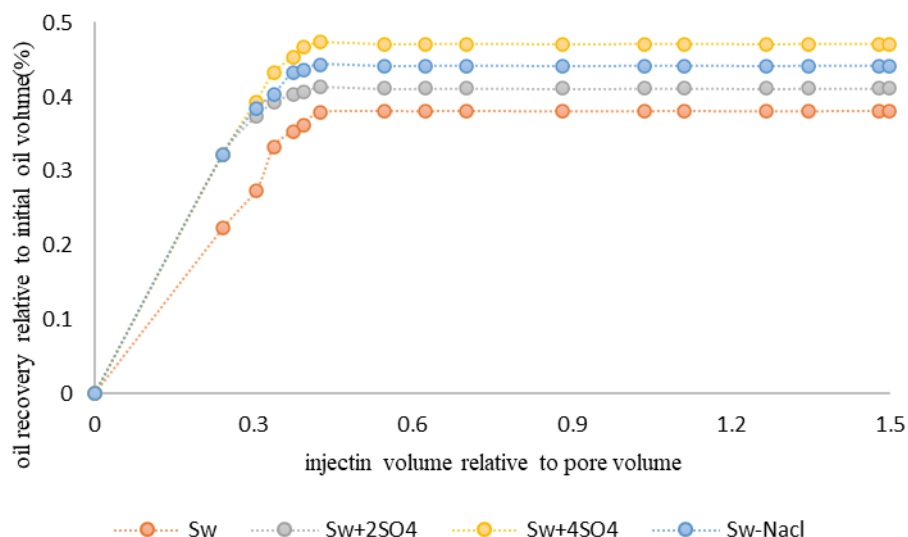


**Figure 8.** Oil recovery rate relative to the injected volume of four types of smart water. The results show the oil recovery rate compared to the initial oil volume.

According to Figure 9, after secondary injection, reinjection is carried out using the polymer-smart water solution. The concentration of the polymer for re-injection was chosen in such a way that its viscosity falls between the viscosity of the water and the oil, and the concentration of the polymer is fixed for all cases. The injection of the polymer-smart water solution led to the recovery of the oil in areas where the injection fluids in the secondary injection caused the oil to detach

from the surface, and the detached oil, which had not been produced, was recovered. This is due to the presence of potential-determining ions and the removal of non-potential-determining ions. Therefore, based on the mentioned reasons, the recovery rates for Sw-NaCl, Sw, Sw+2SO<sub>4</sub>, and Sw+4SO<sub>4</sub> are 15.93%, 12.67%, 9.43%, and 8.57% of OOIP respectively [17].

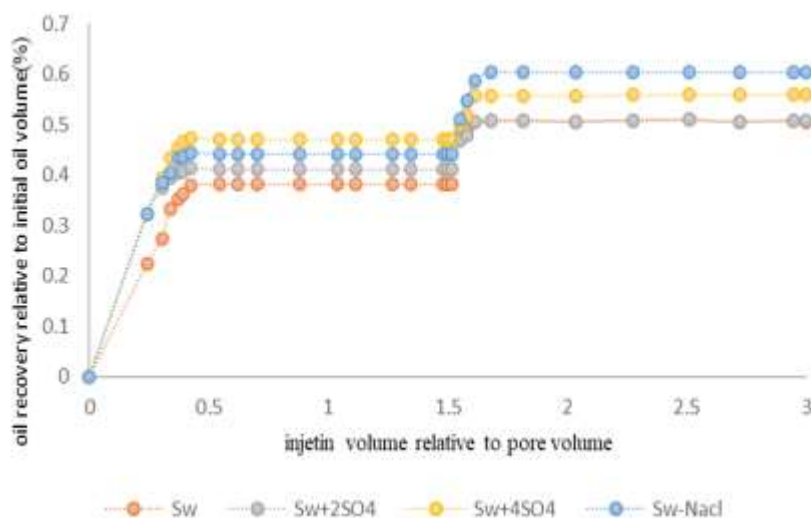


**Figure 9.** Tertiary flooding with the xanthan polymer solution at a constant concentration and smart water at various concentrations.

In Figure 10, it can be seen that in the red columns, when smart water is used as the injection fluid, the sulfate ion significantly increases oil recovery due to its effects on viscosity and changes in the wettability of the carbonate rock surface. However, the relationship between the sulfate ion added to the injection water and oil recovery is not exactly linear. Therefore, having an optimal amount of sulfates suggests that the interaction between formation water and injection water is essential and important. The yellow columns indicate that when polymer is added to the injection fluid, the viscosity increases, reducing the mobility or, in other words, controlling this parameter, which leads to an increase in oil recovery during the secondary flooding. A detailed explanation of this part is provided in Figure 10. Additionally, the total recovery rates for the two injections are as follows: 60.32%, 55.98%, 50.8%, and 50.67% of OOIP for Sw-NaCl, Sw+4SO<sub>4</sub>, Sw+2SO<sub>4</sub>, and Sw respectively. We attribute this to the

enhanced wettability alteration towards water-wet conditions due to the higher concentration of the sulfate. Sulfate ions act as potential-determining ions, adsorbing onto positively charged carbonate surfaces and displacing adsorbed carboxylate groups from crude oil, thereby promoting water-wetness and spontaneous imbibition. This leads to improved oil displacement during the secondary (smart water) flood. While Sw+4SO<sub>4</sub> provides a strong initial boost, the Sw-NaCl brine has the lowest overall ionic strength and TDS. This results in a more significant expansion of the electrical double layer, altering zeta potential and weakening the electrostatic interactions between the oil and the rock surfaces. This may lead to incremental oil recovery during the subsequent polymer flood, resulting in higher ultimate total recovery. The polymer in this case provides the necessary mobility control to efficiently sweep the reservoir.

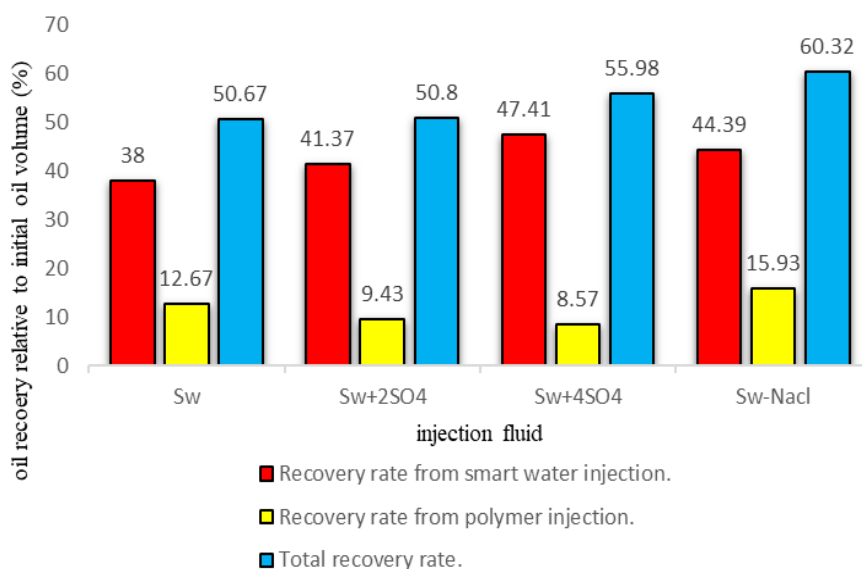


**Figure 10.** Results of flooding with four types of smart water at a constant concentration of polymers, summarizing secondary flooding, tertiary flooding, and the final recovery rate relative to the initial oil.

## 5. Conclusion

At the higher concentrations of xanthan, water molecules are trapped within the polymer structures, and their movement becomes restricted. This phenomenon leads to a reduction in the free flow of water and an increase in the viscosity of the solution.

The increase in the amount of  $\text{SO}_4^{2-}$  ions in seawater slightly increases the viscosity of the polymer. This behavior is due to the formation of viscous layers in the solution. Viscosity layers refer to those formed in viscous liquids, especially in polymer solutions. In the presence of multivalent cations such as calcium ( $\text{Ca}^{2+}$ ) or magnesium ( $\text{Mg}^{2+}$ ), sulfates can increase the viscosity of xanthan. These multivalent cations can serve as bridges, linking xanthan polymer chains together. In this case, sulfate ions indirectly interact with multivalent cations to create inter-chain networks, resulting in the formation of a stronger gel structure, which increases viscosity.

Xanthan contains both hydrophilic (water-attracting) and hydrophobic (water-repelling) sections. In aqueous solutions, its hydrophilic parts tend to interact with water, while its hydrophobic parts tend to interact with the oil phase. This duality causes xanthan to act as a surfactant, helping to reduce IFT. As a result, an increase in the concentration of xanthan leads to a decrease in interfacial tension, as xanthan molecules migrate to the interface and form a protective layer, reducing direct interactions between the two phases. This phenomenon is due to the surfactant properties of xanthan, the formation of molecular layers, the reduction in surface free energy, and the prevention of the accumulation of water molecules at the interface.

Increasing temperature decreases the surface tension of xanthan polymer that is due to the fact that raising temperature increases molecular mobility, reduces viscosity,

weakens hydrogen bonds, and induces structural changes in polymer chains. These changes allow xanthan molecules to be distributed more effectively at the interface between the two phases, thus reducing surface tension.

Increasing salinity generally increases surface tension, but in this case, due to the presence of xanthan polymer and the application of temperature, the addition of potential determining ions such as magnesium, calcium, and sulfates to the xanthan structure leads to a decrease in surface tension. Additionally, in the Sw+2SO<sub>4</sub> solution, an increase in IFT is observed due to the elevated concentration of sulfate ions in seawater (compared to regular seawater). Moreover, the re-increase of sulfate ions in the Sw+4SO<sub>4</sub> solution compared to seawater, can reduce the efficiency of xanthan as a surface tension reducing agent, either through interference with xanthan functionality or competition for the interface, thereby leading to an increase in the surface tension of the solution.

In secondary flooding, the highest oil recovery rate is observed with seawater with added SO<sub>4</sub> (Sw+4SO<sub>4</sub>), which reaches 47.41%. This is due to the increase in the concentration of the sulfate in the injected water and formation water, which influences IFT and viscosity forces. The lowest recovery is observed with smart sea-water (Sw) at 38%.

Moreover, the recovery rate for Sw-NaCl is 44.39%, which can be linked to the potential determining ions (PDI) such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and non-potential determining ions (non-PDI) such as  $\text{Na}^+$ .

In the tertiary flooding, the polymer-water solution recovers the oil from the areas where the injection fluids in the secondary injection process have separated the oil from the surface, but the separated oil was not produced. In this section, the highest recovery is observed for Sw-NaCl, with a recovery rate of 15.93%. This

is due to the presence of potential determining ions and the removal of non-potential determining ions.

We explicitly state that the results are derived from a two-dimensional micro-bed system and acknowledge the inherent limitations of this model compared to those of full-field reservoir conditions. We emphasize that while our findings provide valuable insights into the mechanisms and potential of smart water-polymer flooding in carbonate systems, further studies at core-scale and ultimately field-scale are needed to validate these observations.

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