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Review

# A critical review of low salinity water flooding: Mechanism, laboratory and field application

Allan Katende[a,b,*], Farad Sagala[c]

[a]Department of Energy, Minerals and Petroleum Engineering, Faculty of Applied Sciences and Technology, Mbarara University of Science and Technology (MUST), Kihumuro Campus, 7 km off Mbarara-Kasese Road, PO Box 1410, Mbarara, Uganda
[b]Department of Geoscience and Petroleum, Norwegian University of Science and Technology (NTNU), Sem Sælands veg 1, Trondheim N-7491, Norway
[c]Department of Chemical and Petroleum Engineering, University of Calgary (UC), 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

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ABSTRACT

Low-salinity water flooding (LSW) is a promising new technique for enhancing oil recovery (EOR) in both sandstone and carbonate reservoirs. The potential of LSW has drawn the attention of the oil industry in the past decade. Along with the few successful field applications of LSW, various studies in this field in recent years have been conducted mainly at the lab scale. The main objective of this critical review was to investigate the potential of this EOR technique in improving oil recovery and the mechanism under which it operates. As a result, various mechanisms have been proposed. However, no consensus on the dominant mechanism(s) in neither sandstones nor carbonate reservoirs has been reported, and the oil industry is continuing to discover the leading effects. Herein, we provide the chronicle of LSW, analysis of the proposed mechanisms of enhancing oil recovery using LSW in recent findings, some laboratory observations, and finally, some successful field applications. From this review, despite the promising potential justified by both laboratory studies and field applications, there exists a large number of unsuccessful field case studies. LSW is viewed as an immature EOR technique with many ambiguities because definitive conclusions about which mechanism(s) is responsible for improving oil recovery remains elusive and a bewilderment to the oil industry.

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* Corresponding author at: Department of Energy, Minerals and Petroleum Engineering, Faculty of Applied Sciences and Technology, Mbarara University of Science and Technology (MUST), Kihumuro Campus, 7 km off Mbarara-Kasese Road, PO Box 1410, Mbarara, Uganda.
*E-mail addresses:* allan_katende@hotmail.com, akatende@must.ac.ug, allank@alumni.ntnu.no (A. Katende).

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## 1. Introduction

Water flooding is applied intensively worldwide to improve oil recovery [1-5]. However, the injection of low-salinity water has been found to enhance oil recovery compared to high-salinity water injection [6-14]. This technology has attracted the industry's interest because of its simplicity and low cost. The technique was first introduced by Bernard [15], and co-workers, who discovered an increase in oil recovery when sodium chloride (NaCl) brine in the range of 0 to 1% was used compared to distilled water [15]. Bernard [15], injected different concentrations of NaCl brines and fresh water into the sand packs of Berea core type. The experiments indicated that the oil recovery was almost unaffected when the NaCl concentration was in the range of 1 to 15%. However, incremental oil recovery was observed when the concentration of NaCl was between 0 and 1%. The results showed that when hydratable clays are present, a freshwater flood can produce more oil than the brine accompanied by relatively high-pressure drops across the cores. The incremental oil recovery was attributed to clay swelling and plugging of pore spaces available to oil and water. However, this work did not draw the attention of the petroleum industry at that time. A comprehensive set of experiments started in the 1990s to confirm the performance of low-salinity water flooding (LSW) for improving oil recovery. Similar studies were also performed by; Jadhundan and Morrow [16], Yildz et al. [17], Tang and Morrow [18].

Most coreflood experiments showed increases in oil recovery in both the secondary mode as well as the tertiary mode, as in Zhang et al. [19] and Agbalaka et al. [20]; however, sometimes, tertiary oil recovery improvement was not observed, as in; Rivet et al. [21], Sharma and Filoco [22], and Skrettingland et al. [23]. In those previous studies, the mechanism of oil recovery enhancement remained undefined, and additional laboratory experimental findings supported with field trials for evaluating the potential of LSW at the field scale have been published in the past decade. Nasralla et al. [24] investigated the efficiency of oil recovery by LSW in sandstone reservoirs. The authors conducted core flood experiments to determine the effect of water salinity on oil recovery in the secondary and tertiary modes. Deionized water and three different brines, representing a Middle East field case, in the range of 5000 to 174,000 mg/L were tested. Two different types of crude oils were used to investigate the effect of oil composition on the applicability of LSW. All experiments were conducted on 5 to 6 in.-long outcrop Berea sandstone cores, and the core flood effluent was regularly sampled to follow rock-fluid interactions. This monitoring was achieved by measuring the concentrations of different cations.

From the study in Nasralla et al. [24], the injection of deionized water in the secondary mode resulted in a significant improvement in oil recovery, up to 22%, compared to seawater. However, no additional oil was recovered in the tertiary mode. The authors attributed the increase in recovery to cation exchange, which reduced the electrostatic attraction forces between oil and rock and altered the rock wettability [24]. The authors concluded that fine particle migration during ion exchange can result in formation damage, which can significantly improve the oil recovery; however, according to the authors, the extent of damage depends on the oil composition.

Webb et al. [25] provided the first field evidence of a reduction in residual oil by low-salinity water injection. The log injection tests showed that the residual oil within approximately 4 in of a wellbore was reduced by up to 60% when LSW was used. In addition, various studies on single-well chemical tracer test's (SWCTT) [26-33] have been undertaken. MscGuire et al. [34] conducted a study in Alaska and found a substantial reduction in the remaining oil saturation in the range of 6–12 % of the original oil in place (OOIP) because of LSW injection. The Omar field in Syria showed an incremental recovery of 10–15 % of STOIIP because of LSW [35].

The Powder River basin of Wyoming, which has been flooded with water from low-salinity sources, showed an increase in oil recovery [35]. Moreover, in the North Slope of the Alaskan reservoir, the oil production rate doubled, a measurable drop in the water-oil ratio (WOR) was observed, and the remaining oil saturation also decreased from 30% to 20% under LSW [36]. In general, various mechanisms have been proposed in the literature to explain this additional oil recovery resulting from low-salinity injection. The major mechanisms proposed by the researchers include fine particle migration [18], multicomponent ionic exchange (MIE) [36], the extension of the electrical double layer [37] and pH effects [38].

These mechanisms explain how oil recovery increases because of changes in the wettability of the rock from the mixed wet state toward more water-wet conditions. Thus, this paper gives an overview of the fundamentals of LSW flooding, the experimental design and some field analysis with this new recovery technique for both sandstone and carbonate reservoirs.

### 1.1. Background

In this review of the literature, a chronological comparative study was performed for the application of LSW flooding in sandstone and carbonate reservoirs looking at the proposed mechanisms for LSW flooding in both sandstone and carbonate reservoirs. The proposed mechanism(s) contributing to this increase in oil recovery by LSW are summarized in Table 6.

Waterflooding was first practiced for the purposes of pressure maintenance after primary depletion and displacing oil by taking advantage of viscous forces and has become the most widely adopted improved oil recovery (IOR) technique. Its high availability and simple injection, as well as lower cost and capital investment, are the other key operational and economical features of water flooding. Historically, little attention has been given to the role of injected water chemistry on the displacement efficiency or its impact on oil recovery. However, over the past decade, many studies have shown that injecting brine with a salinity in the range of 1000–2000 ppm can affect crude oil/brine/rock (COBR) interactions in a favorable manner to reduce the remaining oil saturation [39,40].

Low-salinity water injection, on the other hand, is a newly developed EOR process. The recovery process involves injecting brine with a low salinity that is depleted in divalent cations compared with the in-situ brine into the oil reservoirs. Despite growing interest in LSW, a consistent mechanistic explanation has not yet emerged. The complexity and number of parameters behind crude oil/brine/rock (COBR) interactions are the main reasons for confusion about the mechanisms underlying LSW. The variety of circumstances under which LSW may or may not be observed suggests that more than one mechanism may be at play.

### 1.2. Some of the factors affecting low-salinity water flooding

LSW can effectively increase the oil recovery under certain condition. The listed conditions for observing low-salinity effects are mostly related to the systematic experimental work by Tang and Morrow [18]; however, some points are also offered in other studies [34].

1. **Mineral surface**
   According to several studies, the injection of low-salinity water enhances oil recovery only in cores containing clay minerals [18,34,41-44]. The crystal structure of common sandstone reservoir clay consists of a sheet of tetrahedral silica and octahedral aluminium layers. Clay minerals are often characterized as cation exchange materials because of structural charge imbalances either in the silica or in the aluminium layer and at the edge surfaces that produce a negative charge on the clay

surface. To attain a neutral charge, these negatively charged sites attract positively charged ions from the surrounding pore fluid. The capacity of a clay to attract and hold cations from a solution is measured as the cation exchange capacity (CEC). The CEC is defined as the maximum quantity of total exchangeable cations that the clay can hold at a given pH, usually at a pH of 7.

Cations in the solution are attracted and held by weak quasi-bonding forces, including electrostatic and van der Waals forces, and depending on the conditions, cations are exchanged and not held permanently. Various cations have different relative strengths and replacing power. Weakly adsorbed cations may easily be exchanged, and therefore, the relative replacing power of a cationic species depends on its binding strength [18,40]. Tang and Morrow [18] (Fig. 1) and Pu et al. [41] performed experiments on clay-free cores that were fired at 800 °C and acidized to remove the clay, and the results did not show any response to low salinity. The increased oil recovery from low salinity water injection has been proposed to be caused by the tertiary mode being scalable to the amount of kaolinite clay in the rock. However, other results have showed that cores lacking kaolinite still exhibit increases in recovery from low-salinity injection [38]. Researchers have observed increased recovery from low-salinity flooding in cores containing different clays such as illite, muscovite and chlorite [45]. The presence of chlorite has been related to poor results of low-salinity injection in research on Berea sandstone cores [46]. Austad et al. [38] also stated that because of its low CEC, kaolinite may be one of the least advantageous clay types.

Sandstone cores without clay but containing dolomite crystals have also shown positive results from the injection of low-salinity water [41]. A further suggestion is that a negative zeta potential material with CEC seems to be related to a successful low salinity flooding of sandstone rock [47]. Experiments involving a 3D imaging technique indicated that low-salinity brine was able to mobilize the dolomite and anhydrite crystals in the rock [48]. Pu et al. [41] later related low-salinity effects to the dissolution of anhydrite and dolomite cement in three different cores. As a result, it was suggested that the core becomes more water wet from the dissolution and that strongly water-wet cores did not show any low-salinity effects. In recent studies, it has been concluded that anhydrite dissolution is not the main mechanism behind the IOR and is rather simply a contributory mechanism [49]. The use of diluted seawater has been shown to improve recovery in carbonate reservoir rock (80% calcite, 13% dolomite, 6% anhydrite, >1% quartz), and the observed effect was explained by some brine-rock interactions increasing the water wetness of the rock [50]. Reinholdtsen et al. [51] suggest that the presence of certain plagioclase silicates increases the pH of formation

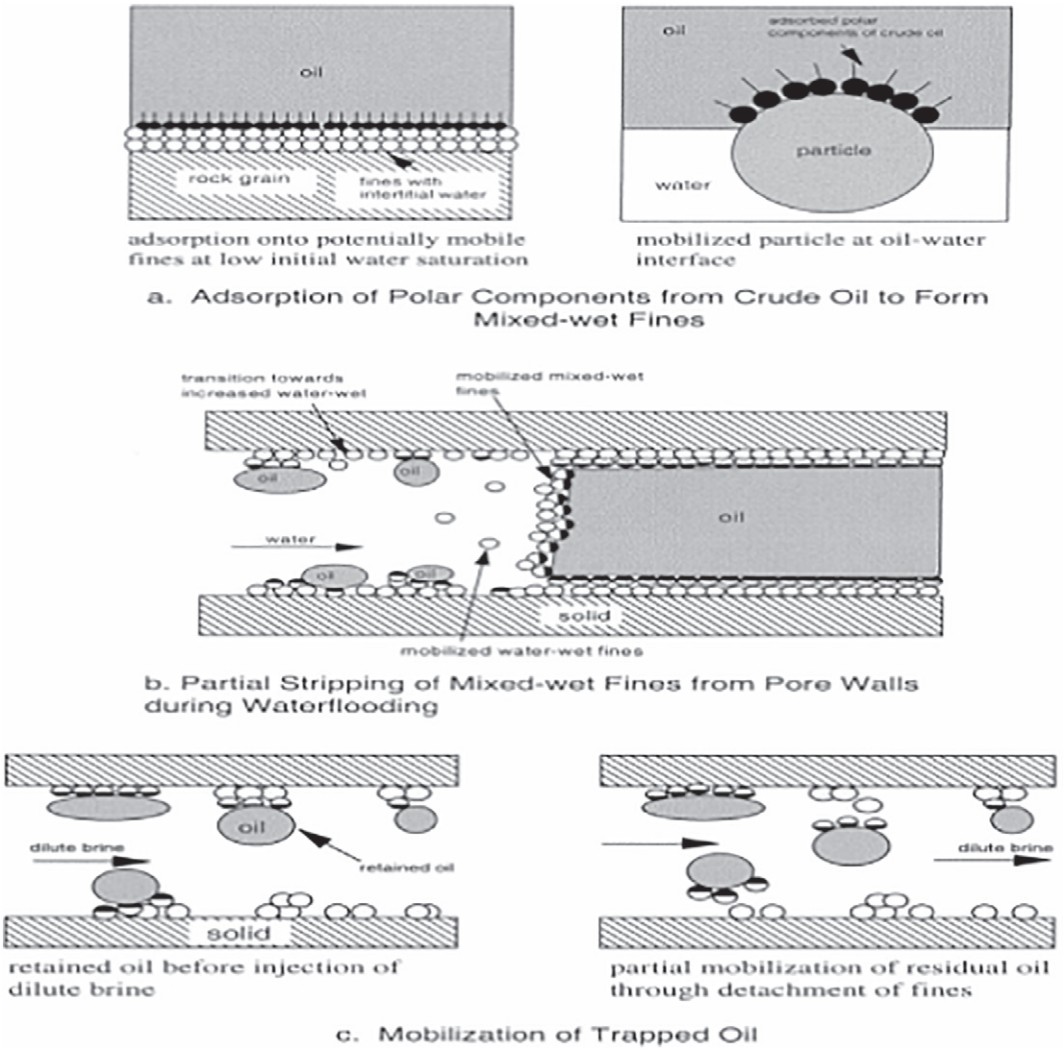



**Fig. 1.** The role of potentially mobile fines in crude oil/brine/rock interactions and the increase in oil recovery with decreasing salinity [18].

water, and therefore, the capacity of clays to adsorb oil during ageing is reduced. Such a situation would lead to an initial water-wet rock and thus prevent the low-salinity effect from occurring.

2. **Brine.**
Numerous studies have revealed that a lower salinity threshold is needed to observe an increased oil recovery, therein being a significant degree less than the salinity of the formation brine [34,36,38,52]. Provided that other required conditions are fulfilled, the research showed that when reducing the salinity of the injected water to 1000–2000 ppm, an effect on oil recovery was observed in almost all instances. An upper salinity threshold of approximately 5000 ppm is most commonly acknowledged to result in increased recovery [25]. Some researchers have observed that the low-salinity brine must contain some forms of divalent and other multivalent cations to work successfully [22,36,53]. Other research indicates that the injection of water with a high concentration of divalent cations stops oil recovery [18]. However, removing the divalent ions in the injection brine has been reported to be insufficient, for example, if the concentration of monovalent ions, such as $Na^+$, is high [19,37]. Some authors have suggested that there should be an optimal low-salinity water composition according to their proposed mechanism responsible for the low-salinity effect [36,38].
3. **Oil**
From experiments with refined oil, keeping all other parameters constant, no extra recovery was observed when adjusting the salinity of the injection brine [18,19,54-57]. Polar components in the oil have been reported as necessary for IOR, as the use of refined oil without polar components did not show any response to low salinity. Similar results were obtained by Morrow et al. [40] when oil with different acid/base numbers was used in flooding. The authors reported that both high-acid-number with low-base-number oil and low-acid-number with high-base-number oil gave similar low-salinity effects, indicating that both acidic and basic oils are usable. It is therefore generally accepted that the oil must contain polar components to confer a low-salinity effect.
4. **Temperature**
The results obtained from LSW seem to be dependent upon the flooding temperature. Recovery was increased by a higher flooding temperature with a high salinity secondary flooding, while recovery from tertiary LSW was reduced. Cissoko et al. [45] and Morrow et al. [40] conducted low-salinity corefloods on North Sea reservoir samples with different ageing and flooding temperatures. Cores aged at 60 °C showed no response to tertiary low-salinity flooding at 60 °C or 130 °C, while cores aged at 90 °C responded to low-salinity flooding at 60 °C, 90 °C, and 130 °C. [23] as well as cores aged at 60 °C followed by flooding with high salinity and tertiary low salinity at 35 °C and 60 °C. In addition, a low-salinity effect was observed only for cores flooded at 35 °C.
5. **Wettability**
Cores have been suggested to become more water wet as mixed wet clay particles are released by low-salinity water [56]. Oil production may be accelerated by a water-wet condition, but it is commonly accepted that a mixed wet condition usually produces the least residual oil saturation after injection of several pore volumes [16]. An experiment conducted by Berg et al. [58] visually revealed the release of oil droplets from the clay surface as the surface was initially exposed to high-salinity water, changing to low salinity; however, the mechanism involved was not identified. Oilfield low-salinity injection resulted in two distinct observed water cuts, which may be an indication of a change in wettability toward a more water-wet case [35]. Wettability may also be altered toward being more oil wet from the injection of low-salinity water [59-66], resulting in an insignificant increase in tertiary oil recovery in their experiments and slower oil production in secondary floods. Because of the wettability change, an increased capillary end effect is expected, and especially with slow rate corefloods, the residual saturation may be distorted.
A mechanism behind the different effects of salinity on wettability has been explained based on the disjoining pressure [22]. According to DLVO theory, salinity may affect the electrostatic forces, and as a result, lower salinity creates a thicker film, increasing the water wetness. Sharma and Filoco [22] suggested that for some crude oil and polar fractions with large surface density where electrostatic forces dominate, the water wetness is increased, as explained by DLVO theory. The authors also suggested that for some less polar oils where electrostatic forces are suppressed, hydration/hydrophobic forces may dominate, and these hydration/hydrophobic forces have been hypothesized to increase with salinity, producing a less water-wet surface. In core flooding experiments on cores with different wettabilities, including water wet, oil wet, neutral wet and neutral wet toward oil wet, a low-salinity effect was observed for all states, after ageing and flooding with high salinity. The strongest effect was however observed for the water wet core.
6. **Injection brine concentration**
The concentration of injected water affects LSW oil recovery [67-75]. For instance, in sandstone reservoirs, the effects of clay migration and clay swelling should be considered as the brine concentration changes. Khilar and Fogler [76] proposed a critical brine concentration of approximately 0.4 wt% for pure NaCl brines in sandstones and suggested that decreasing the concentration below this value may result in clay destabilization, thereby inducing damage within the formation that may impact the success of LSW oil recovery; however, it is important to note that these authors performed measurements on a fully water-wet brine-saturated sample, whereas other authors [77-79] have reported different results regarding the stability of clay in the presence of different wettability systems. For example, Mungan [78] observed that the presence of crude oil in the core may prevent formation damage by fresh water injection.
Additionally, similar findings were reported by Clementz [80], who noted that formation clay stabilizes in the presence of asphaltenes in crude oil. Several other studies on the effects of brine salinity on oil recovery have been reported over the past few years. For example, Chandrashegaran [81] concluded that an injected water salinity of 0.2 wt% is the optimal concentration for most rock types and scenarios. Morrow and Buckley [82] evidenced a moderate increase in oil recovery during the injection of low-salinity water containing approximately 0.2 –0.5 wt% NaCl.
However, not all of these studies included the effects of the injected water salinity on fine particle migration. Consequently, the factors related to whether fine particle migration and possible formation damage occur during LSW injection are not fully understood. A correlation between fine particle migration and wettability was reported by Alagic and Skauge [83], who observed that fine particle migration did not occur during LSW injection in aged cores, whereas particle migration was observed when unaged water-wet cores were used, which is in agreement with the results reported by Clementz [80] and Mungan [78].
7. **Connate water concentration**
Oil recovery during LSW injection greatly depends on the initial reservoir conditions, particularly the connate water saturation, rock physics and connate water salinity. Recently, Zaeri [84] and Mohammadkhani [85] reported the effect of the connate

water saturation on LSW injection; the authors conducted core flooding experiments using carbonate core plugs and found that the oil recovery during the secondary recovery stage reached a maximum for cores with the highest connate water salinity and the lowest connate water saturation. However, in the tertiary scenario, the highest oil recovery was obtained when both the salinity and the saturation of the connate water were low.

The authors concluded that the salinity of the connate brine plays a substantial role in the performance of LSW injection in carbonate rocks. Shehata and Nasr El-Din [86] investigated the role of reservoir connate water in the performance of LSW in sandstone core plugs through spontaneous imbibition experiments and found that cores saturated with connate water containing divalent cations of $Ca^{2+}$ and $Mg^{2+}$ showed a higher oil recovery than did cores saturated with monovalent cations, such as $Na^{+}$. Thus, the authors concluded that the composition of connate water has a substantial effect on LSW oil recovery. The presence of connate water results in the formation of an intermediate layer between the rock surface and crude oil, which is electrostatically attached to the surface. Therefore, the adsorption of oil onto the rock surface is negligible with no intermediate water layer. This effect can facilitate ion transfer between the imbibing fluid and the rock surface, resulting in effective LSW oil recovery [84,87].

### 1.3. Proposed mechanisms of improving oil recovery with low-salinity water flooding

#### 1.3.1. Fines migration

The first mechanism proposed in the literature to explain the additional oil recovery resulting from low-salinity injection was based on mixed wet clay release [18,88-90]. The experiments were performed on several Berea sandstone cores. The cores were fired and acidized in some tests, and the results showed an insensitivity of salinity in oil recovery. This insensitivity was also reported when a refined oil was used instead of crude oil. Moreover, when the cores were initially 100% saturated with crude oil, salinity had no effect on recovery because the fines were initially immersed in the oil phase. The authors concluded that the presence of potentially mobile fines (clay minerals), initial water saturation and adsorption from crude oil are all necessary to achieve an increase in oil recovery with a decrease in salinity. Tang and Morrow [18] reported a reduction in brine permeability caused by fines migration and confirmed that the presence of potentially mobile fines, such as kaolinite, played a key role in increased oil recovery.

Although several experimental observations have been reported, contradictory results have grown in number as well. First, Larger et al. [36] did not notice any fines migration during numerous low-salinity experiments with additional oil recovery both in reduced and reservoir conditions. Zhang et al. [19] showed no evidence of clay content in the production stream or the oil/brine interface in their experiments. Berg et al. [58] proposed that this assumption is not the main mechanism behind LSW, and no fines migration was observed during increased oil recovery in their experiments, thus indicating that the enhanced recovery from LSW is not caused by fines migration. In addition, the experimental findings of Cissokho et al. [45] indicated a substantial incremental LSW recovery in kaolinite-free cores.

#### 1.3.2. pH effect

Austad et al. [38] proposed that the desorption of organic material from the surface of clays by a local increase in pH at the clay-water interface plays an important role in the low-salinity-enhanced oil recovery process. The suggested chemical mechanism for enhanced oil recovery by LSW was based on three experimental observations:

1. clay must be present in the sandstone,
2. polar components (acidic and/or basic material) must be present in the crude oil,
3. and the formation water must contain active ions such as $Ca^{2+}$.

The clays act as a cation exchanger with a relatively large surface area. Initially, both basic and acidic organic materials are adsorbed onto the clay together with inorganic cations, especially $Ca^{2+}$, from the formation water. A chemical equilibrium is then established at actual reservoir conditions with respect to pH, temperature, pressure, and other factors when the low-saline water invades the porous medium with an ion concentration much lower than that in the formation connate water. When the equilibrium associated with the brine-rock interaction is disturbed, a net desorption of cations, especially $Ca^{2+}$, occurs. To compensate for the loss of cations, protons, $H^{+}$, from the water close to the clay surface adsorb onto the clay, and a substitution of $Ca^{2+}$ by $H^{+}$ occurs. This process creates a local increase in pH close to the clay surface. Chemically, the mechanism can be described by Eq. (1) using $Ca^{2+}$ as the active cation as follows:

$$Clay - Ca^{2+} + H_2O \leftrightharpoons Clay + H^{+} + Ca^{2+} + OH^{-} \quad (1)$$

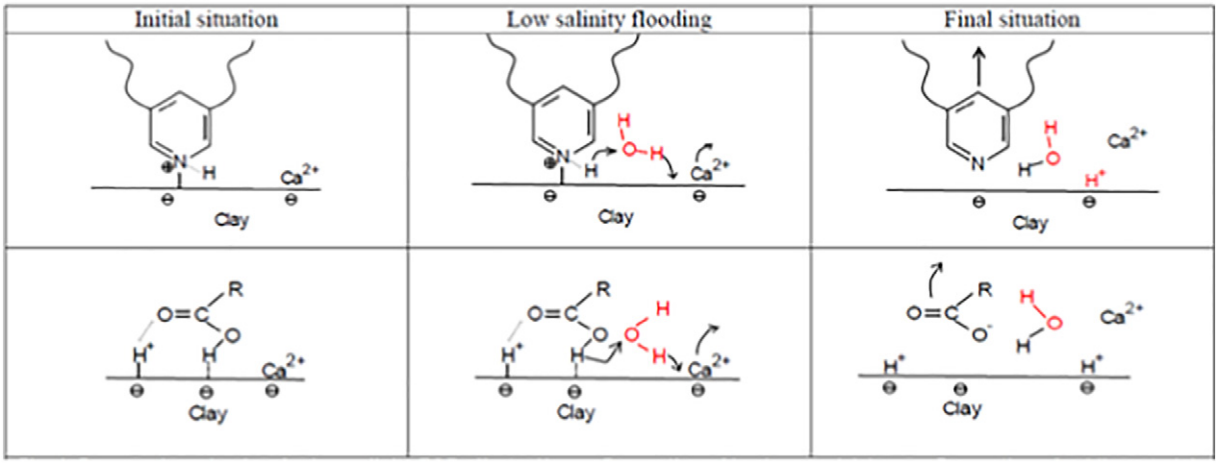



**Fig. 2.** Proposed mechanism for low-salinity EOR effects. Upper: desorption of basic material lower. Lower: desorption of acidic material [38].

The local increase in pH, close to the clay surface, causes reactions between adsorbed basic and acidic material as in an ordinary acid-base proton transfer reaction, as shown by Eqs. (2), (3) and Fig. 2. Both acidic and basic crude oil components are partly desorbed from the surface, changing the wettability toward a more water-wet condition after flooding with LSW [35].

$$Clay - NHR_3^+ + OH^- \leftrightharpoons Clay + R_3N + H_2O \quad (2)$$

$$Clay - RCOOH + OH^- \leftrightharpoons Clay + RCOO^- + H_2O \quad (3)$$

### 1.3.3. Multicomponent Ionic Exchange (MIE)

A mechanism termed multicomponent ionic exchange (MIE) was suggested by Larger et al. [36] (Fig. 3). MIE enables the desorption of both positively and negatively charged organic compounds when low-salinity brine is injected. Their investigations showed that additional oil recoveries occur in the tertiary mode only if the connate brine contains divalent cations ($Ca^{2+}$). Thus, eight adsorption mechanisms for organic compounds are listed in Table 1 to explain this MIE effect.

Studies performed on the magnitude and mechanisms of the adsorption of marine pore water materials onto montmorillonite led to the conclusion that van der Waals interactions, ligand exchange and cation bridging are the dominant adsorption mechanisms of the eight mechanisms proposed by Sposito. According to DLVO theory, high ionic strengths confer low electrostatic repulsion forces, and because the van der Waals attractive forces are significant at high ionic strengths, the particles are allowed to be located close to each other.

Ligand exchange occurs when carboxylate groups of acidic material substitute hydroxyl groups on the surface [91-94]. Cation bridging occurs when a negatively charged surface and functional groups of the organic material are connected by a cation acting as a bridge; this is a weak adsorption mechanism. During the injection of low-salinity brine, two different observations were produced. The first observation was that the presence of divalent cations in the formation brine, especially $Ca^{2+}$, was essential to observing an increase in recovery [95]. The second observation was that the effluents from low-salinity tests showed a strong reduction in the concentration of $Mg^{2+}$, indicating a strong adsorption to the rock matrix and suggesting that the increase in oil recovery was caused by competition between all the ions in the brine for ionic exchange with the rock surface. There are two different mechanisms by which the polar components can adsorb onto the clay. The first is where polar components adsorb onto the clay by multivalent cations and form an organometallic complex. The second is direct adsorption, in which the most labile cations are displaced at the clay surface [45]. Direct adsorption is a bridging mechanism where the negatively charged clay surface and negatively charged molecules in the oil are bridged together by divalent cations [96].

**Table 1**
Mechanism of organic compound adsorption onto minerals [97].

| Mechanisms | Organic functional group involved |
|---|---|
| Cation Exchange | Amino, ring NH, heterocyclic N (aromatic ring) |
| Protonation | Amino, heterocyclic N, carbonyl, carboxylate |
| Anion Exchange | Carboxylate |
| Water Bridging | Amino, carboxylate, carbonyl, alcoholic OH |
| Cation Bridging | Carboxylate, amines, carbonyl, alcoholic OH |
| Ligand Exchange | Carboxylate |
| Hydrogen Bonding | Amino, carbonyl, carboxyl, phenolic OH |
| Van der Waals Interactions | Uncharged organic units |

### 1.3.4. Extension of the electrical double layer

Winsauer and McCardell [99] introduced the concept of ionic double layer conductivity in reservoir rock, and their results showed that excess double layer conductivity is dependent on the particular ions in the electrolyte as well as their concentration.

Alias [98] demonstrated the relation between the electrical double layer and the zeta potential in Fig. 4 as a phenomenon where oppositely charged ions (counterions) are preferentially attracted toward the surface and where ions of the same charge (coions) tend to be repelled.

Ligthelm et al. [37] proposed that wettability modification toward water wetness was the main mechanism of LSW and results from electrical double-layer extension. Knott [100] also provided a theory about a double-layer expansion mechanism in Fig. 5. When a negatively charged clay particle in the porous rock structure of an oil-bearing reservoir is immersed in water, an electrical double layer forms around it. The double layers consist of an inner adsorbed layer of positive ions and an outer diffuse layer of mainly negative ions.

The thickness of the double layers depends on the ion concentration in the surrounding water. Under high-salinity water containing more ions, the double layer is more compact, but when low-salinity water is introduced, the double layer tends to expand, as seen in Fig. 5 (1 and 2). The adsorbed layer of positive ions contains divalent calcium ($Ca^{2+}$) or magnesium ($Mg^{2+}$) ions, which act as tethers between the clay and oil droplets. Injecting reduced-salinity water opens the diffuse layer, enabling monovalent, ions such as sodium ($Na^+$), carried in the injection water, to penetrate the double layer, as shown in Fig. 5 (3). Here, the monovalent ions displace the divalent

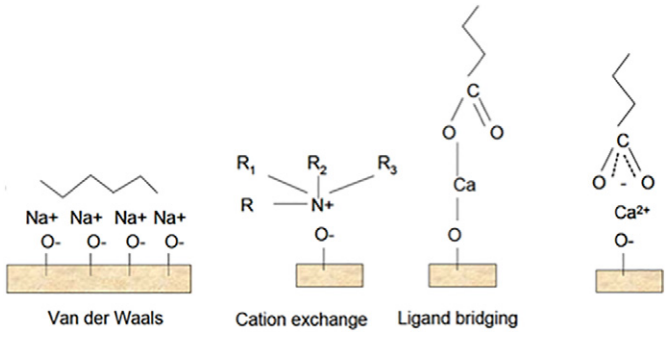



**Fig. 3.** Representation of the diverse adhesion mechanisms occurring between clay surface and crude oil [36].

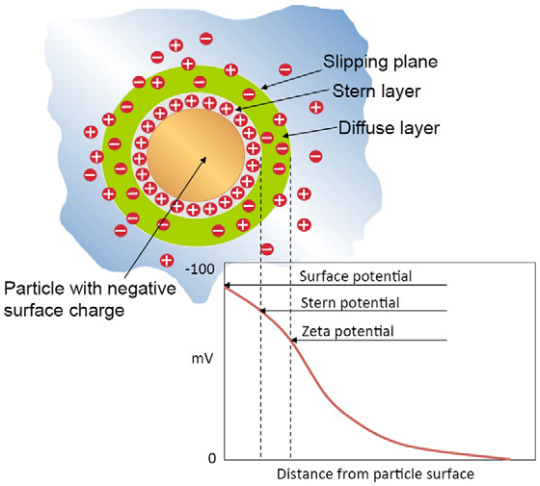



**Fig. 4.** Electrical double layer and zeta potential [98].

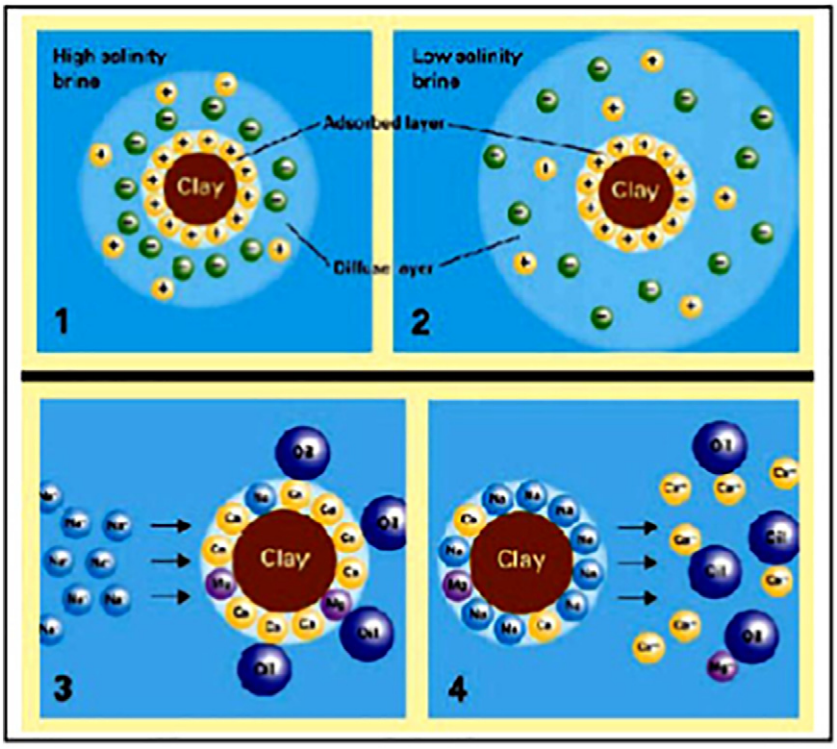



**Fig. 5.** Impact of salinity on electrical double layer [100].

ions, increasing the electrostatic repulsion between clay particles and oil. Once the repulsive forces exceed the binding forces via multivalent cation bridges, the tethers between oil and clay particles are broken, and the oil particles can be desorbed from the clay surfaces. This process changes the wetting state because of the reduction in the rock surface, which is coated with oil and allows the oil to be swept out of the reservoir, as shown in Fig. 5 (4).

Ligthelm et al. [37] made several observations supporting the proposed mechanism. During flooding experiments, after oil production with high-salinity brine containing sodium, calcium and magnesium had stopped, the brine composition was changed to include only sodium chloride with the same ionic strength, and a small increase in oil recovery was observed. The results were associated with the cation exchange mechanism as the pure sodium chloride brine stripped off the divalent cations attached to the rock surface. The brine was then diluted to a 100-times-lower salinity, and a subsequent large increase in recovery was observed. This increase is believed to be related to the expansion of the electrical double layer. The contribution of the cation exchange mechanism was believed to be small compared to the expansion of the electrical double layer.

Nasralla and Nasr-El-Din [101,102] deduced that the expansion of the electrical double layer is a dominant mechanism of oil recovery improvement by LSW. However, a recent molecular study conducted by Mehana and Fahes [103] on double-layer expansion during LSW refuted the double-layer expansion as a mechanism during LSW.

### 1.3.5. Wettability alteration

The wettability of any rock can be reversed toward being oil wet to release oil capillary trapping or toward being water wet to enhance water imbibition and oil counter-current production.

Cassie and Baxter [104], Buckley et al. [105], and Chen et al. [106] indicated that the water film separating crude oil from the mineral surface is not always stable and that the original water wetness of the rock can be altered by destabilizing the water film. Therefore, to destabilize and rupture the water film, the disjoining pressure must be overcome by altering the wettability.

Zhang et al. [107] examined the role of divalent cations, namely, calcium and magnesium, and sulphate ions on wettability alteration in carbonates. The results revealed that divalent anions were found to have a stronger effect on wettability alteration than their monovalent counterparts such as chlorides. The ratio of $Ca^{2+}/SO_4^{2-}$ was found to have a more pronounced effect on wettability alteration and hence recovery than individual anions.

Mohammed and Babadagli [108] , Saikia et al. [109] and Ding and Rahman [110] provided a comprehensive review of the various methods for wettability alteration during LSW.

Fig. 6 shows an overview of the proposed low-salinity recovery mechanisms and how they contribute to oil recovery.

### 1.3.6. Osmosis

Buckley [111] hypothesized that osmosis may be a mechanism for enhanced oil recovery during LSW whereby the clays separating brines with different salinities are able to create an osmotic pressure that can enhance the water drive. Later, the studies by Yousef and Ayirala [67], Callegaro et al. [112], Rotondi et al. [113], Fredriksen et al. [114], Sandengen et al. [115], Fredriksen et al. [116], and Pollen and Berg [117], supported these findings, providing evidence of osmotic water transport and oil mobilization under various wettability conditions.

### 1.3.7. Salting effect

According to Austad [118], salting in implies that the polar components are more soluble in water when the ionic strength of the water is low, whereas salting out means that polar components are less soluble in water when the ionic strength of the water is high.

RezaeiDoust et al. [119] hypothesized about salting as a mechanism by performing adsorption and desorption studies of quinoline

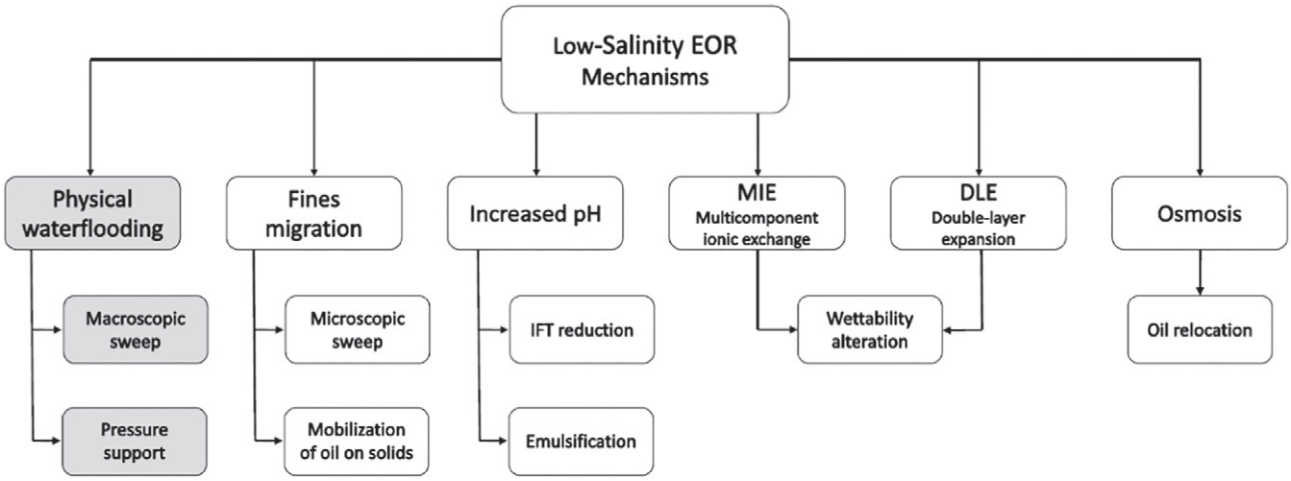



**Fig. 6.** Overview of some proposed low-salinity recovery mechanisms and how they contribute to oil recovery [117].

onto kaolinite at room temperature, and their assumption was that low-salinity effects are linked to the improved water wetness of the clay.

There have been very few studies supporting the salting in mechanism in relation to LSW. Austad et al. [38], Nasralla and Nasr-El-Din [102], and Kakati and Sangwai [120], argue that there is a need for additional experiments to validate the theory of action for this effect.

## 2. Laboratory investigations and field analysis of low-salinity water flooding

Studies have been conducted [6,23,34,113,121-124] on LSW, and promising results have been reported from laboratory and field applications. Reducing the overall salinity, especially the concentration of divalent cations in the injected water, has been reported to significantly improve oil recovery.

Yang et al. [125] investigated wettability alteration during LSW and how wettability is affected by the concentration of divalent cations. In their study, experiments on spontaneous imbibition, zeta potential ($\zeta$), and the static adsorption/desorption of benzoic acid (BA) onto crushed Berea sandstone were conducted. The results provide a better understanding of the underlying mechanisms of LSW injection.

The spontaneous imbibition results showed that the initial wettability of the core system was dominantly controlled by the initial concentration of $Ca^{2+}$ rather than $Na^{+}$ in brine. The concentration of NaCl in initial water had minimal effect on the initial wettability. Moreover, the authors found that reducing the salinity of the imbibing brine influenced the oil recovery of cores that were aged in $CaCl_2$ brine, whereas no considerable improvement in oil recovery by low-salinity water was observed for cores aged in NaCl brine.

**Table 2**
Core properties of the rock used in AlQuraishi et al. [126] .

| Sample | Pore vol. ($cm^3$) | $\phi$ | k |
|---|---|---|---|
| | | % | md |
| **Carbonate** | 9.73 | 17.9 | 205.81 |
| **Sandstone SS1** | 18.84 | 23.03 | 314.79 |
| **Sandstone SS2-1** | 16.85 | 22.42 | 77.75 |
| **Sandstone SS2-2** | 17.42 | 22.58 | 87.23 |

Yang et al. [125] also found that decreasing the concentration of either $CaCl_2$ or NaCl brine can make the oil/brine and brine/rock interfaces less positively charged or even more negatively charged based on $\zeta$ potential measurements. This is caused by electrostatic repulsive forces between the oil/brine and brine/rock interfaces. Their study suggests that the anionic groups of organic acid from crude oil, such as carboxylate, adsorb onto negatively charged mineral surfaces mainly through calcium bridges instead of van der Waals forces or sodium bridges and that reducing salinity can increase the electrostatic repulsive forces between mineral surfaces and carboxylate groups. As a result, calcium bridges break, wettability is altered, and recovery is enhanced.

AlQuraishi et al. [126] investigated the effects of LSW for both sandstone and carbonate formations in Saudi Arabian reservoirs to explore the possible mechanisms behind the enhanced oil recovery. In their study, synthesized formation brine at 20% salinity and Saudi medium crude oil were used as formation fluids (the core and fluid properties are listed in Tables 2 and 3. Seawater collected from the Arabian Gulf and different dilutions were used as displacing fluids in tertiary and secondary flooding modes. Their results indicated the potential of LSW for both carbonate and sandstone samples in both tertiary and secondary flooding modes. In addition, interfacial tension (IFT), zeta potential and contact angle measurements were performed to investigate the possible recovery mechanisms. No significant reductions in the IFT of oleic and brines were observed with

**Table 3**
Properties of formation water in AlQuraishi et al. [126] .

| Parameters | Seawater | Formation water |
|---|---|---|
| **pH** | 7.1 | 7.37 |
| **Density, gm/cc** | 1.0256 | 1.038 |
| **Viscosity, cp** | 1.08 | 1.031 |
| **Turbidity, NTU** | 2.21 | – |
| **Total Alkalinity (as $CaCO_3$ )** | 174 | – |
| **Bicarbonate, mg/L** | 212 | – |
| **Calcium, mg/L** | 766 | 28,035.05 |
| **Magnesium, mg/L** | 2648 | 5241.18 |
| **Sodium, mg/L** | 22,353 | 51,809.52 |
| **Potassium, mg/L** | 810 | – |
| **Chloride, mg/L** | 36,585 | 112,365.3 |
| **Sulphate, mg/L** | **5015** | – |
| **Nitrate, mg/L** | 37 | – |
| **Fluoride, mg/L** | 2.19 | – |
| **TDS, mg/L** | 68,358 | 197,451 |

changes in salinity. The zeta potential and contact angle measurements confirmed that wettability alteration was the main mechanism for improving oil recovery in both carbonate and sandstone samples. The authors noticed a shift in wettability from intermediate wetting conditions to preferentially water-wet conditions in the presence of sea water diluted ten-fold for both rock types.

Multi-ion exchange with increasing sulphate concentration in injected water and the sulphate generated in situ caused by anhydrite dissolution were two major mechanisms that resulted in substantial improvements in oil recovery in carbonates by LSW. The recovery mechanism in sandstones was attributed to fines migration and the release of existing oil and mixed wet kaolinite clay particles exposing the underlying water-wet surface. The petrophysical properties of the rocks used in this study are listed in Table 2. The authors conducted a core flooding test in secondary and tertiary modes at reservoir conditions of 60 °C and 2000 psi. The samples were cleaned, dried, and saturated using the appropriate techniques to restore the reservoir conditions. To calculate the saturated pore volume and quality of the saturation, the weight of the dry and saturated sample was measured. The saturated sample was placed in a core holder in which reservoir conditions were applied.

The core sample was flooded with several pore volumes of synthetic formation brine, and the steady-state flow rate and pressure drop were used to calculate the sample absolute permeability using Darcy's law. The fully brine-saturated core was then flooded with crude oil at 1 $cm^3$/min. Flooding was continued until water production ceased, and the irreducible water saturation ($S_{wirr}$) was determined through a volumetric material balance. The steady-state pressure drop was measured to calculate the end-point relative permeability to oil using Darcy's law. The core sample was flooded with sea water at 1 $cm^3$/min. The secondary flooding process continued until oil production ceased, and effluents were collected in graduated tubes mounted in a fraction collector.

The injected brine volume and the volumes of oil and water produced were continuously recorded to construct the oil recovery curve and to determine the final fluid saturations. Tertiary flooding was started at the point of residual oil saturation with twice-diluted seawater followed by ten-times-diluted sea water, while secondary flooding was conducted by injecting ten-times-diluted sea water. The results of the study indicate that salinity reduction promoted an IFT drop of 2.5 mN m when formation brine was replaced with sea water. Fig. 7 presents the IFT measurements in the oleic phase with different brines as a function of time. A further drop of 2.6 IFT units

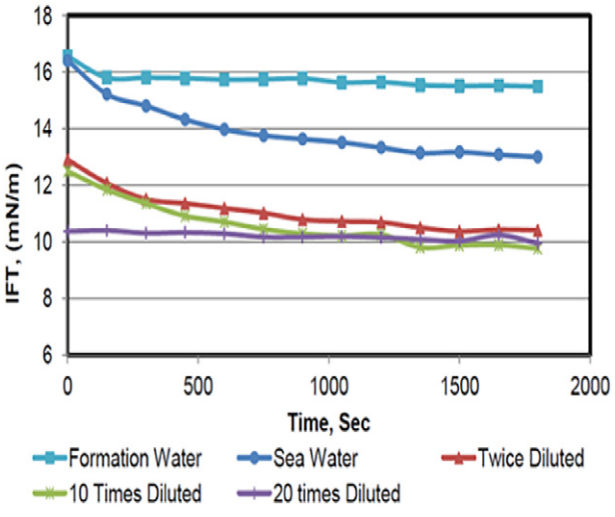



**Fig. 7.** IFT measurements for different brines [126].

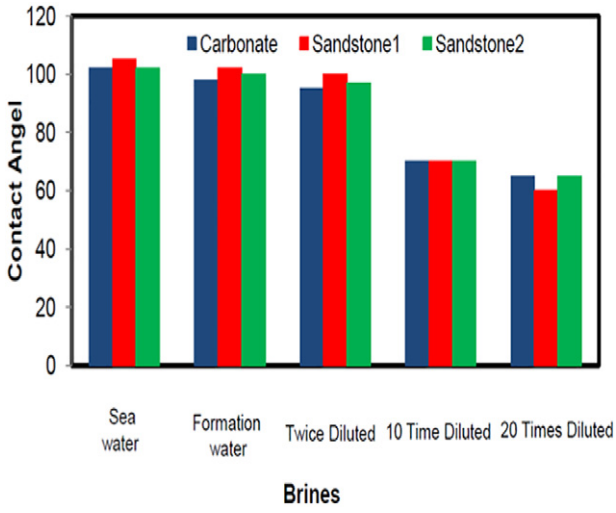



**Fig. 8.** Contact angle measurements of sandstone and carbonate samples [126].

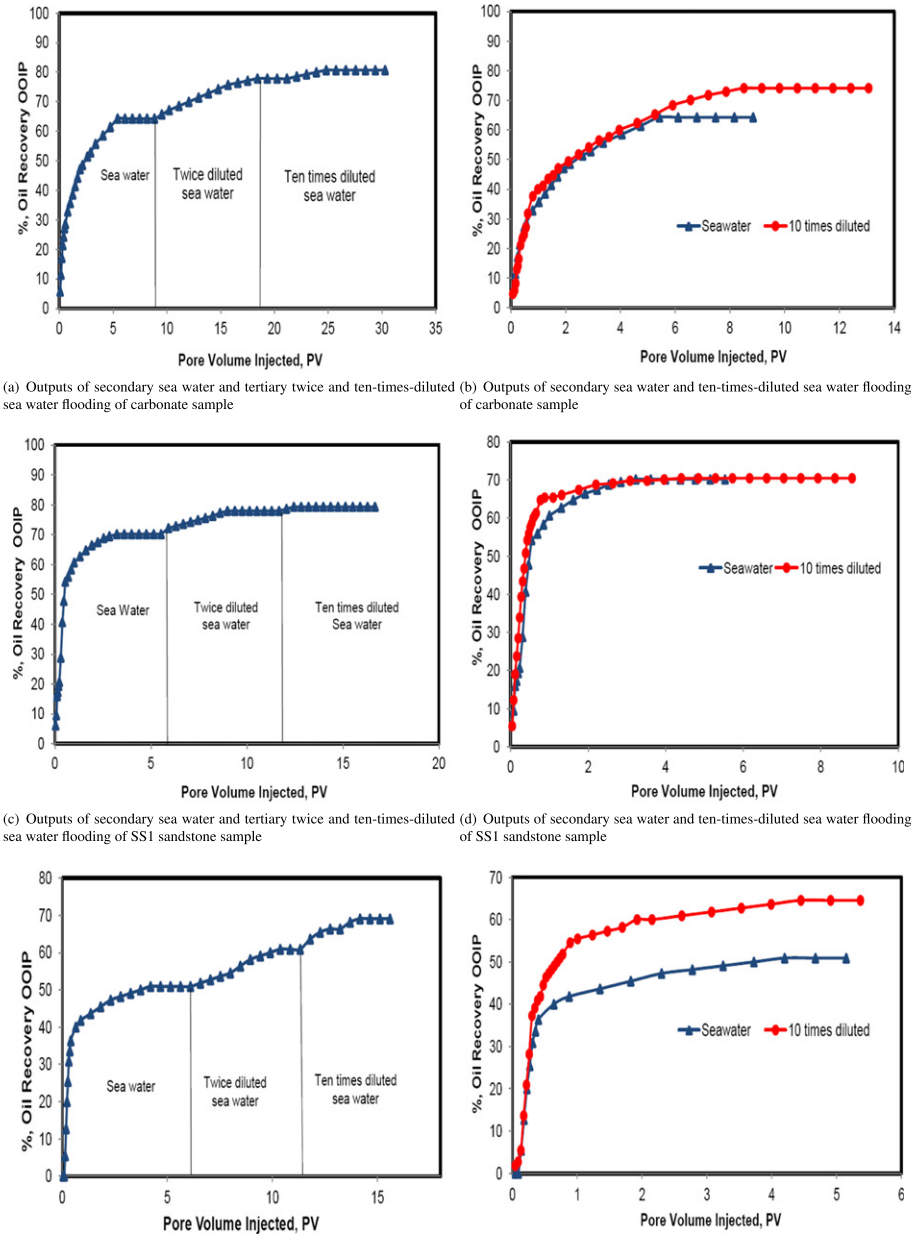
was obtained when twice-diluted seawater was used in an aqueous phase, but further ten- and twenty-fold salinity drops indicated minor IFT effects. The authors concluded that the IFT drop caused by salinity reduction did not contribute to oil recovery.

Fig. 8 summarizes the contact angle measurements for substrates representing the three rock samples in different brines. The carbonate sample showed intermediate wetting characteristics in the presence of formation brine with a contact angle of 102°. This finding is explained by the existence of divalent cations in the formation brine resulting in more positive charges on the calcite surface, which attract the negative components of crude [127].

Contact angle studies indicated that reducing the seawater salinity by a factor of two does not result in a change in wettability. However, further dilutions resulting in brine salinities of approximately 5000 ppm showed significant wettability changes. Surface charge alteration is one of the key mechanisms proposed for wettability shifts in carbonates [128]. As seawater is injected, sulphate is adsorbed to the rock surface, decreasing the positive charge density and leading to the release of negatively charged carboxylic organic materials, which shifts the wettability toward more water-wet conditions. The same measurements were conducted for sandstone samples, denoted as $SS_1$ and $SS_2$, and the results are presented in Fig. 9.

The formation brine and seawater samples were both in a state of intermediate wetting. A slight change in contact angle was observed for twice-diluted seawater, but as the salinity dropped further by diluting sea water ten and twenty times, the rock wettability shifted to preferentially water-wet conditions. Different mechanisms have been proposed for sandstone wettability alteration, including MIE [50]. The authors note that exposure to low-salinity brine can result in a double-layer expansion that promotes the desorption of oil-bearing divalent ions from the rock surface. Clay dispersion, when induced by low-salinity brine, was also proposed as a contributing factor.

AlQuraishi et al. [126] conducted Zeta potential measurements to determine and verify the potential mechanisms behind wettability alteration. The authors measured the zeta potential of suspended particles in various dilutions of seawater at 60 °C. Fig. 10 shows the results of zeta potential measurements for different rock types and various brine salinities. The figure indicates that changing the salinity and ionic strength of seawater increased the negative surface charge for all rock types with higher negative values for the carbonate sample. This substantial effect was seen with 10-times-diluted seawater and correlates well with the contact angle measurements.




(a) Outputs of secondary sea water and tertiary twice and ten-times-diluted sea water flooding of carbonate sample

(b) Outputs of secondary sea water and ten-times-diluted sea water flooding of carbonate sample

(c) Outputs of secondary sea water and tertiary twice and ten-times-diluted sea water flooding of SS1 sandstone sample

(d) Outputs of secondary sea water and ten-times-diluted sea water flooding of SS1 sandstone sample

(e) Outputs of secondary sea water and tertiary twice and ten-times-diluted sea water flooding of SS2-1 sandstone sample

(f) Outputs of secondary sea water and ten-times-diluted sea water flooding of SS2 core samples

**Fig. 9.** Core flooding results for sandstone and carbonate rocks with different salinity for reused cores [126].

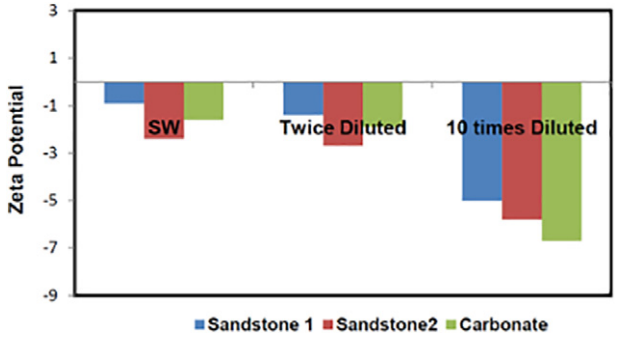



**Fig. 10.** Zeta potential measurements of sandstone and carbonate samples [126].

AlQuraishi et al. [126] concluded that LSW recovered more oil compared to seawater. From their findings, the increase in recovery was higher for 10-times-diluted seawater followed by twice-diluted seawater. The original seawater gave the lowest oil recovery for both secondary and tertiary recovery in sandstone and carbonate cores, as shown in Fig. 9. This result confirmed that injecting diluted seawater results in a higher recovery than injecting non-diluted seawater, and the proposed mechanism was wettability alteration caused by cationic exchange.

Nasralla et al. [24] conducted a study on the efficiency of oil recovery by LSW in sandstone reservoirs. In their study, they conducted core flood experiments using eight cores, deionized water and three different brines with salinities ranging from 5000 to 174,000 ppm. These salinities were selected to cover the full salinity spectrum for fields in the Middle East. The rock and fluid properties used in this study are listed in Table 4. All the experiments were conducted

**Table 4**
Mineral composition of the Berea sandstone cores used [24].

| Mineral | Concentration, wt% |
|---|---|
| Quartz | 86 |
| Dolomite | 1 |
| Calcite | 2 |
| Feldspar | 3 |
| Kaolinite | 5 |
| Ilite | 1 |
| Chlorite | 2 |

**Table 5**
Chemical composition of brines [24] .

| Ions | Formation brine | Seawater | Aquifer water |
|---|---|---|---|
| $Na^+$ | 54,400 | 16,877 | 1504 |
| $Ca^{2+}$ | 10,610 | 664 | 392 |
| $Mg^{2+}$ | 1610 | 2279 | 66 |
| $Sr^{2+}$ | 0 | 0 | 5 |
| $Cl^-$ | 107,000 | 31,107 | 2577 |
| $HCO_3^-$ | 176 | 193 | 192 |
| $SO_4^{2-}$ | 370 | 3560 | 700 |
| TDS, mg/L | 174,156 | 54,680 | 5436 |

using 5- to 6-inch-long cores from Berea sandstone outcrops with a porosity and permeability between 17.9% and 19.3% and 67 md to 95 md, respectively. Two types of crude oil A and B with different viscosities 7.21 cp (A) and 20.4 cp for crude (B) were used, and to mimic reservoir conditions, the experiments were conducted at 100 °C.

Four cores were flooded with less viscous oil at 7.21 cp (A) to determine the effect of viscosity on oil recovery, and the other four cores were flooded with crude (B) at 20.4 cp. Fig. 11 summarizes the results of the core flooding experiments.

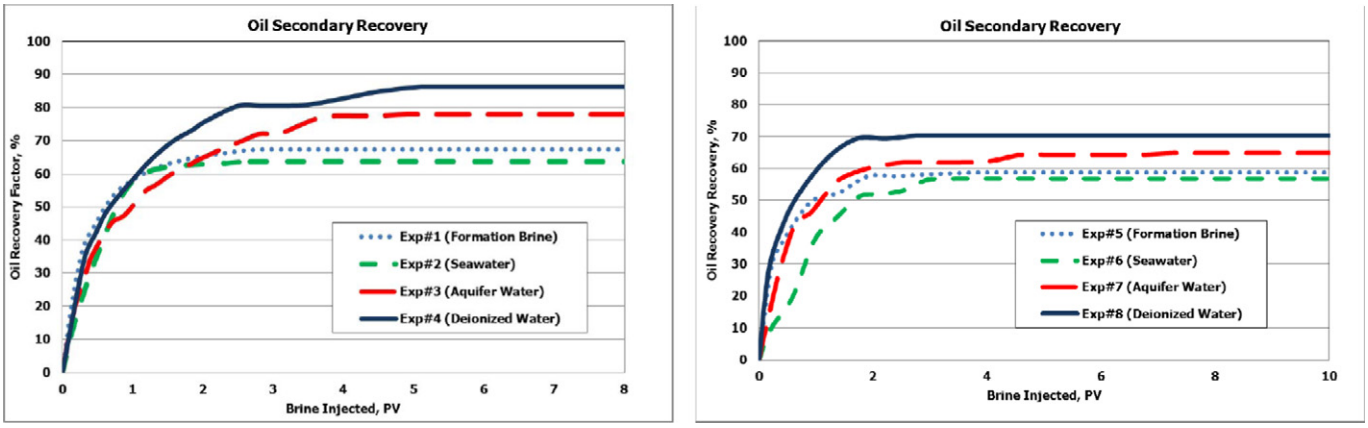
Formation water (FW), seawater (SW), aquifer water (AQW) and deionized water (DIW) were the synthetic brines used in Nasralla et al. [24] study, (Table 5). Deionized water alone recovered more oil compared to the other brines. No significant difference in oil recovery was observed when the injections of formation and seawater were compared. The authors concluded that the salinity of water has a significant impact on oil recovery in sandstone reservoirs at high temperature.

Low-salinity water recovered more oil in the secondary mode than higher salinity water. However, in the tertiary mode, no oil was recovered, and therefore, cation exchange was proposed as the major mechanism responsible for improving the oil recovery. Cation exchange led to a reduction in electrostatic attractive forces between oil and rock surface charges, resulting in a change in wettability. The authors proposed that formation damage may occur during low-salinity water injection and that damage is correlated with oil composition. An effluent analysis using ICP confirmed the reduction in ion concentrations after the injection of low-salinity water, as shown in Fig. 12.

## 3. Field analysis of low-salinity water flooding

The potential of LSW to increase oil recovery has been verified through some field applications [6,23,34,113,121-124,129]. LSW has been recently applied in the Omar oil field in Syria [35]. The results indicate that a recovery increment of 10–15 % OOIP could be obtained. This result was attributed to the change in wettability from oil wet to water wet. The change in wettability was evidenced by an observation of a “dual-step” in the water cut, which is a known indicator of wettability alteration, as shown in Fig. 13. The figure presents the saturation profile between a typical injector and producer well for an originally oil-wet system. As a result of wettability alteration caused by the injection of low-salinity water, the microscopic displacement efficiency was improved. This phenomenon was verified by observing a second oil bank (shock front) in the production. Delayed water breakthrough because of oil banking ahead of a low-salinity shock front caused by the accumulation of desorbed oil lead to a reduction in residual oil saturation behind the flooded zone.

The British Petroleum company, which is known as a pioneer in LSW, conducted extensive studies in the early twenty-first century [130]. These studies were followed by an extensive field application conducted at Endicott field (the north slope of Alaska). This trial was implemented in a single reservoir zone with the injector and producer with a swell spacing of 1040 ft. The producer was monitored for changes in water cut and ionic water composition after the injection of low-salinity water, and data from the wellhead water cut meter and test separator confirmed a decrease in water cut from 95% to 92%. In addition, 10% of the additional oil was recovered from the zone that was swept with low-salinity water, and in the pilot area, a




(a) Secondary recovery for experiments on crude A

(b) Secondary recovery for experiments on crude B

**Fig. 11.** Comparison of secondary oil recovery on crude (A and B); [24].

**Table 6**
Summary of previous studies on low-salinity water flooding.

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Bernard [15] | Sandstone (Berea) | Ambient conditions | 100–15,000 | 15,000 | – Wettability alteration | 1. If the fresh waterflood does not develop a high-pressure drop, no additional oil is produced. 2. A higher recovery is achieved in water-sensitive cores with a fresh waterflood than with brine largely because hydratable clays are present. 3. A decrease in salinity causes an increase in oil recovery. |
| Jadhunaiidan [135] | Sandstone (Berea) | Ambient conditions at 26, 50 and 80 °C | 200–18,000 | 18,814 | – Wettability alteration | 1. Temperature and initial water saturation are dominant variables with respect to wettability. 2. Intermediately wet systems show the lowest residual oil saturation and the greatest amount of oil recovered by water flooding. |
| Yildiz and Morrow [39] | Sandstone (Berea) | Ambient conditions at 110 °C | 6370 | 63,700 | – Wettability alteration | 1. Rock-brine interactions are responsible for the wettability changes. 2. Oil recovery is dependent on the initial and injected brine composition. |
| Tang and Morrow [136] | Sandstone (Berea) | Ambient pressure at 75 °C | <8000 | 24,168 | – Wettability alteration | 1. The transition toward a more water-wet system occurs when the temperature is increased during the course of dispersement, although the wettability changes with thermodynamic conditions in the reservoir. |
| Tang and Morrow [18] | Sandstone (Berea) | 2000 psi and 55 °C | 36,960 | 15,150 | – Fines mobilization. – Limited release of mixed wet particles. | 1. Recovery of crude oil at a high water cut could be initiated or curtailed based on the composition of the injection brine. 2. Changes in oil recovery with salinity can be partly ascribed to the effect of brine chemistry on the forces needed to strip these particles from the pore walls during the course of waterflooding. |
| McGuire et al. [34] | Sandstone (Berea) | Ambient conditions at 40 °C | 1500 | 15,000 | – Saponification | 1. Low-salinity water flooding appears to be effective at salinity levels of approximately 5000 ppm TDS or less. 2. The EOR mechanisms underlying low-salinity water flooding appear to be similar to those of alkaline flooding, i.e. the, generation of surfactants, changes in wettability, and reductions in the interfacial tension; in addition, the detachment of clay particles may also be involved. |
| Lager et al. [95] | Sandstone | Ambient and Reservoir Conditions | 1550 | 20,000 | – Cation exchange | 1. Cation-exchange explains why low-salinity water flooding is not effective when a core is acidized and fired as the cation exchange capacity of the clay minerals is destroyed. 2. Cation-exchange explains why low-salinity water injection has no effect on mineral oil, as no polar compounds are present to strongly interact with the clay minerals. 3. Cation exchange explains why low-salinity water flooding is not effective on carbonate reservoirs. |
| Zhang and Morrow [46] | Sandstone (Berea) | Ambient conditions | Not mentioned | Not mentioned | – Increased pH – Saponification | 1. The properties of sandstone influence oil recovery via the injection of low-salinity water. 2. Effluent pH influences oil recovery. |
| Zhang et al. [19] | Sandstone | Ambient conditions at 60 °C | 1479 | 29,690 | – Wettability alteration – Cation exchange | 1. The effluent pH is clearly dependent on the crude oil and its role in the crude oil/brine/rock interactions, but there was no obvious relationship between effluent pH and oil recovery 2. Additional recovery is obtained via the addition of divalent ions to the injection brine. 3. For mixed wet cores, there was little or no oil recovery as a result of injection of low-salinity brine. |
| Loahardjo et al. [137] | Sandstone | Ambient conditions at 60 °C | <5000 | 35,000 | – Wettability Alteration – Cation exchange | 1. Low-salinity water flooding changes core properties during several flood cycles. |
| Seccombe et al. [138] | Carbonates | Ambient and Reservoir conditions | 3983 | 54,720 | – Multicomponent Ion Exchange – Expansion of the electrical double layer | 1. A 40% low-salinity water flooding is expected to be fully effective based on coreflood studies, single-well chemical tracer tests in multiple wells, numerical simulations and geochemical modelling. |

**Table 6** (*continued*)

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Lebedeva et al. [48] | Sandstone (Tensleep) | Ambient Conditions | 1316.3 | 38,651 | – Cation exchange | 1. The application of DLVO (Derjaguin-Landau-Verwey-Overbeek) theory at the salinity seen in most reservoirs is questionable because of the very high concentrations of the brine. |
| Soraya et al. [139] | Sandstone | Ambient conditions at 90 °C | 1170 | 58,320 | – Multicomponent ion exchange – Increase in pH – Influence of temperature | 1. The multicomponent ion exchange proposed by Larger et al. [95] , can be used for screening different types of adsorption mechanisms of organic compounds on mineral surfaces and to explain how salinity can influence oil/rock interactions. 2. There was no direct relationship between the pH of the effluent and additional oil recovery. 3. Low-salinity injection is sensitive to initial wettability. |
| Ligthelm et al. [37] | Sandstone (Berea) | Ambient Conditions | 100 times diluted Dagang brine | 240,000 | – Wettability altertaion toward increased water-wet conditions. | 1. Designer waterflooding in mixed wet/oil wet sandstones causes wettability modification toward an increased water-wet state and in abscence of an efficient water/oil gravity drainage process, application on the reservoir scale may yield an increased displacement sweep efficiency of several magnitudes. |
| RezaiDoust et al. [119] | Sandstone and Carbonates | High pressure and temperature $> 90^{\circ}C$ | <5000 | 25,000 | – Wettability alteration – Salting out effect – Multicomponent Ion Exchange | 1. For carbonates, salinity water is able to improve water wetness at high temperature. 2. For sandstones, improved water wetness is associated with the presence of clay materials. 3. The adsorption strength of organic materials in both carbonates and sandstones is attached to the rock. 4. The MIE mechanism for low-salinity flooding in sandstones only occurs under low salinity conditions. 5. The MIE in carbonates is dependent on the ions $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$ |
| Lee et al. [140] | Clay | Not mentioned | <4000 | Not mentioned | – Expansion of the electrical double layer | 1. Expansion of the double layer supports the theory presented by Lager et al. [95] . |
| Austad et al. [38] | Sandstone | Ambient conditions at 40°C | Not mentioned | Not mentioned | – Wettability alteration toward increased water wetness – Cation Exchange | 1. At low water-wet conditions, a substantail increase in oil recovery of 75% by low-salinity water flooding can be obtained in the laboratory if the core preparation is optimized. 2. Cation exchange is an important parameter for low-salinity effects. |
| Sorbie and Collins [141] | Pore-Scale Modelling | Not mentioned | Not mentioned | Not mentioned | – Wettability alteration toward increased water wetness. | 1. The wetting change in the oil wet pores from some degree of oil wetness to a more water-wet state may be affected by any of the precise surface chemistry mechanisms that may occur. |
| Vledder et al. [35] | Ambient contions | | 2200 | 90,000 | – Wettability alteration | A change in wettability leads to a significant increase in recovery of the STOIIP. |
| Alotaibi et al. [142] | Carbonates | Ambient temperature at 1000 psi and 500 psi | 5436 | 54,000 | – Wettability Alteration | 1. The effect of pressure on wettability is not significant. 2. There is a lower contact angle for acquifer water (TDS 5436 ppm) than formation water (TDS 54,000 ppm). |
| Berg et al. [58] | Montmorillonite clay | Ambient Conditions | 2000 | 25,950 | – Wettability Alteration | 1. Experiments were not specific enough to determine whether the actual weakening of the adhesion forces is caused by the double-layer expansion or the ion exchange reactions. 2. Interfacial tension, fines migration and the selective plugging of water-bearing pores using clay swelling are not relevant mechanisms for the low-salinity water flooding effect. 3. Oil is released under very low salinity. |
| Cissokho et al. [45] | Clayey Sandstone | Ambient conditions at 90 °C, 60 °C and 35 °C | 2500 | 50,000 | – Increase in temperature – Cation exchange | 1. Temperature has a significant effect on oil recovery, and the recovery occurs even if no divalent ions are present in the low-salinity brine. 2. Experimental results show that additional oil recovery can be obtained without the presence of kaolinite as proposed by Tang and Morrow [18] . |

(*continued on next page*)

**Table 6** (*continued*)

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Wang and Alvarado [143] | Sandstone | 1000 psi and 30 °C | 5749.1 | 57,491 | – Interfacial effect through analysis of capillary hysteresis. – Wettability alteration | 1. The low-salinity effect can still act in the abscence of wettability alteration. 2. At low temperatures, low-salinity brine suppresses capillary hysteresis. |
| Morrow [82] | Sandstone (Berea) | Ambient conditions | <5000 | 24,168 | – Cation exchange and wettability alteration | 1. Significant clay fraction 2. Presence of connate water 3. Exposure to crude oil to create mixed-wet conditions |
| Yousef et al. [50] | Carbonates (Chalk) | 1804 psi and 212 °F | Twice, 10, 20, 100-times-diluted formation water | 213,000 | – wettability alteration – Significant pressure drops were related to fine particle migration. | 1. Approximately 7–8.5% additional oil recovery for twice-diluted water. 2. 10 times diluted 9–10% additional oil. 3. 20 times diluted 1–1.6%. 4. 20 times diluted 1–1.6%. 5. Tertiary oil was obtained after 0.5–0.7 PV. 6. No noticeable IFT reduction; hence, LSW has no effect on IFT reductions. |
| Nasralla et al. [24] | Sandstone (Berea) | 500 psi and 100°C | 5000–174,000 | 174,156 | – Cation exchange resulting from wettability alteration. – Reduction of electrostatic forces between oil and rock. | 1. Additional 22% in the secondary mode but no recovery in tertiary mode. 2. Recommend LSW for secondary flooding injection. |
| Li [144] | Sandstone (Berea) | Room temperature and pressure | 1780 | 33,540 | – Increased pH – and reduced IFT similar to alkaline flooding. | 1. In either secondary or tertiary oil recovery, the EOR associated with the injection of low-salinity water is obtained under a negative pressure gradient higher than that during the brine injection at the same flow velocity, as the water permeability is reduced because of the blockage of pore networks by swelling clay aggregates or migrating clay particles and crystals. 2. For the injection of low-salinity water, the EOR is strongly dependent on flow velocity and flow acceleration. |
| Alotaibi et al. [145] | Sandstone (Scioto and Berea) | 2000 psi and Temperatures from (50 °C, 90 °C and 132.2 °C) | 5,436 | 174,156 | – Wettability Alteration | 1. For Berea Sandstone, the interfacial energies of solid/fluid and fluid/fluid interfaces are affected by different ion strength solutions, and as such, the wettability and contact angle are altered. 2. For Scioto sandstone rocks, the wettability was not affected by low-salinity water. |
| Hassenkam et al. [146] | Sandstone | Ambient Conditions | 1400 | 36,500 | – Wettability alteration to a more water wet system. – Expansion of the double layer | 1. The pH of the solution did not play a critical role in the low-salinity effect. 2. The response to changes in salinity is not uniform. |
| Sandengen et al. [62] | Sandstone | ~20 bar and 124 °C | 1741 | 40,075 | – Wettability alteration to a more oil wet system because of ion exchange | 1. Experimental core flooding shows that the introduction of low-salinity water yields an end to oil production as a result of capillary end effects and a significant change in the capillary pressure curve that parallels the wettability alteration toward a more oil-wet system. |
| Suijkerbuijk et al.(2012)[147] | Sandstone (Berea) | Ambient conditions at 60°C | 1,681 | 237,858 | – Wettability alteration | 1. Increasing the concetration of divalent cations in the formation brine makes the crude/oil/brine/rock system oil wet. 2. When the imbibing phase was either higher or lower in salinity than the formation brine, there was an increase in oil recovery. |
| Fjelde et al. [63] | Sandstone (Berea) | 725 psi and 80°C | Prepared by diluting FW 100 times using distilled water | 105,096 | – Low-salinity water altered the wetting state of the rock. – Cation exchange. | 1. Oil was produced over much longer periods in LSW. 2. Estimated permeability and capillary curves indicated that the rock was water wet in the high-salinity floods and mixed wet in the low-salinity floods. |
| Zahid et al. [148] | Carbonates (Chalk) | Ambient conditions and at 90 °C | 20-times-diluted formation water | 213,734 | – Fine particle migration – Dissolution of the rock material – Wettability alteration based on contact angle measurements | 1. No oil recovery under ambient conditions 2. Increased pressure drops detected over the core plugs 3. At 90 °C, more oil was recovered. 4. Pressure drops were attributed to fine particle migration. 5. Substitution reactions seem to not be a mechanism that controls oil recovery in chalk. |

**Table 6** (*continued*)

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Romanuka et al. [49] | Carbonates | Ambient conditions at 85 °C | <5000 | 230,000 | – Wettability alteration | 1. Oil recovery for carbonates can be increased by lowering the ionic strength of the brine. 2. Information on water and oil relative permeability curves is vital before and after wettability alteration for determining the benefit of low-salinity waterflooding on a field scale. 3. Conditions under which wettability alteration takes place are not identified. |
| Mahani et al. [149] | Sandstone | Ambient conditions | 6487.5 | 25,950 | – Wettability alteration toward a more water-wet state. | 1. The kinetics of wettability change are slow, and the time scales observed were approximately 10–20 times longer than expected by diffusion only. |
| Suijkerbuijk et al. [150] | Sandstone | Ambient Conditions | Not mentioned | Not mentioned | – Wettability alteration – Expansion of the double layer | 1. Multicomponent ion exchange is not an economically viable mechanism behind low-salinity water flooding because it occurs at the retardation front, which requires several magnitudes of the injection of low salinity brine to result in a significant production. 2. Low-salinity water flooding leads to wettability alteration toward a more water-wet system; however, it requires a longer time scale. |
| Nasralla and Nasr-El-Din [102] | Sandstone (Berea) | Ambient conditions at 212 °F | 5000 | 174,156 | – Expansion of the double layer – Salt in effect | 1. The behavior of the rock wettability versus the brine salinity and pH was correlated to the change in the double layer thickness based on the $\zeta$–potential results. 2. The high-salinity seawater resulted in an intermediate-wet mica surface, whereas 10% AQ and 5000 mg/L NaCl conditions made the mica surface water wet, which demsostrates the effect of water salinity on wettability alteration and hence the potential for oil recovery improvement. |
| Xie et al. [151] | Core plugs extracted from the Chang-8 formation of the ChangQing Oilfield | Ambient Conditions at 65 °C | 2777 | 58,430 | – Expansion of the double layer. | 1. Ionstuningwater flooding showed a high potential to improve oil recovery in both secondary and tertiary injection modes for low-permeability reservoirs in the ChangQing oilfield. 2. Multi-component might be one of the mechanisms in recovering additional oil. |
| Bartels et al. [152] | Micro-models with active clays as a model system for sandstone. | Ambient Conditions | 6393 | 25,574 | – Wettability alteration | 1. Low-salinity effect is not driven by a change in interracial tension. 2. The role of osmosis is not the primary mechanism behind the occurrence of the low salinity effect. |
| Mahani et al. [153] | Carbonate | Ambient conditions at 25 °C | 1759 and 2540 | 43,731 | – Wettability alteration | 1. The low-salinity change causes a wettability shift to a more water-wet state. |
| Brady et al. [154] | Sandstone | Ambient Conditions | <5000 | 24,000 | – Simultaneous effect of pH and ion exchange on oil and mineral surface electrostatics | 1. This DLVO approximation omits, among other things, short-range, repulsive, and structural forces. 2. Linking reservoir morphology, surface chemistry, wettability, and crude oil/brine/rock interactions to oil recovery can be readily utilized to predict waterflood recoveries in sandstone reservoirs containing clays other than kaolinite and to carbonates. |

(*continued on next page*)

**Table 6** (*continued*)

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Mahani et al. [155] | Carbonate | Ambient conditions at 25 °C | 1759 | 179,855 | – Wettability alteration toward a more oil-wet system. – Impact of mineral dissolution. | 1. Low-salinity effect occurs even in the absence of mineral dissolution and depends on electrostatic interactions between the crude oil and the rock. |
| Ouden et al. [156] | Carbonate | Ambient conditions | 1000–5000 | 33,390 | – Mineral Dissolution – Wettability alteration | 1. pH increase has a significant effect on calcite dissolution 2. Increase in salinity of the injected brines caused by calcite dissolution makes low-salinity waterflooding effective. |
| Xie et al. [10] | Sandstone (Berea) | Ambient Conditions | 2000 | 174,000 | – Cation exchange – Expansion of the double layer | 1. Low-salinity water triggers positive disjoining pressure in a system of crude oil/brine/rock as a result of double layer expansion. 2. The cation type dominates the disjoining pressure of the oil/brine/rock system instead of the salinity level. 3. Removing divalent cations from the injected brine is essential to observing the low-salinity effect. 4. The disjoining pressure based on extended DLVO theory could be applied to preliminary screen the candidate reservoirs for low-salinity water flooding. |
| Sandengen et al. [115] | Sandstone | Ambient conditions | Not mentioned | Not mentioned | – Osmosis | 1. Osmotic gradients are present across oil films, and the increase in oil production is largely caused by osmosis rather than a wettability change. |
| Torsaeter et al. [79] | Sandstone (Berea) | 45 bar and 60 °C | 3106 | 31,061 | – Wettabilility alteration | 1. Low-salinity water flooding with only NaCl resulted in a more water-wet system with divalent cations. |
| Fredriksen et al. [116] | Sandstone and Carbonates | Ambient temperature and pressure | Not mentioned | Not mentioned | – Osmotic pressure – Wettability alteration | 1. The growth of water in emulsions is a result of osmosis. 2. The low-salinity effect is more relevant under oil-wet conditions, and there are a variety of circumstances under which the low-salinity effect may or may not be observed, which suggests that more than one mechanism is at play. |
| Xie et al. [157] | Sandstone | 20 MPa, 30 MPa, 40 MPa, 50 MPa and temperatures of 60 °C, 100 °C and 140 °C | 1424.31 | 142,431 | – Wettability alteration variation with temperature. – Expansion of the double layer. | 1. Water chemistry, temperature and pressure affect the contact angle; however, water chemistry plays a dominant role in determining the contact angle and thus the wettability. 2. Low-salinity water flooding can be applied to high-temperature (> 100°C.) reservoirs |
| Kakati and Sangwai [158] | Sandstone | Ambient conditions at 25 °C, 40 °C and 55 °C | 1900 | 19,000 | – Wettability alteration | 1. The ageing time has a considerable effect on the contact angle in a sense that the contact angles increase with the ageing time, while quartz surfaces become more oil wet when the temperatures increase. 2. |
| Salehi et al. [159] | Sandstone | 1700 psi and 80 °C | up to 200,000 | 200,000 | – Wettability alteration | 1. Oil recovery increases with the injection of salinity, while the interfacial tension decreases with salinity. |
| Kim and Lee [160] | Sandstone | Ambient conditions at 60 °C | 3000 | 30,000 | – Wettability alteration | 1. The shift in relative permeability curves is proportional to the clay contents in kaolinite, and thus, low-salinity water flooding should be considered an EOR scheme for reservoirs with a high kaolinite content. |
| Xie et al. [161] | Carbonate | Ambient conditions at 25 °C, 60 °C and 100 °C | 10-times-diluted formation brine | 252,244 | – Increased pH combined with wettability alteration. | 1. pH scales with contact angle and the oil/brine/rock system wettability. |

**Table 6** (*continued*)

| Reference | Porous medium | Pressure and temperature | Injected water salinity (ppm) | Reservoir formation salinity (ppm) | Proposed mechanism of oil recovery | Remarks |
|---|---|---|---|---|---|---|
| Nasralla et al. [162] | Carbonates (Chalk) | 400 psi and 100 °C | 10 times diluted Salinity water | 239,000 | – Reduction in residual oil saturation – Dilution of sea water | 1. Spontaneous imbibition tests showed minimal oil production with FW, which indicates that the rock wettability of the tested samples is non-water wet. 2. Secondary mode Amott tests showed higher oil production by seawater than formation brine, which demonstrates the wettability alteration by SW. 3. Diluted seawater gave higher spontaneous imbibition than both FW and SW, which proves that diluting seawater has a greater potential to improve oil recovery than FW or SW. 4. Tertiary mode Amott tests and qualitative USS tests confirmed the wettability alteration by LS brines and the greater potential of diluted SW to improve oil recovery than seawater. |
| Suleimanov et al. [163] | Sandstone | 16 MPa and 62 °C | 3587.45 | 18,738.24 | – Cation exchange – Wettability alteration | 1. There are slight differences in ionic adsorption caused by LHAW and LSW; however, the changes in contact angle for the LHAW were greater than for LSW, as were the changes in interfacial tension, suggesting that the LHAW waters will release more oil than LSW. 2. In a tertiary treatment model, LHAW-2 and LHAW-1 as displacement agents increased oil recovery (%OOIP) by 13% and 10% respectively in comparison with LSW. |
| Chen et al. [164] | Carbonates | 2000 psi and 60 °C | <5000 | 100,000 | – Multicomponent ion exchange – pH increase | 1. Multicomponent ion exchange triggers a pH increase during low-salinity water flooding in the presence of basal-charged clays, and a more water-wet system is obtained. |
| Chen et al. [165] | Carbonate | 2000 psi and 60 °C | 10-times-diluted formation brine and 100-times-diluted formation brine | 252,244 | – Wettability alteration – Increased pH | 1. Conventional dilution triggers an oil-wet system at a lower pH 2. pH plays a fundamental role in the surface chemistry of oil/brine interfaces and wettability. |
| Pooryousef et al. [12] | Sandstone | 200 bar at 50 °C and 100°C | 2000 | 50,000 | – Wettability alteration – Influence of temperature | 1. Wettability shifts from oil wet to slightly water wet with increasing temperature. 2. A low concentration of $Ca^{2+}$ produces an oil-wet system, and a high concentration of $Ca^{2+}$ produces a water-wet system. 3. Contact angle varies with increasing temperature in the presence of softened brine. 4. Zeta potential of brine/muscovite increases with increasing salinity 5. Wettability alteration doesnot support the theory of multicomponent ion exchange proposed by Lager et al. [95] . |
| Sharma and Mohanty [166] | Carbonate | Ambient conditions at 120°C | 511 and 1,600 | 149,160 | – Wettability alteration – Mineral dissolution | 1. Wettability of the surface is dependent on surface concentration of the acids. 2. Mineral dissolution is important for determining the wettability alteration |
| AlHammadi et al. [167] | Carbonate | 1000 psi and 80 °C | 1000–35,000 | 208,600 | – Wettability alteration – Micro-dispersion formation | 1. Additional recovery is predominantky controlled by the formation of micro-dispersions and is linked to the interaction between polar components with brine molecules. 2. |
| Saiia et al. [109] | Carbonate | 700psi and 82°F | 2times, 10 times, 50 times and 100 times diluted formation brine | 10,780 | – Wettability alteration | 1. Wettability of carbonates depends on the iso-electric point of the carbonate rock surface, pH and inter-facial energy between the aqueous brine solution and the rock surface. 2. Reducing the interfacial energy manifests as a wettability change. |
| Pollen and Berg [117] | Sandstone | Ambient Conditions at 22°C and elevated temperatures of 70°C | Not mentioned | Not mentioned | – Osmosis | 1. At ambient conditions, no clear correlation was found between IOR and the surface-to-volume ratio. However there is a correlation between IOR and the pore volume. 2. Elevated temperatures result in low values of IOR which do not correlate with either surface are or pore volume. |

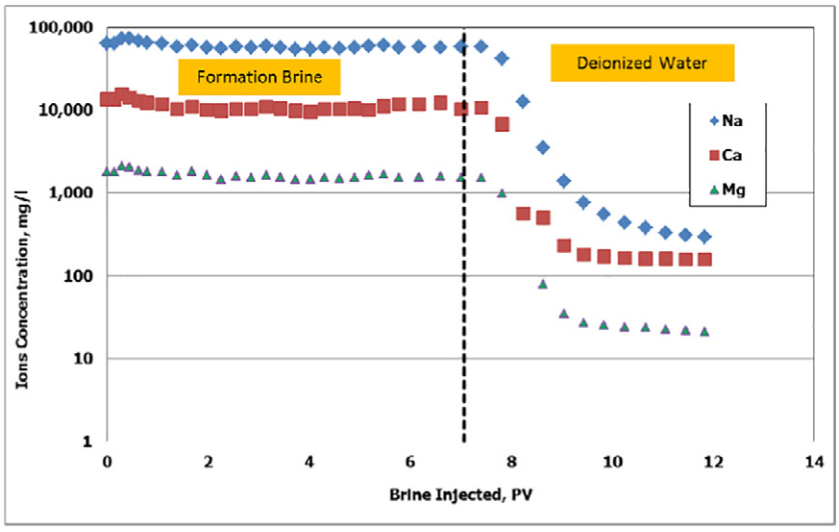



**Fig. 12.** Concentrations of $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ from effluent samples for one of the experiments [24].

significant drop in residual oil saturation of 41% to 28% was observed as a result of LSW [130]. Fig. 14 presents the water cut and oil recovery profiles. The slight drop in water cut from 95% to 92% after a few months of injection was observed in the test separators followed by a gradual rise to the previous value of 95%. This dynamic was attributed to the formation of a second oil bank ahead of the flooded zone. As shown in the figure on the right-hand side, daily production was improved significantly from reducing the salinity of the injected water.

Based on the water analysis conducted on the produced fluids, the concentration of most ions declined linearly as the salinity of the produced water decreased, as shown in Fig. 15.

For LSW in this field, LSW resulted in an additional oil recovery of up to 13%. The unfavorable mobility ratio caused by the lower viscosity of LSW could be a concern; however, no significant effect could be observed in the field-scale application.

Conversely, there is a large number of unsuccessful field cases studies such as the: Bastrykskoye Field in Russsia [131-134] where the insignificant IOR due to LSW was as a result of the large volume of high salinity water that is produced before the start of LSW; Sijan Field in Syria [8] and the reasons for the insignificant response were the strong buoyancy effect caused by the higher permeability of the block, and the significant effect of injectant mixing with the highly saline aquifer; Snorre Field in the North Sea of Norway [23,51] and lack of response to LSW was related to formation brine pH.

## 4. Conclusions, critique and recommendations

Significant work investigating LSW has been conducted by major oil field companies and research institutes for the past 20 years. These studies have covered laboratory core floods, single-well reactive chemical tracer tests (SWCTTs) and well-to-well pilots of tertiary LSW. In addition, data on earlier low-salinity secondary water floods have been analyzed.

The main conclusions to be drawn from this study are as follows.

1. LSW is an immature EOR technique with considerable potential for increasing oil recovery, as verified through various laboratory studies and field applications. The incremental recovery reported in the literature ranges from 0 to 15% OIIP

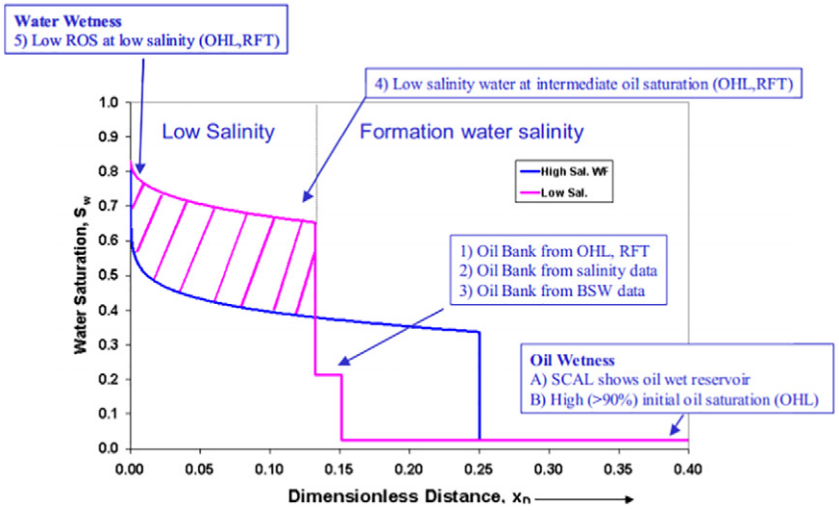
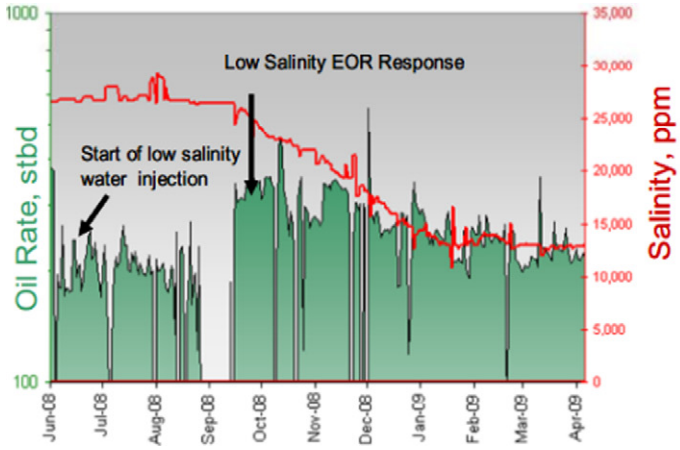
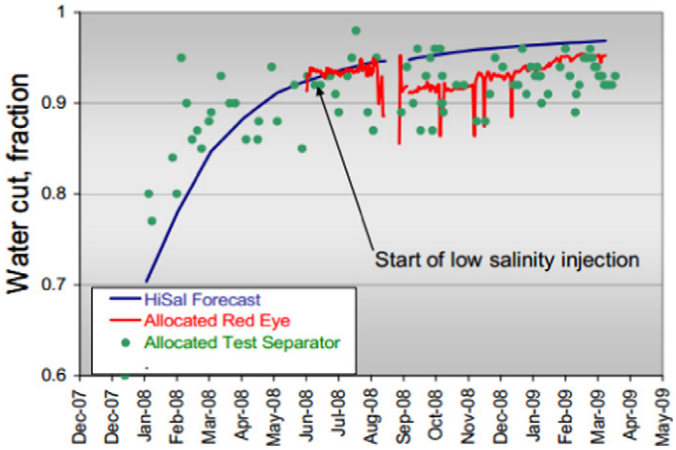



**Fig. 13.** Water saturation in oil-wet system for high-salinity water and low-salinity water based on Buckley theory [35].




(a) Oil Rate Increase, Pilot Producer




(b) Water cut decrease, Pilot Producer

**Fig. 14.** Water cut and oil recovery changes under low-salinity injection [130].

depending on the rock and fluid properties and reservoir conditions.

2. Several recovery mechanisms have been proposed by various researchers; however, no consensus exists as to which mechanisms are dominant in improving oil recovery during low-salinity water injection. Therefore, prior to any field-scale application, extensive laboratory studies should be conducted on the representative rocks and fluid samples to investigate the potential of LSW to increase oil recovery.
3. The provision of a low-salinity water supply in a field can act synergistically with other water-based EOR processes such as alkaline/surfactant/polymer flooding with the potential for even greater incremental recoveries. The injection of low-salinity water can also help in overcoming conventional problems such as souring and scaling.
4. Although not yet proven, LSW either alone or in conjunction with other water-based EOR techniques has the potential to be a "game changer" in both offshore and onshore reservoirs, and therefore, the potential benefits of switching to LSW should be studied for all fields in which water flooding is ongoing or planned. Such research should be undertaken systematically and consistently through independent laboratories.

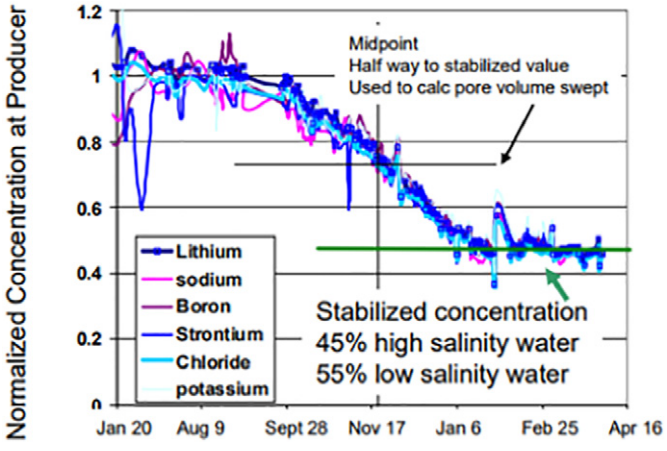



**Fig. 15.** Normalized ion concentration in produced brine; 1 = reservoir water, 0 = reduced salinity injection water [130] .

## Nomenclature

| | |
|---|---|
| $\zeta$ | Zeta Potential |
| NTU | Nephelometric Turbidity Units |
| pH | Potential of Hydrogen |
| $S_{wirr}$ | Irreducible Water Saturation |
| ICP–OES | Inductively coupled plasma–optical emission spectrometry |
| DIW | De-Ionized Water |
| AQW | Aquifer Water |
| FW | Formation Water |
| IOR | Increased Oil Recovery |
| EOR | Enhanced Oil Recovery |
| MIE | Multicomponent Ion Exchange |
| IFT | Interfacial Tension |
| CEC | Cation Exchange capacity |
| STOIIP | Stock Tank Oil Initial In Place |
| SWCTT | Single Well Chemical Tracer Test |
| COBR | Crude/Oil/Brine/Rock |
| LSW | Low Salinity Water Flooding |
| LSE | Low Salinity Effect |
| TDS | Total Dissolved Solids |
| DVLO | Derjaguin, Landau, Verwey, and Overbeek-theory |

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