Abstract

Low-salinity waterflooding (LSWF) is a potential new method for enhanced oil recovery (EOR) in sandstone and carbonate rock formations. LSWF approach has gained an attention in the oil and gas industry due to its potential advantages over the conventional waterflooding and other chemical EOR technologies. The efficiency of waterflooding process is effected via reservoir and fluid parameters such as formation rock type, porosity, permeability, reservoir fluid saturation and distribution and optimum time of water injection. Combined effect of these factors can define the ultimate recovery of hydrocarbon. The main objective of this chapter is to review the mechanism of LSWF technique in improving oil recovery and the mechanism under which it operates. Various laboratory studies and few field applications of LSWF in recent years have been presented mainly at the lab scale. Also it will explore numerical modeling developments of this EOR approach.

Keywords: low salinity, enhanced oil recovery, reservoir and fluid properties, LSWF modeling development

1. Primary recovery

The hydrocarbon fluid, crude oil, is a naturally occurring non-renewable resource, and it is one of the fossil fuels which the world’s economy mostly depends on. Crude oil is composed of hydrocarbon deposits and other organic materials that can be refined and processed further to produce various chemical products. The production process of hydrocarbon fluid is divided into three stages, which are, namely, primary, secondary and tertiary recovery. The primary recovery of the crude oil is driven via the natural source of energy available in the reservoir such as solution gas drive, aquifer drive, gravity drainage, gas cap drive and rock and fluid expansion. Moreover, the extracted oil by artificial lift technologies (i.e. gas lifts, electrical submersible pump (ESP)) is considered a primary recovery. This stage of recovery is very limited to only 5–15% of the original oil in place (OOIP) which is produced [1]. When the available natural energy in the reservoir decreases overtime resulting in a significant drop of oil production, thus an external
energy must be added to the reservoir to maintain the reservoir pressure in order
to produce additional oil. This stage is called secondary oil recovery, which utilizes
various mechanisms including gas injection and waterflooding into the reservoir to
force and displace the remaining residual oil. This process is typically successful in
producing around 30% of the oil reserves after natural depletion, leaving 50–80% of
oil still unrecovered [2].

The last stage of hydrocarbon recovery is known as enhanced oil recovery
(EOR), which uses different practices such as chemical flooding, miscible flood-
ing and thermal methods to extract the hydrocarbon fluid left behind the pri-
mary and secondary recovery. EOR has the capability of increasing oil recovery
up to 75% of OOIP by improving the mobility of oil via modifying fluid proper-
ties [3]. Some examples of EOR techniques implemented in the oil industry are
polymer flooding, steam injection, alkaline flooding, in situ combustion and
modified waterflooding.

2. Secondary recovery using waterflooding

Conventional waterflooding is a secondary oil recovery approach that consists
of water injection to improve the oil production from the subsurface. It is typically
performed after the primary recovery which utilizes the natural energy available in
the reservoir. The main purpose of secondary recovery is to displace hydrocarbons
towards the production wells while maintaining the reservoir pressure.

The improved oil production using waterflooding was first discovered in early
1865 following an accidental flooding of water in Pithole City, Pennsylvania.
This was the result of leaks from surface water and shallow water which entered
the drilled holes. It is revealed that the oil recovery factor by waterflooding is
significantly high compared to the natural depletion. The first applied applica-
tion of waterflooding was attempted in Pennsylvania’s Bradford field, in 1924,
which then grew and was widely applied in many fields in the subsequent
decades [4]. Following nationwide waterflooding implementation in petroleum
industry, many attempts were conducted in understanding mechanism, planning
and optimizing the process. Due to its simplicity and reliability, the waterflood-
ing technique has been worldwide implemented and been considered for most
of conventional oil reservoirs to extract more hydrocarbon after the primary
recovery process.

The conventional waterflooding process involves water injection into the
reservoir formation in which the process is generally done with consideration of the
economic factors and also based on the water compatibility with the present res-
ervoir brine to avoid formation damage. However, in the early 1990s, a number of
researchers experimentally investigated the effect of water composition and found
that it plays a significant role in the oil recovery. After this, the potential of low-
salinity waterflooding (LSWF) in EOR applications was observed and developed by
Morrow and his coinvestigators [5].

Furthermore, extensive water coreflood experiments have been conducted and
addressed the benefits of low salinity in the EOR process. Most of these experiment
results showed that when the injected water salinity is lower than the formation
water salinity, a higher oil recovery up to 40% is achieved for both secondary and
tertiary recoveries [6]. However, LSWF has gained vast interest in the petroleum
industry due to its practical advantages compared to other chemical EOR methods.
LSWF is an emerging EOR technology, and it has a promising future since half of
the world’s petroleum originates from sandstone reservoirs.

Next section will cover LSWF process in details.
3. Enhanced oil recovery using low-salinity waterflooding

3.1 Concept of mobility ratio

As seen earlier, waterflooding involves the injection of water into the reservoir, which is by far the most widely utilized solution for improving oil recovery. Practically any oil field which does not have an aquifer support will be considered for waterflooding to maintain the reservoir pressure and improve production rate [7]. A reservoir’s compliance or suitability for waterflooding to increase oil production can be done by evaluating formation and fluid parameters such as formation rock type, porosity, permeability, saturation and distribution of reservoir fluids and optimum time of water injection [8]. Combined effect of these factors can determine the ultimate recovery of hydrocarbon and its economic revenues depicting the viability of carrying out waterflooding for a specific reservoir condition.

The efficiency of a flooding process can be qualitatively evaluated via defining the mobility ratio, especially end-point mobility ratio. As the term implies, end-point mobility ratio is measured at the end-point saturation of a single-phase fluid and can be written as shown in Eq. (1).

\[ M = \frac{\lambda_{\text{water}}}{\lambda_{\text{oil}}} = \frac{k_{r_{\text{w}}}}{k_{r_{\text{o}}}} = \frac{k_{r_{\text{w}}} \mu_{\text{o}}}{k_{r_{\text{o}}} \mu_{\text{w}}}, \]

where,

- \( M \) = end-point mobility ratio
- \( \lambda_{\text{water}} \) = water mobility (mD)
- \( \lambda_{\text{oil}} \) = oil mobility (mD/cP)
- \( k_{r_{\text{w}}} \) = relative permeability of water (mD)
- \( k_{r_{\text{o}}} \) = relative permeability to oil (mD)
- \( \mu_{\text{o}} \) = oil viscosity (cP)
- \( \mu_{\text{w}} \) = water viscosity (cP)

When the value of end-point mobility ratio is less than one, it indicates that the performed flooding is stable, while for a value of more than one, flooding process is unstable due to a phenomenon known as ‘viscous fingering.’ Considering an oil–water system, stable flooding signifies that oil displacement will effectively take place if the injected water behaves like a piston and pushes oil to the intended point [9]. On the other hand, viscous fingering refers to early and continuous breakthrough of injected fluid as a result of large difference in viscosity between water and oil phase. A higher value of mobility ratio implies reducing waterflooding effectiveness as the volumetric sweep efficiency reduces [10].

3.2 Concept of wettability

In understanding the process of oil recovery, formation wettability knowledge is important as it describes the reservoir performance via defining the fluid flow and distribution. Being one of the most significant factors of LSWF, it is important to comprehend wettability phenomenon appropriately to prevent any incorrect assumptions which may lead to permanent formation damage.

Wettability can be defined in a system which consists of two immiscible fluids in contact with a solid surface (rock). In the presence of such system, wettability can be described as the tendency of one fluid to adhere to the rock surface to be in contact with one fluid than the other. In the situation of two-phase immiscible fluid, one fluid attaches strongly to the rock surface while displacing the other fluid [11]. In reference to wettability concept, fluids can be classified into wetting or non-wetting fluid. A wetting fluid balances its forces and adheres to the rock at a
specific contact angle, while the non-wetting fluid will have minimal or no contact with the rock.

In a reservoir system, when the reservoir fluids present in the porous medium are oil and water, wettability can be described as the preference of the rock to be in contact with either oil or water or both fluids. In an oil field, reservoir rock wettability is typically described as either water-wet or oil-wet. If the reservoir is described to be water-wet, it means that the water phase is retained on the pore wall either small or large by capillary pressure, while the oil phase occupies the pore space [12]. On the other hand, an oil-wet reservoir implies that oil phase is adhered to the rock pores, while water phase occupies the centre of pores. There are a number of techniques in which wettability can be quantitatively measured by the determination of contact angle, the Amott method and US Bureau of Mines (USBM) method [13]. The surface energies of a water, oil and solid system can be expressed by Young’s equation; Eq. (2) can be deduced.

\[ \sigma_{ow} \cos \theta = \sigma_{os} - \sigma_{ws} \]  

where,

- \( \sigma_{ow} \) oil and water interfacial energy (dyne/cm)
- \( \sigma_{os} \) oil and solid interfacial energy (dyne/cm)
- \( \sigma_{ws} \) water and solid interfacial energy (dyne/cm)
- \( \theta \) contact angle (degree)

As a typical practice, the contact angle measurement is performed through the aqueous phase, and it identifies wettability as seen in Figure 1. For a reservoir rock containing only oil and water, a contact angle of less than 90° indicates that the reservoir rock is water-wet, but when the contact angle is more than 90°, it denotes the reservoir rock is oil-wet. Moreover, a strong water-wet rock system can present when the fluid-rock contact angle approaches to 0°, while a strong oil-wet rock can be described when the contact angle approaches to 180° [13]. When both fluids (oil, water) are in contact with the rock surface, the reservoir rock can be described to be in intermediate/neutral-wet condition.

![Figure 1. Wettability of the crude oil/brine/rock system [13].](image-url)
Wettability could greatly affect the reservoir rock petrophysical properties, for instance, residual saturation, capillary pressure, relative permeability and end point of relative permeability curves [14]. The crossover point and the relative permeability end points of wetting and non-wetting phases are related to wettability as shown in Figure 2. For a strong water-wet rock, the relative permeability curves will crossover at a wetting phase saturation point of greater than 0.5, while a strong oil-wet rock relative permeability curves will crossover at a wetting phase saturation point of lesser than 0.5. A crossover point at a saturation of 0.5 and equal end points of relative permeability curve imply that the reservoir rock is in neutral-wet condition [16].

The alteration in reservoir rock wettability may possibly occur naturally during production, or it can be modified using thermal or chemical method. Initially, most of the reservoir formations are in the state of strong water-wet due to the deposition process that saturates reservoir completely with water [17]. The migration of hydrocarbon fluid (especially oil) may cause a change in the rock wettability to oil-wet, or the rock may maintain its wettability as water-wet. Mugele et al. [18] reported that the rock wettability can be altered to be more water-wet via the adsorption of divalent cations, subsequently allowing better mobilization of oil for production. In addition, several studies strongly suggest that the adsorption of divalent cations such as Ca$^{2+}$ and Mg$^{2+}$ changes the initial rock wettability towards more water-wet [19]. This is an important observation that describes the LSWF mechanism which results in incremental oil recovery and will be deeply discussed in the upcoming sections.

3.3 Role of crude oil, brine and reservoir rock on wettability

It is commonly known that oil reservoirs can have various alterations of wettability depending on the oil and rock and also the composition and amount of the brine phase. Crude oil/brine/rock (COBR) interactions are utilized to produce wetting conditions in laboratory core samples which are more representative of wetting in an oil reservoir than either a strongly oil-wet or water-wet. Anderson [20] stated that the original strong water-wetness of most reservoir minerals can be changed via the polar compounds adsorption and/or the deposition of organic matter that was initially in the crude oil. He also reported the surface-active agents present in

![Figure 2.](#)  
*Effect of wettability on relative permeability curve [15].*
the oil that are widely believed to be polar compounds that comprise nitrogen, oxygen and/or sulfur. Such compounds have a polar and a hydrocarbon end. He noted that the polar end is adsorbed on the rock surface, exposing the hydrocarbon end and making the rock surface more oil-wet. Furthermore, to the oil composition, the degree of wetting conditions which is altered by these surfactants can also be determined by various factors that are the temperature, pressure, mineral surface and brine chemistry, including pH and ionic composition.

Buckley et al. [21] found that some factors are affecting the rock wetting upon contact with crude oil, including composition of both the oil and brine, temperature and duration of aging in oil and initial water saturation. The chemistry of the brine phase was noticed to change the rocks wettablility, which shown that the brine pH is also significant in verification of wettablility and other interfacial properties of the COBR system. They also indicated that similar factors affect measurements of contact angle using asphaltic crude oil and two sodium chloride solutions of different pH to alter the wetting of two core formations. They noted in cores that there are further complexities in wetting related to rough surfaces, converging and diverging pore shapes and heterogeneous mineralogy. Superimposed on all these sources of heterogeneity in the porous media is the ability of crude oil components to adsorb onto mineral surfaces and change their wetting properties. They summarized that changing pH of aqueous phase affects initial water saturation (Swi) in cores with low-ionic-strength NaCl solutions. Moreover, pore coatings may control wetting alteration in the porous media thus the COBR interactions are not similar to predicted values.

Tang and Morrow [22] performed a study on the effect of salinity and oil composition on wettability behaviour and observed that there are some possible mechanisms by which COBR interactions control wettablility and efficiency of oil recovery. They noted that acid–base interactions can define oil-brine and brine-solid surface charges, and also direct adsorption from crude oil onto a dry surface is ascribed to polar interactions. It is noticed that alterations in wettablility resulting from instability of a water film take place almost instantaneously. Furthermore, adsorption by ion binding takes place through attachment of polar components in the crude oil to specific surface sites on the solid surface by multivalent ions. Surface precipitation is recognized by conditions of poor solvency of asphaltenes in the oil phase. They noted that molecular association, including ion binding of crude oil components at the interface of oil–water, could promote lateral aggregation and the formation of an organic mat that may still be largely separated from the solid surface by a thin water film. They concluded that wetting variations of a rock induced by crude oil are related to changes in solvency of the crude oil with respect to its heavy polar components.

Cuiec [23] explained many experimental condition contributions to understand oil/rock interactions, which are responsible on the occurrence of oil-wet reservoirs. He noticed that some intermediate fractions of crude oil samples might change the rocks’ surface properties depending on the type of formation. He also reported the role of asphaltenes in crude oil/solid interactions through correct correlation between wettability and asphaltene content for a set of reservoirs.

Clementz [24] observed that clay mineral properties are irreversibly altered by adsorption of heavy crude ends. Therefore, this alteration causes reduction in rock sensitivity to injected fluids since rock wettability is altered from water-wet to neutral. He noted further that adsorption of surfactants is decreased, while rock property measurements are changed from irreversibly altered cores. The extent of this interaction is subjected to the type of clay minerals in the rock, the composition of heavy crude ends and the interaction environment. He had seen that after the adsorption took place, a clay-organic complex is formed which is hydrophobic.
and very stable. The development of swelling clays is decreased, and clay surface area and cation exchange capacity are decreased as well. As a result, he revealed that the practical implication of these problems indicates some sort of spotted coverage of the surface and leads to discuss the role of an adsorbed layer on the rock wettability. The existence of this surface film would certainly affect oil recovery in a rock system. He recommended that it cannot be stated a priori that oil recovery from the rock having a neutral wettability will be less than that from the water-wet system. In addition, he reported that the recovery would most undoubtedly rely on the nature of drive fluid and its interaction with reservoir minerals. Finally, he concluded that it is very important to identify potential alterations to core properties, which take place as a result of core handling. The absorbed layer can either be formed or damaged, and any rock property measurements, which count on the nature of the clay minerals present, would be affected by the existence of the adsorbed layer.

Brown and Neustadter [25] studied the wettability performance of oil/water/silica systems based on contact angle measurements. They reported that the recovery efficiency of crude oil from a porous media using water displacement depends on the rock wettability. This conclusion was based on the relative tendency of both the aqueous and oil phase to coat the solid surface and, therefore, to occupy the rock pores under the action of capillary forces. They also found that the existence of monovalent ions can affect wetting conditions by suppressing the charge effects with no effect at low concentration of NaCl and behave differently at high concentration and extremes of pH. By contrast to the effect of monovalent ions, they have seen that the seawater can provide a strongly oil-wetted surface, independent of pH, even when it is diluted with distilled water. Furthermore, they noticed the same performance with synthetic seawater that was applied to determine if the original seawater can affect the wettability by reason of its protein or other nonsalt components. The results obtained with NaCl were as expected considering the charge interaction model, but using seawater indicated that divalent ions had a very noticeable effect. In addition, they conducted a study to examine the effect of divalent ions and observed that there are specific interactions between different oil crude samples and the divalent ions can take place. They suggested that alterations in wettability are not contributed to general electrical double-layer compression at low electrolyte concentrations. They also observed that divalent ions can create bridges between specific petroleum crude surfactant species and the silica surface. In conclusion, for systems of crude oil/silica/distilled water, the wettability strongly depends on pH due to activation of the crude oil surfactants by the aqueous phase. When pH value is high, the water film can stabilize between the oil film and the silica surface by charge repulsion, while at low pH values, charge attraction between the positively charged crude oil surfactants and the negative rock surface promotes wetting oil surface. Moreover, crude oil/rock systems, which are preferentially oil-wet, show large hysteresis between the advancing and receding angles. Due to the low solubility of the crude oil surfactants in the aqueous phase, the crude oil has to adhere to the surface before the surfactants, which promote oil wettability, can be adsorbed.

3.4 Low-salinity enhanced oil recovery

The recovery of hydrocarbon fluid from subsurface formations is a complex process that associates multiple length scales. In typical water flooding process, seawater is injected on a macroscopic scale into the reservoir formation which carries hydrocarbon fluid (oil) to sweep the oil away from injection wells towards production wells. On the microscopic scale, the injected water displaces the oil in
the porous reservoir formation in a typical microfluidic two-phase flow of water and oil. Due to the large ratio of surface-to-volume, the efficiency of this process of microfluidic is strongly influenced by the surrounding porous rock matrix wettability. The rock formation ingredient, typically sandstone or limestone, is made of naturally hydrophilic material. Throughout millions of years of exposure to petroleum fluid, a layer of organic material adsorbed onto the surfaces and thus rendered the rock more hydrophobic. These molecular scale adsorption developments (as seen in Figure 3) thereby impede the oil displacement via water phase in the hydrophobized rock pores. This is understood to be one of the major causes why the secondary oil recovery is a rather inefficient process that leaves more than 50% of the oil unrecovered in the reservoir [26].

Since the 1970s, oil operator companies have examined several techniques to improve the low recovery rate by injecting various additives combined with the water aqueous phase. More recently, it was found that the recovery rate can be improved by desalinating the seawater before injecting it into the reservoir. The following sections will explore experiment and numerical developments of low water salinity approach.

3.5 Experimental observation of low salinity

Upon the observation that the injection of freshwater in sandstone reservoirs reduces the oil recovery due to clay swelling, extensive laboratory researches were conducted in the 1940s to evaluate the influence of fluid’s physical and chemical properties on oil recovery [27]. Reiter [28] observed that low-salinity waterflooding obtained an additional oil recovery of 21.3% more than higher-saline floods conducted on Nacatoch sandstone cores. Further investigation by [29] on the effect of salt water on oil recovery containing clays concluded that the pressure drop across cores and oil recovery increased as the concentration of salt-in injection water decreased.

The true EOR potential of LSWF was recognized by Morrow and his experimental co-workers from the studies conducted on the effect of wettability on oil recovery via waterflooding [30]. They confirmed that the composition of injection

Figure 3. Molecular scale adsorption processes [26].
brine affects oil recovery, but the amount of recovery depends on the conditions of crude oil, injection brine and reservoir rock. Further investigation by [30] on LSWF observed that the oil recovery obtained from conventional water flooding with high-salinity brine was similar to that of LSWF when initial formation water saturation was zero. It was concluded that the positive effects of low salinity could only be obtained with the existence of connate water, and the salinity of connate water plays a significant role in the amount of oil recovery. It was observed from the experiment that additional oil recovery could be achieved when the injection water salinity is relatively lower than formation water salinity.

However, this was not observed in all the studies conducted on the effect of brine composition on oil recovery. Zhang [31] presented their report showing that the injection of low-salinity brine on Berea sandstone resulted in lower recovery than that of high-salinity waterflooding, although more cases showed better recovery with the application of low-saline brine injection. The salinity level of 1500 ppm NaCl showed higher oil recovery, while the injection of 8000 ppm had zero effect although both the salinity levels were below the connate water salinity. Nevertheless, in most of the published cases, LSWF showed positive benefits on oil recovery in sandstones.

Based on practices in the laboratory, Jerauld et al. [32] proposed that brine composed of 10–25% of connate water or salinity of 1000 to 2000 ppm will be an appropriate estimation in determining the composition of injection brine. A total of 214 and 188 laboratory scale studies conducted in the secondary mode and tertiary mode, respectively, which confirmed the positive effect as an increment of 5–20% in oil recovery was observed [33]. The application of LSWF evaluated in West Salym field, Russia, through coreflood tests on sandstone cores resulted in elevated oil recovery of 4% OOIP and 1.7% OOIP in the tertiary mode [34]. A summary of experimental research that has been conducted to study the benefits of LSWF in improving oil recovery is shown in Table 1.

| Reference | Rock type              | Injected water salinity (ppm) | Formation water salinity (ppm) | Mode of injection | Incremental oil recovery achieved (%) |
|-----------|------------------------|------------------------------|--------------------------------|------------------|---------------------------------------|
| [35]      | Sandstone              | 1480 SW 1500 NaCl            | 29,690 FW                      | Secondary        | 29                                    |
|           |                        |                              |                                | Tertiary         | 7–14                                  |
| [36]      | Sandstone              | 50–5500 SW 22,000 SW         |                                | Secondary        | 14–28                                 |
| [37]      | Berea sandstone        | 10,000 NaCl 40,000 NaCl      |                                | Secondary        | 5–6                                   |
|           |                        |                              |                                | Tertiary         | 25–35                                 |
| [38]      | Berea and field sandstone | 870–1140 SW 30,510 SW       |                                | Secondary        | 15                                    |
|           |                        |                              |                                | Tertiary         | 0                                     |
| [39]      | Berea and field sandstone | 1% FW FW                    |                                | Secondary        | 10–22                                 |
|           |                        |                              |                                | Tertiary         | 2–6                                   |
| [40]      | Sandstone              | 1054.96–105.49 SW 105,496 FW |                                | Secondary        | 9                                     |
|           |                        |                              |                                | Tertiary         | 3                                     |
| [34]      | Sandstone              | —                            | FW                             | Secondary        | 6                                     |
|           |                        |                              |                                | Tertiary         | 5                                     |

Note: SC, standard conditions of temperature (60°F) and pressure (1 atm); RC, reservoir condition of temperature and pressure; SW, seawater; FW, formation water.

Table 1. Summary of laboratory experimental observation on low-salinity waterflooding.
3.6 Proposed mechanism of low-salinity waterflooding

3.6.1 Fine migration

Clay is subjected to swelling when it is exposed to freshwater. Early studies conducted in understanding the mechanisms of low-salinity water injection are associated with clay swellings and fine migration. According to Sheng [41], fine mobilization takes place when the strength of ions in injected brine is lower than the concentration of critical aggregate lump. Divalent cations play a major role in determining the critical flocculation concentration. These cations stabilize clay by reducing the zeta potential and repulsive force. The injection of solution with a low-saline concentration destabilizes and disperses clay from the wall of pores causing it to flow with water. Clay that flows in water tends to stick on the surface of small pores resulting in the reduction of permeability. This phenomenon increases the sweep efficiency as water is forced to flow on new paths.

Jackson et al. [42] reported similar mechanism stating that low-salinity effect arises from the removal of mixed-wet fines from the surface of formation and accumulation of oil-wet fines at the oil–water interface. This increases oil recovery as it stimulates the mobilization of oil and changes the wettability of the formation towards more water-wet by exposing the water-wet surfaces beneath the stripped fines as denoted by Figures 4–6.

Based on their experimental studies, Tang and Morrow [43] reported that incremental oil recovery obtained through LSWF was due to fine mobilization especially kaolinite. The conclusion was made upon their observation that unfired Berea sandstone showed improvement on oil recovery during low-saline brine injection, while acidized Berea core did not show any improvements. It was also observed in their research that the increase in oil recovery was more significant for sandstones containing clays than clean core samples.

However, numerous LSWF carried out by British Petroleum (BP) on cores under reduced and reservoir condition in sandstones did not indicate any fine mobilization despite the increment in oil recovery [32]. Zeinijah et al. [44] reported that minimal to zero amount of clay production was observed during their experiment of flooding cores with low-saline brine. The variation in the composition of injected brine, minerals and lithology might be the reason for the conflicting findings.

3.6.2 Increase in pH and reduction in interfacial tension

Mcguire et al. [45] suggested that similar to the mechanism of alkaline flooding, increase in the pH value and reduction in interfacial tension (IFT) could be one of the LSWF mechanisms. The exchange of adsorbed sodium ions with hydrogen ions in water results in elevation of pH. Various experiments conducted by researchers indicated an increase in pH value of about pH 2 to pH 4 upon the injection of low-saline brine. In situ surfactant that lowers oil or water IFT is produced when organic acids in the crude oil react under high-pH conditions [46]. The formation of surfactants and reduction of IFT forms either oil–water emulsion or water–oil emulsions which results in the improvement of water sweep efficiency [33].

However, in several cases, in the injection of low-saline water, the pH value was lower than 7, and in some cases pH remains unchanged. Zhang et al. [31] reported that no obvious relationship was observed between effluent pH and oil recovery, and only slight change in pH was observed during low-salinity injection. The measured IFT value was above 10 mN/m with pH less than 9 during the course of LSWF which was concluded to be very low to reduce residual oil saturation.
Figure 4.
Formation of mixed-wet fines due to adsorption of polar components from crude oil [42].

Figure 5.
Stripping of mixed-wet fines from pores during waterflooding [42].

Figure 6.
Mobilization of trapped oil [42].
A chemical mechanism proposed by Austad [46] signifies the role of clay at low pH values. Thermodynamic chemical equilibrium that initially exists at reservoir condition at low pH increases the adsorption of anions and cations onto the clay surface. The injection of low-salinity brine disturbs this chemical equilibrium causing reaction between rock and brine to occur especially during the presence of Ca\(^{2+}\) ions. Compensating for the loss of cation into the low-saline water, H\(^+\) ions reacts and increases the pH near to the clay surface. Thus, an increase in pH is introduced by the tendency of low-salinity brine in changing the chemical structures initially present.

3.6.3 Multicomponent ion exchange

Multicomponent ion exchange (MIE) mechanism describes the alteration in the wettability of reservoir rock towards more water-wet due to the release of oil particles from the clay surfaces. Low-salinity water expands the double layer and eases the process of desorption of divalent ion on oil bearing to take place. Divalent cations such as Ca\(^{2+}\) and Mg\(^{2+}\) from the injected low-salinity brine control this process that results in ion exchange [17]. The requirements of this process are the presence of negatively charged surface on the rock, polar components on oil phase and divalent cations in the injection brine. MIE takes places during LSWF by removing organometallic complexes and polar compound from the clay surface and substituting them with noncomplex cations.

This theory was supported by experimental work carried out by Lager et al. [30] on core samples from North Slope composed of dead crude oil and initial connate water. Initially, the experiment was conducted at a temperature of 25°C, flooding the core with high-salinity brine followed by tertiary low-salinity flood, resulting in oil recovery of 42% OOIP for conventional high-salinity waterflooding and 48% OOIP for LSWF. A second experiment was run at 102°C, flooding the core samples with high-salinity water, and it resulted in an oil recovery of 35% OOIP. Divalent cations were removed from the cores by flushing it with brine containing high concentration of NaCl. The initial water saturation and oil condition were restored, and a high-salinity waterflood without the presence of divalent cations in the cores resulted in 48% OOIP, while no additional oil recovery was observed during LSWF.

From the experiment, it was concluded that the injection of low-salinity water into a sandstone reservoir in which mineral structure are not present will not result in incremental oil recovery. The findings also explained the reason why LSWF has no positive effect on acidized or fired sandstone as observed by Tang and Morrow [43] in their research. This was due to the absence of polar compounds that did not promote the interaction of clay minerals to release oil particles.

3.6.4 Limited release of mixed-wet particles

Limited release of mixed-wet particles is a combined mechanism of fine migrations proposed by Tang and Morrow [43] with DLVO theory. The name of DLVO theory originated upon the proposal of the theory by Derjaguin, Landau, Verwey and Overbeek. As explained by previous mechanisms, it is known that crude oil is originally bonded with clays which are attached on the pore surface. Due to the introduction of reduction in the salinity upon low-salinity water injection, the likelihood of these fines to be detached increases as the electrical double layer in the aqueous phase between is expanded. The migration and aggregation of stripped fines result in oil coalescing [38]. Oil recovery is enhanced due to the limited elimination of mixed-wet particles from the wall of pores because of local heterogeneous wetting conditions.
3.6.5 Wettability alteration

The alteration of the wettability of the reservoir is considered the primary mechanism of LSWF that results in incremental oil recovery. Previously explained mechanism such as fine migration, increase in pH and decrease in IFT, multi-component ion exchange and salt-in effect were related to the alteration of initial wettability of reservoir towards more water-wet. Suijkerbuijk et al. [34] related the changes in wettability in sandstone rocks with the presence of clays, composition of oil and high divalent cation concentration in formation water. The requirements for the positive effect of LSWF to take place were that the injection water also should contain divalent cations with the injection water salinity to be relatively lower than the salinity of formation water.

During low-salinity water injection into sandstone core, the mechanism of wettability alteration reported were similar to the process that occurred during alkaline flooding and surfactant flooding. The conducted experiment indicated an increase in pH value up to 10 that resulted in the generation of surfactant. This lowers the IFT between the water phase and the oil phase, thus increasing the water wettability promoting higher oil recovery [47]. Similar reaction mechanism occurred during the salting-in phenomenon with the decreasing salinity of injection brine.

The investigation of the effect of type of cation and its concentration in the injection water conducted by a researcher on the oil recovery of Berea sandstone concluded that wettability alteration was the main mechanism resulting in improvement in oil recovery [48]. The changes in the electrical charge upon LSWF in both the brine/oil and brine/rock interfaces to be more negative promote further stability of water film and result in water-wet state in the reservoir.

Moreover, several experiments conducted indicated that the contact angle between the oil and rock surfaces increases as the temperature and pressure increase and decrease with decreasing injection water salinity. As reported by Nasralla et al. [49], this observation was also supported by the increase in oil relative permeability end point and decrease in water relative permeability end point.

The low-salinity water flooding is an attractive eco-friendly and a promising technique for oil recovery in sandstone reservoirs in recent years. It can change the ion composition or brine salinity for improving oil recovery. However, the optimum conditions that improve oil recovery by low-salinity flooding are related to the understanding of fluid–rock interaction mechanisms. Low-salinity waterflooding might be effectively considered in special conditions for improving hydrocarbon recovery when the following factors are met: clay should be present in the sandstones, polar components (acidic and/or basic material) also should be present in crude oil, and formation water should contain divalent ions like Ca$^{2+}$ [43, 50].

3.7 Aspects of modeling and simulation on low-salinity waterflooding

One of the earliest developments of the model to conduct studies on LSWF was accomplished by Jerauld et al. [32] through the modification of Buckley and Leverett conventional waterflooding model. In their model, the salinity of injection brine was made as a function of relative permeability and capillary pressure. The model built also includes the effects of secondary drainage water, relative permeability and hysteresis between imbibition and connate water. A similar LSWF model for sandstone and fractured media was presented by Wu and Bai [51] mathematically and numerically using MSFLOW general simulator. Results generated on the alteration
of both models matched the experimental results, confirming the incremental oil recovery obtained via LSWF.

A semi-quantitative model developed by Sorbie [52] based on pore-scale theoretical considerations describes the multicomponent ion exchange mechanism of LSWF. This model was built with the purpose of demonstrating the effects of electrical double-layer expansion and polar organic species adsorption on the wettability alteration. Nevertheless, the predictions of the model were not convincing, and it was concluded that further experimental studies are required to validate it.

Omekeh [40] presented a mathematical model based on ion exchange and mineral dissolution and precipitation in LSWF. The model considered two-phase flow of oil and brine. From the research conducted, it was also demonstrated that the presence carbonate minerals may reduce the positive impact of LSWF in improving oil recovery. It was also proposed that cations are involved in an ion exchange process with the negatively charged clay surface and the release of cations from the surface of the rock increases relative permeability and mobility of oil. Desorption of divalent ions was suggested to be the main mechanism of LSWF. However, according to Suijkerbuijk [34], the proposed theory from the model contradicts with the experimental studies conducted on the mechanism of LSWF. Adsorption of divalent ions on the clay minerals was reported to be the process that alters wettability resulting in LSWF benefits.

Recently, a systematic study of LSWF mechanism and its potential in improving oil recovery was presented by Dang et al. [52] using a mechanistic model that was developed using Computer Modeling Group’s GEM™ reservoir simulator validated against PHREEQC geochemistry software and few other experimental coreflooding tests. In this model, the role played by clay was captured in investigating the geological effects in the process of LSWF, and the field-scale benefits of LSWF in both secondary and tertiary injection modes were proven. Changes in wettability condition due to ion exchange and clay effects were proposed to be the primary mechanism of LSWF, and nominal optimization of the process was presented in this research. Table 2 summarizes past modeling and simulation studies that were conducted to understand the process of LSWF.

| Author       | Software used                                                                 | Research scope                                                                 |
|--------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| [32]         | Buckley and Leveret model                                                      | Effect of injection water salinity on relative permeability and capillary pressure |
| [47]         | PHREEQC geochemical software                                                   | Changes in pH of reservoir during LSWF                                          |
| [51]         | Buckley and Leveret model                                                      | Relationship between injection salinity concentration and wettability alteration |
| [52]         | PHREEQC geochemical software                                                   | Description of the multicomponent ion exchange process at the pore scale        |
| [40]         | Mathematical and salt reaction model                                           | Modeling of ion exchange and mineral solubility in LSWF                         |
| [53]         | IPHREEQC geochemical module coupled with UTCHEM chemical flooding reservoir simulator | Multicomponent ion exchange mechanism and effect on LSWF                         |
| [54]         | PHREEQC geochemistry software coupled with CMG’s GEM                           | Investigation on effect of clays and ion exchange process on LSWF and process optimization |

Table 2. Summary of previous modeling and simulation studies related to low-salinity waterflooding.
4. Conclusion

The evaluation on the prominent ideas and aspects of LSWF were presented in this paper mainly focusing on sandstone reservoir. Different characteristics of LSWF have been thoroughly reviewed including the industrial application, field studies, mechanisms, laboratory and modeling works that have been conducted. Based on previous reports, LSWF has a beneficial effect on oil recovery in both laboratory and field-scale studies. The mechanisms that resulted in incremental oil recovery compared to standard high-salinity waterflooding that have been proposed by several researches over the years are fine migration, increase in pH and reduction in IFT, multicomponent ion exchange, limited release of mixed-wet particles and wettability alteration. Some of these mechanisms are related to each other with the main process being wettability alteration.

It can be deduced that there is no general agreement regarding which mechanism results in incremental oil recovery, and these mechanisms work under a specific condition during low-salinity water injection. The magnitude of incremental oil recovery obtained via LSWF is highly dependent on the reservoir condition as the working mechanism directly relates to the specifics of the reservoir because the wettability can be changed from oil-wet to water-wet or from water-wet to mixed-wet. Although in either way oil recovery factor could be improved, the magnitude of oil recovery may vastly vary. Another fact is that generally LSWF is used together with chemical flooding. LSWF is largely environmentally friendly compared to chemical methods and has higher oil recovery benefits than conventional waterflooding method. However, considering the incremental oil recovery from chemical EOR projects, the incremental oil recovery from LSWF alone should not be too high.

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