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Chapter

Hybrid EOR Methods Utilizing Low-Salinity Water

Peyman Pourafshary and Nikoo Moradpour

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Abstract

Low-salinity water (LSW) flooding has been applied in sandstone and carbonate formations to improve oil recovery. Wettability alteration by LSW has been identified as the dominant driving mechanism for the incremental oil recoveries. LSW flooding has been combined with other EOR methods to develop new hybrid approaches to improve crude/brine/rock (CBR) interactions with the objective of overcoming some of the LSW flooding downsides, which include oil trapping and fine migration. Hybrid methods can provide higher oil recovery than each stand-alone technique. For instance, changes in gas solubility during LSW injection positively affect the performance of LSW/gas hybrid injection. LSW/surfactant flooding can contribute to incremental recovery by simultaneously lowering interfacial tension (IFT) and wettability alteration. The synergistic effect of fluid redistribution by LSW and enhanced water mobility by polymer flooding improves oil detachment and displacement in porous media through the application of the hybrid approach LSW/polymer flooding. Nanoparticles (NPs), mainly SiO_2, can alter wettability toward more water wetness in combination with LSW, and hot LSW can improve heavy oil production by reducing viscosity. Hence, the synergistic effect of hybrid EOR methods based on LSW flooding is considered a novel EOR approach to improve oil recovery.

Keywords: hybrid EOR, LSW, WAG, surfactant, polymer, nanofluid, hot water, wettability, IFT

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1. Introduction

Waterflooding is the most widely used method to increase oil recovery. Recent studies show that in many cases, by modifying the salinity and ionic content of the injected water, oil recovery by waterflooding improves. The injection of water with lower salinity or adjusted ion composition triggers different mechanisms that modify the wettability of sandstone and carbonate formations. The bonding of polar components in the crude oil with the carbonate or sandstone rock surface is affected by the salinity and composition of the injected water, which generally produces wettability alteration of the rock surface. Several mechanisms have been proposed in the literature for low-salinity water flooding EOR, such as fine migration, rock dissolution, pH increase, multicomponent ion exchange, and double-layer expansion. The combination of these mechanisms is believed to affect the oil recovery in carbonate and sandstone formations. For more information on LSW and the governing mechanisms, the reader is referred to [1].

The idea of combining two (or more) EOR methods, known as hybrid methods, has been investigated recently to promote the activation of several oil recovery mechanisms to increase the ultimate oil recovery, tackle operational challenges, reduce environmental damage, and lower the production costs. Hybrid methods can be optimized for different injection scenarios to achieve the highest feasible recoveries. LSW flooding has been found to be effective when combined with gas injection (mainly CO_2), surfactant and/or polymer flooding, nanofluid injection, and hot water injection, each of which can improve the oil recovery through several mechanisms such as mobility control, wettability alteration, IFT reduction, etc. Experimental and modeling studies reviewed in this chapter have found that LSW hybrid methods can provide up to 30% original oil-in-place (OOIP) incremental oil recovery.

2. LSW/gas hybrid EOR technique

The application of hybrid LSW/gas flooding has recently attracted the attention of different researchers. Various injection schemes have been studied using experimental and simulation approaches. LSW can be injected into water alternating gas (WAG) or simultaneous water alternating gas (SWAG) modes. Moreover, gas may be injected after completion of LSW injection to improve the total oil recovery. CO_2 is generally used as the injection gas in this hybrid approach as it is cheap, has a lower minimum miscibility pressure (MMP), and provides environmentally positive results. Injection of LSW affects the solubility of gas in water and, consequently, the gas/oil interaction and oil recovery. There are two different observations during the hybrid injection of gas and LSW. Some researchers reported benefits from the application of this hybrid method, while others did not observe any incremental recovery compared to continuous gas injection (CGI).

Experimental and modeling studies show that the solubility of gas, especially CO_2, in brine increases with decreasing salinity of water due to the salting out effect [2–5]. Hence, higher CO_2 solubility results in lower amount of free gas available to come into contact with the oil and improve oil mobility, which reduces the oil recovery. On the other hand, many other experiments resulted in higher oil recovery at lower water salinities, as higher solubility increases the gas diffusion in water, which affects the waterfront, mobility ratio, and stability of the injection fluid. Improvement in these parameters leads to lower fingering of the injected fluid that increases its contact with previously bypassed oil droplets in the porous media. Therefore, dissolved gas in water changes the shape of the waterfront which contacts unswept oil more easily than free gas.

In both carbonate and sandstone formations, hybrid LSW/gas injection can be beneficial if it can alter the mobility of the injected fluid. Aleidan and Mamora [6] investigated different schemes of water/CO_2 injection such as SWAG and WAG at different salinities to study the effect on oil recovery in carbonate core samples. They observed higher oil recovery for both injection schemes when switching to LSW, as shown in **Figure 1**. More dissolution of gas in brine reduces the mobility of the injected fluid. An important observation in this study was that the LSW alone was not effective; hence, the observed incremental oil recovery was due to the hybrid method and the synergy between gas injection and LSW injection.

The same trend was observed by Jiang et al. [7]. They investigated the effect of water salinity on the performance of WAG during miscible flooding in sandstones using a highly viscous crude oil. Higher solubility of gas in low-salinity water controls the mobility of the water and reduces the mobility ratio of water and viscous oil. Hence, they observed better oil recovery, as shown in **Figure 2**.

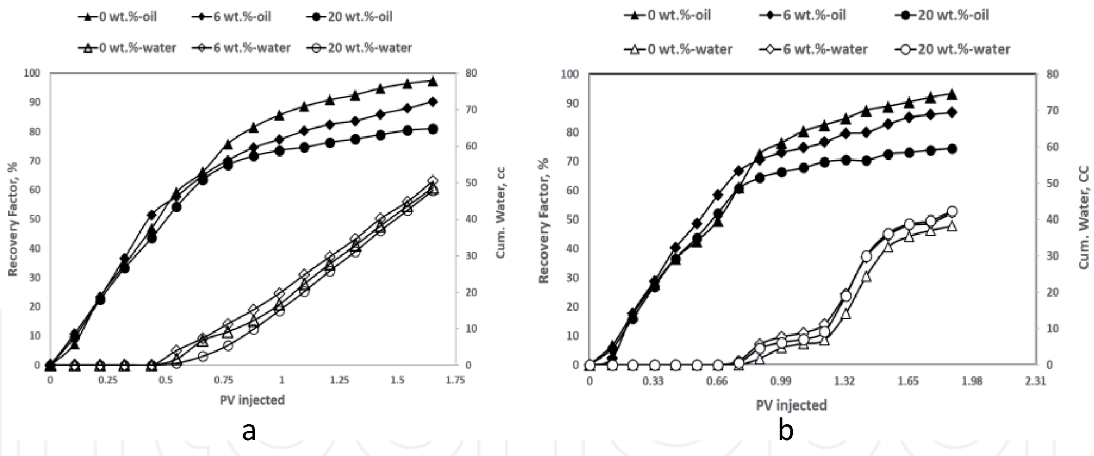

Figure 1.
Recovery factor of oil and cumulative water production at different salinity levels (0, 6, and 20%) (i.e., 0 wt.%-oil and 0 wt.%-water are oil production and water production by water injection with salinity of 0%, respectively): (a) SWAG, (b) WAG [6].

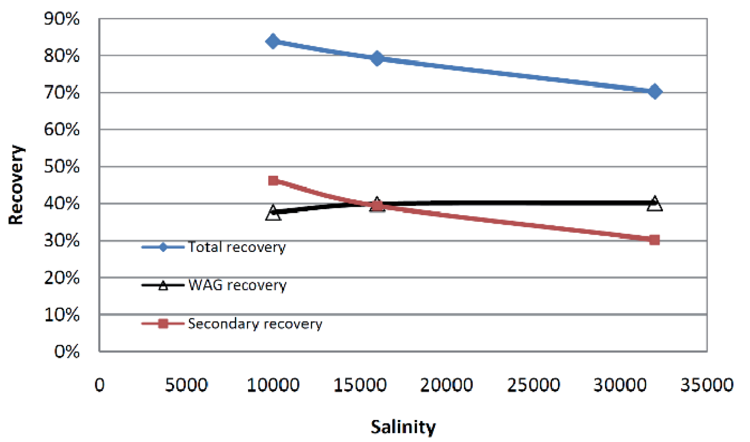

Figure 2.
The effect of brine salinity (in ppm) during hybrid LSW/gas WAG injection on oil recovery at secondary (waterflooding) and tertiary modes [7].

Kumar et al. [8] experimentally studied the effect of hybrid smart water/CO_2 flooding into sandstone samples with high clay content. 0.5 NaCl, 0.5 KCl, and 0.5 wt% $MgCl_2$ solution were used as smart brines for the hybrid method. They observed that smart water alternating gas injection controlled the mobility ratio of the fluids injected and reduced fluid channeling and oil bypassing effects. Hence, smart water alternating immiscible gas flooding recovered more oil than the stand-alone smart water and continuous gas injection (CGI) in their experiments. It should be noted that the rock samples in their study were initially water wet; therefore, wettability alteration by smart water was not the dominant mechanism during the hybrid EOR.

If the initial mobility ratio of water and oil is favorable, application of the hybrid method does not provide any benefit, as it does not affect the flow front stability. In these cases, salting out effect becomes more dominant, which reduces the amount of free gas contacting oil during the hybrid method. Hence, switching to LSW alternating gas (LSWAG) reduces the oil recovery. In [7], the LSWAG method was used to improve the recovery of a model oil composed of *n*-decane and *n*-hexadecane in sandstones. Due to the low viscosity of the oil and the homogeneity of the small artificial cores used in their experiments, the initial sweep efficiency was high, and LSWAG did not have a noticeable effect on oil recovery as shown in **Figure 3**. Hence, LSWAG is not recommended at these conditions.

Another factor that should be considered for an effective hybrid LSW/gas method is the performance of CGI. Wherever the recovery by stand-alone gas injection is high, application of the hybrid method does not provide noticeable incremental oil. For example, Al-Shalabi et al. modeled the hybrid injection of LSW and miscible CO_2 into carbonates using UTCOMP simulator. In their studies, the recovery factor by CGI was 98.9%, and shifting to the hybrid method just changed it to 99.7% by viscous fingering control [9]. Hence, in similar conditions, where the dominant mechanism is the miscibility of the gas, application of the hybrid method is not recommended.

An important parameter that affects the success of the hybrid LSW/gas method is the initial wettability of the rock. Wettability alteration from oil wet to water wet is considered as one of the main reasons for the positive performance of LSW, especially in sandstones [10]. Hence, if the initial wettability of the rock is water wet, LSW and consequently the hybrid method do not work. In this condition, the salting out effect controls the recovery mechanism during hybrid injection. Ramanathan et al. experimentally studied seawater alternating gas (SeaWAG) and LSWAG injection to recover oil from water-wet sandstone [11]. The recovery factor in LSWAG was lower than SeaWAG as the rocks were initially strongly water wet. Conversely, in an aged oil wet core, recovery by WAG changed from 76 to more than 97% when the water utilized changed from seawater to low-salinity brine, as shown in **Figure 4**.

The importance of the initial wettability was also confirmed by Teklu et al. [1]. They did several contact angle measurements for carbonate, sandstone, and shale samples at different initial wettability conditions, as shown in **Figure 5**, in which, case A shows the initial contact angle of an oil-wet disk, while case D shows the original water-wet condition of rock before aging by the oil. B and C cases show alteration in the contact angle by sample aging in seawater and CO_2 and in low-salinity brine and CO_2, respectively. LSW/CO_2 is more effective in the presence of CO_2 because the wettability of the rock changes toward a more hydrophilic surface. As shown, this mechanism is more effective when the initial wettability is oil wet.

In [13], Al-Abri et al. experimentally studied the hybrid immiscible CO_2 and smart water injection into sandstone core samples. They investigated the synergistic effects between gas injection and different ions in the water samples. Three synthetic brines were used in their work which contained 5000 ppm NaCl, $MgCl_2$, and KCl, respectively. Considerable improvement in oil recovery was observed, as shown in **Figure 6**. The maximum solubility of CO_2 in brine was observed in the

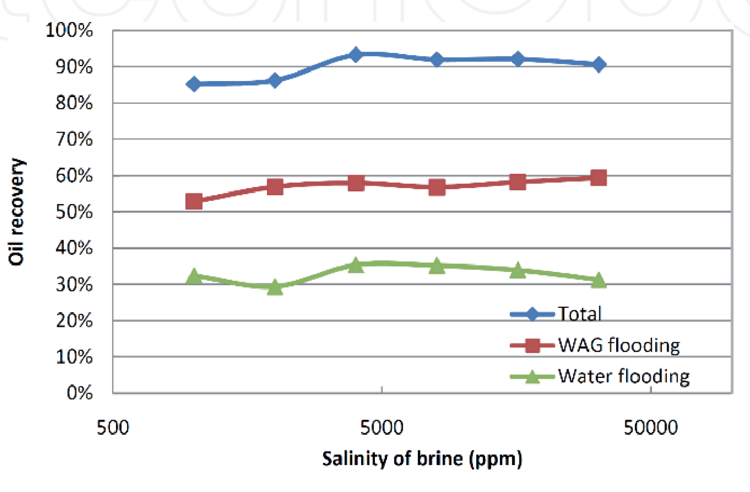

Figure 3.
The effect of salinity during hybrid LSWAG injection on recovery of low-viscosity oil (green curve is for secondary water flooding, red curve is for LSWAG, and blue curve is the total recovery) [7].

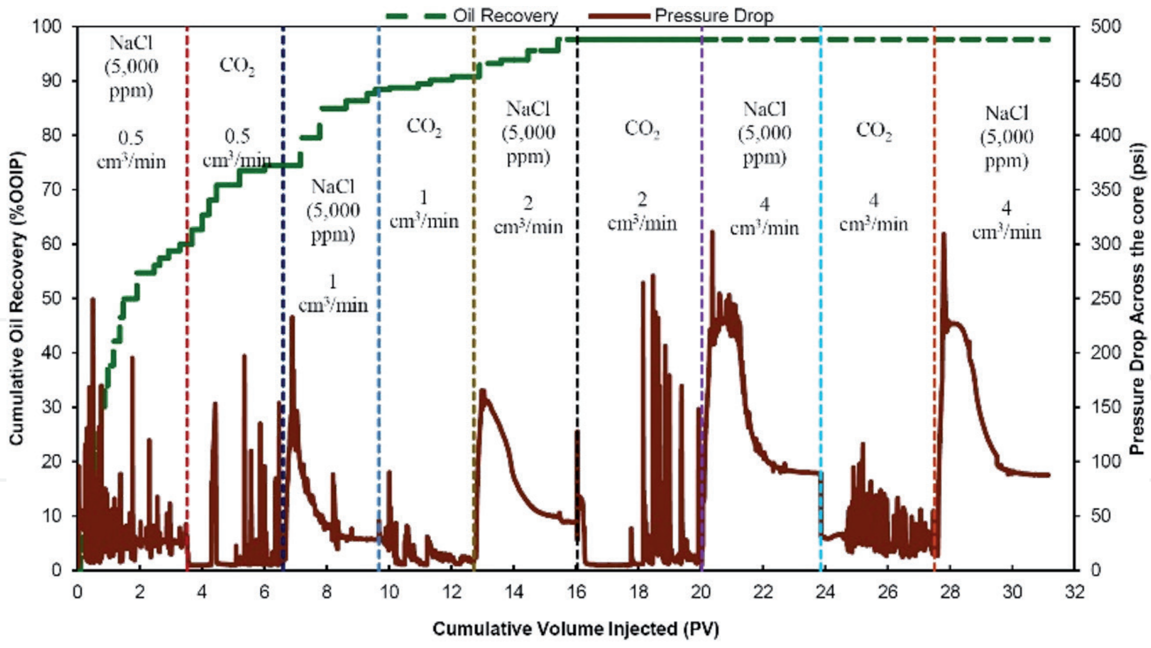

Figure 4.
Oil recovery and pressure drop across an oil-wet core during LSW alternating CO_2 [12].

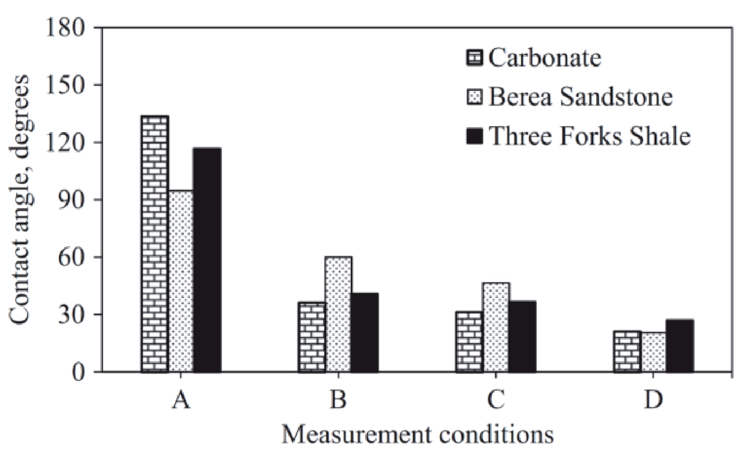

Figure 5.
Contact angle alteration by sample aging in high-salinity brine/CO_2 and low-salinity brine/CO_2 [1].

water containing $MgCl_2$, which also showed the lowest oil recovery among the three tests. In their work, smart water samples were effective, altering the wettability of the rock to more water wet without gas injection due to multicomponent ion exchange.

Hence, generally, wherever the LSW alone is effective, the hybrid method shows good performance and provides higher oil recovery than CGI and high-salinity water alternating gas. This point was also observed and confirmed by [14, 15]. AlQuraishi et al. [14] showed that low-salinity alternating miscible CO_2 method was useless for clay-free sandstones, but wherever clays were present, the recovery value was 35.1% of the OOIP for LSWAG.

A study by Yang et al. [16] showed that at a constant pressure and temperature conditions, the presence of CO_2 reduces the oil/brine IFT. Hence, this may also be considered as one of the mechanisms for incremental oil recovery by the hybrid method. References [1, 12] observed a reduction in IFT of less than 10 dynes/cm. On the other hand, in [8], higher IFT in the presence of CO_2 was reported. It should be noted that the alteration in IFT is not significant and cannot be considered as a dominant mechanism during the hybrid LSW/gas approach. In [17], Bennion

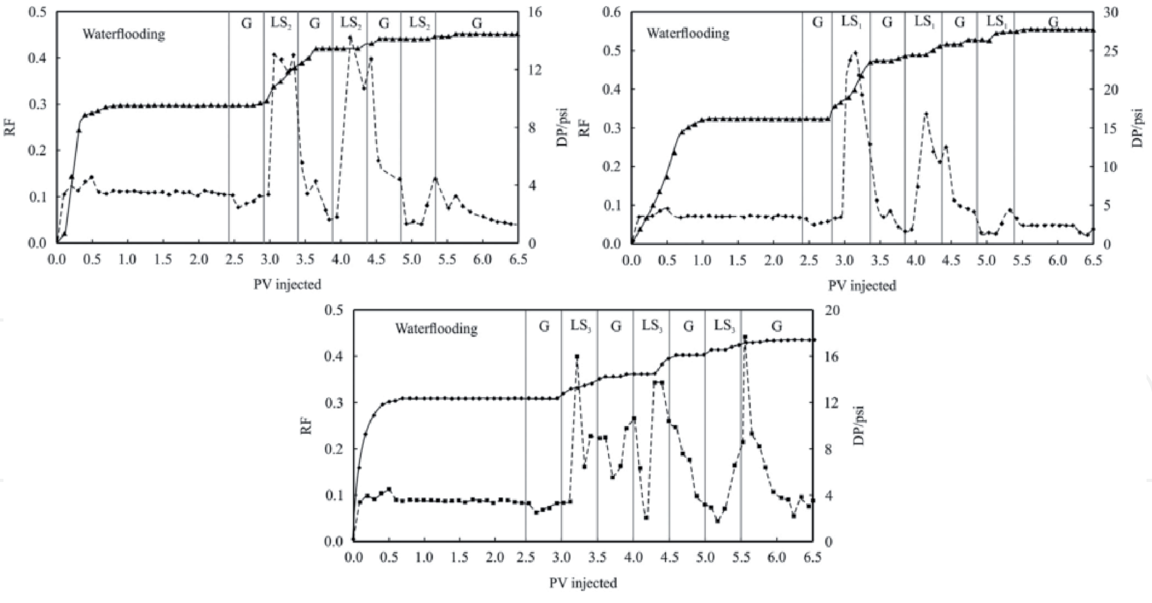

Figure 6.
Oil recovery and pressure drop for hybrid smart water alternating CO_2 flooding. (a) 5000 ppm $MgCl_2$ (top left), (b) 5000 ppm NaCl (top right), and (c) 5000 ppm KCl (bottom) [13].

et al. experimentally concluded that the increase in CO_2 solubility in low-salinity brine reduces the IFT of CO_2 and brine, which may lead to wettability alteration. Therefore, it can be considered that wettability alteration and mobility control are the dominant mechanisms for hybrid LSW/gas methods. In cases in which the initial wettability is water wet, the LSW stand-alone is not effective. In these situations, mobility control is the mechanism that shows the most important effect in improving oil recovery.

Different injection schemes have been applied to study the benefits of hybrid methods. Besides WAG and SWAG, the injection of CO_2 after LSW flooding provides extra oil recovery and can be considered as a novel approach for application in oil fields. Teklu et al. observed more than 20% incremental oil recovery by this approach [1].

Hybrid methods are also beneficial in terms of decreasing the operational costs of enhanced oil recovery processes. Previous research [9] has shown that the application of simultaneous LSW alternating gas leads to faster production of oil, as shown in **Figure 7**. This occurs due to the alteration of the reservoir rock wettability that increases the oil relative permeability. Also, the application of hybrid gas/LSW methods reduces the gas utilization factor. Kulkarni et al. observed a lower gas utilization factor during LSW alternating miscible CO_2 flooding [18]. However, this issue should be considered carefully during immiscible flooding, because the higher solubility of CO_2 in LSW requires more gas to make contact with the oil, which increases the gas utilization factor. Thus, more experimental and modeling studies are required in this area.

Most of the previous research in this area has focused on the performance of hybrid methods in sandstones. Analysis of the special interaction of LSW and gas with carbonate rock needs more investigation. For example, rock dissolution is considered as an effective mechanism during LSW injection in carbonates. Hence, geochemical analysis is essential to study the hybrid LSW/gas injection in rocks with high calcite and dolomite content. An earlier work [19] has performed simulations to compare the geochemical analysis results of LSW, CGI, and hybrid methods for different types of carbonates. Results indicated that hybrid methods can accelerate the dissolution process especially for high dolomite concentrations. Consequently, comprehensive experimental studies are required to investigate the

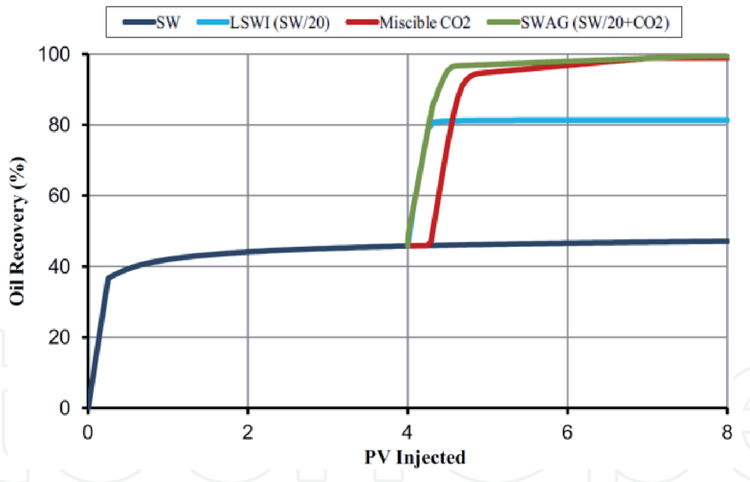

Figure 7.
Faster production of oil by LSW alternating gas injection than CGI [9].

geochemical parameters during hybrid LSW/gas injection methods to explain the oil recovery mechanisms of these processes.

Up to now, most of the work conducted in this area has been experimental research. There are few simulation studies in this field. Dang et al. [20] simulated a hybrid LSW alternating miscible CO_2 flooding injection in a 1D heterogeneous core and then upscaled the model to simulate the process at field scale. Their study showed that the hybrid approach overcomes the WAG late production problem. We recommend a comprehensive field-scale simulation study based on experimental work to analyze the practical benefit of hybrid approaches.

3. LSW/polymer hybrid EOR technique

Polymer flooding, as a well-known and effective EOR method, can also be considered as a complementary method to enhance the capability of LSW flooding as a hybrid approach. Polymer flooding affects the macroscopic sweep efficiency in porous media by improving the displacement mobility ratio. On the other hand, LSW flooding affects the microscopic sweep efficiency by changing CBR interactions and wettability. Hence, the hybrid low-salinity/polymer flooding provides the benefits of both methods and can be considered as a novel EOR approach.

Different injection schemes were experimentally studied and modeled in the literature. LSW can be injected as a preflush before polymer flooding, or polymer can be injected prior to LSW. The first approach is more effective than the second one because the injection of LSW changes the wettability to more water wet, which alters the distribution of the remaining oil saturation in the porous medium. Oil droplets are detached from small pores and accumulated in bigger and middle-sized pores. Hence, the injection of polymer recovers the redistributed oil more easily. Torrijos et al. [21] experimentally investigated the synergy between LSW flooding and polymer flooding in sandstones. Both injection modes were studied by injecting a low-salinity polymer (LSP), which was prepared by dissolving 1000 ppm hydrolyzed polyacrylamide (HPAM) in 1000 ppm NaCl brine as LSW. **Figure 8** shows that the hybrid LSW/LSP provides around 20% higher total oil recovery than the LSP/LSW method.

A similar trend was observed by Alsofi et al. [22] who studied the synergy between LSW/polymer flooding in a carbonate formation. In this work, heavy crude oil, high-salinity (69,000 mg/L) brine, and low-salinity brine (6900 mg/L)

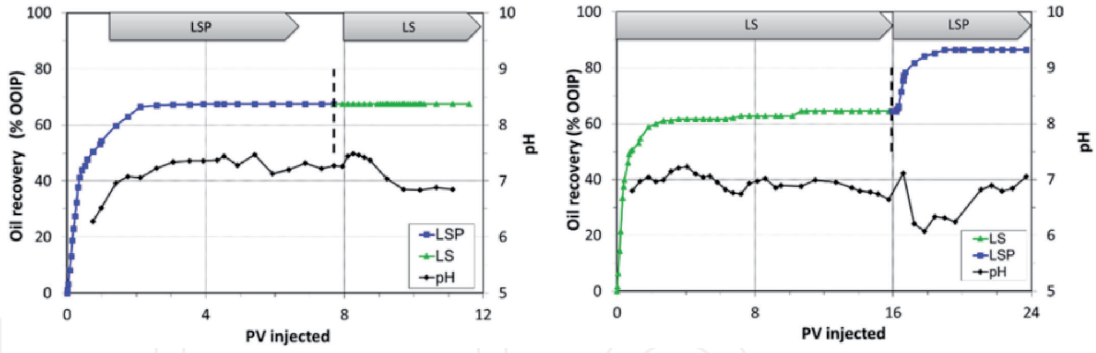

Figure 8.
Oil recovery by two combinations of polymer flooding and LSW flooding [21].

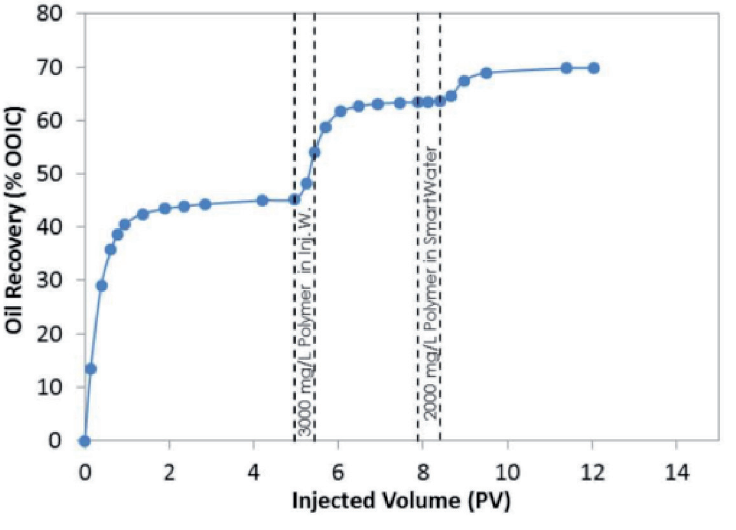

Figure 9.
Recovery profile for tertiary hybrid flooding method [22].

were used. After secondary waterflooding, polymer flooding followed by polymer-LSW flooding provided more than 24% OOIP additional recovery, as shown in **Figure 9**. The same findings were reported by [23–25].

Hence, the sequence of injection affects total oil recovery. Almansour et al. experimentally investigated the hybrid LSW/polymer flooding method in Berea and Bentheimer sandstone samples. Persian Gulf brine and a 10 times diluted sample were used as the high-salinity and low-salinity brines, respectively. The hybrid method recovered more than 12% extra oil by switching from LSW to polymer in the Berea sandstone and more than 29% for the Bentheimer sample. Continuing LSW as the tertiary method and then converting to polymer flooding were also recommended based on their results [26]. Likewise, Tahir et al. showed that injection of polymer after LSW or smart water provides higher oil recovery than the oil recovery obtained by polymer injection before LSW. It is speculated that in this flooding sequence (i.e., polymer flooding before LSW), the LSW may follow the same paths as the polymer fluid, which inhibits the direct contact of LSW with the oil/rock interface. In contrast, the preinjection of LSW can alter the wettability of the rock by direct contact making oil detachment from rock surfaces easier, which aids the displacement of oil in the subsequent polymer flooding stage [27].

In addition to experimental studies, modeling approaches have also confirmed the benefits of hybrid LSW/polymer flooding. Khorsandi et al. [28] developed the first analytical solution for combined LSW/polymer flooding in sandstone to describe the synergy of this hybrid process, which allows recognizing the effective parameters and the mechanisms controlling oil recovery. This hybrid method was also simulated by Mohammadi and Jerauld [29], who showed higher oil recovery as displayed in **Figure 10** that shows that injection of polymer after LSW gives better performance than polymer injection and stand-alone LSW flooding. Furthermore, this study showed that wettability alteration by LSW and the simultaneous increase in brine viscosity, reduction of the relative brine permeability, and mobility control during polymer flooding improved the fractional flow of the process, as shown in **Figure 11**. The adjustment in fractional flow was also modeled by [30], which confirms the stable shock fronts during LSW/polymer flooding. As polymer cannot invade the inaccessible pore volume, the water remaining after LSW will be immobile in these pores, which reduces the channeling in the formation [31]. Hence, the hybrid method can control the unstable front and the channeling of low-viscosity LSW into the viscous oil. This makes the LSW/polymer hybrid method even more effective in heavy oil formations.

Other injection schemes have also been discussed and studied as reported in the literature. For example, Lee et al. modeled the process of polymer-assisted carbonated LSW flooding (PCLSWF) as a new hybrid method [32]. Different mechanisms are involved during PCLSWF, such as wettability modification by LSW, oil swelling, oil viscosity reduction by the gas, and mobility enhancement by the polymer. Also, higher pressure in the porous media in the presence of polymer leads to more dissolution of CO_2 in the brine and more transport of gas to the oil phase. Hence,

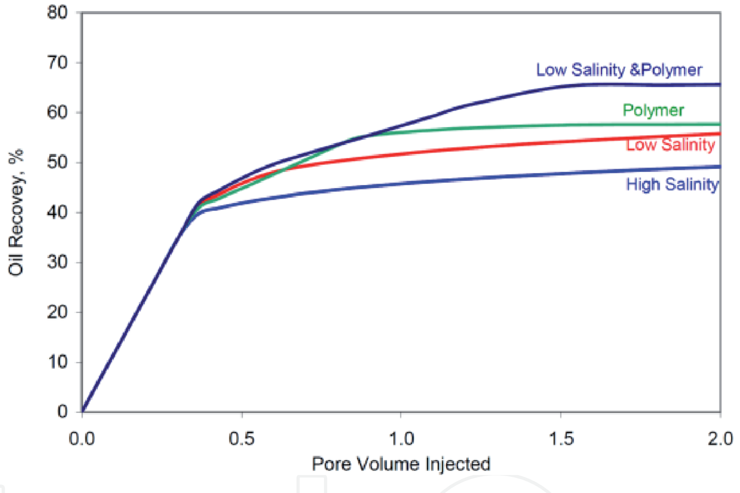

Figure 10.
Oil recovery modeling by hybrid method injection and comparison to other EOR approaches [29].

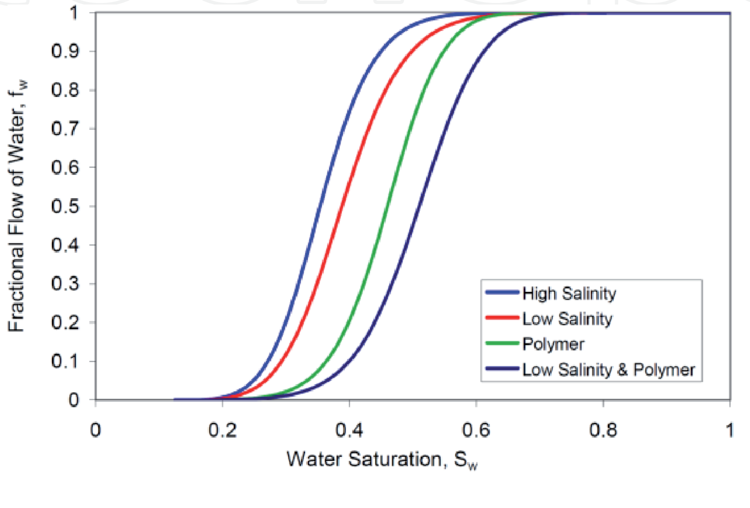

Figure 11.
Comparison of fractional flow of high-salinity, low-salinity, polymer, and hybrid flooding by modeling [29].

PCLSWF showed better performance than LSW flooding, hybrid low-salinity polymer flooding (LSPF), and hybrid carbonated LSW flooding (CLSWF), as shown in **Figure 12** [32]. Another study was conducted by Eikrem to analyze oil recovery by combining low-salinity injection and surfactant/polymer (SP) flooding. Cores with different initial wettability were flooded initially by the high-salinity water (HSW) and then with a surfactant solution in tertiary mode, followed by a polymer injection for mobility control. They found that injecting a 600 ppm HPAM polymer solution after the surfactant injection improved the ultimate recovery of oil [33]. Mjøs observed a similar behavior [34].

Interactions between polymer and LSW affect different governing parameters in the EOR process. Lower salinity has an influence on the polymer injectivity, retention, polymer stability, and rheological factors such as viscosity. Alsofi et al. studied the effect of LSW on the polymer solution properties by single-phase core flooding tests in carbonate samples. Anionic sulfonated polyacrylamide polymer was used as the polymer, and two samples of water with salinity of 244,000 and 24,400 mg/L were used as high- and low-salinity brines, respectively. They found that at lower-salinity concentration, coiling of the polymer backbone is reduced due to lower existing ions in LSW. Therefore, there are more repulsive interactions among the polymer chains causing the expansion of the polymer backbone, which results in higher viscosity of the polymer solution that leads to pressure buildup and slightly lower polymer injectivity [35].

The better solubility of polymer in LSW leads to the alteration of the polymer retention, which is critical for the technical and economical design of the process. In [35], it was indicated that the polymer retention decreased by 10–28%, which was noticeable. Expansion of the polymer chains due to repulsion results in the fitting of fewer polymer molecules on the adsorption rock surface sites, which reduces the retention. In [26], Almansour et al. also confirmed a reduction in the retention of polymer by using LSW. A decrease in polymer adsorption was also reported by [36]. Modeling has also showed that lower concentrations of polymer are required to establish a stable displacement front in the LSW/polymer approach than the HSW/polymer [29].

This synergistic effect also reduces the consumption of polymer, which is a positive point. At lower salinity, a lower polymer concentration is required to achieve the target viscosity, which makes the polymer flooding process more cost-competitive. In addition to the reduction of transportation costs, storage, and polymer handling, this behavior was also confirmed by [22]. Brine salinity also affects the stability of the polymer solution in some special conditions. Levitt et al. [37] showed that at lower ion composition, especially at low calcium concentration, HPAM is more stable at higher temperatures.

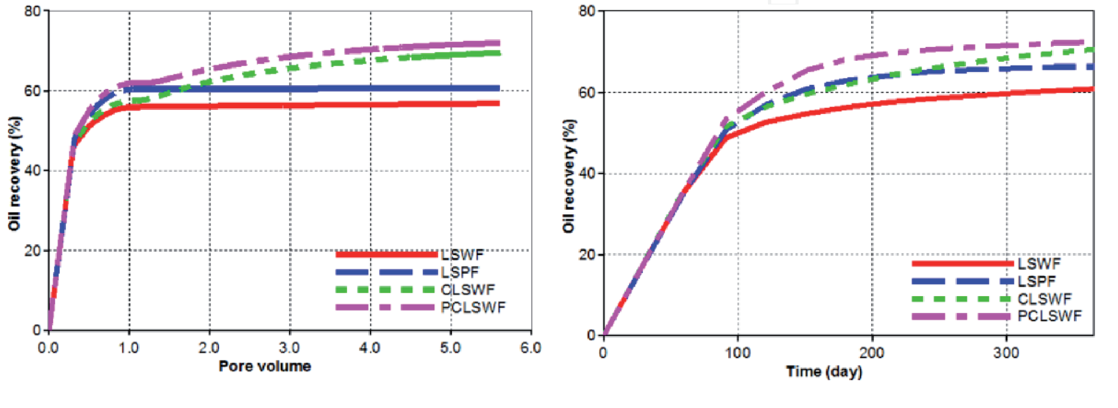

Figure 12.
Oil recovery of PCLSWF compared to other EOR methods in core scale (left) and pilot scale (right). LSWF is LSW flooding, LSPF is low-salinity polymer flooding, and CLSWF shows the carbonated LSW flooding [32].

Different operational parameters affect the performance of the LSW/polymer hybrid method, which should be considered at the design stage of the flooding process. The main parameters that should be studied are the initial wettability of the rock, smart water design (salinity concentration and composition), and the hybrid method initiation time. Shiran et al. studied the synergy of LSW/polymer flooding by core flooding experiments in sandstone samples [31]. The LSW was obtained by diluting 10 times seawater. Flopaam 3630S polyacrylamide with a hydrolysis degree of 25–30% was added to the LSW in concentrations of 300 and 1000 ppm to prepare the polymer solution. Aluminum citrate was added to the polymer solution to cross-link the polymer chains. This study revealed that the initial wettability of the porous medium was a critical factor affecting the success of the hybrid method, because incremental oil recovery was not observed during the polymer flooding step in the hybrid LSW/polymer injection scheme in core plug samples that were strongly water wet. However, the injection of polymer after LSW was effective for intermediate water-wet core samples, as shown in **Figure 13**. In water-wet formations, there are more adsorption sites available on the rock surfaces; thus, polymer retention is higher, which affects the performance of the method. Moreover, it was observed by [34] that the performance of the hybrid method was better in less water-wet conditions.

Another important parameter in the design of the hybrid method is the appropriate time to switch from conventional waterflooding to the hybrid method. A numerical simulation study of the hybrid LSW/polymer flooding conducted in 1D, 2D, and 3D reservoirs indicated that the hybrid method should be started at water cuts less than or equal to 75% to achieve improvement in oil recovery [30]. Hence, a comprehensive economic study is required to design the optimum case for field applications.

Ion management is a critical parameter to design smart waters and improve the performance of the diluted LSW/polymer flooding. Alteration in ion concentrations and ion types can affect the properties of the polymer solution, which must be considered during the design of hybrid polymer and smart water flooding. Experiments in [27] aimed to study the effect of active ions such as sulfate on the performance of the hybrid methods. The presence of sulfate affects the polymer solution viscosity, as shown in **Figure 14**.

The application of the LSW/polymer flooding offers economical and technical benefits for EOR applications. For example, the water cut is reduced compared to the stand-alone polymer or LSW flooding, as confirmed by simulations conducted

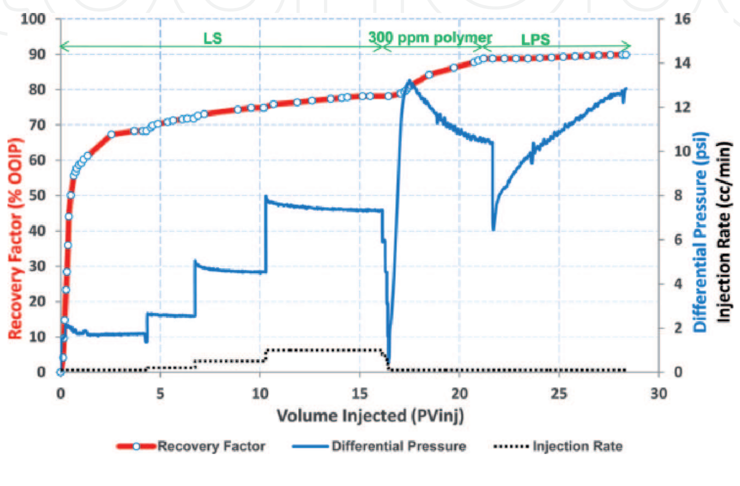

Figure 13.
Oil recovery during secondary mode LSW flooding followed by polymer flooding and linked polymer solution (LPS) flooding [31].

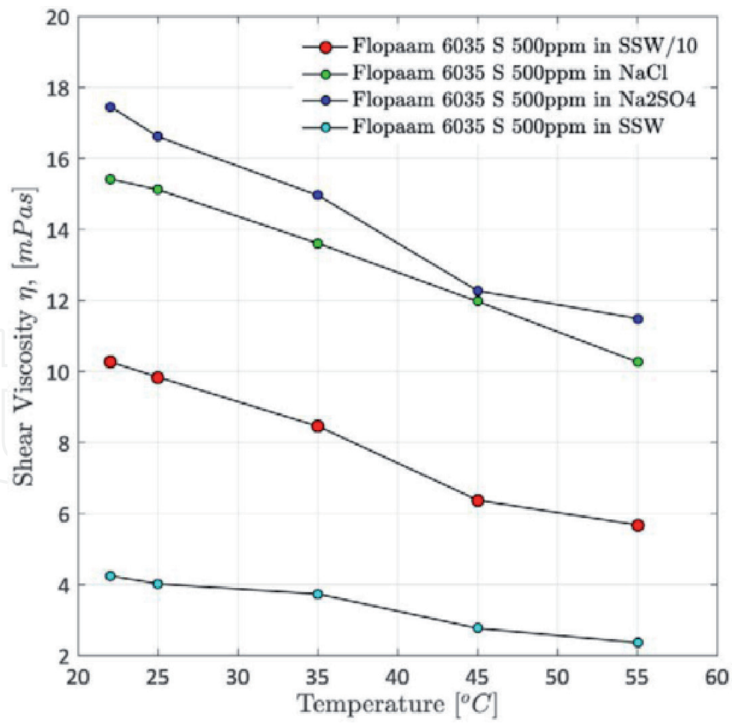

Figure 14.
Polymer steady-state viscosity at different temperatures for different types of solution brines (SSW stands for synthetic seawater) [27].

by Santo and Muggeridge [30]. Also, the oil recovery by LSW/polymer flooding was established to be slightly better than the conventional surfactant/polymer chemical flooding [22]. This is an important observation because the hybrid method could provide higher oil recovery at a lower cost. The studies reviewed in this section confirm the synergistic effect of combining LSW/polymer flooding.

4. LSW/surfactant hybrid EOR technique

The main mechanism responsible for the effectiveness of LSW in improving oil recovery is the alteration of the wettability of the rock toward more water wet that causes the detachment of oil films from the rock surface. The injection of surfactant reduces the interfacial tension (IFT) between crude oil and brine and alters the wettability of the rock reducing the capillary forces that have trapped oil in the porous media. Therefore, the combination of LSW and low-salinity surfactant (LSS) in LSW flooding could be an efficient approach by combining the effect of oil layer destabilization by LSW and reduction of the IFT by the surfactant. This hybrid method provides higher incremental oil recovery than either stand-alone techniques.

LSW makes the environment more favorable for an effective surfactant flooding, while LSS solubilizes some of the residual oil via Winsor type II microemulsion. Several studies have reported high tertiary oil recovery values by surfactant injection after LSW flooding in both carbonate and sandstone formations. For example, according to [38], 5–7% incremental oil recovery was observed by injection of sodium dodecyl benzene sulfonate surfactant (SDBS) after LSW into sandstones. Similarly, Alameri et al. observed up to 10% incremental oil recovery by LSS after LSW injection into carbonate core samples [39].

Application of the LSW/LSS hybrid method results in lower surfactant consumption, lower operational costs, and fewer operational problems. For instance, it is less challenging to achieve a low IFT during surfactant flooding at low-salinity conditions. Likewise, in these conditions, there is reduced surfactant retention and increased surfactant stability and solubility.

In this hybrid process, the dominant mechanisms for increased oil recovery are wettability alteration by LSW and IFT reduction between the crude oil and brine by LSS. Alagic et al. studied this hybrid method through core flooding tests and analyzed the performance of LSS injection after LSW into sandstone samples. Olefin sulfonate was used as the surfactant in these tests. The results show more than 90% oil recovery of the OOIP when surfactant is injected after LSW. This injection sequence produces higher oil recovery than the injection of surfactant after high-salinity water (74% OOIP), as shown in **Figure 15** [40]. Injection of LSW makes the system more water wet, which aids the detachment of oil droplets and reduces the capillary force, making easier the displacement of oil during the surfactant flooding process. Surfactant injection in a low-salinity environment is more effective, as the presence of the divalent ions contained in high-salinity water attenuates IFT reduction due to the formation of water-in-oil microemulsions.

The achievement of ultralow IFT during LSS is critical; however, several studies have demonstrated that wettability alteration by the hybrid LSW/LSS approach can be very effective. Therefore, in this process, wettability alteration is considered the dominant mechanism for oil recovery. Johannessen et al. [41] used branched C12–13 alcohol-xPO-sulfates as the surfactant, olefin sulfonate as the co-surfactant, and secondary butanol (SBA) as the cosolvent to evaluate the performance of LSW/LSS flooding from Berea sandstone cores in terms of oil recovery. Two flooding conditions were studied: in the first case, the core was flooded using low-salinity brine corresponding to 0.07 times the seawater salinity (diluted case), and the other one was flooded at the optimum salinity of surfactant flooding obtained from phase behavior screening and IFT measurements (optimum salinity case). The same oil recovery was observed for both cases, as shown in **Figure 16**. Incremental oil recovery beyond expectations by the capillary number changes is explained by the synergistic effect of the low-salinity surfactant flooding, even at IFT values above ultralow IFT values.

The same behavior was observed by Khanamiri et al. during LSW/LSS flooding of sandstone samples [42]. The incremental oil recovery by LSS after LSW was in the range of 2–6% OOIP. They observed that the oil mobilization in the process was mostly due to wettability alteration by LSW and LSS and IFT reduction cannot be considered as the dominant mechanism. As the salinity of the solution was not at the optimum salinity condition, ultralow IFT was not achieved; however, the significant wettability alteration caused by LSS flooding verified from contact angle measurements (quartz crystal microbalance (QCM) on silica-coated crystals) compensated the effect of having a value of IFT higher than the desired ultralow IFT

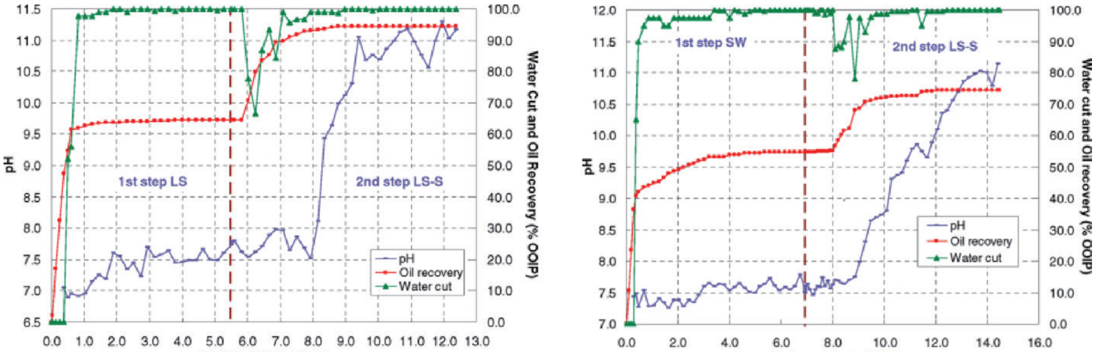

Figure 15.
Oil recovery, water cut, and effluent pH during LSW/LSS injection (left) and synthetic seawater (SSW)/LSS flooding (right) [40].

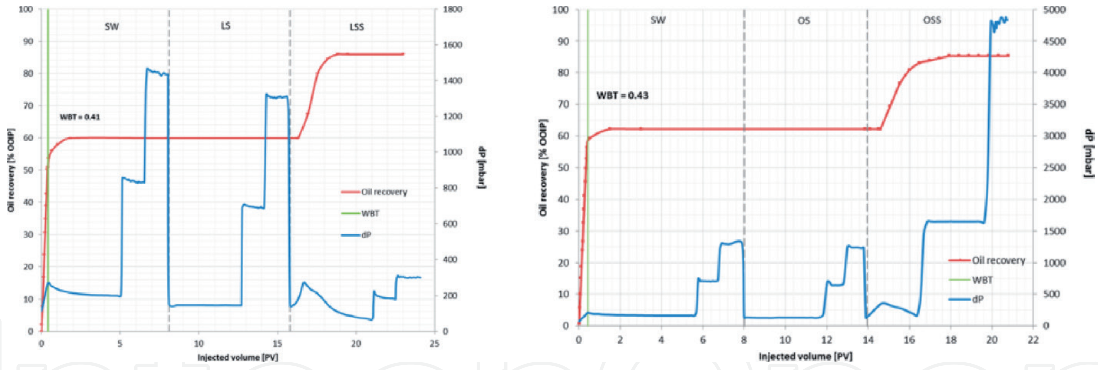

Figure 16.
Oil recovery and dP profiles for injection of seawater followed by LSW and low-salinity surfactant at diluted case (left) and optimum salinity (right) [41].

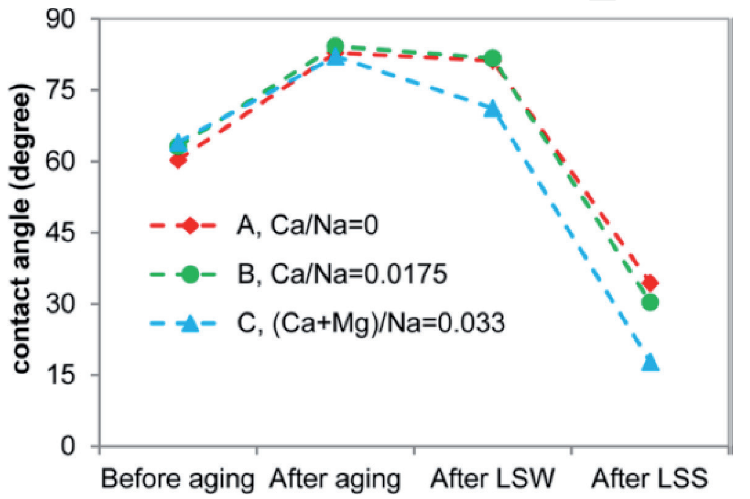

Figure 17.
Contact angle for deionized water droplet/air/silica after different treatments [42].

value. **Figure 17** shows the alteration in contact angle for different treated brines. This figure indicates the initial contact angle and the angles after aging in high-salinity water, in LSW, and in LSS. As can be seen, wettability alteration toward water-wet condition occurred for all cases with different types of LSW. However, different ion contents affected the magnitude of wettability alteration.

The effect of surfactant on wettability alteration was also observed by Teklu et al. [43]. They measured the contact angle of different carbonate and sandstone rock disks saturated with oil in low-salinity brine in the presence and absence of nonionic ethoxylated alcohol surfactant. They found that the presence of surfactant decreases the contact angle and makes the system more water wet. Reduction in IFT and alteration of rock wettability by LSS can increase oil recovery in cases when LSW is not effective alone. For example, core flooding experiments conducted by Spildo et al. showed that the application of surfactant-free LSW does not increase oil recovery, while LSS produces incremental oil recovery, as shown in **Figure 18** [44].

These synergistic mechanisms (i.e., wettability alteration and reduction of IFT) in the hybrid LSW/LSS method provide higher oil recovery than the recovery expected from the capillary desaturation curves (CDC). Studies in [44, 45] showed that during the LSS after LSW, the capillary number was about 10^{-4}, which is not high enough to achieve noticeable incremental oil recovery, as observed in the experiments [46]. Hence, oil detachment and redistribution due to rock wettability alteration during LSW make the LSS performance better than the estimation from the CDC.

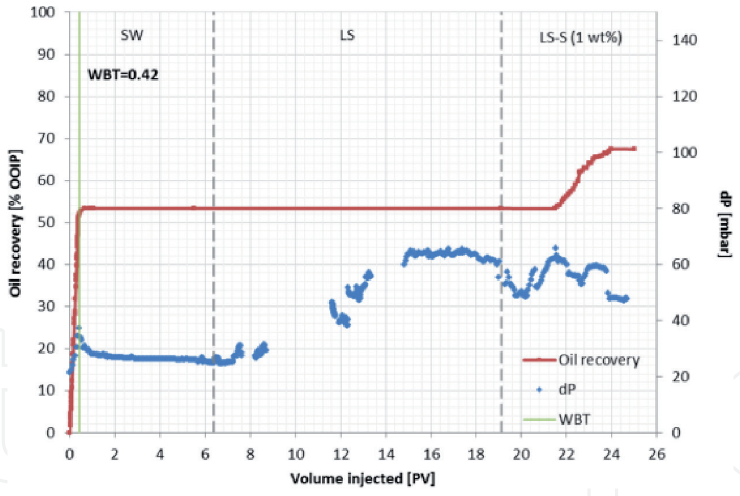

Figure 18.
Oil recovery and pressure drop profile as a function of pore volume injected into sandstone core during SW/LSW/LSS injection [44].

Shaddel et al. evaluated the incremental oil recovery obtained from LSW, LSW/surfactant, and LSW/alkali injection in Berea and Bentheimer sandstones in tertiary mode. Sodium hydroxide and sodium dodecyl sulfate dissolved in 0.01 LSW were used as alkali and surfactant solutions, respectively. The authors considered that the LSW/alkali is a convenient process as a hybrid method due to the lower operation costs [47].

Brine composition is an important variable during the design of surfactant flooding. The retention (i.e., adsorption) of surfactant molecules onto porous media is considered a critical issue; thus, the reduction of surfactant adsorption onto the porous media enhances the quality of a surfactant flooding project from the technical and economical points of view. Glover et al. reported that low-salinity brine surfactant adsorption is reduced [48]. Lower surfactant retention at lower salinities was also observed in [43, 45]. Additionally, Johannessen et al. [41] observed that the surfactant retention values were lower at very-low-salinity brines than at the optimum salinity condition, as measured by retention tests, which are shown in **Figure 19**. The greater area under the production curve for the LSS condition corresponds to lower surfactant retention. This implies that the hybrid LSW/LSS method is more economically efficient than the injection of surfactant at the ultralow IFT formulation. Tests performed by Araz and Kamyabi showed that precipitation of SDBS surfactant in LSW occurs when salinity concentration is above 1000 ppm [49].

The type and concentration of divalent cations also influence the performance of surfactant flooding. For example, Enge [38] showed that the content of divalent ions in brines affects the precipitation of surfactant. Calcium cations affect the behavior of surfactant adsorption and surfactant precipitation due to interactions with calcium (negative effect) and the stabilization of micelles (positive effect). Hence, there is a limit for divalent cation concentration which must be considered during the LSS design stage. Other properties of surfactant solutions are affected in a low-salinity environment, such as solubility and retention. For instance, Alagic et al. observed that the surfactant solubility is improved in low-salinity brine, especially in the absence of divalent cations [45].

The initial wettability of the porous media is a key parameter in the success of most hybrid LSW EOR methods. Alagic et al. [45] studied the effect of crude oil aging on LSW/LSS flooding in sandstones. They used a sulfonate surfactant added to the low-salinity brine in the LSS injection period. The performance of the LSS

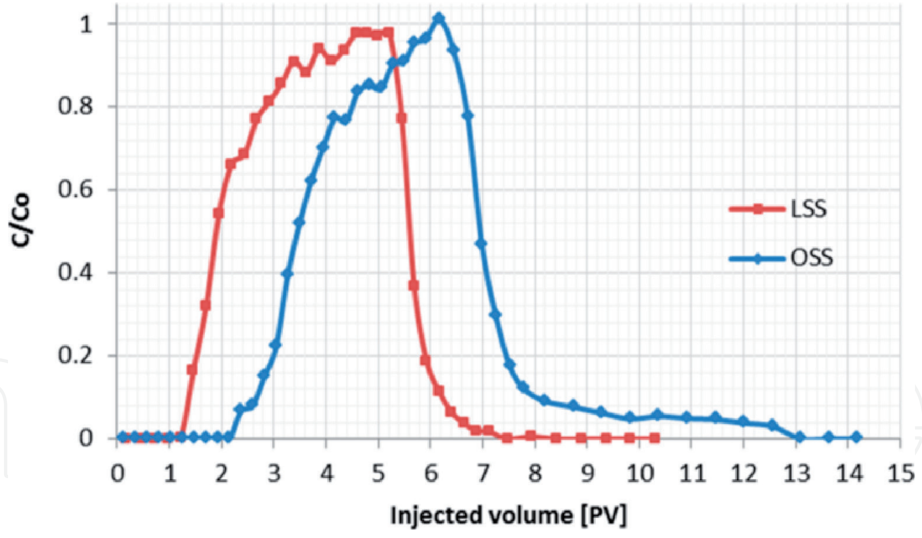

Figure 19.
Normalized produced surfactant concentration for surfactant in very LSW (LSS) and in water with the optimum salinity (OSS) [41].

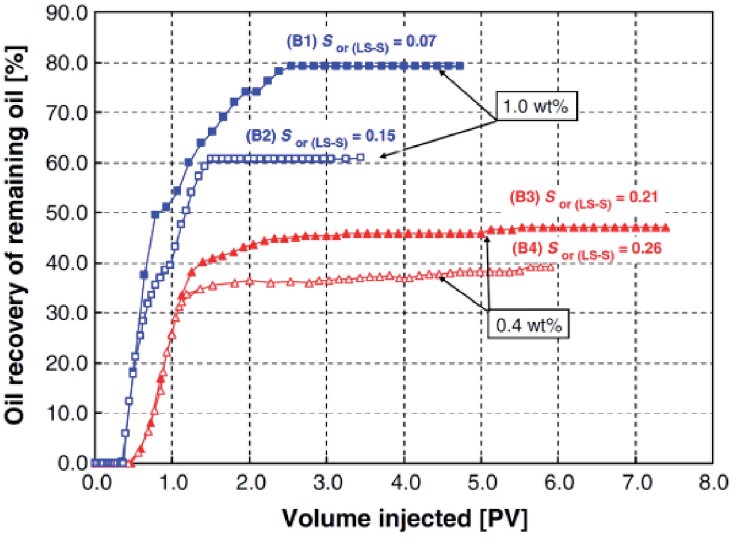

Figure 20.
Oil recovery of remaining oil (after LSW flooding) in aged (B1, B3) and unaged (B2, B4) sandstone samples for two surfactant concentrations (1 and 0.4 wt%) [45].

was observed to be better in cores aged by oil. In addition, LSS recovered more oil at a higher concentration of surfactant. **Figure 20** shows the performance of oil recovery in the LSS stage for aged and unaged samples. The same trend was also observed in [33, 34]. Another variable affecting the performance of hybrid methods is the composition of the LSW. Araz and Kamyabi examined the effect of the LSW composition on the performance of core flooding by LSW/LSS in sandstones. They found that alteration in the composition of different ions in LSW and LSS affected oil recovery [49]. Therefore, it is essential to study the effect of ion composition in the LSW/LSS process in terms of oil recovery.

The stability of the displacement front in the LSW/LSS process is a critical issue to achieve a successful recovery. Tavassoli et al. [50] showed that unstable fronts of surfactant floods due to the high velocity result in slow oil recovery. This problem can be solved through the combination of LSW with surfactant/polymer (SP). In this process, three different oil recovery mechanisms are active such as wettability alteration, reduction in IFT, and mobility control. In [51], Wang et al. studied the hybrid low-salinity surfactant/polymer flooding as an EOR method in carbonates.

They observed more recovery by LSW/SP in LSW than HSW/SP. This study confirmed the destabilization of oil layers after LSW injection prior to SP flooding by pressure drop analysis. The pressure drop was more significant due to the formation of an oil bank after LSW injection.

Most of the research conducted in the area of hybrid LSW/LSS or LSW/SP processes has been based on experimental studies. There are few simulation studies published on the effectiveness of the hybrid LSW/LSS method. The lack of modeling and optimization of the process through simulation studies is obvious in this field. In [50], Tavassoli et al. applied UTCHEM-IPhreeqc to model LSW as a function of geochemical reactions and surfactant flooding. Their simulations were in good agreement with experiments carried out by [27]. This study demonstrated the importance of the surfactant selection, injection sequences, and operational parameters such as brine salinity and surfactant solution injection rate to achieve incremental oil recovery. Therefore, more modeling studies are justified.

5. LSW/nanofluid hybrid EOR technique

Nanoparticles are used in EOR processes due to their size and high surface area; thus, nanoparticles flow without difficulty through the pore/throat network in porous media. Nanoparticles enhance oil recovery by the following mechanisms: IFT reduction, wettability alteration, improvement of mobility ratio, and in situ emulsification [52, 53]. For example, SiO_2 particles are hydrophilic and can be injected into the porous media to alter the rock wettability toward more water wet [54, 55].

Despite the positive effects of LSW on oil recovery, LSW flooding changes the chemical environment (pH, ionic strength, and temperature) in the porous media, which may lead to the detachment of reservoir particles. As the salinity of the injected brine becomes less than the critical salinity concentration, fine migration initiates, which leads to formation damage [56, 57]. Fine migration can enhance oil recovery by mobility control through the blockage of high-permeability layers, but fine migration can also cause severe damage to the near-wellbore zone. Therefore, it is desirable to control fine migration and to take advantage of its positive effects far from the wellbore to minimize its damaging effects near the wellbore. Some researchers have stated that combining LSW and NPs may help to overcome the detrimental effects of formation damage associated with low-salinity flooding [58, 59]. Hence, nanoparticles in nanofluid form can be used as a hybrid approach with LSW flooding to improve the performance of this method.

Nanoparticles enhance the attractive forces between fine particles and grain surfaces, particularly by changing the surface zeta potentials of fine particles [60]. Nanofluid pretreatment prior to the injection of LSW can reduce the side effects of fine migration by decreasing the injection pressure drop [53]. Abhishek et al. [52] studied nanoparticle adsorption at different salinities and observed that during hybrid LSW and nanofluid injection, the adsorption of nanoparticles prevents fine migration.

Another approach is to apply the hybrid nanofluid/LSW method to alter wettability and interfacial tension. Hydrophilic nanoparticles adsorb on the rock surface, and water molecules accumulate around them. This changes the wettability of the rock to be more water wet and improves oil recovery. Sadatshojaei et al. [60] coupled silica nanoparticles with LSW prepared by dilution of Persian Gulf brine. In this study, IFT, wettability, and zeta potential were measured to analyze the carbonate rock-low-salinity fluid interaction in the presence of nanofluid. It was observed that the influence of the nanofluid on the wettability of the porous media was dominant relative to the IFT reduction; thus, wettability alteration can be considered as the main mechanism for oil recovery. Moreover, Ding et al. [61] introduced nanoparticle-assisted low-salinity hot water (LSHW) injection for heavy oil recovery. Flooding tests were conducted on silica sand packs saturated with heavy oil to compare the effect of LSW flooding, 0.05 wt% SiO_2 nanoparticle-dispersed LSW flooding, and 0.05 wt% Al_2O_3 nanoparticle-dispersed LSW flooding on oil recovery. They observed higher oil recovery by the injection of NP/LSW than LSW alone. Also, they found that Al_2O_3 NPs were more effective in recovering oil due to the greater reduction in IFT.

Generally, the average nanoparticle size, specific surface area, and stability of nanofluids are important in the performance of this hybrid method. The issue of nanofluid stability at low-salinity conditions is challenging and should be considered in the application of this hybrid method. The range of stability constraints (such as zeta potential) of colloidal systems of nanofluids coupled with ions (i.e., LSW) is typically wider so that in the presence of both elements (nanoparticles and ions), longer-lasting stable solutions can be attained [60].

6. LSW/hot water hybrid EOR technique

Heavy oil is conventionally recovered by thermal-based approaches. Thermal energy in combination with LSW water flooding, in the form of hot LSW water flooding, can be applied to simultaneously decrease the viscosity of the heavy oil and alter the wettability of the porous media to attain higher oil recovery. Alotaibi et al. and Tang et al. reported lower contact angle and higher oil recovery, respectively, after increasing the displacement temperature in LSW injection [62, 63]. Contrary to this observation, Soraya et al. [64] found lower oil recovery at higher temperatures by tertiary LSW. However, another study [65] demonstrated that the injection of hot LSW yielded significant incremental oil recovery. In this work, hot LSW at a concentration of 200 ppm salinity was injected after hot HSW at a concentration of 15,000 ppm salinity, which yielded about 25% OOIP incremental oil recovery, as shown in **Figure 21**. In addition, in this study the injection of steam is proposed after hot LSW flooding to further enhance the oil recovery.

A similar trend was reported by Ding et al. by injecting nanoparticle-assisted low-salinity hot water (LSHW) into silica sand packs to recover heavy oil. Temperatures of 17, 45, and 70°C were applied under different scenarios of high- and low-salinity brines and nanofluids. LSW was found to provide better

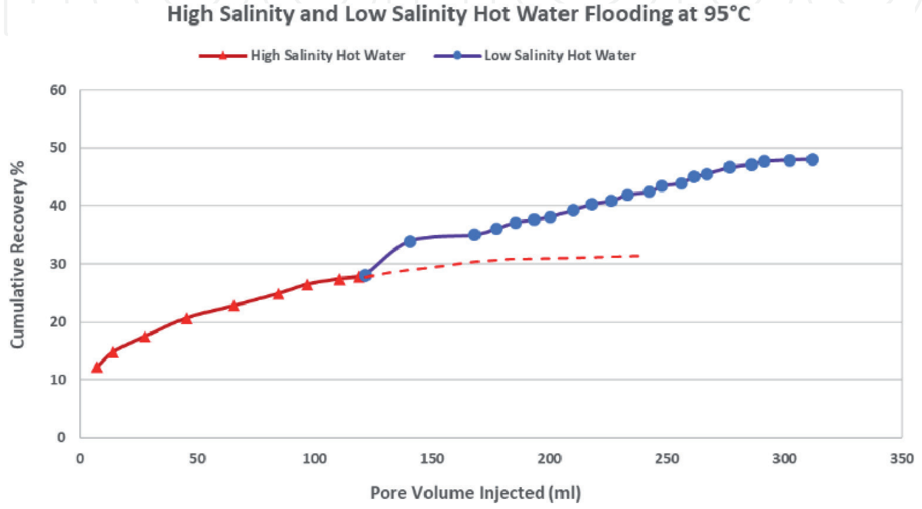

Figure 21.
Oil recovery by hot HSW and hot LSW [65].

performance than the HSW under ambient temperature. Moreover, in all cases in the presence or absence of nanoparticles, increasing the displacement temperature yielded higher ultimate oil recoveries up to 23%. Increased temperature also restrains the growth rate of water cut [65].

The results to date in terms of enhanced oil recovery for all hybrid LSW-based EOR methods are promising. So far, experiments at laboratory scale have been carried out, while modeling studies and pilot field applications are scarce. Numerical simulation studies are necessary to provide more practical insights on the effectiveness of hybrid methods especially important for field implementations.

7. Conclusion

The main idea of this chapter is to demonstrate the synergistic EOR effects of combining chemical/gas-based/thermal methods with low-salinity water and the related underlying mechanisms in both sandstone and carbonate rocks. Hybrid EOR methods are utilized to bypass or improve operational, environmental, and economical shortcomings of individually implemented methods. Many experimental and modeling studies have confirmed this potential synergy by mentioning wettability alteration toward more water-wet condition as the main mechanism of LSW method.

Lower ion concentration of LSW allows gas (typically CO_2) molecules to dissolve in water phase in higher extent which results in gas/oil contact and improved front stability. However, some studies cast doubt on this idea as the more gas dissolves in water, the lower free gas is available to decrease oil viscosity and ultimately improve oil mobility.

Surfactants are known as the agents which are utilized to decrease the IFT, consequently capillary forces, between oil and water in order to enhance microscopic sweep efficiency. LSW provides more detached oil droplets to be produced due to lowered capillary forces by surfactants.

Polymers cause higher oil recovery by increasing water viscosity which lowers mobility ratio after reservoir fluid redistribution by LSW injection due to wettability alteration.

Thermal methods are applied in heavy oil reservoirs to help oil recovery under the mechanism of improved oil mobility, which can be more advantageous if higher detached oil droplets are provided by LSW injection. Lastly, nanoparticles have been introduced to be beneficial as they can improve wettability alteration process by LSW injection.

Despite the extensive promising works mentioned in this chapter, many contradictions, ambiguities, and unexamined issues, especially in carbonate rocks, require more investigation in LSW hybrid methods regarding underlying mechanisms, field implementation viability, operational considerations, and economical feasibility by both experimental and modeling assessments.

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Author details

Peyman Pourafshary* and Nikoo Moradpour
School of Mining and Geosciences, Nazarbayev University, Nur-Sultan, Kazakhstan

*Address all correspondence to: peyman.pourafshary@nu.edu.kz

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