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Review

Hybrid Engineered Water–Polymer Flooding in Carbonates: A Review of Mechanisms and Case Studies

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Abstract: The fast depletion of oil reserves has steered the petroleum industry towards developing novel and cost-effective enhanced oil recovery (EOR) techniques in order to get the most out of reservoirs. Engineered water–polymer flooding (EWPF) is an emerging hybrid EOR technology that uses the synergetic effects of engineered water (EW) and polymers to enhance both the microscopic and macroscopic sweep efficiencies, which mainly results from: (1) the low-salinity effect and the presence of active ions in EW, which help in detachment of carboxylic oil material from the rock surface, wettability alteration, and reduction in the residual oil saturation; (2) the favorable mobility ratio resulting from the use of a polymer; and (3) the improved thermal and salinity resistance of polymers in EW. Various underlying mechanisms have been proposed in the literature for EW EOR effects in carbonates, but the main driving factors still need to be understood properly. Both polymer flooding (PF) and EW have associated merits and demerits. However, the demerits of each can be overcome by combining the two methods, known as hybrid EWPF. This hybrid technique has been experimentally investigated for both sandstone and carbonate reservoirs by various researchers. Most of the studies have shown the synergistic benefits of the hybrid method in terms of two- to four-fold decreases in the polymer adsorption, leading to 30–50% reductions in polymer consumption, making the project economically viable for carbonates. EWPF has resulted in 20–30% extra oil recovery in various carbonate coreflood experiments compared to high-salinity water flooding. This review presents insights into the use of hybrid EWPF for carbonates, the main recovery driving factors in the hybrid process, the advantages and limitations of this method, and some areas requiring further work.

Keywords: hybrid engineered water; low salinity; polymer; surfactant; wettability; interfacial tension; mobility ratio; carbonates

1. Introduction

The World Energy Outlook has reported that about 60% of oil reserves globally are concentrated in carbonate reservoirs [1]. However, due to the presence of organic and polar acidic compounds in crude oil, the majority of carbonate reservoirs tend to be oil-wet [2–4]. This results in higher residual oil saturations in carbonates, even after water flooding. During the primary recovery phase, only 10–15% of oil originally in place (OOIP) is recovered. Secondary recovery using water or gas injection can further extract 10–30% of the remaining oil. However, almost 40–60% of oil remains trapped and inaccessible, even after secondary recovery. Various enhanced oil recovery (EOR) practices are in use to recover the trapped oil volume, such as polymer flooding (PF), surfactant EOR, miscible gas injection, and steam injection. Each EOR method modifies the rock–fluid interaction (oil–water–rock, OWR) properties in a certain manner, resulting in improved recovery. For example, polymer flooding increases the displacing fluid viscosity, resulting in a favorable mobility ratio, whereas surfactant EOR causes reductions in the oil–water interfacial tension (IFT) and residual oil saturation (S_{or}) [5].

Engineered water flooding (EWF) is a relatively new EOR technique, which involves the injection of properly designed low-salinity water (LSW), disturbing the original equilibrium state of the OWR system, resulting in incremental oil recovery, which is mainly caused by the wettability modification. Additional oil recovery resulting from EWF in sandstone was first documented in 1967 [6]. In 2004, the first ever field application of EWF in sandstone as an EOR technique was published. The idea of EWF as a potential EOR process in carbonates was triggered first in the 1980s, when exceptionally high oil recovery rates were observed from the injection of seawater into fractured chalk formations under the North Sea [7–9]. Engineered water for use in carbonates is designed by tuning the injected water salinity, ionic strength, and the concentrations of potential determining ions (PDIs) Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$. EWF also has some inherent limitations, such as viscous fingering due to unfavorable mobility ratios, oil trapping, and fines migration [10]. Hence, this method may not qualify as an optimum EOR option under certain conditions, even though it is a low-cost technique.

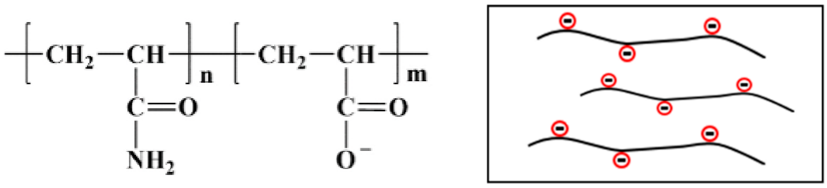
The development and implementation of novel, cost-effective EOR methods is critical for the sustainable growth of the oil industry. Research is underway on various levels to develop economically viable hybrid EOR methods and overcome the limitations of individual methods, such as hybrid engineered water–polymer flooding (EWPF) or surfactant flooding. The idea behind hybrid EWPF is to enhance oil recovery via the combined effects of optimization of the injection water composition and PF, mainly through two mechanisms. (1) Engineered water modifies the wetting characteristics of the rock surface due to the salinity and composition differences, which affects the bonding of the crude oil polar components (carboxylic material, -COOH group) with the carbonate surface and helps in oil detachment [11–13]. (2) Polymer flooding improves the macroscopic sweep efficiency by decreasing the mobility ratio [14]. In addition, EW promotes polymer stability and a reduction in the polymer concentration requirement, making PF applicable to high-salinity, high-temperature carbonate formations [15]. Hence, the hybrid method results in greater incremental oil recovery than that obtained by standalone methods.

This review paper is focused on the experimental and modeling work performed in the field of hybrid EWPF for carbonates. This paper is divided into four sections. The first section consists of a brief overview of polymer flooding, its recovery mechanism, and its associated limitations. The second part provides an overview of EWF, the mechanisms involved in recovery enhancement for carbonates, and some downsides of this EOR method. The hybrid EWPF method is discussed in the third section, including modeling studies and lab-scale examples available in literature. The review is concluded with recommendations for future work required in this area.

2. Polymer Flooding (PF)

The use of polymers in EOR as mobility control agents was first investigated in 1964 [16]. Later, various laboratory studies of polymer properties were performed [17–19]. The first field applications of polymers were carried out during 1960–1970 in the United States. Many researchers have conducted detailed reviews regarding PF projects implemented worldwide [20–23]. A successful PF project was implemented in the Marmul sandstone oil field in Oman, where PF helped reduce the water cut rate and improve the oil recovery rate [24]. As far as the implementation of PF in carbonate reservoirs is concerned, the literature shows a very small number of field projects [25,26]. In a review by Standnes and Skjevrak [27], only 5% of field projects were conducted in carbonate formations. Some of these carbonate reservoirs included the Upper Shaunavon Unit of the Rapdan field [28], ember formations in the Byron and North Oregon basin fields [29], the Eliasville Caddo Limestone Unit [30], and the Pettit formation crane zone of the Northeast Hallsville field [31].

Polymers are high molecular weight materials with specific properties based on their structures, such as their viscosification, toughness, and viscoelasticity. In contrast to water, polymer solutions exhibit non-Newtonian fluid behavior, i.e., either shear thinning or shear thickening as a function of the shear rate [32]. Two fundamental types of polymers used widely in EOR are synthetic polymers and biopolymers [33]. Hydrolyzed polyacrylamide (HPAM) is used extensively as a synthetic polymer due to its low cost and high molecular weight [34]. Standnes and Skjevrak [27] conducted a comprehensive review of the implemented EOR projects involving polymers and reported that HPAM was used in ~79% of the projects studied. HPAM is formed by copolymerization of acrylamide and acrylic acid [35,36]; its chemical and physical configurations are shown in Figure 1. HPAM consists of long flexible chains with negatively charged carboxylic groups on backbones, which repel each other and keep the polymer chains stretched, resulting in high solution viscosity [37].



(**a**) (**b**)

Figure 1. (**a**) The chemical structure [38] (**b**) physical structure of hydrolyzed polyacrylamide (HPAM) polymer.

2.1. Recovery Mechanism

The main recovery mechanism involved in PF is viscosification of the displacing fluid resulting from the addition of polymer, which is favorable for hydrocarbon recovery [39]. The addition of polymer to the displacing fluid increases its viscosity, resulting in a decreased mobility ratio, as per the fundamental relationship shown below:

$$Mobility\ ratio,\ M = \frac{Mobility\ of\ the\ displacing\ fluid,\ \lambda_D}{Mobility\ of\ the\ displaced\ fluid,\ \lambda_d} = \frac{\mu_o k_{rw}}{\mu_w k_{ro}} \quad (1)$$

where μ_o and μ_w are the viscosity values of oil and water, respectively; while k_{ro} and k_{rw} are the corresponding relative permeability values of oil and water. For the mobility ratio $M > 1$, the water moves faster, causing an unstable front advancement, early breakthrough of water, and lower ultimate oil recovery. The polymer on the other hand has relatively stable front movement, delayed water breakthrough, and better sweep efficiency. Much research has been performed in the area of PF to improve its applicability and outcomes [40,41]. Many researchers have studied the chemical and physical properties of polymers and their dependence on various subsurface reservoir conditions [42,43].

2.2. Challenges Associated with Polymer Flooding

The viscosification ability of a polymer (particularly HPAM) is dramatically affected by the ionic strength and salinity of the makeup brine, as well as the formation water. This is because the polymer chains undergo severe coiling and distortion in highly saline water due to the shielding or neutralization of charges present on the backbone. As a result, the polymer solution loses viscosity. Similarly, hard water also has a deteriorating effect on the viscosity of the HPAM for the same reason, i.e., divalent ions (Ca^{2+} and Mg^{2+}) reduce the polymer chain expansion by consuming negative backbone charges, resulting in polymer precipitation if the Ca^{2+} concentration is more than 200 ppm. High temperature also poses a challenge for HPAM, as it causes hydrolysis of the polymer. Many researchers have studied the effects of these critical parameters on the polymer performance [14,44–48]. Some of the important challenges for PF, including challenges related to the salinity and hardness, are given below:

- The adsorption of HPAM in carbonate reservoirs is higher than for sandstones, possibly due to the strong attraction forces between the negatively charged carboxylates on the HPAM backbone and the positively charged calcite surface (Figure 2);

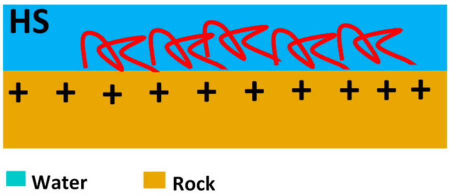


Figure 2. Schematic illustration of polymer degradation and adsorption in high-salinity water.

- The degree of polymer adsorption increases with increasing brine salinity (NaCl concentration), as seen in Figure 3 [43];

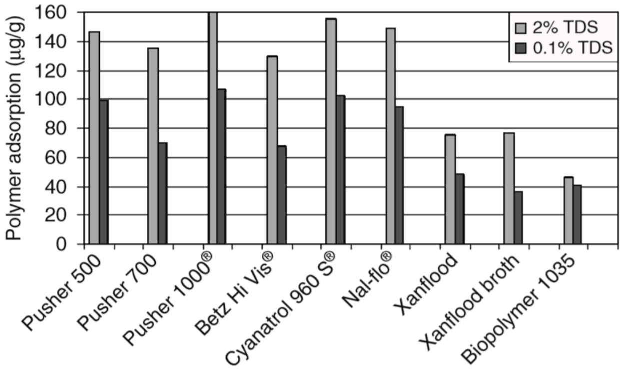


Figure 3. Effects of salinity on the adsorption of different polymers [43]. TDS: Total dissolved solids.

- High-salinity and high-temperature conditions are major challenges for conventional PF due to the instability and degradation of polymers under such conditions [49];
- Extraction and recycling of polymer from the production stream is a major operational challenge, which can substantially increase the project cost [50–52].

Scientists and researchers have put forth a great deal of effort and the PF technique has greatly improved over the years. Despite these advancements, there are several limitations that need to be carefully evaluated in order to make this method an economically viable solution for carbonates. The applicability of polymer flooding in carbonates is primarily limited by the formation water salinity, makeup water salinity, hardness, formation temperature, and high chemical degradation of polymers [21,53,54]. These constraints need to be addressed to accomplish oil recovery objectives, hence leading us to the idea of a novel hybrid EOR method that includes both PF and EWF.

3. Engineered Water Flooding (EWF)

At present, research work on enhanced oil production involving the modification of the chemistry of the injected brine is being extended to carbonates, which is apparent from an increasing number of related research publications [55–59]. A number of coreflood studies have shown incremental oil recovery ranging values from 5 to 30% from different carbonate rocks, including limestone and dolomite, using low-salinity or chemically tuned water (Table 1). Despite the variation in additional oil recovery rates, the EOR effect of EW is supported by all of the studies. Table S1 in the Supplementary Materials provides incremental recoveries by EWF obtained in different studies. The different recovery percentages can be attributed to variations in the oil, rock, compositions of the formation and injection water, and temperature. The EWF method gives better performance in strongly oil-wet to intermediate-wet systems and at temperatures greater than 70 °C [60]. Spiking of the low-salinity water with SO_4^{2-} ions has led to higher incremental recovery in most of the studies [61–63]. Despite the increased interest in the use of EWF EOR in carbonates, there is still a debate on the principal driving mechanisms. In some cases, mineral dissolution acts as a primary mechanism for wettability change [64,65] and incremental recovery, while in other cases multi-ion exchange (MIE) reactions and surface charge modifications are dominant [66–68]. The characteristics of a reservoir fluid system have a strong influence on the success or failure of the EWF process.

The research conducted to date indicates that more than one mechanism is responsible and that certain conditions need to be met to achieve the desired effects of EWF EOR. Additionally, the mechanisms in carbonates are different from those reported in sandstones, possibly due to the absence of clay in the carbonates [69,70]. In sandstones, the presence of clay is considered to be critical to achieving the low-salinity EOR effect, as the clay particles are released from the rock's surface due to the salinity difference between the injected and in situ brines, detaching the organic oil components and altering the sandstone's wettability [6,60,71]. However, low salinity alone may not be enough to recover trapped or adsorbed oil in carbonates due to their positive surface charge.

Table 1. Summary of corefloods where incremental oil recovery was achieved using engineered water flooding (EWF) in carbonates.

Study	Rock Type	Brine TDS (g/L)	Potential Determining Ions (PDIs)	Acid Number (AN) (mg KOH/g)	Temperature (°C)	Injection Mode	Incremental Recovery (%OOIP)	Remarks
Bagci, Kok [72]	Unconsolidated limestone	FW: Nil EW: 20	KCl	-	50	Secondary	18,4	2 wt% KCl case resulted in maximum recovery due to reduction in pH
Fathi, Austrad [61]	Outcrop chalk cores	FW: 62.80 EW: 16.79	4 times the amount of SO_4^{2-} and 4 times the amount of Ca^{2+}	Oil A: 2.0 and Oil B: 0.5	70–120	Secondary	24	The highest recoveries using EW were observed in 90–120 °C temperature range with SO_4^{2-} ions. Effect of Ca^{2+} was observed only at 120 °C. indicating that Ca^{2+} is less active at lower temperatures.
Gupta, Smith [73]	Limestone and dolomite	FW: 181 EW: 33	4 times the amount of SO_4^{2-}	0.11	70 °C for dolomite and 120 °C for limestone	Tertiary	9% in dolomite and 5.1% in limestone	The lower recovery for the limestone core was attributed to anhydrite precipitation at higher temperatures.
Yousef, Al-Saleh [74]	Limestone	FW: 213 EW: 5.7	SO_4^{2-}, Ca^{2+}, and Mg^{2+} present in sea water	0.25	100	Tertiary	18	The highest tertiary recovery by LSW is attributed to improved connectivity between pore systems due to mineral dissolution by salinity gradient.
Zahid, Shapiro [60]	Reservoir carbonate and outcrop chalk	FW: 213 EW: 57	SO_4^{2-}, Ca^{2+}, and Mg^{2+} present in sea water	0.96	Ambient and 90 °C	Tertiary		LSW did not result in any incremental oil at ambient temperature because of negligible activity of potential ions. Higher recovery from carbonate at 90 °C was possibly due to dissolution reactions. Poor recovery from chalk was due to water wet nature of cores.
Chandrasekhar and Mohanty [62]	Limestone	FW: 179 EW: 5.7	SO_4^{2-}, Ca^{2+}, and Mg^{2+}	2.45	120	Secondary and tertiary	32–36	LSW with SO_4^{2-} and Mg^{2+} gave best results in terms of oil recovery and wettability alteration. Ca^{2+} ions were not effective. Ion exchange and mineral dissolution were dominant mechanisms. Higher EW recovery can also be due to higher AN oil.
Al-Attar, Mahmoud [63]	Limestone	FW: 197 EW: 5	SO_4^{2-}, Ca^{2+}	-	25	Secondary	24	SO_4^{2-} addition gave the highest recovery. However, addition of Ca^{2+} had a negative effect on recovery
Awolayo, Sarma [75]	Limestone	FW: 261 EW: 43.9	4 times the amount of SO_4^{2-}	-	110	Tertiary	10	Increasing SO_4^{2-} beyond 4 times the original amount did not give any incremental recovery possibly due to $CaSO_4$ precipitation triggered at higher temperatures.
Alameri, Teklu [76]	Fractured limestone	FW: 100 EW: 12.8	-	-	90.6	Tertiary	7	LSW can work for low permeability rocks, but the incremental recovery is high in less heterogeneous reservoirs
Puntervold, Strand [77]	Outcrop chalk cores	FW: 62.83 EW: 20.24	4 times the amount of SO_4^{2-}	0.5	90	Secondary	20	LSW spiked with 4-fold amount of SO_4^{2-} ions gave maximum incremental oil as compared to original seawater.
Qiao, Li [78] and Fathi, Austad [79]	Chalk	Molarity FW: 2.198 EW: 0.794	4 times the amount of SO_4^{2-} and 4 times the amount of Ca^{2+}	1.9	110	Secondary	14–22	Effective LSW design should include higher amount of SO_4^{2-} and small amount of divalent ions to increase water-wet fraction of rock.

Table 1. *Cont.*

Study	Rock Type	Brine TDS (g/L)	Potential Determining Ions (PDIs)	Acid Number (AN) (mg KOH/g)	Temperature (°C)	Injection Mode	Incremental Recovery (%OOIP)	Remarks
Mohsenzadeh, Pourafshary [80]	Limestone	FW: 136 EW: 4.5	-	-	87	Tertiary	22.5	IFT reduction was observed to be the main LSW recovery mechanism at low reservoir temperature and lower concentration of active ions.
Fani, Al-Hadrami [81]	Limestone	FW: 102.5 EW:7.7	4 times the amount of SO_4^{2-}	-	87	Tertiary	22.2	Smaller tertiary EW slugs can provide comparable recovery to larger slugs if reasonable soaking time is given for EW to interact with the rock.
Nasralla, Mahani [82]	Limestone	FW: 239 EW: 4.4	SO_4^{2-} and Mg^{2+} present in seawater	-	100	Secondary and tertiary	7	LSW performance varies with rock properties and minerology. In low-permeability formations, LSW results in accelerated oil production at lower injection rates.
Sarvestani, Ayatollahi [83]	Limestone	FW:150 EW: 4	SO_4^{2-}, Ca^{2+}, and Mg^{2+}	0.14	90	Secondary	12	Mg^{2+} affected the oil recovery more than Ca^{2+}. The $(SO_4^{2-})/(Mg^{2+})$ ratio is the controlling factor in the wettability modification.
Masalmeh, Al-Hammadi [84]	Limestone	FW:204 EW: 0.24	-	9.25	127	Secondary and tertiary	6.5–12.5	Crude oils with high AN lead to extra oil recovery by LSW in both secondary and tertiary modes due to formation of microdispersions.

The presence of active ions, e.g., Ca^{2+} and SO_4^{2-}, in injected water is necessary to aid oil detachment from the carbonate surface [85]. Different factors govern incremental oil recovery using EW, and those that are discussed in the literature are summarized in the next section.

3.1. Recovery Mechanisms

In carbonates, the main parameter contributing to whether the carbonate is slightly water-wet or highly oil-wet is the acid number (AN; mg KOH/g of oil, -COOH group) of the crude oil [2,86,87]. The rock tends to be more oil-wet if it contains crude oil with a higher AN due to the high attraction force between the negatively charged carboxyl group (COO-) of oil and the positively charged carbonate surface [88,89]. Consequently, oil recovery is reduced with increasing AN [90]. The main mechanism governing EOR using chemically tuned water or LSW is the change of the carbonate rock's wettability to more water-wet conditions, subsequently improving the relative permeability and fractional flow of the oil [12,88,91–93]. However, the extent of this wettability change depends on many factors, including the presence of potential active ions in the low-salinity water, the reservoir temperature, the type of rock, and the composition of the crude oil.

3.2. Wettability Modification

In carbonate reservoirs, the main factors in the wettability modification are the potential determining ions (PDIs; Mg^{2+}, Ca^{2+}, and SO_4^{2-}), particularly SO_4^{2-}, in the injected water, along with the reduction in salinity. The decrease in NaCl results in a reduced ionic density in the electric double layer, which formed on the positively charged carbonate's surface, making surface access of the PDIs easier. SO_4^{2-} adsorption makes the carbonate's surface less positive, and consequently the negatively charged carboxylic group in the oil is detached, making the rock more water-wet [11,13,77,94–96]. Hence, EWF results in improved microscopic displacement. However, the macroscopic efficiency is generally poor for EWF if the mobility ratio is unfavorable. This can result in early water breakthrough, meaning incremental oil recovery may not be achieved [95,97,98]. No EW EOR effect will be observed when the system is strongly water-wet under initial equilibrium conditions.

3.2.1. Mineral Dissolution Reactions

Another mechanism involved in the alteration of the wettability is the enhanced connectivity between micropores and macropores due to mineral dissolution by EW at the micro level [9,65,99,100]. The study conducted by Den et al. [101] showed that more calcite was dissolved as the pH of the injected low-salinity brine decreased. The effluent brine pH was higher in this case, leading to crude rock surface charge modification and additional oil recovery. Another study also documented similar results, showing that increases in the effluent pH and Ca^{2+} concentration were observed after injecting different dilutions of seawater, which could lead to incremental oil production caused by modification of the wettability or alkali formation [64]. Reductions of the IFT instead of the wettability alteration have also been reported in some cases [80,102]. Experiments performed by Mohsenzadeh et al. [80] showed a reduction of the IFT of around 42% using seawater that had been diluted 20 times in a low-temperature carbonate reservoir.

3.2.2. Fluid–Fluid Interactions (Microdispersion)

Not all crude oils facilitate incremental oil recovery using EWF. It is necessary to consider the oil composition and interaction with the injected LSW in the screening criteria for carbonate reservoirs and to assess the suitability of the reservoir for EWF. Recently, Masalmeh et al. [84] carried out a comprehensive study of almost 30 offshore and onshore carbonate formations in Abu Dhabi to develop robust screening criteria for low-salinity water flooding (LSWF) based on oil–brine interactions and analysis of the resulting microdispersions. Some oils formed microdispersions with LSW (positive crude oils), which also resulted in incremental oil recovery, while others did not form microdispersions (negative crude oils) and provided negligible additional recovery upon LSWF. Similar studies by have also confirmed the role of fluid–fluid interactions in incremental recovery using LSWF [83,103,104].

3.2.3. Conditions for Engineered Water Flooding (EWF)

Chemically altered water injection results in extra oil production from carbonate rocks if favorable conditions exist. Firstly, the salinity of the injection water should be appreciably less than the salinity of the formation water in order to disturb the initial equilibrium of the system [105]. Secondly, the injection water must contain active ions, most importantly SO_4^{2-}, in order to change the carbonate rock surface charge and release adsorbed oil [85]. Temperature also has a strong influence on EWF performance, with most of the studies suggesting the temperature to be in the range of 70–120 °C for effective oil production using engineered water [106,107]. The reservoirs containing crude oil with organic acidic components are better candidates for EWF, as these reservoirs tend to be oil-wet and more residual oil saturation is available to be displaced by low-salinity engineered water [84].

3.3. Limitations of EWF

The results reported in the literature show that EWF can potentially be used as an EOR technique for carbonate rocks. The corefloods performed by Ravari et al. [108] showed ~28% incremental oil recovery using chemically tuned water. Experiments performed by Yousef et al. [109] also showed encouraging results using diluted versions of seawater. However, there have also been unsuccessful cases where EWF did not lead to any incremental oil recovery in either sandstone or carbonate reservoirs [97,98,110–113]. The injection of low-salinity water (440 ppm) in the North Sea Snorre field single-well pilot test resulted in negligible extra oil, despite a 2% incremental recovery of OOIP in laboratory corefloods. The main reason was the initial reservoir wettability, which was more water-wet.

As with conventional water flooding, the problem involving unfavorable mobility ratios also exists with EWF due to the viscosity difference between the displaced and displacing fluids [97]. The use of LSWF in four different fields in Russia resulted in very little to negligible incremental oil recovery. Field tests in the Pervomaiskoye field showed a three-fold reduction in the relative permeability of the water and 3.5% extra oil recovery using LSWF. However, no incremental recovery was achieved using LSW (1.0 mol/L ionic strength) in the Bastrykskoye sandstone field pilot test, despite a five-fold reduction in the relative permeability of the water in corefloods. Furthermore, 2.7% additional oil was recovered in the Romashkinskoye field pilot tests using diluted seawater, whereas no LSW effect was observed in the Arkhangelskoye field [97]. One of the reasons for such discouraging results is the viscosity contrast between oil and injected LSW, which leads to an unfavorable mobility ratio and poor sweep efficiency. This problem may be even worse in pilot or field-scale applications if high permeability channels or layers exist in the reservoirs [114]. Hence, EWF has the potential to enhance the microscopic displacement efficiency, but on the other hand it can result in a poor volumetric sweep efficiency if a mobility control treatment is not considered.

4. Hybrid Engineered Water–Polymer Flooding (EWPF)

Literature and field case studies have proven that the synergistic combination of two or more EOR techniques provides better results in terms of oil recovery and economics. For instance, the combined use of an alkali, surfactant, and polymer in the alkaline–surfactant–polymer (ASP) flooding technique results in enhanced macroscopic and microscopic sweep efficiencies, owing to the favorable mobility ratio of the polymer, the microscopic sweep efficiency due to pH change caused by alkali, and the reduction in IFT caused by surfactants [115,116]. Any EOR method involving two or more EOR techniques is known as a hybrid EOR method. Much research is being carried out in the field of hybrid EOR, particularly aiming to increase the applicability of chemical methods. As discussed in previous sections, both PF and EWF have associated challenges that limit their field-scale applications.

In order to overcome these limitations and take advantage of the synergetic effects of the two methods, the hybrid EWPF technology comes into play. The hybrid process can be simply represented as:

$$Engineered\ Water\ (EW) + Polymer\ Flooding\ (PF) = Incremental\ Oil\ Recovery$$
$$(\text{Wettability}ttability\ Modification)\ (Reduction\ in\ Mobility\ Ratio)$$

This hybrid EWPF method provides the following obvious benefits:

- The addition of a polymer to low-salinity water flooding enhances the volumetric sweep and can also mobilize the oil released due to wettability modification after LSWF, which otherwise would be trapped [117];
- Various studies have shown the added benefit of the reduced polymer concentration needed to attain the desired in situ viscosity by using low-salinity brine compared to high-salinity water [118]. This can result in a significant cost reduction;
- Other advantages include the improved polymer stability (particularly at high temperatures), reduced sensitivity to shear-rate-induced degradation, less polymer adsorption, improved viscoelasticity of the polymer, and decreased scaling and souring tendency [119,120];
- Most of the studies have been conducted on sandstones [121–124], however the experiments performed on carbonates have also proved the synergetic effects of EWPF.;
- Recently, osmosis was proposed as the mechanism for the LSW EOR effect instead of wettability alteration in a sandstone sample [125–128].

Various experiment-based and modeling studies have been carried out in recent years to prove the effectiveness of hybrid EWPF as an EOR method [15,119,129–135]. These studies have shown an average of 11% incremental oil recovery using the hybrid method in different carbonate formations (Figure 4). The supporting data and references for the figure can be found in Table S2 of the Supplementary Materials.

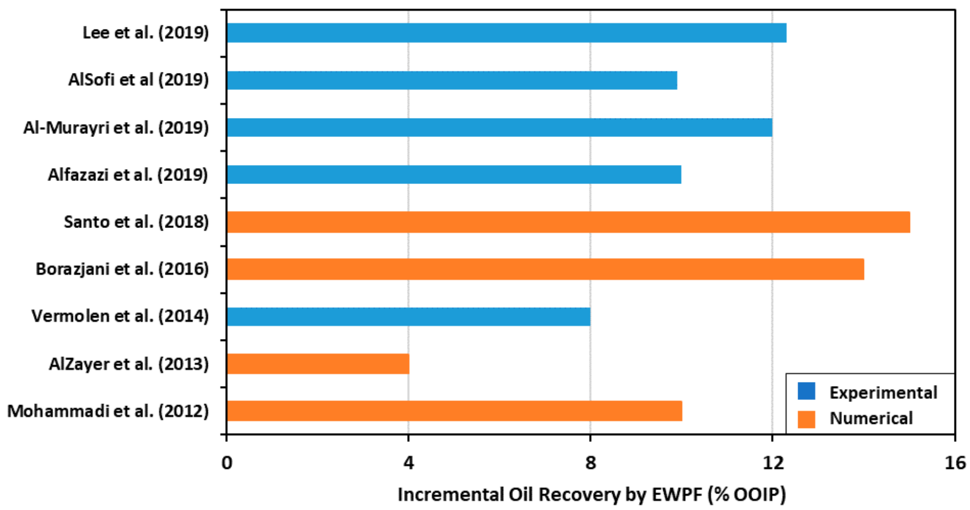


Figure 4. Summary of experimental and simulation studies involving incremental oil recovery using engineered water–polymer flooding (EWPF) in carbonates.4.1. Enhanced Oil Recovery using Hybrid EWPF in Carbonates.

The limited literature on the application of EWPF EOR in carbonates shows that it can increase oil recovery by equal to or more than the sum of the recovery from each process. Rivet [10] and Seright et al. [136] studied the combined effects of EWPF in terms of the better polymer stability and yield, improved microscopic and macroscopic sweep efficiency, and reduction in chemical costs. A seawater desalination process was developed for combined EWPF applications in an offshore field [137]. EW hybrid methods can achieve up to 30% of OOIP incremental recovery [138].

Lee et al. [135] performed experiments on carbonate samples using LSW with ion adjustments followed by PF. The S_{or} value was considerably decreased by using low-salinity polymer flooding (LSPF) compared to conventional high-salinity water flooding and EWF. All designed injection water (IW) solutions (IW-1: pH 7, 1000 ppm SO_4^{2-}, IW-2: pH 7, 4000 ppm SO_4^{2-}, IW-3: pH 4, 4000 ppm SO_4^{2-}, IW-4: pH 7, 100 ppm Ca^{2+}, IW-5: pH 7, 1000 ppm Ca^{2+}, and IW-6: pH 4, 1000 ppm Ca^{2+}) reduced the S_{or} value, however the neutral low-salinity water containing only SO_4^{2-} ions gave the lowest S_{or} value (Figure 5a).

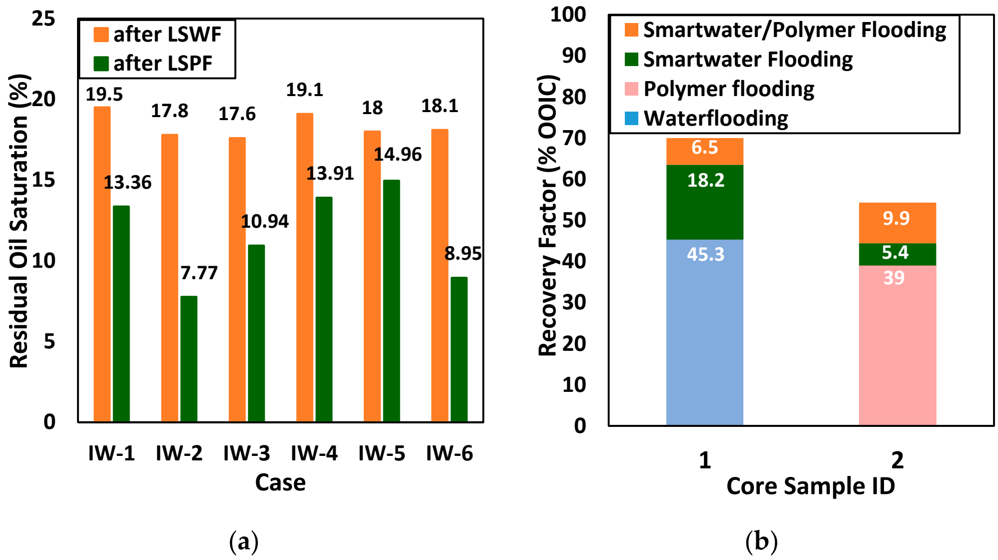


Figure 5. (**a**) Reduction in S_{or} after LSPF [135] (**b**) additional recovery using EWPF in carbonate reservoir cores [139].

Incremental oil recovery resulting from the synergy between smart water (SW) and polymer in carbonates was also confirmed by AlSofi et al. [139]. Hybrid EWPF resulted in 6–10% OOIP recovery after PF, showing that LSW modifies fluid–rock interactions, creating a moveable oil volume that is displaced easily by the polymer in EWPF (Figure 5b). Similarly, Vermolen et al. [119] conducted oil displacement experiments on reservoir cores, resulting in ~45% incremental oil recovery using LSPF. An incremental OOIP recovery value of 8% was achieved by further reducing the salinity of the water, confirming the synergistic effect of the hybrid process.

4.1. Effect of Hybrid EWPF on Residual Oil Saturation: Capillary Desaturation

Capillary desaturation is the process of recovering capillary-trapped residual oil. Generally, conventional PF is considered to affect only the macroscopic efficiency. A typical procedure for examining the microscopic sweep efficiency of any improved oil recovery (IOR) process is to construct a capillary desaturation curve (CDC) by performing corefloods at different rates. The residual oil saturation at the end of each stabilized pressure interval is plotted against the capillary number (N_c) [140,141]. The capillary number is the ratio of viscous to capillary forces [142–147], as given in Equation (2) [148]:

$$N_c = \frac{K\Delta p}{\sigma L} \tag{2}$$

where K is the absolute permeability, $\Delta p/L$ is the pressure gradient across the core, and σ is the oil–water IFT. Equation (1) shows that in order to have an acceptable range of N_c, either the pressure gradient should be high enough or the IFT should be extremely low, both of which are generally not achievable by conventional water flooding (WF) and PF. From the CDC, the critical N_c can be identified for the process under study. The critical N_c is usually in the range of 10^{-4} to 10^{-3} [143,149], whereas the typical N_c obtainable using WF and PF in the field ranges from 10^{-7} to 10^{-5} [150]. Analysis of CDCs from different coreflood studies has shown that the typical field operating constraints for PF are generally not sufficient to cause any reduction in capillary-trapped residual oil [33,151–154].

A comparison of the capillary desaturation tendency of PF [155–159] and LSPF [15,117,119,122,124,134,135,160] has been made by plotting the coreflood end-points from various LSPF studies. It was observed that LSPF can result in a significant S_{or} reduction, even at smaller values of N_c (Figure 6). Almost all the points in Figure 6 fall below PF CDCs, indicating that the S_{or} values are lower than standalone PF and that the hybrid method is more effective in recovering trapped oil. This can be attributed to the synergetic effects of wettability modification and efficient oil bank displacement using EW and polymer. Data for Figure 6 can be found in Table S3 of the Supplementary Materials. Recently, it has been suggested by some researchers that the viscoelastic properties of polymers can cause a reduction in S_{or} by stripping the trapped oil [155,156,159,161–167]. However, this is debatable and beyond the scope of this review.

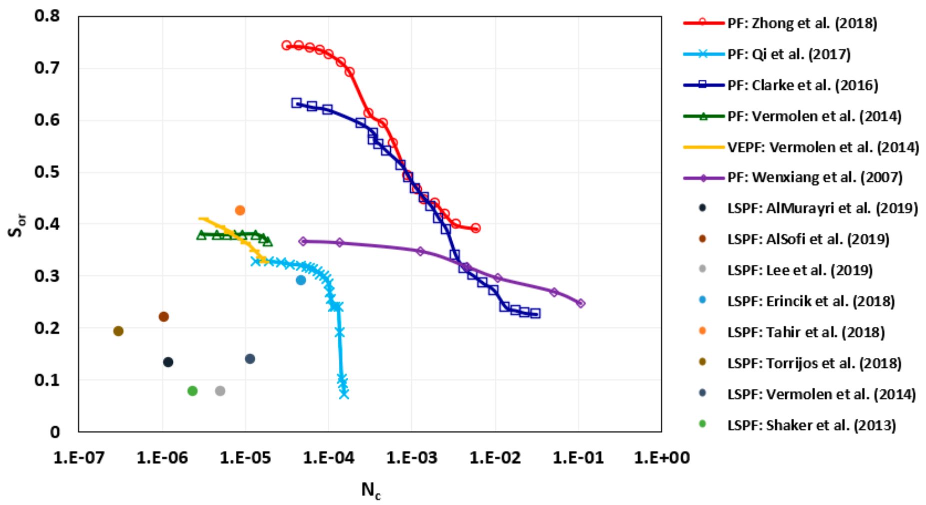


Figure 6. Capillary desaturation curves (CDCs) showing the higher microscopic efficiency of LSPF compared to conventional PF based on coreflood studies. VEPF: viscoelastic polymer flooding.

Hence, different researchers have confirmed the synergy and additional oil recovery that can be achieved by combining low-salinity or engineered water with polymer in carbonates, but more work is required to fully understand the recovery mechanisms driving incremental oil recovery using this hybrid process. The dominant recovery mechanisms for EWPF are discussed in the following section.

4.2. *Recovery Mechanisms*

The hybrid method under study involves combined mechanisms of both EW and polymer methods. EW helps to detach oil from the rock surface, creating moveable oil saturation areas in situ, which are later displaced by polymer flooding. Figure 7 shows the main mechanisms known to be responsible for EOR using the hybrid method. However, in order to obtain the maximum benefit from the hybrid method, there should be an optimum design in terms of the EW composition, selection of PDIs to be used in a certain carbonate rock type, polymer concentration, slug sizes for EW and PF, optimum injection rate for PF, and injection scheme used for the hybrid process (continuous or slug-wise injection). The mechanisms reported in the literature are briefly discussed in the following section.

4.2.1. Wettability Modification Using Engineered Water

One of the two governing mechanisms of the hybrid process is the effect of ion-adjusted, low-salinity water, which changes the wettability of carbonate rock from oil-wet or intermediate-wet to water-wet by disturbing the initial equilibrium of the formation of the water–oil–rock system [168]. In this way, the EW plays its part in enhancing the microscopic sweep efficiency via desorption of oil from the rock. It is important to consider various factors when designing the EW for a particular OWR system and polymer type. For example, the selection of PDIs is very critical and must be decided based on the specific rock type (limestone, chalk, and dolomite) under study. The pH of the injection brine is also a critical parameter that must be considered in the design process. The factors that govern the wettability modification mechanism of EWPF are briefly discussed below.

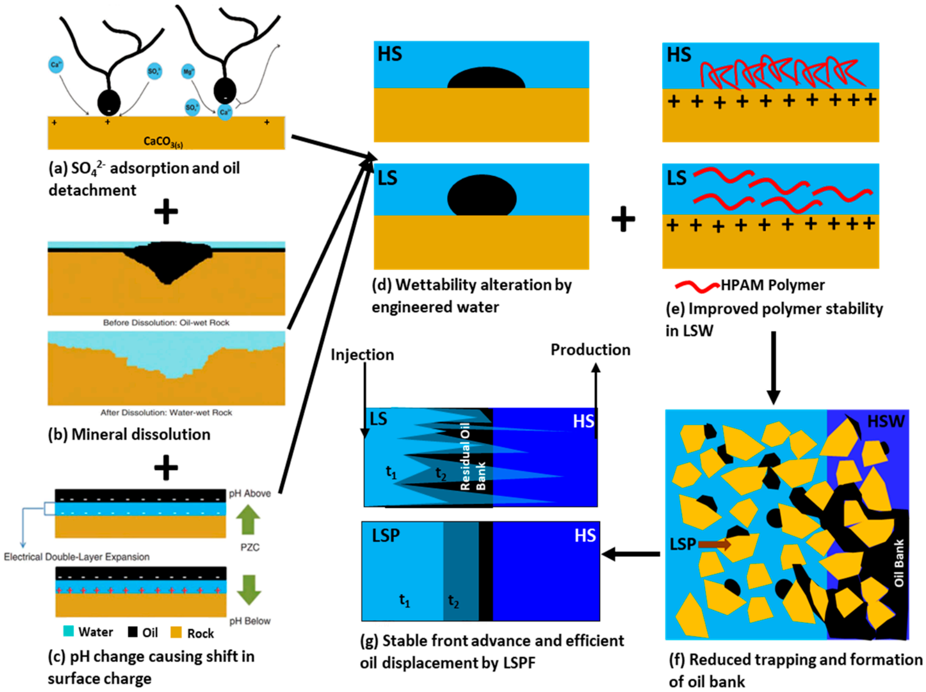
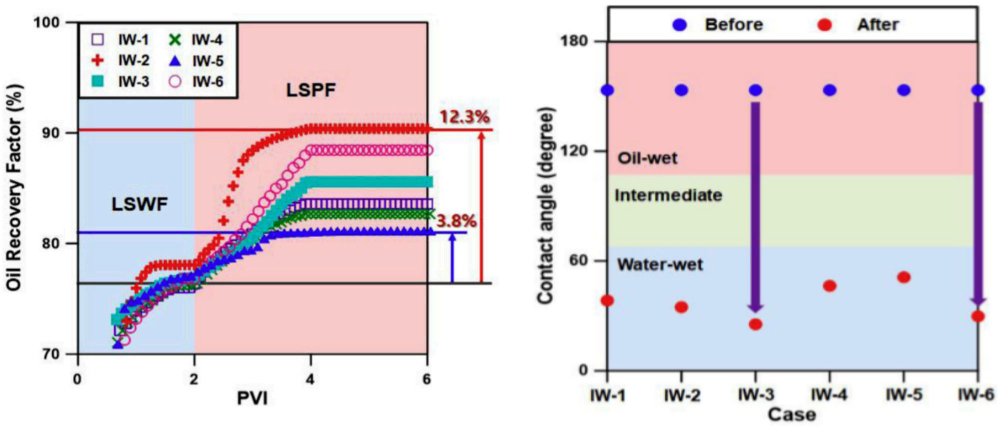


Figure 7. Illustration of governing mechanisms for incremental oil recovery using hybrid LSPF: (**a**–**d**) the functions of LSW [58,169] (**e**) the polymer stability in LSW; (**f**) the formation of the oil bank [170]; (**g**) the final outcomes of the process, i.e., detachment, mobilization, and displacement of the residual oil bank by combined LSPF.

4.2.2. Role of Potential Determining Ions (PDIs)

The PDIs in the EW polymer solution affect the polymer adsorption and incremental recovery differently. The presence of SO_4^{2-} ions in seawater or EW is the key factor for wettability modification, as it reduces the carbonate rock surface potential, promoting oil detachment by Ca^{2+} or Mg^{2+} [61,171–174]. Lee et al. [135] performed a detailed study in order to analyze the effects of the PDIs and the pH on oil recovery using EWPF in a carbonate reservoir. Coreflooding experiments showed that use of the neutral HPAM polymer solution containing SO_4^{2-} ions resulted in a considerable decrease in S_{or} and less polymer adsorption compared to Ca^{2+} ions (Figure 5a). The incremental oil recovery was 12.3% for this case, the highest value among all cases (Figure 8a). Contact angle measurements using the captive droplet method also confirmed the wettability change towards more water-wet conditions in the case of the neutral polymer solution with a higher SO_4^{2-} concentration (Figure 8b). The reason for the lower oil recovery in the case of the polymer solution containing Ca^{2+} ions was the higher polymer adsorption and permeability reduction due to the precipitation of Ca^{2+} ions.



(**a**) (**b**)

Figure 8. Effects of the potential determining ions (PDIs) and the pH of water on (**a**) oil recovery and (**b**) wettability alteration using EW [135].

4.2.3. Effect of Brine pH

The pH of the solution also has a strong influence as it controls mineral dissolution reactions involved in wettability alteration using EW in carbonates. An analysis of effluent pH values by Lee et al. [135] showed a higher pH increase resulting from acidic solution injection due to calcite dissolution in acid–base reactions. However, the pH increase must be sufficient (≥11) for wettability modification and incremental oil recovery. The polymer adsorption was also significantly increased in the acidic medium, indicating that acidic conditions are not favorable for PF.

4.2.4. Favorable Mobility Ratio from Polymer Flooding

Another mechanism involved in EOR using EWPF is the improved fractional flow resulting from the use of polymer. EW alone may not be able to displace the moveable oil; however, with the addition of polymer, the formed residual oil bank can be easily displaced by the polymer solution due to stable front movement. Hence, the polymer plays a critical role and must be compatible with the EW designed for the reservoir. Fortunately, EWPF harnesses the supplementary benefits of enhanced polymer stability and decreased retention in the presence of EW, leading to higher incremental oil recovery rates and cost savings by reducing polymer consumption. As a result, the hybrid EWPF EOR method can be successfully applied to carbonate reservoirs with harsh temperature and salinity conditions. However, careful design of the EW and polymer must be applied for each field, as the composition of the EW can have both positive and negative impacts on the polymer performance. The critical factors for the polymer performance in the hybrid process include the polymer viscosity, retention, degradation, and consumption. These factors and their dependence on the EW composition are discussed in the following sections.

4.2.5. Enhanced Polymer Stability using EW

The HPAM properties are strongly dependent on the makeup brine salinity, hardness, pH, and ionic composition. HPAM polymers are the cheapest and most widely used polymers, however they start losing viscosity and behave more like Newtonian fluids under high-salinity and high-temperature conditions, thus limiting their application in such formations [119]. Low pH conditions promote HPAM adsorption due to the coiling of polymer chains as more molecules are adsorbed onto an available surface area. Similarly, high salinity conditions result in the charge screening effect, reducing the polymer viscosity and stability. Ca^{2+} ions promote HPAM precipitation, which can have a detrimental effect on the rock permeability and polymer degradation. The recommended Ca^{2+} concentration in EW should be below 200 ppm [175]. In contrast, $SO_4{}^{2-}$ ions, being negatively charged, promote the stability of the anionic HPAM polymer in carbonate formations. A number of studies on polymer rheology have shown ~30–50% reductions in the polymer concentration [15,119,120,134,176–178] were needed in order to achieve the target viscosity when low-salinity makeup brine was used (Figure 9). Data for Figure 9 are given in Table S4 in the Supplementary Materials.

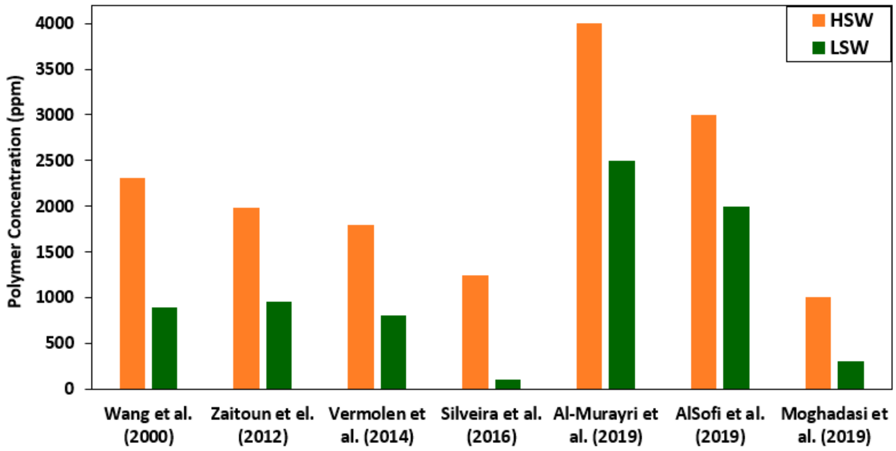


Figure 9. Studies showing reductions in the required polymer concentrations using LSW compared to high salinity water (HSW).

Lee et al. [179] developed a comprehensive database based on detailed rheological experiments using HPAM polymers. This database clearly demonstrates the higher polymer viscosity and enhanced stability caused by reducing the brine salinity and hardness. Vermolen and Pingo-Almada [119] performed coreflooding experiments to assess the impact of LSW on the polymer concentration and incremental oil recovery, showing a 50% reduction in the polymer concentration needed to attain the desired viscosity, mainly because of the improved polymer stability and reduced coiling in LSW (Figure 10). The cost savings will be even higher in high-salinity formations.

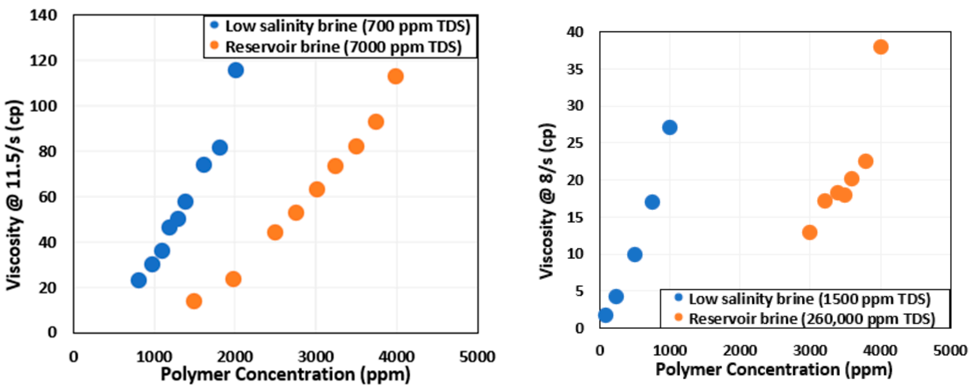


Figure 10. Reductions in HPAM concentrations using LSW as the makeup brine [119].

Considering a high-salinity and high-temperature scenario in an Arabian carbonate reservoir with slightly heavy oil (25 °API), AlSofi et al. [139] showed the positive effects of LSW on polymer the rheological properties and thermal resistance. The smart water (7000 ppm TDS) resulted in a ~30% decrease in the polymer concentration needed to maintain the target viscosity and also improved the thermal tolerance of the polymer (Figure 11) as compared to the injection water (70,000 ppm TDS).

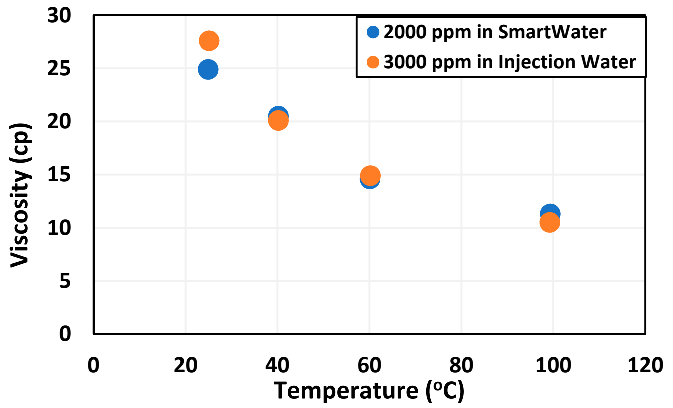


Figure 11. The effect of smart water on the polymer concentration required to achieve the target viscosity [180].

The improved polymer stability in LSW spiked with SO_4^{2-} ions (2935 ppm TDS with 1155 ppm SO_4^{2}) was confirmed by Al-Murayri et al. [15]. The target viscosity of 3 centipoise (cp) was achieved at a relatively lower polymer concentration (2500 ppm) using LSW compared to high-salinity brines (polymer concentration 4000 ppm). This resulted in a ~37% reduction in polymer consumption in reservoir conditions. Similarly, the LS polymer solution also retained 94% of its original viscosity after 188 days of aging at reservoir temperature, showing the better thermal stability of the polymer in low-salinity makeup water (Figure 12). The results of his work showed that a carefully designed low-salinity polymer (LSP) solution can provide both improved polymer stability and the required viscosity needed for efficient oil displacement at high temperatures, as well as the desired molecular weight needed for better polymer injectivity in low-permeability carbonate formations. Hence, the PF application envelope can be extended to severe reservoir conditions using LSW, which otherwise may not be technically or economically viable using high-salinity formation water.

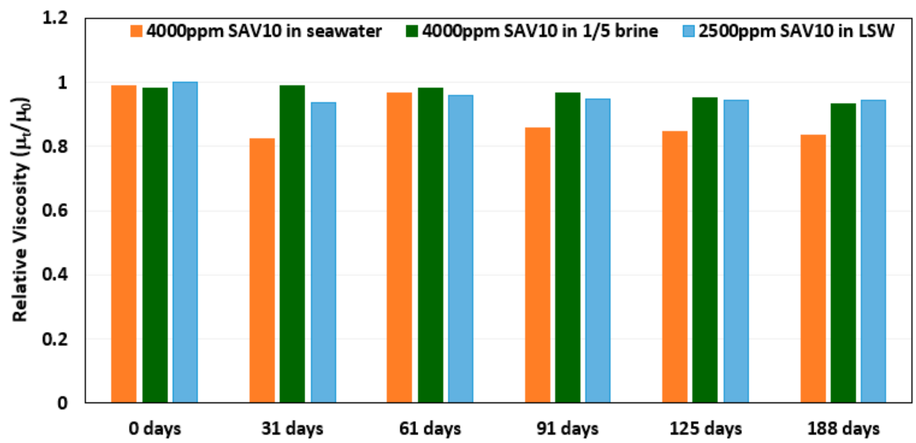
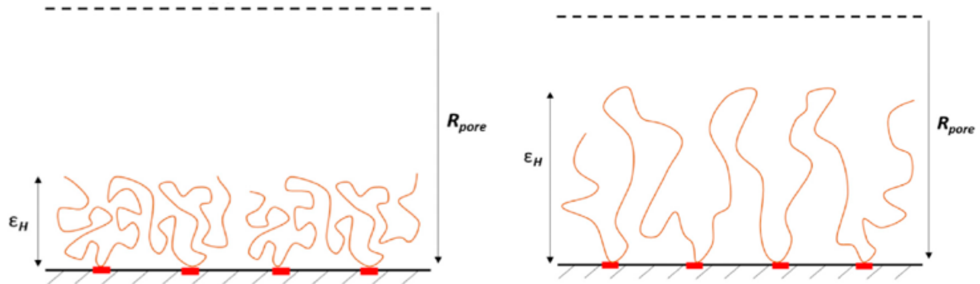


Figure 12. Better thermal stability of Superpusher Terpolymer of Acrylamide, Acrylamido-Tert-Butyl-Sulfonate and N-Vinyl-Pyrrolidone (SAV10) in LSW at 113 °C. LSW = 2935 ppm of TDS; 1/5 brine = 47,869 ppm of TDS; seawater = 49,878 ppm of TDS [15].

4.2.6. EW Effect on Polymer Retention

AlSofi and Wang [180] also investigated the effects EW has on polymer adsorption and frontal acceleration under reservoir conditions by performing two injectivity experiments on carbonate cores at a constant frontal velocity of 3.5e-06 m/s ft/day using polymer solutions prepared in injection water (70,000 ppm salinity), smart water (7000 ppm salinity), and a tracer. The results were in line with other relevant literature [15,119,135] in that EW provided a 10–28% reduction in polymer adsorption due to increased polymer coil expansion, which resulted in less polymer molecules being required to occupy the surface adsorption sites (Figure 13). Similarly, the larger polymer expansion in the presence of LSW resulted in a slightly higher inaccessible pore volume (IPV). Hence, the smart water had no significant negative impacts on the polymer front or oil bank acceleration.



(**a**) (**b**)

Figure 13. Polymer retention in the presence of (**a**) injection water and (**b**) smart water [180].

Substantial decreases in polymer retention have also been shown in several studies [118,119,178,180–182] in the presence of LSW (Figure 14). The data for Figure 14 are given in Table S5 of the Supplementary Materials.

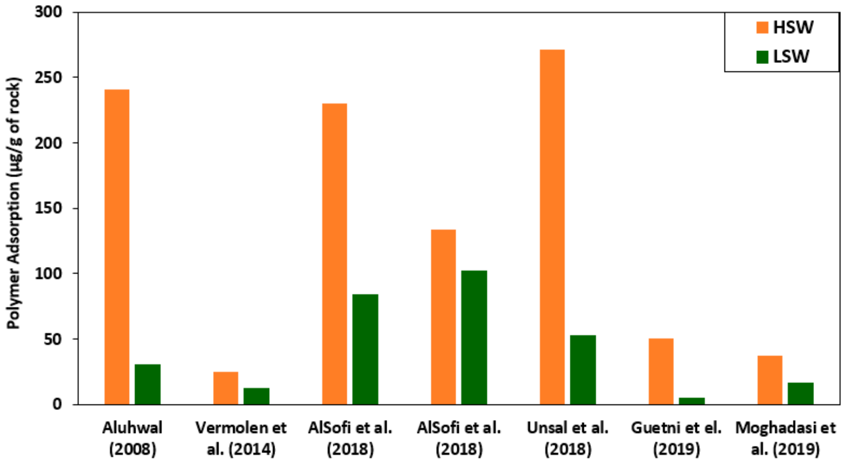


Figure 14. Studies showing reductions in the required polymer adsorption using LSW.

4.2.7. Impact of Polymer on EW Performance

While EW improves the polymer stability, the polymer can also have positive or negative effects on the EW performance, which can be qualitatively assessed using electrokinetic surface potential (zeta potential) and contact angle measurements. The zeta potential is a measure of the overall surface charge in a system and is an indicator of wettability alterations in the system. A higher negative zeta potential for carbonates shows a higher net repulsion force between the carboxylic oil material and carbonate surface, resulting in oil detachment and a wettability shift towards being water-wet. In cases where it is not possible to measure the zeta potential, the electrophoretic mobility can be used as an indication of wettability alteration as it is directly proportional to the zeta potential.

Electrophoretic mobility and contact angle experiments were performed by AlSofi et al. [180] to show the positive impact polymer has on the LSW performance. The HPAM polymer solution prepared using smart water (10-fold dilution of injection water) resulted in the highest decrease in electrophoretic mobility, and hence in the zeta potential, as well as the greatest wettability shift towards the water-wet state (contact angle of 88.9° for smart water–polymer compared to 102.4° for smart water only), for an aged carbonate reservoir material (Figure 15). The reasons for the reduced electrophoretic mobility and contact angle in the presence of polymer could be the negative charges on the polymer backbone or adsorption of anionic polymer molecules onto the positive carbonate rock particles suspended in the solution. These experiments confirmed that polymer has no adverse effects on the LSW the wettability alteration capability; in fact, the polymer can slightly enhance the LSW effects.

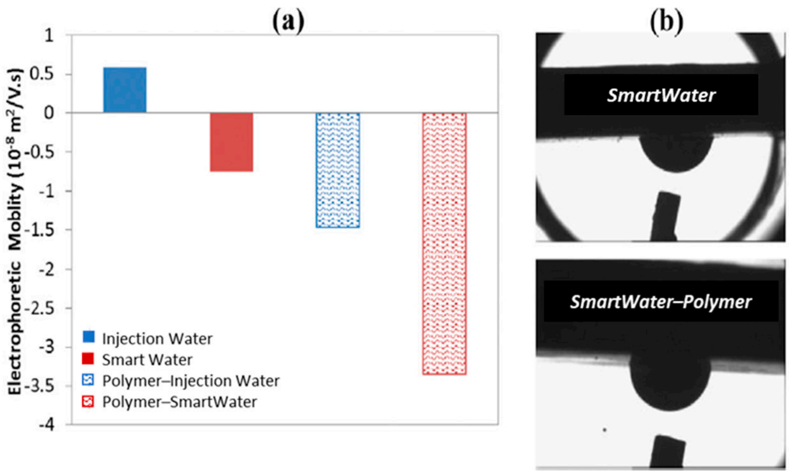


Figure 15. (**a**) A higher reduction in the zeta potential and (**b**) an increased wettability shift to water-wetness in the presence of HPAM polymer in smart water [180].

4.3. Potential Risks Associated with EWPF

The potential risks associated with EWPF, as investigated by Vermolen et al. [119], are as follows:

- The viscosity of a LSP solution is more sensitive to brine salinity compared to a solution containing high-salinity water (HSW). A slight increase in the brine salinity can reduce the polymer viscosity significantly, making it necessary to consider this factor while designing a LSPF project;
- The contamination of the LSP slug with already present high-salinity formation water also poses risks for polymer viscosity loss and increased adsorption;
- Another risk in this process is a delay of the incremental oil recovery due to the higher polymer slug needed to reach the required adsorption level as a result of a lower polymer concentration;
- The reduced injectivity levels of polymer and chase fluid in the presence of EW can also be a potential limitation involved in this hybrid method [180].

However, these risks can be partially or completely offset by lowering the maximum adsorption and increasing the hydrodynamic acceleration of the polymer in the LSW. Vermolen et al. [119] carried out a de-risking study in order to minimize the risks of using LSW for PF and showed that due to polymer adsorption, a LS slug is formed in between the HSW and LSP, which prevents direct contact of the polymer with the HSW, meaning the polymer slug efficiently displaces the HSW slug without deterioration. Despite the risk of delayed oil production, a two- to four-fold reduction in the polymer concentration and the resulting cost savings could be enough to justify the economic feasibility of LSPF, particularly in high-salinity formations, which otherwise may not satisfy the criteria for conventional PF.

Several variable-rate coreflood experiments were conducted by AlSofi et al. [180] to assess the effects of smart water on polymer injectivity. Resistance factors and residual resistance factors for smart water cases were slightly higher than those for injection water cases, indicating a negative impact of smart water on polymer injectivity. Although polymer and chase fluid injectivity rates were slightly reduced due to increased polymer chain expansion in the smart water, the reduced polymer consumption and retention still showed that the hybrid method has potential for successful field-scale implementation in high-salinity, high-temperature carbonate formations, as it can result in significant cost savings.

4.4. Lab-Scale Studies

In order to establish the EOR potential of hybrid EWPF in carbonates, a number of lab-based studies were carried out over the past ten years [133,135,183–185]. Vermolen et al. [119] presented a detailed experimental workflow for an LSPF field design at the lab scale. The experiment involved an aged reservoir core and confirmed that using LSW in PF can reduce the project cost by lowering the polymer concentration, also providing additional oil recovery resulting from the wettability modification and the improved viscoelastic behavior of the polymer. Figure 16 shows the recovery and pressure drop profiles for sequential injection of three polymer solutions of different salinities and concentrations. LSPF resulted in ~52% additional oil recovery compared to HSW.

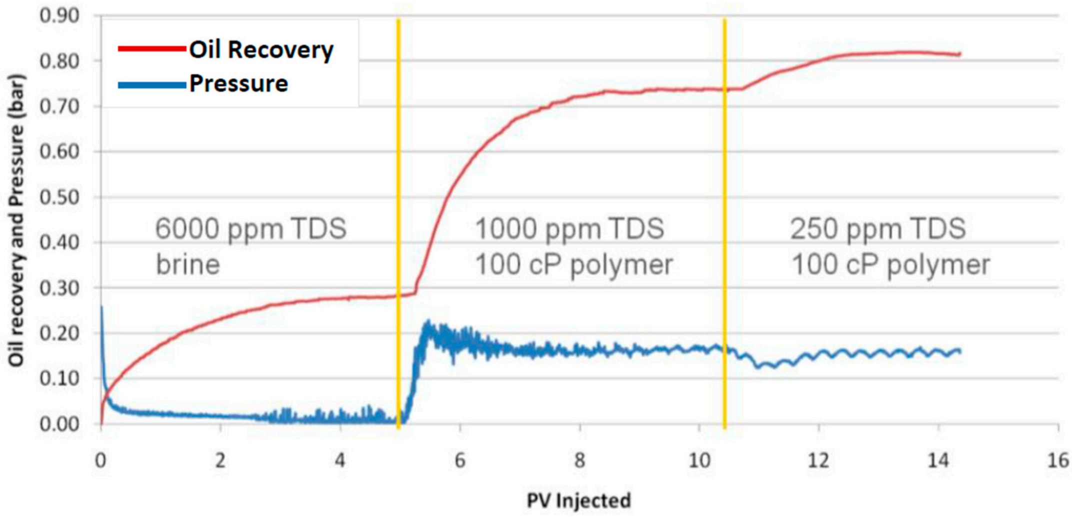


Figure 16. Oil recovery and pressure trend values for LSPF in a reservoir core [119].

Oil displacement experiments conducted by AlSofi and Wang [139] at reservoir conditions (99 °C) for Arabian carbonate reservoir aged cores showed ~6 to 10% higher oil recovery for the hybrid LSW and sulfonated polyacrylamide polymer process compared to the recovery using the standalone processes (Figure 17). The higher negative zeta potentials for LSP solutions indicated the presence of more repulsive force in the system, which helped to detach the adsorbed oil and increased the recovery factor. Based on their results, oil recovery can be directly related to zeta potential, whereby the higher the negative zeta potential value, the higher the oil recovery from that system. In addition, the higher recovery values in coreflood-1 were because the pore system in the core sample had good connectivity.

Laboratory experiments were conducted on a reservoir composite core to assess the feasibility of using the polymer SAV10 combined with LSW (2935 ppm TDS) for a high-salinity and high-temperature carbonate oil reservoir in Kuwait (113 °C and 239,000 ppm) with a relatively low permeability of <10 md [15]. Secondary LSWF reduced the S_{or} to 23%, followed by a further 10% reduction by LSPF, whereas the pressure drop data suggested no significant plugging by the polymer (Figure 18). The results showed that LSPF can be applied to harsh reservoir conditions and low permeability reservoirs if the process is designed carefully.

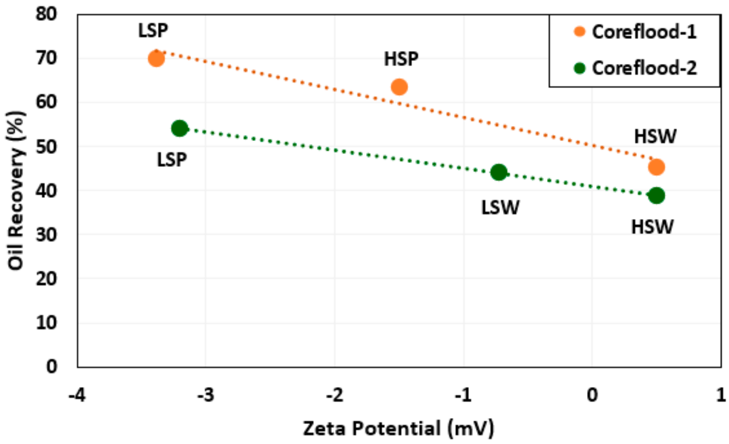


Figure 17. Oil recovery as a function of the zeta potential, showing higher recovery using the hybrid method compared to standalone processes. Coreflood-1 shows a comparison between PF and LSPF, while coreflood-2 displays a comparison between LSW and LSPF [139].

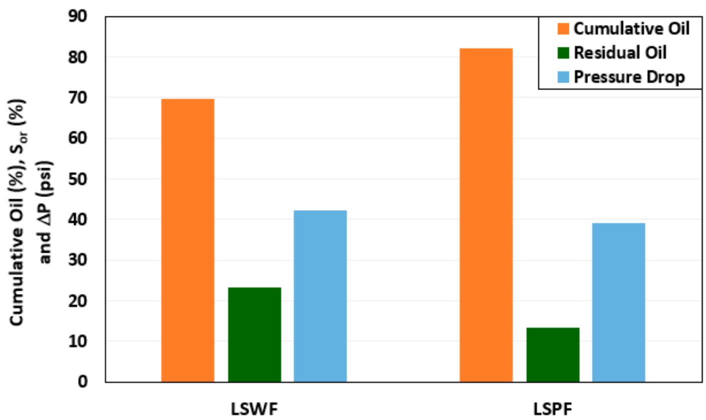


Figure 18. Comparison of oil recovery, S_{or}, and pressure drop values using LSWF followed by LSPF in a Kuwaiti carbonate oil reservoir composite core [15].

4.5. Numerical Modeling Studies

A systematic analytical and numerical modeling study was conducted to investigate the potential synergy between LSW and PF [132]. The comparison of conventional WF, HSW–PF, and LSW–PF showed that the combined LSPF method gave the best results, having the highest incremental oil recovery rate and lowest water cut rate. This can be attributed to the improved fractional flow, stable frontal advance, and reduced viscous fingering for the LSPF method. Overall, the combined EOR process resulted in incremental oil recovery values of 15–42% and 11–48% reductions in the water cut after one pore volume (PV) of injection, depending on the extent of the reservoir layering and heterogeneity. Figure 19a presents the correlation between the shock front mobility ratio and the cumulative oil production. As the mobility ratio decreased from 1.1 (for high-salinity water flooding) to 0.9 (for LSPF), the total oil recovery increased from 48% to 70%, proving the better polymer performance in low-salinity environments. The effect of salinity on oil recovery using PF was also studied and the 3D numerical modeling results for different injection water salinity rates clearly showed the higher ultimate recovery rates for low-salinity–polymer cases, as highlighted in Figure 19b. A reduction in salinity from 30,000 to 700 ppm resulted in 23% extra oil production compared to the high-salinity base case, confirming the synergy between the two processes.

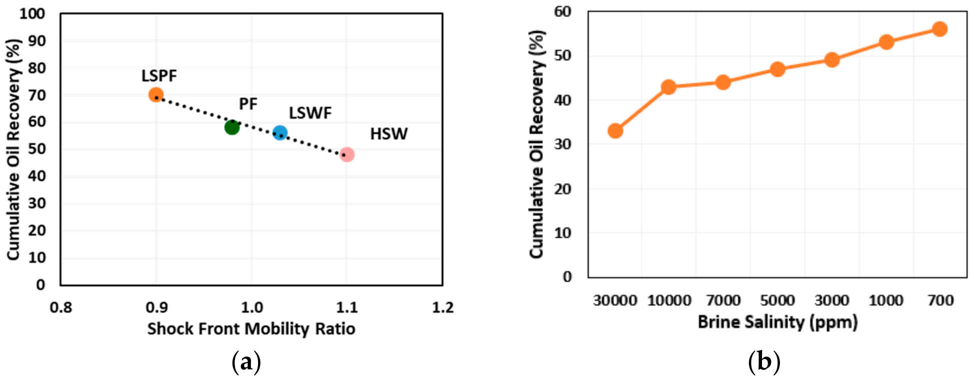


Figure 19. Numerical modeling results showing oil recovery as a function of (**a**) the mobility ratio for different flooding scenarios and (**b**) the brine salinity used for PF [132].

Borazjani and Bedrikovetsky [131] presented an analytical solution for modeling LSPF by incorporating the non-Newtonian properties, adsorption, and ionic strength of water of the polymer. Henry's sorption equation and modified Darcy's law were used to formulate the model. To study the effect of the LSP slug size, a splitting technique presented by Pires and Bedrikovetsky [186] was used to solve problems that were non-self-similar. The results showed ~14% higher ultimate oil recovery when using LSPF, delayed water breakthrough, and the lowest water cut (Figure 20). Polymer adsorption was also higher with the high-salinity polymer (HSP) method, as polymer breakthrough occurred later (after 8.1 PV) compared to LSPF (after 7.8 PV). The results showed that the hybrid LSPF technique performed better than conventional PF, both in terms of the reduced polymer consumption and higher oil cut rates.

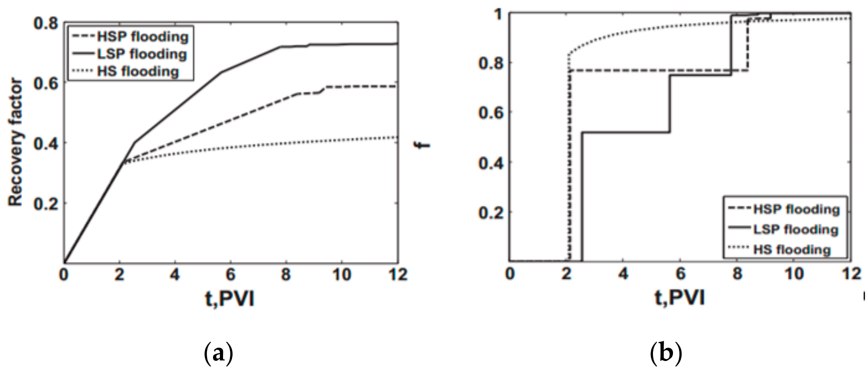


Figure 20. Analytical solution results showing the effects of LSPF on (**a**) oil recovery and (**b**) water cut rates [131]. Reproduced with permission from Borazjani et al., *J. Pet. Sci. Eng.*; published by Elsevier, 2016.

A comprehensive numerical simulation study using empirical modeling of LSWF was carried out by Mohammadi and Jerauld [129] to simulate the hybrid LSPF process in Landmark Solutions and Computer Modeling Group Ltd. (CMG) reservoir simulators. Polymer rheology and adsorption measurements were included to model the effects of salinity and hardness on the viscosity degradation, reduction in permeability, and IPV caused by polymer retention in porous media. The study investigated the influences of the injection sequence, polymer and LSW slug sizes, oil viscosity, and heterogeneity of the reservoir on oil recovery (Figure 21). The hybrid method was more beneficial for high-viscosity oil. Based on the simulation results, the optimum LSP slug size was 0.5–0.7 PV. An additional 20% of oil recovery was obtained using LSPF as compared to the conventional WF, mainly due to the wettability modification using LSW, the better polymer stability, and the efficient front displacement caused by polymer, improving the overall fractional flow. The 1D simulation results showed the improved fractional flow and better performance of the hybrid process compared to LSWF and PF alone. Higher oil recovery and better timing results were obtained in secondary mode than in tertiary mode (oil breakthrough at 0.3 PV compared to 0.5 PV for tertiary mode), whereas the synergy of the hybrid process was more pronounced in tertiary mode than in secondary mode. The study also showed that due to the better performance of the polymer in LSW, the chemical cost can be reduced by five times.

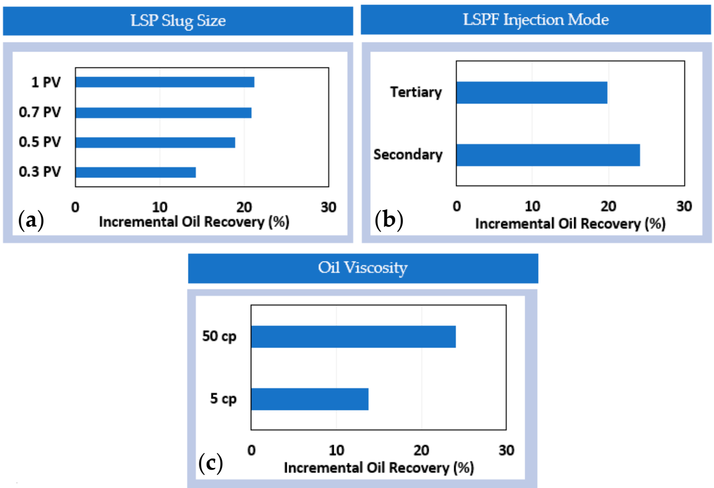


Figure 21. Effect of (**a**) slug size; (**b**) injection mode; and (**c**) oil viscosity, on the performance of LSPF in terms of incremental oil recovery [129].

Alzayer and Sohrabi [130] conducted a numerical simulation study using the correlation between the residual oil saturation after water flooding (S_{orw}) and the salinity of water, as developed by Webb et al. [187], utilizing the relevant published data in the literature. The objective of the study was to improve the oil recovery from a heavy oil reservoir (80 cp and 20° API oil) using LSWF followed by PF. A comparison of the different injection schemes showed that the combination of LSWF and PF provided an additional 4% estimated ultimate recovery (EUR) of the OOIP with significantly lower injection volumes required compared to both methods simulated separately (Figure 22). The synergetic effects of hybrid EWPF were also confirmed by the modeling studies conducted by Hirasaki and Pope [188], Han and Lee [189], and Khamees and Flori [190]. Based on this review, the main parameters to be considered regarding the applicability of each EOR technique are summarized in Table 2.

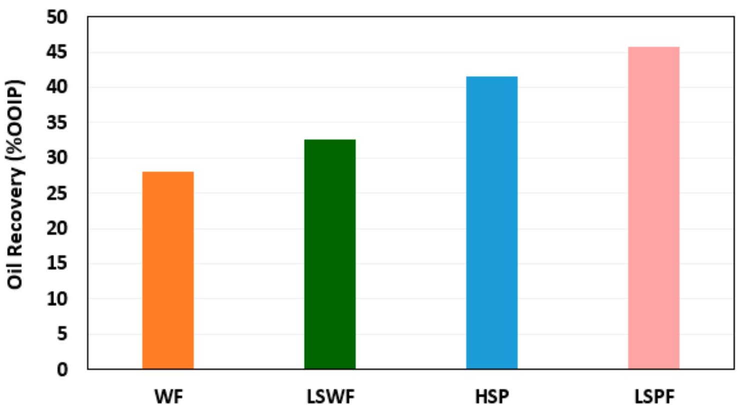


Figure 22. Comparison of LSPF with high-salinity WF (50,000+ ppm), LSWF (2000 ppm), and HSP flooding after 0.6 PV injection [130].

Table 2. Key conditions for polymer, engineered water, and engineered water–polymer flooding.

Parameter	Conditions
Polymer Flooding	
Porous Medium	Mostly sandstone. Limited application in carbonates mainly due to the high-salinity formation water associated with carbonates [25–27].
Formation Water	Salinity should be < 100,000 ppm [43]. Chlorides should be < 20,000 ppm, Ca^{2+} and Mg^{2+} divalent ions must be < 500 ppm [47]. Low salinity (LS) is preferred to avoid polymer degradation [44].
Permeability	Value range of 20 to 2300 md. Polymer adsorption can cause permeability reduction [14,45,191].
Temperature	Should be < 93 °C. HPAM undergoes thermal degradation at high temperature [32,46,49].
pH	High pH is favorable for HPAM due to increased electrostatic repulsion [192,193].
Engineered Water Flooding	
Oil	Must have polar organic components in order to observe EW EOR effects [84,106,194].
Injection Fluid	Salinity must be between 2000 and 5000 ppm [105,195], but can work up to 33,000 ppm [70,79]. Injection water must have PDIs, Mg^{2+}, or Ca^{2+} and $SO_4{}^{2-}$ [74,85,196].
Temperature	Should be > 70 °C [92,106,107,196].
Initial Wettability	Oil-wet to mixed-wet [194,197,198].
Engineered Water Polymer Flooding	
Formation Water	This method can be applied to reservoirs containing high-salinity and high-hardness formation water in the range of 167,000–239,000 ppm [15,133].
Injection Water	Salinity should be low as compared to formation water. A value range of 300–9750 ppm has been reported in the literature [133,184].
PDIs	Injection water spiked with 4 times the amount of $SO_4{}^{2-}$ ions gives the best results. Increase in Ca^{2+} concentration can cause polymer degradation [135].
Temperature	Can be as high as 120 °C [133].
Permeability	EWPF can also provide incremental recovery from low permeability formations (< 10md) [15,183].

5. Conclusions

The synergy between polymer and low-salinity or engineered water has significant potential to improve the oil recovery and extraction of residual oil from highly abundant oil-wet carbonate rocks. However, more research is still required to make this hybrid process practically applicable in large-scale field projects, particularly from an economic point of view. One important parameter in this regard is the understanding of the principle driving mechanisms responsible for EWPF and how this hybrid process can be designed to achieve the maximum possible oil recovery. There is still a debate in the literature regarding EWF mechanisms for carbonates and the main drivers for EOR need to be properly identified. The mechanisms reported in the literature include multi-ion exchange, mineral–rock dissolution, oil–water microdispersions, and pH increases.

Different experimental and modeling studies have shown that the performance and economics of PF can be improved by using LSW as a makeup brine, especially in high-temperature, high-salinity formations. The review of various studies demonstrates that the technique can result in an appreciable reduction in polymer consumption (30–50%) and more than 20% incremental oil recovery from high-salinity, high-temperature formations. The presence of $SO_4{}^{2-}$ in the low-salinity injection water has the most promising effect on both the HPAM stability and the oil recovery, whereas Ca^{2+} and Mg^{2+} play supporting roles in the wettability alteration of rocks using $SO_4{}^{2-}$. The hybrid EWPF can provide both economic and environmental benefits by reducing the chemical consumption and cost, while improving oil recovery. The above reasons make the hybrid EWPF approach a promising EOR method, however the research on its application for carbonates is very limited due to the heterogeneity and complexity of rock–fluid interactions. These factors require more in-depth research, particularly regarding the composition of the injection water, the injection scheme design, and the economic output, in order to justify field-scale implementation of the EWPF approach.

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