A review on low salinity waterflooding in carbonates: challenges and future perspective

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Abstract
Low salinity waterflooding has gained significant attention and importance in the last decade, as it is seen as an impactful method for recovery of additional oil from carbonate reservoirs. Existing literature does not do justice to the underlying mechanisms that aid in the recovery of additional oil from such rock types. In this paper, we present a comprehensive review of the research conducted on low salinity waterflooding in carbonates and further provide a detailed and critical analysis on the same. The intention of this paper is also to present a condensed research summary on the said topic, and to chart out a detailed roadmap for future work, thereby opening the possibilities of new avenues of research in the field.

Keywords Low salinity waterflooding · Reservoir engineering · Wettability alteration · Potential determining ions · Carbonates

Introduction
Traditionally waterflooding has always been used as a way of recovering the oil that otherwise cannot be recovered through primary mechanisms that use natural energy of the reservoir. Injection of seawater or formation water into the reservoir is a cost-efficient way of recovering the additional oil as the injection water is readily available in most fields (usually produced from the same reservoir) and does not require any exhaustive chemical treatment to make it compatible with the reservoir environment. Other reasons such as better displacement efficiency, ease of injection, reservoir pressure maintenance and minimum operating expenditure make waterflooding an attractive alternative to any other EOR method. In the current age of globalization, when the energy demand and consumption is rising globally, the need of the hour is to meet the rising energy demand by application of cost efficient EOR techniques that will help produce maximum oil and gas from the available reserves.

Low salinity waterflooding is a method of improved oil recovery wherein the injected water, which has substantially lower salinity (less than 10,000 ppm) than conventional sea water or formation water, is injected in the reservoir. The injected low salinity water interacts with crude oil and reservoir rock in a way which results in an improvement in the final recovery of oil. Low salinity water injection (LSWI) as a method of improving the oil recovery was first tested in the 60s (Bernard 1967). Since then, significant research has been undertaken to develop a better understanding of the mechanisms behind LSWI that result in additional oil recovery.

LSWI in carbonates has been a topic of much debate as the underlying mechanisms that contribute to oil recovery from carbonates have not been completely understood. Carbonates are complex in nature due to their heterogeneous pore structure, mixed to oil wet conditions and existence of naturally occurring micro-fractures that contribute to secondary porosity. Various mechanisms have been proposed which contribute to enhanced recovery from these rock types, which include wettability alteration, fines migration, pH change, interfacial tension (IFT) reduction, emulsion formation, electrostatic repulsion, etc. (Tang and Morrow 1999; Webb et al. 2005; Strand et al. 2006; Zhang and Morrow 2006a; Zhang et al. 2007; Zhang et al. 2007; Austad et al. 2008; Ligthelm et al. 2009; Hiorth et al. 2010; Austad et al. 2010; Yousef et al. 2010; Romanuka et al. 2012; Mahani et al. 2013; Al-Shalabi et al. 2014; Heberling et al. 2014; Mahani et al. 2015; Jackson et al. 2016; Alroudhan et al. 2015). Although there are various mechanisms that
have been researched to result in additional oil recovery, there has been a common understanding that the main mechanisms that contribute involve physical and chemical interactions between fluids and rock surface such as wettability alteration and/or IFT reduction.

The primary objective of this work is to provide a comprehensive and critical review of the experimental and simulation studies performed so far since research got initiated on low salinity waterflooding in carbonates. It compares as well as carefully and critically investigates the previous studies to benchmark them against the state of the art, thereby assisting present researchers in gaining a perspective about the current status of work being done. Further, this study will be supplemented by a critique on the previous investigations conducted so far, thereby leading to possible future recommendations on directions of study.

Low salinity waterflooding as enhanced oil recovery method: brief history

Several core flood and simulation studies have been performed since the study conducted by Bernard in 1967 to understand the impact of low salinity flooding in carbonates. Because of the complexities involved in carbonates, a relatively less number of studies have been performed compared to sandstones to recognize the effect of low salinity waterflooding for improved oil recovery. We have added a study here as a representative of the studies performed on carbonates to highlight the potential of low salinity flooding for higher oil recovery in carbonates.

(Sanchez-Rodriguez et al. 2015) integrated the experimental studies with simulation studies to understand if the results obtained from the laboratory studies could be upscaled and applied to reservoir scale. Core flood studies were performed as secondary and tertiary processes to investigate whether low salinity waterflooding results in additional oil recovery or not. The core flood studies revealed that low salinity waterflooding results in as much as 37% higher oil recovery when the flooding process is employed as a secondary process rather than as a tertiary process.

The data obtained from laboratory studies were used to perform simulation and sensitivity studies at reservoir scale. The sensitivity studies were performed on parameters such as well spacing, heterogeneities, reservoir temperature, injection rate, and injection salinity. It was observed that reservoir temperature and injection rate play important roles in successful implementation of low salinity waterflooding, especially at reservoir scale.

Many such studies have been conducted over the period of last two decades which point toward the usability and implications of low salinity waterflooding in carbonates. Overall, the advantages of application of low salinity waterflooding outweigh the drawbacks. In the following sections, we will critically go through the literature to understand the processes/mechanisms that have proven to result in additional oil recovery and present the audience a know-how of where the literature stands for the application of low salinity waterflooding in carbonates.

Principles of low salinity water injection

The focus of the following subsections is to discuss main principles that contribute to removal (desorption) of oil molecules from the carbonate mineral surface and the mechanisms that cause the desorption. Wettability alteration, fines migration and rock dissolution, and fluid–fluid interactions will be discussed in depth, and their importance will be addressed.

Wettability alteration

Impact of potential determining ions (PDIs)

Potential determining ions (PDIs) are those which can alter the crude oil/rock/brine interaction by altering the surface chemistry and aid in achieving favourable conditions for wettability alterations which results in incremental oil recovery in the case of low salinity waterflooding. The most common PDIs for low salinity waterflooding in carbonate include calcium, magnesium, and sulphate respectively (Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$).

Importance of zeta potential as a tool for assessing the wettability alteration

Zeta potential is defined as the electro kinetic potential that exists between the particle surface and bulk phase surrounding the surface. As shown in Fig. 1, an electrical double layer exists at every surface particle in contact with
solution. The double layer consists of two parts: stern layer and diffuse layer (also known as slipping plane). The stern layer is where ions with equal and opposite charge as that of surface charge will be bound rather tightly to the surface (Ricci et al. 2013). The net charge acting on stern later is known as stern potential. Zeta potential of the particle is the electrical potential at the boundary of the double layer on the particle surface. Zeta potential is the measure of electrostatic attraction or repulsion between the particle and the ion. Since the ions inside of slipping plane are loosely dispersed near the stern layer, the electric potential decreases as we move away from the surface of the particle toward the slipping plane, and it becomes close to zero inside of the solution.

As for the carbonate surfaces are concerned, for pH less than 8, the surface of the carbonate is positively charged. The zeta potential measurement at the interface of surface particles and the solution will show existence of positively charged surface. If such surface is exposed to oil with negatively charged carboxylic groups (COO\(^{-}\)), this results in oil being adsorbed on to the carbonate surface. This is the reason why carbonates tend to exhibit mixed to oil wet behaviour.

The two most popular methods for zeta potential measurement are: streaming potential method (SPM) and electrophoretic mobility method (EPM). The EPM method is most commonly employed in current studies wherein samples are crushed to a powder and suspended in the electrolyte of interest. Potential difference is applied across the electrolyte, and the resulting oscillating movement of the solid particles is used to interpret zeta potential using Helmholtz–Smoluchowski equation. The disadvantage of using the EPM method is that it does not use the core samples in its natural state and crushing of the samples may expose those mineral surfaces which otherwise will not get exposed to the formation brine. Also, this method requires the overall ion concentration of the brine (< 0.5 M) and the temperature (< 60 °F) to be at much lower level compared to the actual formation brine concentration. Therefore, the zeta potential measurement may not be an accurate reflection of the real number. The SPM method which was first introduced by (Fuerstenau 1956) is less popular but can overcome the limitations of EPM as it uses the cores in their intact state, can be used at elevated temperatures, and can be employed on a multiphase system of brine and water of high ionic strength.

**Lab Studies focusing on Wettability Alteration:**

**Impact of ion concentration and brine composition** Low salinity studies conducted on carbonates provide evidence that the main processes which are dominant in altering the rock wettability are as follows:

- Decreasing the salinity of the injection brine
- Increasing the concentration of PDIs in the injection brine
- Lowering the ionic strength of the injection brine
- Combination of the above

Wettability measurements of the brine-rock system showed that decreasing the brine salinity results in additional oil recovery and that if the brine salinity is maintained constant, brines having higher sulphate concentration tend to change rock wettability to more water wet, thus resulting in higher oil recovery (Webb et al. 2005; Al-Attar et al. 2013; Nasralla et al. 2014; Nasralla et al. 2018).

The potential determining ions (PDIs) such as Ca\(^{2+}\), Mg\(^{2+}\) and SO\(_4^{2-}\) tend to have a positive impact on final oil recovery through wettability alteration from oil wet to water wet. In experiments conducted on Stevns Klint carbonates from North Sea, it was observed that the increase in Ca\(^{2+}\) concentration in injection brine results into additional oil recovery. Increase in temperatures enhances the oil recovery even more due to the substitution reaction between Ca\(^{2+}\) and Mg\(^{2+}\) at elevated temperatures. (Zhang et al. 2007)

\[
2\text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg(CO}_3)_2 + \text{Ca}^{2+}
\]

SO\(_4^{2-}\) also plays a major role as a potential determining ion such that increasing the concentration of SO\(_4^{2-}\) ions increases the oil recovery. This is due to chemical mechanism between SO\(_4^{2-}\) and Ca\(^{2+}\) which is as follows (Fig. 2):

1. The sulphate present in seawater will adsorb onto the positively charged chalk surface, thus reducing the electrostatic attraction between carboxylic group and rock surface. The Ca\(^{2+}\) can get adsorbed on the chalk surface due to relatively higher affinity of these ions toward the sulphate ions. These Ca\(^{2+}\) ions then will displace some
of the carboxylic groups by reacting with them, thus releasing them from the surface. (Zhang et al. 2006a; Zhang et al. 2006b; Puntervold et al. 2009).

2. At higher temperatures, Mg$^{2+}$ will substitute Ca$^{2+}$ from the chalk surface and are linked to carboxylic groups. Also, SO$_4^{2-}$ will be active due to lowered electrostatic repulsion. The ionic interaction between Mg$^{2+}$ and SO$_4^{2-}$ will increase the concentration of Mg$^{2+}$ close to the chalk surface.

This may result into enhanced weakening of the rock, and thus, an appropriate balance between temperature and concentration of sulphate ions is critical (Austad et al. 2008; Puntervold et al. 2009). This observation is important from the PDIs perspective as it discusses the limitation of sulphate ions at reservoir conditions. Since sulphate ions are understood to have a major impact on wettability alteration, researchers have ignored the impact of the ions on the mechanical strength the rock. More focused research is required in this field to understand this effect in a better way for better design of treatments (Zhang et al. 2007).

Contrary to the research discussed so far related to enhanced weakening of the rock due to substitution reaction between Ca$^{2+}$ and Mg$^{2+}$, (Madland et al. 2011) suggested that the formation of a new mineral (hunltite) through precipitation of Ca$^{2+}$ results in the weakening of the rock. Through the development of 1-D model, they suggested that enhanced strain on the rock cannot be caused by substitution of calcium by magnesium in presence of sulphate, but it was proposed to be of chemical in nature. As seen here, a lot of discrepancies are present in the current research. Researchers have found contradicting results after having conducted similar experiments. There is little agreement regarding what causes the additional recovery oil, is it magnesium ions in isolation or in conjunction with calcium ions? Is it anhydrite precipitation that causes additional recovery? Is it precipitation of the new mineral that causes the additional oil recovery? This requires detailed research with focus on interaction between Mg$^{2+}$ and Ca$^{2+}$ ions, especially at elevated temperatures.

(Gomari et al. 2006) studied the impact of potential determining ions, namely Mg$^{2+}$ and SO$_4^{2-}$, on calcite surface and found out that Mg$^{2+}$ has a greater impact on wettability alteration compared to SO$_4^{2-}$ through mechanisms such as adsorption of magnesium as a hydrated ion on active site, and induction of surface reaction with surface Ca$^{2+}$ ions. (Romanuka et al. 2012) suggested that high concentration of SO$_4^{2-}$ ions in the injection brine can lead to potential scale formation in the production tubing, if the reservoir water contains barium and strontium. Thus, through imbibition studies they demonstrate that oil recovery can be increased through reducing the ionic strength of the injection brine.

Surface complexation model (SCM) coupled with experimental work has proven to be a useful way of determining the possible mechanisms behind successful low salinity waterflooding. Zeta potential is an electrostatic charge at the rock-liquid interface, and is a useful parameter for determining the wettability of the rock. The zeta potential measurements show that with brine dilutions the zeta potential at the rock-brine interface becomes more negative which is an indicator of rock surface becoming more water wet. With the help of SCM, it can be revealed that at lower salinities, the calcite surface becomes more negative due to increase in the concentration of negatively charged >CO$_3$ ions, decrease in the concentration of positively charged species such as >CO$_3$Mg$^+$ and formation of neutral species such as >CaOH. (Mahani et al. 2016).

Ions other than Ca$^{2+}$, Mg$^{2+}$ and SO$_4^{2-}$ have also been studied as PDIs. Ions such as Borate and Phosphate have been experimented with, and proven to have a positive impact on oil recovery (Gupta et al. 2011); however, limited research has been conducted to prove the usability of these ions as PDIs.

**Impact of NaCl**

The oil recovery can be improved even at lower temperatures by spiking the sulphate ion concentration and by removing the non-active ions such as NaCl as per the studies from (Fathi et al. 2011). The non-active ions such as NaCl are usually found in the electric double layer close to the Stern layer. They can reduce the accessibility of sulphate ions by the positively charged calcite surface by reducing the electrostatic attraction between the surface and the sulphate ions. In the absence of these non-active ions, the sulphate ions act as potential determining ions by getting adsorbed onto the calcite surface, thus reducing the attractive forces between oil and mineral surface. This phenomenon is more prominent when the sulphate concentration in the imbibing fluid is spiked to a higher level. The authors concluded that both NaCl and sulphate ion concentration has a significant impact on wettability alteration and oil recovery.

It is important to note that brines of equal salinity can lead to varying contact angles in the same rock, which indicates that apart from brine salinity, there are other factors such as brine composition that play major role in determining the wettability of the rock. The NaCl and CaCl$_2$ salts also alter carbonate wettability towards more water wet (Al-Shaikh and Mahadevan 2014). The acid number which indicates the amount of carboxylic acid groups present in the crude is an important factor in wettability alteration as it has been observed that the rate of water imibition and ultimate oil recovery is higher in cores which are saturated with low acid number oil, depleted in water-soluble acids (Fathi et al. 2010).

(Alroudhan et al. 2015) created ‘equilibrated’ NaCl brine solutions to study the impact of concentrations of
PDIs on pH and polarity of zeta potential. It was observed that increasing the concentrations of positive divalent ions makes the zeta potential more positive, while for negative divalent ions, it becomes more negative. Also, previous studies argued that the IEP (Iso-Electric Point: point of zero zeta potential) is independent of the NaCl concentration, but this is the first study where it was showed that the IEP decreases with increasing NaCl concentration over the range of 0.05–0.5 M. This could be due to the reduced ability of the calcium ions to interact with the calcite surface due to the collapse of the double layer and occupancy of the hydrated sodium ions in the diffused part of the double layer.

Presence of Na\(^+\) and Cl\(^-\) ions affects only the magnitude and not the polarity of the zeta potential. The impact of Ca\(^{2+}\), Mg\(^{2+}\) and SO\(_4\)^{2−} ions on zeta potential revealed that these two ions behave identical to each other within experimental error and for a given NaCl concentration. Increasing p(SO\(_4\)) (p representing negative logarithm) or in other words decreasing the SO\(_4\)^{2−} concentration results in more positive zeta potential; however, the sensitivity of the change is much less compared to p(Ca) or p(Mg). Al-Mahrouqi et al. (2016) demonstrated that the IEP obtained in an open-air system is larger than in a closed system due to the absence of or limited access to CO\(_2\) in closed system experiments, which causes a decrease in carbonic acid formation. They argued that equilibrium pH and pCa/pMg are related at fixed p(CO\(_2\)) as shown by surface complexation reactions before, and concluded that a lot less dilution is required to change the polarity of zeta potential as the IEP can be encountered at relatively higher concentration of Ca or Mg ions compared to what was shown in previous studies.

The temperature dependence of zeta potential is a less researched area; however, the studies reveal that at elevated temperatures and at low ionic strength of the NaCl electrolyte, the zeta potential becomes less negative as the Ca ion concentration increases. No such trend is observed at relatively higher concentration of Ca or Mg ions compared to what was shown in studies undertaken previously.

Studies based on zeta potential measurements

The electrostatic charge at the mineral–brine and oil–brine interface is one of the important factors in determining success of low salinity waterflooding. (Jackson et al. 2016; Alroudhan et al. 2015; Al-Mahrouqi et al. 2016; Jackson et al. 2019; Collini et al. 2019). The pH is unaffected irrespective of the temperature and ionic strength of the NaCl brine. (Al-Mahrouqi et al. 2016). A prior understanding of these zeta potential values and their polarity is important, and thus, an integrated approach of zeta potential measurement with coreflood studies is advisable (Jackson et al. 2016; Jackson et al. 2019). It has been recommended to use ‘inverse’ low salinity waterflooding (low salinity followed by seawater followed by formation brine injection at the last) for oils which showed ‘positive’ zeta potential at the oil–brine interface. This is because introducing the divalent ions (SO\(_4\)^{2−}) during conventional flooding may not result in additional oil recovery for these oils. Table 1 summarizes the studies undertaken wherein zeta potential and its impact were primarily studied from the low salinity waterflooding perspective.

If the zeta potential of the water wet sample (100% water saturated) is:

- Positive and becomes more positive after ageing, then it indicates positive oil brine zeta potential.
- Negative and becomes more negative after ageing, then it indicates negative oil brine zeta potential.
- Positive and becomes negative after ageing, then it indicates negative oil brine zeta potential.
- Negative and becomes positive after ageing, then it indicates positive oil brine zeta potential.
- Positive and becomes less positive after ageing, this could indicate a negative or less positive zeta potential at the oil brine interface.
- Negative and becomes less negative after ageing, this could indicate a positive or less negative zeta potential at the oil brine interface.

Some ambiguities related to zeta potential measurement at the oil–brine interface:

- The samples which showed more negative zeta potential after ageing were interpreted to have negative zeta potential at the brine–oil interface unambiguously, but the samples which showed less negative zeta potential after ageing were interpreted to have either positive or less negative zeta potential at oil–brine interface.
- (Jackson et al. 2016) suggest that the oil–brine interface for oil wet cores is always negative irrespective of the type of oil, brine, or rock sample used. However, (Collini et al. 2019) observed that it may not always be negative, and it depends upon the rock type and oil sample used for aging.
- In one of the experiments conducted by (Collini et al. 2019), it was observed that inverse low salinity flooding did not result in any additional oil recovery although the oil–brine interface polarity was negative and became less negative after aging in low salinity brine.
| Zeta Potential Studies on Carbonates and Key Points | Temperature Range | IEP (pCa) | PDIs Investigated | Effluent Brine pH | ZP Measurement Method | Key Points | Reference |
|-----------------------------------------------|------------------|-----------|-------------------|------------------|-----------------------|------------|-----------|
| Synthetic Calcium                              | Ambient          | +6 to −8  | 2                  | –                | SPM                   | PDI at the crude oil-brine interface play a major role in EOR during low-salinity flooding. | Jackson et al. (2016) |
| Natural Calcium                                | Ambient          | +5 to −20 | 0.6               | –                | EPM, SPM              | Increasing Ca concentration increases the zeta potential. | Alroudhan et al. (2015) |
| Natural and Synthetic Calcium                  | Ambient          | +20 to −24 | 1.9–4.5           | –                | EPM                   | Zeta potential is independent of the pH of the system if the Ca ion concentration stays the same. | Al-Mahrouqi et al. (2016) |
| Natural Calcium                                | 22°C to 120°C    | −17 to 17  | 1.9 to 12°C       | –                | SPM                   | Temperature dependence of zeta potential is simple and depends on the ionic strength of the electrolyte. | Jackson et al. (2019) |
| Natural Calcium                                | 23°C to 100°C    | +10 to −20 | 2°C to 9°C        | –                | SPM                   | Strongly water saturated formations with high salinity consistently showed positive zeta potential, while saturating with low salinity brines consistently returned negative zeta potential. | Jackson et al. (2019) |
Table 1 (continued)

| Calcite  | Zeta Potential Range (mV) | Temperature Range | Experiment System | IEP (pCa) | PDIs Investigated | Effluent Brine pH | ZP Measurement Method | Key Points | Reference |
|----------|---------------------------|-------------------|-------------------|-----------|-------------------|-------------------|------------------------|------------|-----------|
| Natural  | +10 to −20                | 70˚C, 80˚C, 100˚C | Open              | –         | Ca²⁺, Mg²⁺, SO₄²⁻ | 7                 | SPM                   | Oil–brine zeta potential value and magnitude is important before deciding the injection scheme as crudes with positive zeta potential may not show EOR. | Collini et al. (2019) |
| Synthetic| +17 to −15                 | Ambient           | Open              | –         | Ca²⁺, Mg²⁺, SO₄²⁻ | 6                 | SPM                   | Crystal face exposed to pore walls will adsorb more Ca ions thus returning positive zeta potential, while Crystal edges exposed to brine will return anomalously negative zeta potential | Li et al. (2020) |
This could be due to ambiguity in the interpretation of the zeta potential.

(Li et al. 2020) explored the reasons behind negative zeta potential after saturating the rock samples in formation brine and suggested that the negative zeta potential could be due to the calcite faces getting exposed in the pore spaces. If the pore spaces are dominated by calcite faces, then Ca\(^{2+}\) adsorption will be larger, which will be reflected in higher values of zeta potential.

In summary, the following important points can be noted about zeta potential and its importance for low salinity waterflooding:

- Zeta potential is the electric potential between mineral–brine and oil–brine interfaces, the mineral–oil interface generally returns zeta potential of the water-wet surface, while the oil–brine interface returns the zeta potential of the oil-wet surface.
- It has been observed that saturating the core sample in the formation brine returns the positive zeta potential with the exception of a few studies (Li et al. 2020) wherein negative zeta potential is observed.
- Cores saturated with oil generally returns negative zeta potential with exception of a few studies (Collini et al. 2019) where positive zeta potential is observed.
- In order to remove oil molecules adsorbed on the mineral surface, electrostatic repulsion between mineral–brine and oil–brine interfaces is a must. This requires both the interfaces to be of the same charge (positive or negative) such that a stable water film will be established on the mineral surface.
- The zeta potential of the core saturated with low salinity brines returns negative zeta potential with a few exceptions where a positive zeta potential has been observed.
- Zeta potential is independent of the pH of the electrolyte if the p(Ca) remains constant.
- The PDIs such as Ca\(^{2+}\) and Mg\(^{2+}\) behave identically, zeta potential changes linearly (Nernstian) as a function of p(Ca) and p(Mg). Zeta potential becomes more positive with decrease in p(Ca) and/or p(Mg) and vice versa.
- The SO\(_4\)\(^{2-}\) ion exhibits linear (Nernstian) relationship with zeta potential, and the zeta potential becomes more negative with decrease in p(SO\(_4\)).
- Surface complexation reactions show that for a fixed p(CO\(_2\)), there exists a linear (Nernstian) relationship between pH and p(Ca) and/or p(Mg).
- Using the equilibrated electrolyte solution is recommended since it has been observed that the IEP is encountered at much lower values of p(Ca) and p(Mg) (higher concentrations of Ca\(^{2+}\) and Mg\(^{2+}\)) when using equilibrated solutions. This will warrant polarity inversion at the oil–brine interface with a lot less dilution that was mentioned in the literature before.
- The relationship between zeta potential and temperature is such that the zeta potential and Ca\(^{2+}\) ion concentration decrease linearly (becomes less negative) with the increase in temperature at low ionic strength of the brine. No such relationship is observed in brines of high ionic strength as both zeta potential and Ca\(^{2+}\) ion concentration remain constant irrespective of temperature.

**Modelling studies focusing on wettability alteration**

Simulation study conducted by (Al-Shalabi et al. 2013) on the data from (Yousef et al. 2010) showed large change in the relative permeability for water and oil for each cycle of seawater injection. Successive injection of more diluted seawater resulted in shifting of the relative permeability curves towards the right side of the X-axis. This is an indication that the rock was becoming more water wet with each diluted seawater injection cycle. The oil end point saturation (\(S_{or}\)) reduced with each flood from about 0.3 for the first cycle to less than 0.2 for the last, which is also an indication of prevailing water wet conditions in the reservoir.

(Al-Shalabi et al. 2014) extended the previous work and identified three most critical parameters for the success of low salinity waterflooding using design of experiments. According to the study, the three most important parameters for the successful field implementation of low salinity flooding are low salinity injection water slug size, reservoir heterogeneity and salinity of the injection water. The empirical model developed by them (Al-Shalabi et al. 2015) which uses contact angle measurements for making \(S_{or}\) predictions is a better model compared to salinity model as contact angle is a direct indicator of wettability alteration compared to salinity of the injected brine.

Development of a chemical model based on bulk aqueous and surface chemistry is a complex process and requires understanding of surface charge and surface potential for the basis species and their surface complexes. (Hiorth et al. 2010) developed a chemical model to study surface complexes such as (>CaH\(_2\)O\(^+\)) and (>CO\(_3\)) and found out that ageing the sample in MgCl\(_2\) will make the surface more oil wet. This is contrary to the observation made by (Zhang et al. 2007, Gomari et al. 2006) which show that Mg\(^{2+}\) as potential determining ion promotes oil recovery. Therefore, zeta potential alone cannot be used as a method of explaining additional oil recovery in the presence of PDIs. It was observed at elevated temperatures, anhydrite is precipitated from seawater which creates deficiency of Ca\(^{2+}\) ions in the solution. This deficiency is overcome by borrowing additional Ca\(^{2+}\) ions from the mineral surface through dissolution to achieve thermodynamic equilibrium. This also
promotes additional oil recovery through desorption of oil molecules from the surface.

**Rock dissolution and fines migration**

Rock dissolution (calcite) and fines migration have thought to be the possible mechanisms behind additional oil recovery using low salinity waterflooding. The calcite dissolution phenomenon was studied by (Masalmeh et al. 2019) with the help of coreflood experiments conducted on limestone and dolomite rock samples. It was concluded that the mineral dissolution may not be the primary reason behind wettability alteration. In another set of experiments, (Zahid et al. 2012) studied fines migration as the possible mechanism for additional oil recovery, by observing the pressure drops across the cores during the experiments. They concluded that fines migration in isolation cannot be the dominant mechanism and that fines migration and rock dissolution could combine to give additional oil recovery.

**Fluid–fluid interaction**

Various studies have indicated that the crudes that form micro-dispersion with water are good candidates for low salinity flooding as reservoirs with such crude-water system show additional oil recovery by low salinity injection (Sohrabi et al. 2015; Mahzari et al. 2019). In a study conducted by (Masalmeh et al. 2019), two types of crudes were tested: crude showing high degree dispersion and crude showing low or no dispersion at all. It was observed that the crudes which show very low degree of dispersion (or no dispersion) are not suitable for low salinity waterflooding as no additional oil recovery can be observed from cores containing such crudes. On the other hand, crude having high degree of dispersion has a strong impact on oil recovery in both secondary and tertiary stages of low salinity injection. This is an indication that crude from same reservoir can behave differently, and more detailed study is needed to understand the crude oil–brine interaction to assess the success of low salinity waterflooding in carbonates.

As observed here, limited research has been conducted for understanding fluid–fluid interaction as the reason for additional recovery from carbonates. Crude oil–brine interaction is an important aspect of success of low salinity waterflooding as low salinity brine is injected into the reservoir that is saturated with high salinity reservoir brine and contacts both. More efforts are required to characterizing the crude oil as suited for the low salinity project or not via micro-dispersion studies.

**Impact of heterogeneity on LSWF performance in carbonates**

Carbonates are heterogeneous in nature due to the existence of natural fractures that contribute to secondary porosity. This complexity may play an important role in how a low salinity flood front propagates and contacts maximum oil. Although the inherent heterogeneity is an important aspect of carbonates that distinguishes the flow behaviour of these rocks from sandstone reservoirs, this aspect is seldom given importance in research. (Al-Ibadi et al. 2020) have studied the impact of heterogeneity on LSWF performance for both sandstones and carbonates through numerical simulation approach. The authors built a model that incorporated a porosity model randomly distributed using Sequential Gaussian Simulation. The permeability data were built using standard porosity–permeability correlations for both sandstones and carbonates. Each model built for sandstone and carbonate was compared with homogeneous model with minimal numerical dispersion. The flow performance was interpreted in terms of three parameters such as water cut, salinity and oil recovery factor as a function of pore volume injected. Water saturation and salinity distribution profiles were also studied to understand the impact of heterogeneity.

Two salinity ranges were chosen: 1000–10,000 and 1000 to 200,000. Figure 3 shows model behaviour in terms of water cut and recovery factor for a model built using salinity range of 1000–200,000 ppm for both sandstone and carbonate reservoirs. The FU(0) and FU(5) shown here are carbonate flow units. The figure shows that the sandstone model has a higher water cut and carbonate flow units have closer behavior to homogeneous model. Figure 4 shows model behaviour for salinity range of 1000–10,000 ppm for sandstone and carbonate flow units. Figure 4 shows that the sandstone model is closer to homogeneous model for this range. It was observed that the sandstone models were more affected by spatial distribution of petrophysical properties than the carbonate models. Also, the range of effective salinity also plays an important role in determining the effect of heterogeneity on LSWF. It was observed that heterogeneity plays less important role in the case of carbonates compared to sandstones.

(Attar et al. 2015; Attar et al. 2018) studied the impact of heterogeneity on oil recovery and water cut when low salinity waterflood is being employed as a secondary and tertiary method. They observed that the heterogeneity plays an important role in carbonates and that the water cut was being encountered earlier compared to homogeneous model. (Al Dasani et al. 2015) constructed 3-D models to study the impact of wetting characteristics of the carbonate reservoir. They studied the role of heterogeneities and sweep efficiency towards incremental oil recovery. The results
indicated that the recovery is more rapid in oil-wet state; however, the amount of unswept oil is also more compared to other wetting conditions. Their study did not encompass the effect of fractures and diffusion rates on the final oil recovery. (Taheriotaghsara et al. 2020) studied the delay in oil production due adsorptive ion transport and the diffusion-controlled wettability alteration for heterogeneous carbonate reservoirs, when employing low salinity waterflooding in such reservoirs. They tested various types of heterogeneities such as homogeneous reservoirs, layered system, and sector scale model with contrasting physical properties. Their results suggested that for a homogeneous model, as the distance between injection and producing well increases, the normalized cost of delay (cost of delay/maximum cost of delay in oil production) decreases. Also, for the layered reservoir model, as the number of layers in the model increases the delay in oil breakthrough time due to adsorption process decreases. (Adegbite and Al-Shalabi 2021a; Adegbite and Al-Shalabi 2021b) investigated the effect of heterogeneity on the field scale using five spot patterns for the secondary and tertiary ‘Engineered Water Injection (EWI)’ in carbonates. Three types of five spot patterns were studied that included homogeneous, heterogeneous with permeability channelling, and heterogeneous with gravity underride. They concluded that EWI improves volumetric and displacement sweep efficiency which is consistently seen across all the models and that the EWI is best suited as a secondary method compared to the tertiary EWI or secondary formation water injection.
as highest recovery was obtained in secondary EWI. Also, the delay in oil recovery during tertiary EWI can be reduced by increasing the sulphate ion concentration as increase in sulphate concentration leads to release of CH₃COO⁻ due to ionic exchange reaction.

Apart from a few studies mentioned here, very limited work is performed to address the impact of heterogeneity on low salinity flooding in carbonates. This field of research deserves more attention for gaining comprehensive insights into the importance of heterogeneity for better designing the LSWF treatment.

**Field implementation of low salinity waterflood in carbonates**

Low salinity waterflooding projects/field trial/pilots reported in the literature have been dominated by those projects which have been implemented in sandstone reservoirs. Researchers (McGuire et al. 2005; Eric Robertson 2007; Skrettingland et al. 2011; Abdulla et al. 2013a; Erke et al. 2016; Al Qattan et al. 2018; Katende and Sagala 2019) have reported field implantation of low salinity waterflooding in sandstone reservoirs. On the other hand, studies which discuss low salinity projects in carbonates are scarce.

First case of field implementation of low salinity waterflood in carbonates was reported by (Yousef et al. 2012). Several Saudi Aramco reservoirs have peripheral water injection program going on since the 50 s and these reservoirs also exhibit water drive as the primary recovery mechanism. The infrastructure for low salinity project is already in place, and therefore these reservoirs are ideal for implementation of such projects. Yousef et al. conducted comprehensive laboratory investigations for understanding the impact of injection of low salinity water into carbonate reservoirs. These studies have been summarized in a series of papers (Yousef et al. 2010; Yousef et al. 2011; Yousef et al. 2012). Several dilutions (2 times, 10 times, 20 times, and 100 times) of injection seawater as that of stage 1 to make sure no additional oil is mobilized, while for well B, the stage included injection of twice diluted SmartWater followed by injection of SWCT. In stage 3, wells A and B were injected with 10 times diluted SmartWater followed by SWCT injection for residual oil measurement.

For well A, stage 1 injection of field seawater and SWCT indicated oil mobilization. The tracer curve was compared with history matched curve. Stage 3 injection of 10 times diluted SmartWater resulted mobilization of additional oil near the well. The reactive tracer curve for stage 1 and 3 matched since the injection volume was the same; however, a significant shift in product tracer curve was seen (Fig. 6) for stage 1 and stage 3 which is a clear indication of reduction in residual oil saturation. For well B, residual oil saturation was calculated by history matching the reactive and product tracer curves with the actual curves obtained from the well production for stage 1. For stage 2, apparent shift in product tracer curve from base case for stage 1 was observed. This was a clear evidence of reduction in residual oil saturation. The history match and analytical method revealed that there is a 3-saturation unit reduction in residual oil after stage 2.
For stage 3, apparent shift in product tracer curve and history match revealed 3 saturation unit reduction in residual oil saturation. A total of 6 saturation unit reduction in residual oil saturation was observed compared to residual oil saturation at the end of stage 1. Overall, the field trial for both wells was successful and the results obtained from field trials were in line with the laboratory results and the results obtained from the simulation studies.

This is so far the only reported field trial of low salinity injection in carbonate reservoir. The reluctance to conduct field trials in carbonates could be due to lack of reliable data from the laboratory studies. Carbonates being complex in nature, the laboratory studies pertaining to low salinity injection have reported contradictory data. Although a lot of research is being undertaken globally, the research is still in its nascent stage. The process is yet to be fully understood, and therefore the industry is far from design and implementation of pilot studies. Also, in the field application reported by Yousef et al. they have used SWCT as a way to assess the success of the project. The piloting options available are either single well pilot or multi well pilot. The problem with single well piloting methods (SWCT, or log-inject-log LIL) is that these methods are heavily dependent upon estimation of reduction in residual oil. Unless there is significant change in residual oil after low salinity injection, these methods cannot provide reliable results. Also, these by no means can replace the actual flooding using production/injection setup (Masalmeh et al. 2019).

Discussion

Although the objective of this paper is to shed light on the current status of research that focuses on low salinity flooding in carbonates, the paper critically discusses the gaps in the research completed so far.

The current research on effect of low salinity waterflooding on additional oil recovery in carbonates suggests that in majority of the laboratory investigations, the results showed additional oil recovery. This means that the method of waterflooding works in carbonates; however, very little attention has been given to understanding the mechanisms that result in additional oil recovery. Most of the studies indicate that the wettability alteration is the main mechanism behind additional oil recovery; however, some of them fail to give a reasonable explanation behind wettability alteration. Some studies suggest that the potential determining ions play major roles in wettability alteration by changing the surface chemistry of the carbonate rock surface, others suggest that fines migration could be the reason behind additional oil recovery, and some of them also suggest it is the fluid–fluid interaction that causes the additional oil recovery. In general, there is no agreement on underlying mechanism that results in additional oil recovery.

Potential determining ions such as Ca²⁺, SO₄²⁻ and Mg²⁺ have been demonstrated to have positive impact on final recovery of oil as these ions alter the surface chemistry of the carbonate surface and make it more water wet. In fact, injection of sulphate ions may result in scaling problems which is undesired (Romanuka et al. 2012). Also, the size of
Mg$^{2+}$ ions is much smaller compared to Ca$^{2+}$ ions, therefore substitution reaction may result in substantial reduction in mechanical strength of the rock. The literature on PDIs predominantly describes the impact of these three ions as PDIs; however, other ions have seldom been tested to understand if they can be treated as PDIs. Other ions such as borate (BO$_3^{3-}$) and phosphate (PO$_4^{3-}$) have been understood to have positive effect on final oil recovery and thus can be treated as PDIs. Only a few studies (Romanuka et al. 2012; Webb et al. 2005) have demonstrated the impact of using these ions as PDIs; however, more research needs to focus on other ions such as borate and phosphate which can potentially be alternatives to calcium, sulphate, and magnesium ions.

Due to its reactive nature, SO$_4^{2-}$ ions can result in scale precipitation. (Romanuka et al. 2012) have rightly pointed out that injecting the low salinity brine with higher concentration of SO$_4^{2-}$ ions in the formation that contains Barium and Strontium increases the potential of scale formation. This can result into plugging of pore spaces in the reservoir or plugging/choking inside a production tubing. To avoid any such situation, an alternative approach especially for such reservoirs that contain these ions needs to be developed. One approach could be lowering of ionic strength of the injection brine or injection of any other PDI that may have similar effect as that of sulphate ions. This aspect definitely needs more attention than what is being given in the literature right now.

Very few studies have discussed the surface chemistry of carbonates when the rock surface is contacted by low salinity brine. The reactive nature of ions is a function of concentration of that ion in the solution. Various other factors such as salinity (TDS), ionic strength and measured pH are influential in determining the outcome of the experiment. Except a few studies (Hiorth et al. 2010), there has been a lack of research that focuses on the surface chemistry. The difficulties and inherent complexity associated with such studies could be a discouraging factor, but more attention is necessary to be given to this aspect of low salinity waterflooding.

Effect of pressure and temperature could be a significant factor in determining success or failure of low salinity flood in carbonates. Pressures and temperatures in conjunction with other mechanisms have demonstrated a positive impact on the final recovery. (Zahid et al. 2012) demonstrated through their experimental work that the impact of low salinity flooding is not seen at ambient temperatures and that increasing the temperatures to 90 °C results in significant recovery. At elevated temperatures, the Mg$^{2+}$ ions are demonstrated to have more reactive nature to replace Ca$^{2+}$ ions from the carbonate surface (Zhang et al. 2007). Other studies also point toward increased recovery of oil when the tests are conducted at reservoir pressure and temperature conditions and with live oil (Webb et al. 2005). (Al-Mahrouqi et al. 2016b), on the other side, have found out that at low ionic concentration of electrolyte, the zeta potential and Ca$^{2+}$ ion concentration becomes less negative with the increase in temperature but at high ionic strength (> 0.5 M NaCl), there exists no such relationship between zeta potential, Ca$^{2+}$ ion concentration and increasing temperature. Therefore, temperature in isolation may or may not have the positive impact on results but it is necessary to study other aspects (Ca$^{2+}$ ion concentration, ionic strength etc.) to understand the relationship between these parameters and temperature. High temperature can also have a negative impact, as at elevated temperatures, anhydrite precipitation can result from interaction between calcium and magnesium ions. Anhydrite precipitation can reduce the mechanical strength of the rock. This aspect of chemistry is not thoroughly studied yet.

Zeta potential studies on limestone and dolomites have shown that due to the presence of additional Mg$^{2+}$ ion (CaMg(CO$_3$)$_2$), the dolomite surface is higher positively charged compared to limestone surface. Therefore, while the impact of low salinity on carbonates is being studied, distinction between limestone and dolomite must be considered. Some studies indicate through zeta potential studies that the impact of low salinity is evident in limestones, it not so much obvious in dolomites. The dolomite surface charge may remain positive at the end of flood experiments and such rock may still be oil wet although with relatively less affinity towards oil. Therefore, care must be taken while designing the experiments and interpreting the results for dolomite rock surfaces.

Zeta potential studies (Jackson et al. 2016; Jackson et al. 2019; Alroudhan et al. 2015; Al-Mahrouqi et al. 2016a; Al-Mahrouqi et al. 2016b; Collini et al. 2019 etc.) have also shown that the electrostatic charge at the mineral–brine interface and oil–brine interface should be such that an electrostatic repulsion must act between interfaces. Prior information about these interface polarities will be helpful in successful design of the low salinity process, thereby resulting in additional oil.

Although heterogeneity is an integral part of a carbonate rock and its impact of final recovery cannot be ignored, it is observed that very limited studies have so far been conducted that focus on heterogeneity. Heterogeneity plays a major role in dictating the flow through porous media and thus its impact on waterflood needs more attention.

Although it is well understood that the polar components in oil (COO$^-$) have greater affinity toward the positively charged carbonate surface, very few experiments have been designed by keeping the oil composition as the variable. Mineral oil cannot be used for such studies as it does not have carboxylic groups, and such oil will never get adsorbed on the rock surface to imitate the actual oil wet condition. Therefore, crude oil, especially with heavier fraction, should
be used. Chemical models developed by researchers have ignored the chemistry of the oil phase and its interaction with rock and brine interface. Shortcoming of such studies must be addressed by developing more a complex and robust chemical model which will be universal. Oil viscosity is another important aspect of crude oil that should be given more importance. Limited studies have focused on application of low salinity flooding to heavy crude oils (Sanchez-Rodriguez et al. 2015) although the studies indicate that the flooding method is equally successful in heavy oils.

**Conclusion**

Following conclusions can be drawn from the studies performed to understand effect of low salinity waterflooding in carbonates:

- Majority of studies mention wettability alteration as the main cause of additional oil recovery but fail to explain the mechanism/s that yield wettability change in the carbonate rock.
- Potential determining ions such as Ca$^{2+}$, SO$_4^{2−}$ and Mg$^{2+}$ have shown to have positive impact on additional oil recovery, some studies indicating Ca and Mg ions behave identically as far as surface chemistry is concerned.
- Zeta potential plays an important role in wettability alteration consequence of which is additional oil recovery, the electrostatic repulsive force between mineral–brine and oil–brine interface stabilizes the water film and repels the oil molecule resulting in oil recovery.
- Majority of the studies have been conducted at ambient temperatures, very few have focused on understanding the impact of reservoir temperatures on final recovery. Contradictions in final results from their studies exist and require further investigation.
- Distinction between limestones and dolomites needs to be made as both behave differently when low salinity brine contacts the mineral surface of these rocks. Due to existence of Mg$^{2+}$ ion in its crystal lattice, dolomites tend to exhibit more oil wetness compared to pure limestones.
- Surface complexation models suggest that calcite surface is negatively charged over the pH range between 5.5 and 11 and in most studies, pH does not have any effect on zeta potential and wettability of the rock. For a constant p(CO$_2$), the zeta potential varies linearly as a function of p(Ca) or p(Mg).
- Studies focusing on effect of carbonate rock composition and impurities in carbonates are scarce although researchers have found that these factors affect the surface chemistry and impact the final wettability.

**Appendix**

| Sr no. | Paper number | Paper title                                                                 | Year | Authors               | Rock type | Inferred mechanisms          |
|-------|--------------|------------------------------------------------------------------------------|------|-----------------------|-----------|-----------------------------|
| 1     | SPE 1725     | Effect of Floodwater Salinity on Recovery of Oil from Cores Containing Clays | 1967 | Bernard               | Carbonate | History of LoSal            |
| 2     | IPTC 10,506  | A laboratory study investigating methods for improving oil recovery in carbonates | 2005 | Webb et al.           | Carbonate | Wettability Alteration       |
| 3     | SPE-93903-MS | Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope | 2005 | McGuire et al.        | Carbonate | Field Application           |
| 4     | SPE 99,628   | Mechanistic Study of Interaction between Water and Carbonate Rocks for Enhancing Oil Recovery | 2006 | Gomari et al.         | Carbonate | PDI                         |
| 5     | JPSE vol 52 187–197 | New wettability test for chalk based on chromatographic separation of SCN$^{−}$ and SO$_4^{2−}$ | 2006 | Strand et al.        | Carbonate | PDI                         |
| 6     | Energy & Fuels 2006, 20, 2056–2062 | Wettability Alteration and Improved Oil Recovery in Chalk: The Effect of Calcium in the Presence of Sulfate | 2006 | Zhang et al.         | Carbonate | Wettability Alteration       |
| Sr no. | Paper number | Paper title | Year | Authors | Rock type | Inferred mechanisms |
|-------|--------------|-------------|------|---------|-----------|---------------------|
| 7     | Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 301, Issues 1–3, 2007, Pages 199–208 | Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca$^{2+}$, Mg$^{2+}$, and SO$_4^{2-}$ | 2007 | Zhang et al. | Carbonate | PDI |
| 8     | SPE109965    | Low-Salinity Waterflooding to Improve Oil Recovery – Historical Field Evidence | 2007 | Robertson | Carbonate | Field Application |
| 9     | SPE-118431-PA | Seawater in Chalk: An EOR and Compaction Fluid | 2008 | Austad et al. | Carbonate | PDI |
| 10    | SPE 121,569  | Effect of brine salinity on reservoir fluids IFT | 2009 | Altoaibi and Nasr El-Din | Carbonate | |
| 11    | Energy & Fuels 2009, 23, 2527–2536 | Coinjection of Seawater and Produced Water to Improve Oil Recovery from Fractured North Sea Chalk Oil Reservoirs | 2009 | Puntervold et al. | Carbonate | Wettability Alteration |
| 12    | SPE 137,634  | Lab investigation for novel oil recovery method for carbonate reservoirs | 2010 | Yousef et al. | Carbonate | Wettability Alteration |
| 13    | Tran Por Med (2010) 85:1–21 | The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability | 2010 | Hiorth et al. | Carbonate | PDI |
| 14    | Energy Fuels 2010, 24, 2974–2979 | Wettability Alteration in Carbonates: The Effect of Water-Soluble Carboxylic Acids in Crude Oil | 2010 | Fathi et al. | Carbonate | Wettability Alteration |
| 15    | SPE 137,634  | Lab investigation of the impact of injection water salinity and ionic content on oil recovery from carbonate reservoirs | 2011 | Yousef et al. | Carbonate | Wettability Alteration |
| 16    | SPE 142,668  | Enhanced Waterflood for Carbonate Reservoirs—Impact of Injection Water Composition | 2011 | Gupta et al. | Carbonate | PDI |
| 17    | Transp Porous Med (2011) 87:679–702 | Chemical Alterations Induced by Rock-Fluid Interactions When Injecting Brines in High Porosity Chalks | 2011 | Madland et al. | Carbonate | PDI |
| 18    | SPE-129877-PA | Snorre Low-Salinity-Water Injection—Coreflooding Experiments and Single-Well Field Pilot | 2011 | Skrettingland et al. | Carbonate | Field Application |
| 19    | Energy Fuels 2011, 25, 5173–5179 | Water-Based Enhanced Oil Recovery (EOR) by “Smart Water”: Optimal Ionic Composition for EOR in Carbonates | 2011 | Fathi et al. | Carbonate | Wettability Alteration |
| 20    | SPE 153,869  | Low salinity EOR in carbonates | 2012 | Romanaka et al. | Carbonate | Wettability Alteration |
| 21    | SPE 155,625  | Experimental Studies of Low Salinity Water Flooding Carbonate: A New Promising Approach | 2012 | Zahid et al. | Carbonate | Fines Migration |
| 22    | SPE-159526-MS | Smart Waterflooding: Industry | 2012 | Yousef et al. | Carbonate | First field trial of LSW flooding |
| 23    | SPE 164,788  | LSW in carbonated reservoir—Experimental approach | 2013 | Al Attar et al. | Carbonate | Wettability Alteration |
| Sr no. | Paper number   | Paper title                                                                 | Year  | Authors                  | Rock type | Inferred mechanisms                      |
|-------|----------------|------------------------------------------------------------------------------|-------|--------------------------|-----------|------------------------------------------|
| 24    | SPE 165,339    | Mechanism behind LoSal waterflooding in carbonate reservoir                   | 2013  | Al Shalabi et al         | Carbonate | Wettability Alteration                   |
| 25    | SPE164341      | First EOR Trial using Low Salinity Water Injection in the Greater Burgan Field, Kuwait | 2013  | Abdulla et al            | Carbonate | Field Application                        |
| 26    | SPE165255      | Kinetics of the Low Salinity Waterflooding Effect Studied in a Model System  | 2013  | Mahani et al             | Carbonate | Wettability Alteration                   |
| 27    | IPTC 17,821    | Optimization of LSW injection process in carbonate reservoirs                | 2014  | Al Shalabi et al         | Carbonate | Wettability Alteration                   |
| 28    | SPE 172,187 MS | Impact of Brine Composition on Carbonate Wettability: A sensitivity Study     | 2014  | AlShaikh and Mahadevan   | Carbonate | Wettability Alteration                   |
| 29    | SPE-172010-MS  | Demonstrating the Potential of Low-Salinity Waterflood to Improve Oil Recovery in Carbonate Reservoirs by Qualitative Coreflood | 2014  | Nasralla et al           | Carbonate | Calcite dissolution                      |
| 30    | SPE 174,391    | LSW in heavy oil carbonates                                                  | 2015  | Sanchez et al            | Carbonate |                                           |
| 31    | SPE-169674-PA  | A Novel Method To Model Low-Salinity-Water Injection in Carbonate Oil Reservoirs | 2015  | Al Shalabi et al         | Carbonate | Empirical model to predict recoveries    |
| 32    | SPE 174,300 MS | Driving Mechanism of Low Salinity Flooding in Carbonate Rock                 | 2015  | Mahani et al             | Carbonate | Mineral dissolution                      |
| 33    | Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 493, 2016, ages 83–98 | Zeta Potential of Intact Natural Limestone: Impact of Potential-Determining Ions Ca, Mg and SO4 | 2015  | Alroudhan et al          | Carbonate | Zeta Potential                           |
| 34    | SPE-176315-MS  | 3D Simulation of Low Salinity, Polymer, Conventional, Waterflooding & Combination IOR Methods – Heterogeneous & Varying Wetting Conditions | 2015  | Aladasani et al          | Carbonate | Heterogeneity                            |
| 35    | Sci. Rep. 6, 37,363; https://doi.org/10.1038/srep37363 (2016) | Zeta potential in oil-water carbonate systems and its impact on oil recovery during controlled salinity water-flooding | 2016  | Jackson et al            | Carbonate | Zeta Potential                           |
| 36    | Volume43, Issue22 Pages 11,578–11,587 | Temperature dependence of the zeta potential in intact natural carbonates | 2016  | Al Mahrouqi et al        | Carbonate | Zeta Potential                           |
| 37    | Advances in Colloid and Interface Science, Volume 240,2017,Pages 60–76,ISSN 0001–8686, | Zeta potential of artificial and natural calcite in aqueous solution | 2016  | Al Mahrouqi et al        | Carbonate | Zeta Potential                           |
| 38    | SPE-179629-MS  | Low Salinity Flooding Trial at West Salym Field                              | 2016  | Erke et al               | Carbonate | Field Application                        |
| 39    | SPE-181745-PA  | Electrokinetics of Carbonate/Brine Interface in Low-Salinity Waterflooding: Effect of Brine Salinity, Composition, Rock Type, and pH on Zeta-Potential and a Surface-Complexation Model | 2016  | Mahani et al             | Carbonate | Zeta Potential                           |
| 40    | Volume 164, May 2018, Pages 640–654 | Low salinity waterflooding for a carbonate reservoir: Experimental evaluation and numerical interpretation | 2016  | Nasralla et al           | Carbonate | Wettability Alteration                   |
| Sr no. | Paper number | Paper title                                                                 | Year  | Authors                          | Rock type | Inferred mechanisms                  |
|-------|--------------|------------------------------------------------------------------------------|-------|----------------------------------|-----------|--------------------------------------|
| 41    | SPE-190481-MS| Low Salinity Waterflood and Low Salinity Polymer Injection in the Wara Reservoir of the Greater Burgan Field | 2018  | Al-Qattan et al.                 | Carbonate | Field Application                      |
| 42    | SPE 197.314 MS| Low Salinity Water Flooding in Carbonate: Screening, Laboratory Quantification and Field Implementation | 2019  | Masalmeh et al.                  | Carbonate | Fluid–Fluid Interaction               |
| 43    | IOR 2019 – 20th European Symposium on Improved Oil Recovery, Apr 2019, Volume 2019, p.1—9 | Zeta Potential in Intact Carbonate Samples: Impact of Brine Composition, Temperature and Wetting State with Application to Controlled Salinity Waterflooding | 2019  | Jackson et al.                   | Carbonate | Zeta Potential                        |
| 44    | Fuel, Volume 266, 2020, 116,927, ISSN 0016–2361 | Zeta potential in intact carbonates at reservoir conditions and its impact on oil recovery during controlled salinity waterflooding | 2019  | Collini et al.                   | Carbonate | Zeta Potential                        |
| 45    | SPE-200547-MS| Heterogeneity Effects on Low Salinity Water Flooding                         | 2020  | Al-Ibadi et al.                  | Carbonate | Reservoir heterogeneity               |
| 46    | Fuel, Volume 276,2020,118,097 | Role of the calcite-water interface in wettability alteration during low salinity waterflooding | 2020  | Li et al.                        | Carbonate | Zeta Potential                        |
| 47    | ACS Omega 2020, 5, 46, 29,780–29,794 | The Impact of Spatially Correlated Heterogeneity and Adsorption on Modified Salinity Water in Carbonates | 2020  | Taheriotaghsara et al.           | Carbonate | Heterogeneity                         |
| 48    | Petroleum, 2021, ISSN 2405–6561, https://doi.org/10.1016/j.petlm.2021.04.001 | Effect of heterogeneity on engineered water injection in carbonates using five-spot sector model: A numerical study | 2021  | Adegbite and Al-Shalabi           | Carbonate | Heterogeneity                         |

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**Declarations**

**Conflict of interest** On behalf of all the co-authors, the corresponding author states that there is no conflict of interest.

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