Capillary Desaturation Tendency of Hybrid Engineered Water-Based Chemical Enhanced Oil Recovery Methods

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Abstract: Several studies have shown the synergistic benefits of combining various chemical enhanced oil recovery (CEOR) methods with engineered waterflooding (EWF) in both sandstones and carbonate formations. This paper compares the capillary desaturation tendency of various hybrid combinations of engineered water (EW) and CEOR methods with their conventional counterparts. Several coreflood experiments were conducted, including EW-surfactant flooding (EWSF), EW-polymer flooding (EWPF), EW-alkali-surfactant flooding (EWASF), EW-surfactant-polymer flooding (EWSPF), and EW-alkali-surfactant-polymer flooding (EWASP). Capillary numbers ($N_c$) and corresponding residual oil saturation ($S_{or}$) for each scenario are compared with capillary desaturation curves (CDC) of conventional CEOR methods from the literature. The results indicate that hybrid EW–CEOR methods have higher capillary desaturation tendency compared to conventional methods. The capillary numbers obtained by standalone polymer flooding (PF) are usually in the range from $10^{-6}$ to $10^{-5}$, which are not sufficient to cause a significant reduction in $S_{or}$. However, the hybrid EW-polymer flooding approach considerably reduced the $S_{or}$ for the same $N_c$ values, proving the effectiveness of the investigated method. The hybrid EWASP flooding caused the highest reduction in $S_{or}$ (23%) against $N_c$ values of $8 \times 10^{-2}$, while conventional ASP flooding reduced the $S_{or}$ for relatively higher $N_c$ values ($3 \times 10^{-3}$ to $8 \times 10^{-1}$). Overall, the hybrid methods are 30–70% more efficient in terms of recovering residual oil, compared to standalone EWF and CEOR methods. This can be attributed to the combination of different mechanisms such as wettability modification by EW, ultralow interfacial tension by alkali and surfactant, reduced surfactant adsorption by alkali addition, and favorable mobility ratio by polymer. Based on the promising results, these hybrid techniques can be effectively implemented to carbonate formations with harsh reservoir conditions such as high salinity and high temperature.

Keywords: capillary desaturation; chemical flooding; engineered waterflooding; hybrid enhanced oil recovery

1. Introduction

Oil recovery during the primary recovery phase is generally poor in carbonate formations, due to their oil-wet nature and geological heterogeneity [1–3]. The secondary recovery methods, such as waterflooding and gas injection, only slightly improve the recovery factor, and as a result, residual oil saturation ($S_{or}$) after the secondary production phase is still quite high in carbonate reservoirs [3]. Tertiary recovery techniques, such as chemical flooding, have been extensively studied and implemented in sandstone reservoirs but have limited applications in challenging carbonate reservoirs. Polymer flooding (PF), surfactant flooding (SF), alkali-surfactant flooding (ASF), surfactant-polymer flooding (SPF), and alkali-surfactant-polymer (ASP) flooding are the most used chemical enhanced oil recovery (CEOR) techniques which recover the remaining oil by various mechanisms, e.g., reduction of oil–water interfacial tension (IFT), wettability alteration, and mobility control [4]. Several...
studies have proved the effectiveness of these CEOR methods in carbonate formations in terms of improvement in oil recovery [5,6]. However, their field-scale applications are still very few, and one significant reason for this is a high degree of chemical degradation and adsorption on calcite surfaces which makes the projects economically unfeasible [7].

Recently, low-salinity waterflooding (LSWF), or engineered waterflooding (EWF), has gained significant momentum in the oil industry, as indicated by an increasing number of studies on this technology [8–12]. In this process, a reduced salinity brine spiked with some key active ions, known as potential determining ions (PDIs), is injected into the reservoir, disturbing the initial equilibrium state of the oil–water–rock (OWR) system and releasing the trapped or adsorbed oil. The LSWF was first implemented in sandstone reservoirs [13,14], but it provided excellent results and quickly became popular in carbonate formations [15,16]. Multicomponent-ion-exchange (MIE) [17–19], mineral dissolution [20–22], fluid–fluid interactions and formation of microdispersion [23–25] are the dominant recovery mechanisms of EWF in carbonate reservoirs, which ultimately alter the carbonate rock wettability towards more water-wet conditions [26,27]. A range from 5% to 30% incremental oil recovery by EWF has been reported in several studies conducted in carbonate reservoirs [28].

The chemically altered low-salinity water provides some additional benefits of lower chemical adsorption and enhanced performance of chemicals in high-salinity high-temperature reservoirs. In this context, research is being conducted to study different combinations of engineered water (EW) and enhanced oil recovery (EOR) chemicals, e.g., surfactant, alkali, and polymer. CEOR techniques have huge potential to recover additional oil, but these methods have some inherent limitations and are not fully exploited for carbonate formations. Surfactant flooding is one of the established EOR techniques in which surfactants are used to unlock low to medium viscosity crude oil potential from petroleum reservoirs. Surfactant flooding technology is not new and has been utilized in the petroleum industry for the last 40 years [29–35]. Application of surfactant effectively lowers the IFT between crude oil and water phase, diminishing the forces which are responsible for capillary trapping, and, hence, decreases the residual oil saturation by altering the wettability [36,37]. However, there are some risks associated with surfactant flooding, such as adsorption of surfactants onto the rock surface and their chemical separation and precipitation under reservoir conditions [38,39]. Furthermore, surfactants are also prone to become unstable and inactive in a high-salinity and high-temperature environment [40].

Therefore, the main objectives of SF design are to achieve the lowest possible IFT with low surfactant concentration, and minimum adsorption on the rock surface [41,42]. This can be achieved by combining SF with EWF, known as hybrid engineered water surfactant flooding (EWSF). This method can minimize the retrapping of the oil mobilized by low-salinity water (LSW) [29,43,44]. Moreover, surfactant solubilization is improved, and adsorption of anionic surfactant on calcite surface is decreased in the presence of LSW, making this hybrid approach both technically and economically applicable to reservoirs with harsh conditions of temperature and salinity [45,46]. Thus, a broader range of inexpensive and biologically safe surfactants can be employed for low-salinity environments. Different studies have shown the effectiveness of hybrid EWSF method in both sandstone and carbonate reservoirs, wherein 10–20% of original-oil-in-place (OOIP) incremental recoveries are reported by the hybrid method [47–49].

Polymer flooding is another extensively used CEOR method in which high-molecular-weight polymer mixed with brine is injected into the formation. The principal recovery mechanism responsible for better hydrocarbon production by PF is the increase in displacing fluid viscosity by the viscous polymer solution, hence, causing a reduction in mobility ratio [50]. Partially hydrolyzed polyacrylamide (HPAM) is a synthetic polymer that is extensively used owing to its high molecular weight and low cost [51]. Considerable research has been carried out in the field of PF to expand its application envelope and improve the performance [52,53]. Several researchers have examined the dependency of physical and chemical characteristics of HPAM polymers on different subsurface parameters such as
reservoir temperature, salinity, and hardness of reservoir brine and injected brine \[54,55\]. The polymers were first applied in 1964 as EOR chemicals to control mobility \[56\]. Later, several laboratory experiments were performed to study polymer properties \[57–59\]. However, most of the work was carried out for sandstones, and the literature contains a limited number of projects \[5,6\] in carbonate fields. Standnes and Skjervak \[7\] conducted a comprehensive review of implemented PF projects wherein only 5% of the total projects were reported in carbonate reservoirs. This is because HPAM viscosity is adversely affected by brine salinity and high concentration of divalent ions, leading to increased adsorption of polymer on positive calcite surface \[55\]. Furthermore, HPAM polymers undergo thermal degradation at high formation temperatures, which is another constraint for their application in carbonate reservoirs \[60\].

The limitations of standalone PF can be overcome by combining it with EW or LSW, and this has been given the term ‘hybrid engineered water polymer flooding’ (EWPF). The effectiveness of EWPF in carbonates has been proven by various experimental \[61–65\] and numerical modeling \[66–69\] studies. EWPF provided incremental recovery of 10% OOIP from carbonate cores in experiments by Al Sofi et al. \[70\]. Similarly, Vermolen et al. reported around 45% OOIP incremental recovery by EWPF during coreflood tests \[63\]. The improvement in oil recovery by hybrid EWPF is caused by the combined actions of EW and polymer. EW aids in altering the carbonate rock wettability by desorption of acidic crude oil components \[71,72\], and PF helps in providing stable oil bank displacement by creating a favorable mobility ratio \[73\]. The adsorption and chemical degradation of HPAM polymer is also reduced in the presence of EW, and therefore, less polymer is required to achieve a desired viscosity \[62\]. A 30–50% reduction in polymer concentration can be achieved by combining EWF and PF, due to a higher solution viscosity and lower polymer adsorption under low-salinity settings \[62,65,74\].

Alkaline flooding (AF) is one of the economical EOR techniques in which an alkali, such as sodium carbonate (Na\(_2\)CO\(_3\)) or sodium hydroxide (NaOH), is mixed with water and injected into the reservoir to increase oil production. The main mechanism of alkaline flooding is emulsification \[75–77\]. A water-mixed alkali reacts with the acidic component of crude oil, forming in situ anionic surfactants which result in the reduction of IFT between oil and aqueous phases and triggers an increase in oil recovery. However, this EOR technique is not popular because of the complications it causes at the field level \[78\]. It is not particularly suitable for carbonate formations because a high concentration of calcium ions can form hydroxide precipitates (a scaling issue) and increase the probability of formation damage \[79\]. Moreover, the emulsification process, which is the main mechanism of alkaline flooding, generates extremely stable emulsions that increase the operating expenses required for the separation and treatment of produced fluids with surface facilities. Therefore, alkaline flooding is usually applied as a hybrid technique with polymer and surfactant, to improve the oil recovery \[4,80\]. Alkali surfactant flooding is a promising CEOR method, and it has been extensively studied by various researchers in recent years \[81–84\]. The combination of alkali and surfactant promotes ultralow IFT, reducing the residual oil saturation (\(S_{or}\)) and improving oil recovery. \(S_{or}\) was dramatically reduced to only 3% in a tertiary ASF test conducted by Mohan et al. \[85\] on tight carbonate reservoir core plugs. However, conventional ASF still has some risks, such as scaling issues, the formation of extremely tough emulsions with oil and precipitation in the reservoir containing high-salinity formation water \[79\].

To counter these risks, EW and ASF can be combined to achieve the simultaneous benefits of wettability alteration, IFT reduction and reduced chemical degradation \[86\]. A few studies have demonstrated the synergy of hybrid engineered water alkali surfactant flooding in porous sandstone media \[86,87\], but its application in carbonates has not been studied in detail. Similarly, combining polymer with other chemical flooding methods provides the supplementary advantage of higher macroscopic sweep efficiency. Surfactant polymer and alkali surfactant polymer methods are the most extensively used combination flooding methods with successful field applications in sandstones \[88,89\]. Wang et al. \[90\]
reported a maximum incremental oil recovery of 33% by an optimized SP flooding design in heterogeneous sandstone cores. Bataweel et al. [91] studied different combinations of CEOR methods in Berea sandstone with high temperature and high salinity and reported around 9% more residual oil recovery by ASP flooding compared to SP flooding. In spite of the promising results from different laboratory-scale studies, the combination flooding is mainly implemented in sandstone formations on pilot and field scale, and there are barely any large-scale projects in carbonate reservoirs because of their inherent complexity and high-temperature, high-salinity environments [92].

The application of SP and ASP can be extended to carbonate formations by combining these methods with ion-tuned EW. The chemicals’ performance and stability can be significantly improved in low-salinity settings by hybrid EW-surfactant polymer flooding (EWSPF) and EW-alkali-surfactant polymer (EWASP) flooding techniques. So far, these hybrid methods have only been studied for sandstones on a laboratory scale. Al-Ajmi [93] reported an incremental oil recovery of 16% OOIP by a hybrid EWSPF test performed on Berea cores, highlighting the efficiency of the hybrid approach. Dang et al. [92] modelled the ASP process by fully capturing the mechanisms involved and validated the model with ASP data available in the literature. The model showed 10% more oil recovery by a hybrid EWASP process, compared to a conventional ASP process with no pre-injection of EW. Ideally, these hybrid methods can be more valuable for oil-wet carbonate reservoirs, but there is insufficient research in the literature for their practical applications. The effectiveness of hybrid EW-based CEOR methods can be clearly demonstrated with the help of the capillary desaturation process.

The term “capillary desaturation” refers to the process of releasing and producing the residual oil that is trapped due to presence of high capillary forces. Usually, conventional PF only affects the volumetric sweep efficiency. On the other hand, conventional AF and SF can only improve the microscopic sweep efficiency. To examine the displacement efficiency of any enhanced oil recovery technique, particularly chemical flooding methods, a capillary desaturation curve (CDC) is constructed by conducting coreflood testing at various flow rates [94,95]. A CDC usually reflects the pore structure, arrangement within the porous media, and fluid distribution inside these pores [96]. To construct a CDC, residual oil saturation for every stabilized flow period is plotted against the capillary number (Nc) [97,98]. The capillary number is defined as the ratio of viscous forces and capillary forces [99–104], and it has several mathematical expressions. The two most commonly used definitions of capillary number reported in the literature are given by Equations (1) and (2) [105]:

\[
N_c = \frac{K \Delta p}{\sigma L} \quad (1)
\]

\[
N_c = \frac{v \mu}{\sigma} \quad (2)
\]

where K is absolute permeability in cm², Δp/L is the pressure gradient across the core in dynes/cm², σ is the oil-water IFT in dynes/cm or mN/m, v is the superficial injection velocity in m/s, and μ is the displacing phase viscosity in Pa.s. The residual oil saturation is inversely proportional to capillary number, i.e., higher the capillary number, the lower the Sor. Critical capillary number for the onset of residual oil mobilization in strong water-wet rocks is around 10⁻⁵, while it increases by one to two orders of magnitude for oil-wet rocks [101,106]. Equation (1) indicates that, to have an adequate range of Nc, either the pressure drop should be significantly increased or IFT should be considerably reduced, both of which are normally not attainable by typical waterflooding (WF) and PF [107]. The possible ways to increase Nc in PF are either to increase the viscosity or injection velocity of the displacing fluid (Equation (2)) both of which are practically constrained by the formation fracture pressure [108]. Thus, conventional PF cannot cause appreciable reduction in Sor owing to field operational constraints [109–111]. Wettability alteration by EW is another option to increase Nc by redistribution of the residual oil inside the pore
spaces, but the existing capillary forces are still high enough to produce an appreciable percentage of residual oil.

IFT reduction is the most realistic approach to have a significant increase in the magnitude of capillary number (up to $10^{-2}$) and the residual oil saturation can drop to nearly zero for ultralow IFT values ($10^{-3}$ to $10^{-4}$ mN/m) [100]. Surfactant flooding and alkali-surfactant flooding come into play at this point as these EOR methods are capable of lowering IFT and increasing $N_c$ beyond the critical capillary number needed to mobilize residual oil. Many researchers have studied the capillary desaturation tendency of various EOR methods and reported an increase in displacement efficiency with increasing capillary numbers [99,104,112]. However, only a capillary number cannot be considered to evaluate the performance of any EOR operation. The volumetric sweep efficiency is another critical factor which is somehow ignored while studying different EOR methods utilizing classical CDC theory [102]. Both the microscopic and macroscopic sweep efficiencies should be given equal importance, especially in heterogeneous oil-wet carbonate formations, which generally have a higher critical capillary number compared to sandstone reservoirs [98]. Finally, a formulation containing both polymer and alkali/surfactant is practically the most effective CEOR design to recover maximum residual oil saturation.

The conventional CEOR methods (such as PF, SF, SPF, and ASP flooding) have limited applications in carbonate reservoirs as higher capillary numbers are required for an appreciable reduction in $S_{or}$ in carbonates. However, the capillary desaturation tendency of the CEOR methods can be improved by combining them with EW. Zivar et al. [108] used experimental data from the literature and showed a higher capillary desaturation capability of low-salinity surfactant flooding compared to conventional waterflooding and SF. Shakeel et al. [28] compared the conventional PF CDCs with experimental data of EWPF available in the literature and showed a higher reduction in $S_{or}$ by EWPF for similar values of $N_c$. In this paper, the capillary desaturation theory has been used to compare the performance of hybrid EW-based chemical EOR methods with the conventional CEOR methods. Several designs of EW and CEOR methods are developed, and coreflood tests are performed to obtain capillary number and $S_{or}$ data. The objective of this paper is to analyze the capillary desaturation tendency of our hybrid designs and present effective EW–CEOR methods for carbonate formations.

2. Methodology

To construct the CDCs for hybrid EW–CEOR methods, several coreflood tests were performed, oil-water IFT for alkali and alkali/surfactant solutions was estimated, and capillary numbers were calculated. Conventional chemical flooding CDC data were gathered from different studies, and a comparison was made between the hybrid designs and conventional CEOR methods. This section provides details of the materials used and procedures followed in this research work.

2.1. Chemicals

The surfactant used in this research work was Soloterra 113-H, which is an anionic surfactant of benzene sulfonic acid. This surfactant was chosen because of its improved performance in combination with EW in a previous study [49]. The optimum surfactant concentration was determined from phase behavior and aqueous stability tests and was found to be 1 wt%. For alkali-surfactant experiments, sodium carbonate ($Na_2CO_3$) is used as an alkali with a concentration of 1 wt% of aqueous phase. The addition of alkali reduces anionic surfactant adsorption on carbonate rock and promotes surfactant and polymer stability [81,113]. For hybrid combinations consisting of polymer flooding, Flopaam 5115 was used, which is a hydrolyzed polyacrylamide polymer. The reason for using this polymer is its higher thermal and salinity tolerance. A previous study has also shown better synergy of Flopaam 5115 and EW compared to other polymers [114].
2.2. Coreflooding

Eight coreflood experiments were conducted on Indiana limestone outcrop samples using a crude oil with a viscosity of 10.8 cp at 80 °C. Color-indicator titration was used to determine the acid number (AN) of the crude oil by using ASTM D974 standard test procedure, and the AN was found to be 4.3 ± 0.2 mg KOH/g of oil. The porosity and permeability of the cores were in the range of 14–16% and 90–135 md, respectively. The initial water saturation (Swi) ranged from 12% to 22%. The injection sequence for different tests is given in Table 1, along with the number of data sets for each case. The formation water (FW) of around 180,000 ppm (180 ppt) salinity was used to saturate the cores, while south Caspian seawater (CSW), with a salinity of 13,000 ppm (13 ppt), was used for waterflooding. In addition, 10 times diluted CSW spiked with 6 times sulphate ions, 1 time magnesium ions, and 3 times calcium ions (10CSW6SMg3Ca) was used as EW in all of the experiments. For alkali-surfactant tests, the EW was further diluted by 1.5 times to obtain the Type III microemulsion, based on a phase behavior study. The details for the phase behavior study are beyond the scope of this paper and can be seen in the work of Samanova A. [115].

Table 1. Number of tests conducted and their respective injection sequences.

| Case     | Number of Data Sets | Injection Sequence                |
|----------|---------------------|-----------------------------------|
| EWSF     | 3                   | WF, EWF, EWSF                    |
| EWPF     | 3                   | WF, EWF, EWPF                    |
| EWSPF    | 1                   | WF, EWF, EWSF, EWPF              |
| EWASF    | 1                   | WF, EWF, EWASF                   |
| EWASP    | 2                   | WE, EWF, EWAS/EWASP-Slug, EWPF   |

In all the corefloods, the injections sequence is almost similar with a slight modification of the chemical flooding stage. Three corefloods were conducted for the EWPF scenario, three for EWSF, one for EWASF, one for EWSFP, and two for EWASP flooding. Initially, CSW was injected to recover maximum oil and reach Sw after waterflooding. EWF was then performed continuously until the oil cut was less than 0.1%. The designed chemical stage was then conducted, and the recovered oil volume calculated. The residual oil saturation at the end of each stage was calculated using initial oil saturation (Soi) and the recovery factor (RF) for that stage. All of the corefloods were performed at 80 °C.

2.3. Interfacial Tension Estimation

To calculate the IFT for surfactant and alkali-surfactant combinations, a phase behavior study was carried out by mixing crude oil and alkali/surfactant solutions in a 1:1 ratio at an optimized brine salinity and alkali concentration of 1% of aqueous phase. The samples were kept in an oven at 80 °C for 6 days, and the volumes of oil, water and microemulsion were noted. The correlation provided by Nelson et al. [116] was then used to estimate IFT for oil/surfactant and oil/alkali-surfactant cases, as given by Equation (3):

$$\log_{10} \sigma_{mo,mw} = \frac{4.80}{1 + 0.10(V_{o,w}/V_s)} - 5.40$$

where $\sigma_{mo,mw}$ is the microemulsion/oil or microemulsion/water IFT in dynes/cm, $V_{o,w}$ is the oil or water volume in microemulsion in ml, and $V_s$ is the surfactant volume in microemulsion phase in ml.

2.4. Capillary Numbers

The capillary numbers for each scenario were calculated by Equation (1) using the experimental data (pressure drop), fluid-rock interaction properties (IFT), and rock properties (permeability and length). The IFT for surfactant and alkali-surfactant cases is the
same as that obtained from the previous step, while a typical IFT value of 30 dynes/cm (30 mN/m), reported in the literature [65], was used for EWF and EWPF scenarios.

2.5. Conventional Capillary Desaturation Curves

For each hybrid EW–CEOR design, the corresponding typical capillary desaturation curves are collected from the literature. The studies consulted for polymer flooding [117–119], surfactant flooding [120,121], alkali-surfactant flooding [122], surfactant-polymer flooding [90], and alkali-surfactant-polymer flooding [123,124] are summarized in Table 2. Almost all of the studies were performed on sandstone cores, and we used the sandstone CDC curves to compare our hybrid designs performed on carbonates. This can be explained by the work of Tang et al. [98], in which typical CDCs for sandstone and limestone were compared and a higher capillary number is needed in limestones to have a same reduction in \( S_{or} \) compared to sandstones. Hence, our idea is that the effective capillary number ranges for hybrid EW–CEOR methods obtained for limestones, can also work for sandstones, as it is easier to release capillary-trapped residual oil in sandstones compared to carbonates. The conventional CDCs are constructed using either of the two equations of capillary number (Equations (1) and (2)).

Table 2. Summary of conventional CDC studies used for comparison.

| Author          | Chemical Agents                  | Reservoir          | Injection Design                                                                 | Results                                                                 |
|-----------------|----------------------------------|--------------------|----------------------------------------------------------------------------------|------------------------------------------------------------------------|
| Abeyesinghe et al. [120] | Surfactant: sodium C\(_{6-10}\) alcohol ether sulfate (anionic) | Sandstone          | Steady and unsteady state experiments: Waterflooding was followed by surfactant flooding | The reduction in \( S_{or} \) is due to an increase in oil-relative permeability with increasing capillary number during SF. |
| Abeyesinghe et al. [121] | Surfactant: sodium C\(_{6-10}\) alcohol ether sulfate (anionic) | Mixed-wet Berea sandstone | Waterflooding followed by surfactant flooding                                    | \( S_{or} \) vs. \( N_c \) plot does not characterize the true CDC behavior. In the mixed-wet case, the most important effect of surfactants can be the acceleration of oil; not necessarily the reduction of \( S_{or} \). |
| Pei et al. [122] | Alkali: Sodium hydroxide (NaOH) Surfactant: SLPS (with a purity of 33.3%) and surfactant ORS (with a purity of 33.5%) | Sandpack            | Sandpack flooding test: Waterflooding followed by slug-wise and continuous injection of alkali and alkali-surfactant solution. | The tertiary oil recovery of AS flooding is lower compared with the only alkaline flooding, and results in a significant reduction in residual oil saturation. |
| Qi et al. [117] | Polymer: HPAM 3630s              | Bentheimer sandstones | Waterflooding followed by glycerin and polymer floods at a constant pressure gradient. | Increasing polymer elasticity results in decreasing residual oil saturation. |
| Zhong et al. [118] | Polymer: AP-P4 hydrophobically associated polymer | Daqing oilfield sandstone | Waterflooding followed by viscous glycerin flood and viscoelastic polymer flood of same viscosity | A higher reduction in \( S_{or} \) is observed for the polymer flooding at the same capillary number compared to glycerin flooding, showing the contribution of polymer viscoelastic behavior in reducing \( S_{or} \). |
| Clarke et al. [119] | Polymer: HPAM 3630S              | Bentheimer sandstone | Waterflooding followed by polymer flooding                                      | HPAM polymer has caused rapid capillary desaturation at relatively lower capillary numbers, indicating some other mechanisms e.g., viscoelasticity in addition to mobility control. |
Table 2. Cont.

| Author                | Chemical Agents                      | Reservoir         | Injection Design                                                                 | Results                                                                                                                                 |
|-----------------------|--------------------------------------|-------------------|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| Wang et al. [90]      | Surfactant: Cocamide Diethanolamine  | Sandstone         | Waterflooding followed by 0.3 PV slug of surfactant-polymer solution, chased by   | An SP formulation with optimum IFT and viscosity can provide higher incremental oil recovery compared to formulation with lowest IFT, largely because of improvement in the sweep efficiency. |
|                       | (nonionic) and Petroleum sulfonate   |                   | waterflooding                                                                     |                                                                                                                                         |
|                       | (anionic)Polymer: HPAM polymer       |                   |                                                                                  |                                                                                                                                         |
| Ghorpade et al. [123] | Alkali: 0.1 wt% NaOHSurfactant: 0.11 | Sandstone         | Waterflooding followed by ASP flooding                                           | An ASP formulation with small concentration of polymer can work better in homogeneous reservoirs containing low-viscosity crude oil.     |
|                       | wt%Polymer: 1500 ppm                 | simulation model  |                                                                                  |                                                                                                                                         |
| Qi et al. [124]       | -                                    | Sandstone         | Waterflooding followed by combination flooding                                   | Classic CDC does not explain the relationship between capillary number and $S_{or}$ for high capillary number conditions and must be corrected before applying desaturation theory to combination flooding.|

3. Results and Discussion

The capillary desaturation tendency of conventional CEOR methods with that of hybrid EW/CEOR methods has been compared by plotting the coreflood endpoints from each EOR injection stage in all experiments studied. It is observed that hybrid EW/CEOR methods resulted in a substantial $S_{or}$ reduction for relatively smaller values of $N_c$.

3.1. IFT Results

The results of the phase behavior study for the effect of alkaline addition are presented in Figure 1. It is clear from Figure 1 that the volume of Type III microemulsion is increased by the addition of alkaline, which can be explained by the significant IFT reduction. Table 3 shows the oil, water, and microemulsion (ME) volumes for both surfactant and alkaline-surfactant mixtures, as well as IFT values. Alkali addition helped to increase the microemulsion ratio and achieve ultralow IFT. The microemulsion ratio is almost 95% higher in the presence of alkaline, compared to the standalone surfactant scenario.

![Figure 1](image.png)

Figure 1. Results of phase behavior study for (a) EW-surfactant solution and (b) EW-surfactant solution with addition of 1 wt% alkali.
Table 3. Results of phase behavior study for alkali addition to surfactant solution.

| Case                        | \( V_o \) | \( V_w \) | \( V_{me} \) | ME Ratio | IFT      |
|-----------------------------|-----------|-----------|-------------|----------|----------|
| Surfactant                  | 1.94      | 1.94      | 0.12        | 0.03     | 0.02     |
| Alkali + Surfactant         | 0.80      | 1.00      | 2.20        | 0.55     | 0.000018 |

The IFT for oil/surfactant is 0.02 dynes/cm while for oil-/alkali-surfactant, the IFT is 0.000018 dynes/cm (0.000018 mN/m). This order of magnitudes reduction in IFT indicates the designed alkali-surfactant formulation is effective for recovering capillary-trapped residual oil.

3.2. Hybrid EW-Surfactant Flooding

The first comparative analysis carried out for hybrid EWSF design is shown in Figure 2. Three EWSF tests were performed with almost the same injection scheme but a slightly different salinity of the injection fluids. The effect of salinity gradient is not discussed in this paper, and the work carried out by Samanova A. [115] can be referenced for more details. The CDCs for conventional surfactant flooding obtained from Abyesinghe et al. [120,121] were plotted, and our experimental EWSF data from three corefloods were overlain on the same graph. All the points fall below the conventional SF curves, showing a higher capillary desaturation tendency of the hybrid method. The highest reduction in \( S_{or} \) for conventional CDC is obtained for a capillary number of \( 1.2 \times 10^{-2} \), while the \( S_{or} \) is dramatically reduced for \( N_c \) ranging from \( 9.5 \times 10^{-3} \) to \( 1 \times 10^{-2} \) in the case of hybrid EWSF method. Hence, this hybrid design is more efficient than standalone SF in terms of improving microscopic sweep efficiency. The higher recovery of residual oil by hybrid method is attributed to the combined action of ion-tuned EW and surfactant. EWF promoted wettability alteration of the oil-wet carbonate medium and EWSF successfully lowered the oil-water IFT, thereby improving the oil recovery factor. Moreover, this hybrid design effectively reduced the \( S_{or} \) by 15–16% at the end of the test compared to only 6–10% reduction in \( S_{or} \) by conventional SF.

![Figure 2. Comparison of capillary desaturation tendency of hybrid EWSF with conventional SF.](image)

3.3. Hybrid EW-Alkali-Surfactant Flooding

One coreflood was conducted to obtain the capillary number and \( S_{or} \) for a combination of EW, alkali, and surfactant. Figure 3 shows the experimental results compared with the
conventional CDC of alkali-surfactant flooding (ASF), extracted from the experimental work of Pei et al. [122]. The initial points of conventional CDCs in Figure 3 show the $S_{or}$ without alkali addition, while the subsequent points show the $S_{or}$ with increasing alkali concentration in the surfactant solutions. Figure 3 clearly depicts that the hybrid method has recovered more residual oil with a smaller magnitude of capillary forces ($1 \times 10^1$), whereas conventional ASF required a larger capillary force of around $1.3 \times 10^2$ to produce the residual oil. Our hybrid EWASF test shows much lower $S_{or}$ for the same capillary number, compared to conventional ASF. This is due to the added benefit of alkali which helps minimize the adsorption of anionic surfactant on carbonate surface [81,113,125]. Furthermore, wettability alteration by EW in the case of hybrid EW-alkali-surfactant flooding leads to reduced adsorption of anionic surfactant on less positive carbonate surfaces. The low-salinity environment created by EW has contributed to enhanced surfactant performance in terms of IFT reduction. Finally, alkali addition helped achieve an ultralow IFT of 0.000018 dynes/cm, which augmented the residual oil recovery process by the hybrid method. The lower $S_{or}$ at the end of our experiment indicates that EW-based alkali-surfactant flooding is a better option for oil-wet carbonate reservoirs, since conventional ASF can undergo chemical degradation and increased surfactant loss in such high-salinity, high-temperature formations.

![Figure 3](image3.png)

Figure 3. Comparison of capillary desaturation tendency of hybrid EWASF with conventional ASF.

### 3.4. Hybrid EW-Polymer Flooding

Three coreflood tests were performed for hybrid EW-polymer flooding (EWPF) design. The residual oil saturation as a function of capillary number for the three cases is plotted in Figure 4, along with conventional PF CDCs extracted from various studies [117–119]. The hybrid EWPF experiments have recovered more residual oil compared to conventional tests. Most of the researchers are of the view that standalone PF cannot reduce the residual oil saturation as it does not affect fluid–rock interaction properties, such as IFT or contact angle [107]. By the CDC curve, critical $N_c$ for the process under investigation can be determined. The critical $N_c$ usually ranges from $10^{-4}$ to $10^{-3}$ [100,126], while the typical $N_c$ achievable in the field by WF and PF is in the range from $10^{-7}$ to $10^{-5}$ [107]. Evaluation of CDCs from various coreflood tests revealed that the normal field operating constraints for PF are not enough to trigger any decrease in capillary-trapped residual oil [109–111,127,128]. To cause a reduction in $S_{or}$ and increase microscopic sweep efficiency by any EOR method, the capillary number should be in the range from $10^{-4}$ to $10^{-3}$, which is not attainable by typical PF.
However, our paper shows that by combining PF with low-salinity ion-tuned water, a considerable reduction in $S_{or}$ is possible for lower $N_c$ values. The conventional PF in the studies of Zhong et al. [118], Qi et al. [117], and Clarke et al. [119] lowers the $S_{or}$ by 25–40% for capillary numbers ranging from $1.5 \times 10^{-4}$ to $3.1 \times 10^{-2}$. The hybrid EWPF, on the other hand, has reduced the $S_{or}$ by 27% for a relatively lower capillary number range from $4.0 \times 10^{-6}$ to $4.5 \times 10^{-5}$. This indicates that almost three orders of magnitude increase/decrease in viscous/capillary forces are required to obtain a reasonable residual oil recovery by conventional PF compared to hybrid EWPF. Thus, hybrid EWPF may provide a reasonable reduction in $S_{or}$ for a capillary number range obtainable in the field. This is because of favorable synergy between EW and HPAM polymer; EW alters rock wettability and reduces polymer degradation; and PF helps in efficient displacement of the residual oil bank.

3.5. Hybrid EW-Surfactant-Polymer Flooding

The experimental results of $N_c$ vs. $S_{or}$ for this test are presented in Figure 5, together with conventional surfactant-polymer flooding (SP) CDCs from the study of Wang et al. [90]. The hybrid design has caused higher $S_{or}$ reduction against the same capillary number compared to the conventional SP flooding. A higher recovery of residual oil in this case compared to previous designs can be attributed to the addition of polymer which has resulted in improved fractional flow and better volumetric sweep efficiency. The EW is used as the makeup brine for all chemical injection fluids, which has further increased the stability of the surfactant and polymer, providing higher incremental recovery compared to conventional SP flooding scenario. Our hybrid design has successfully lowered the $S_{or}$ to 5% for a capillary number $2.7 \times 10^{-2}$, while the conventional method requires a higher $N_c$ range (from $4 \times 10^{-5}$ to $2.2 \times 10^{-1}$) to cause an appreciable reduction in $S_{or}$ (7–10%), which is still lower than that obtained in the hybrid EWSPF case. According to this comparison, it is evident that EW-based hybrid SP flooding is more beneficial for reservoirs with harsh conditions where typical chemical flooding techniques cannot be implemented because of increased chemical consumption.

3.6. Hybrid EW-Alkali-Surfactant-Polymer Flooding

To study the capillary desaturation tendency of hybrid EW-alkali-surfactant-polymer (EWASP) flooding technique, two corefloods were conducted. The alkali-surfactant and polymer average IFT are used in the calculation of $N_c$ for both tests, and the final chemical
flooding stage is considered for capillary desaturation analysis. The CDCs for conventional ASP flooding are taken from the studies of Ghorpade et al. [123] and Qi et al. [124]. The final CEOR stage in our corefloods includes the combined action of alkali, surfactant, and polymer. That is why a remarkable reduction in $S_{\text{or}}$ is observed during this stage for relatively lower $N_c$ values, compared to conventional ASP flooding, as shown in Figure 6.

![Figure 5. Comparison of capillary desaturation tendency of hybrid EWASP flooding with conventional SPF.](image)

![Figure 6. Comparison of capillary desaturation tendency of hybrid EWASP flooding with conventional ASP flooding.](image)

The residual oil bank formed during the alkali-surfactant flooding stage is effectively displaced by a viscous polymer front. Only 4–6% residual oil saturation is left in the core at the end of hybrid EWASP flooding, indicating that this design is the best in terms of oil recovery and chemicals consumption. Interestingly, hybrid EWASP method has shown an excellent capillary desaturation tendency by reducing the $S_{\text{or}}$ by 23% for $N_c$ values of $8 \times 10^{-2}$. The conventional ASP flooding has also helped to reduce $S_{\text{or}}$ but for a higher capillary number range from $3 \times 10^{-3}$ to $8 \times 10^{-1}$ compared to hybrid EWASP flooding.
The CDCs developed by Ghorpade et al. [123] and Qi et al. [124] show that a threshold capillary number ($N_c$) is required to observe a considerable reduction in $S_{or}$ by typical ASP flooding, which is in the range from $1.7 \times 10^{-4}$ to $2.7 \times 10^{-1}$. A threshold or critical capillary number in this context is the minimum capillary number at which a reduction in $S_{or}$ is observed by a certain EOR process [102].

However, this threshold $N_c$ value is significantly reduced in the case of hybrid EW/CEOR methods because of the synergetic effects of wettability alteration, IFT reduction, sweep improvement, and lower surfactant adsorption. There is also a possible contribution of the viscoelastic properties of polymer in achieving low $S_{or}$ in these cases because of the high-pH environment created by the alkali/surfactant flooding stage. Basic conditions promote HPAM viscoelastic behavior, causing a reduction in $S_{or}$. Recently, some researchers have suggested that $S_{or}$ can be reduced by using viscoelastic polymers as they can strip off the trapped oil from pore throats and walls [118,129–137]. However, this discussion is beyond the scope of the current paper. These results prove the usefulness of combining CEOR methods with low-salinity, ion-tuned EW over conventional CEOR methods. Carbonate reservoirs are particularly known for higher residual oil saturations after waterflooding due to their heterogeneous nature and oil-wet surface properties. Hybrid EW-based CEOR methods are promising applications for such challenging environments, as our work has clearly demonstrated a higher capillary desaturation tendency of these hybrid methods over their conventional counterparts.

3.7. Comparison of Threshold Capillary Number

Figure 7 presents a comparison of threshold capillary numbers for all combinations of EW/CEOR methods and conventional CEOR methods except SF and ASF, since $S_{or}$ continuously decreases and there is no threshold $N_c$ for these cases. Figure 7 shows that the threshold capillary numbers for conventional CEOR methods are higher compared to our studied hybrid EW/CEOR methods. EWPF, EWSPF, and EWASP flooding has helped to overcome capillary forces and initiate recovery of residual oil for at least one order of magnitude smaller $N_c$ values because of reduced retrapping of the residual oil in the presence of alkali/surfactant and more stable oil bank displacement by the polymer.

![Figure 7. Comparison of threshold capillary numbers of hybrid EW/CEOR methods with conventional ones.](image)

On average, a 7–10% reduction in threshold capillary number is observed by hybrid methods, whereas the resulting reduction in $S_{or}$ is even higher than that obtained by
conventional methods, as can be seen in Figure 8. This can be attributed to the combined effects of the constituents involved in the hybrid EW/CEOR methods. The $S_{or}$ at the end of EWSF is almost 30% higher compared to conventional SF. Similarly, EWPF has caused 55% more reduction in $S_{or}$ than its conventional version. Finally, the $S_{or}$ reduction by EWSPF and EWASP is 70–80% more, compared to conventional SPF and ASP flooding. Figure 8 also highlights the importance of mobility control mechanism as the hybrid CEOR methods consisting of both alkali/surfactant and polymer have resulted in higher recovery of residual oil, indicating that mobility control is as critical as IFT reduction or wettability alteration in the efficient recovery of capillary-trapped residual oil.

**Figure 8.** Effectiveness of hybrid EW/CEOR methods in reducing $S_{or}$ compared to conventional CEOR methods.

4. Conclusions

This paper presents the performance comparison of EW-based hybrid CEOR methods with the conventional CEOR methods. This is achieved by conducting coreflood tests for various EW–CEOR combinations and comparing our experimental capillary number and residual oil saturation data with CDCs of conventional methods gathered from the literature. This comparison has helped to investigate the active mechanisms for recovery of residual oil in different CEOR designs as a function of capillary number. The $S_{or}$ at the end of a certain test is also compared for both hybrid and conventional methods to quantitatively assess the effectiveness of our designed hybrid methods.

Analysis of capillary desaturation data has revealed that hybrid EW–CEOR methods are more effective in recovering the capillary-trapped residual oil with relatively lower capillary numbers, compared to conventional CEOR methods. Overall, a 7–10% reduction is observed in threshold capillary numbers, and the resulting $S_{or}$ is quite lower, compared to conventional methods.

Alkali addition to the EW surfactant solution has remarkably reduced the oil–water IFT by three orders of magnitude, and the hybrid EWSF method has caused 4% more reduction in $S_{or}$ compared to EWSF design. Hybrid EWASP flooding has resulted in a maximum reduction in $S_{or}$ of 23% for a capillary number of $8 \times 10^{-2}$, whereas conventional ASP flooding has reduced the $S_{or}$ by 10–23% for a relatively higher capillary number range (from $3 \times 10^{-3}$ to $8 \times 10^{-1}$). This comparative study shows a 30–70% higher reduction in capillary-trapped residual oil saturation by our designed hybrid EW–CEOR methods, compared to their conventional equivalents, and therefore, these hybrid methods have a higher capillary desaturation tendency.
Hybrid EWSF and EWPF have shown higher capillary desaturation tendency compared to conventional SF and PF because of reduced chemical degradation and adsorption in a low-salinity environment and the supplementary benefit of wettability alteration by EW. Similarly, combination flooding techniques (ASF, SPF, and ASP) have exhibited improved performance and recovered more residual oil when combined with EW. This is due to the synergistic behavior of EW and chemicals; for instance, alkali has helped to lower surfactant adsorption, create ultralow IFT, and promote HPAM viscoelastic behavior, and polymer has improved the volumetric sweep by providing a favorable mobility ratio for efficient residual oil displacement. Collectively, the hybrid EW–CEOR methods have proved to be promising for applications in heterogeneous, high-temperature carbonate formations containing high-salinity formation water.

Author Contributions: Conceptualization, investigation, writing—original draft preparation, M.S. and A.S.; writing—review and editing, supervision, P.P. and M.R.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge Nazarbayev University for aiding this research through the NU Faculty Development Competitive Research Grants program (Award number: 110119FD4541).

Acknowledgments: The authors would like to thank respectable reviewers for their valuable feedback and comments to enhance the quality of manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

- $\Delta \pi$: Pressure drop, psi
- $L$: Length of core sample, cm
- $\mu$: Viscosity of displacing fluid, Pa.s
- $N_c$: Capillary number
- $N_{ct}$: Threshold capillary number
- $\sigma$: Interfacial tension, dynes/cm (mN/m)
- $\sigma_{\mu_0,\mu_\omega}$: Microemulsion/oil or microemulsion/water IFT, dynes/cm (mN/m)
- $S_{or}$: Residual oil saturation
- $\gamma$: Superficial velocity, m/s
- $V_{me}$: Volume of microemulsion
- $V_{o,w}$: Oil or water volume in microemulsion, ml
- $V_s$: Surfactant volume in microemulsion
- ASP: Alkali-surfactant polymer flooding
- EWSF: Engineered water surfactant flooding
- PF: Polymer flooding
- SF: Surfactant flooding
- SPF: Surfactant polymer flooding

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