

Step II: Exposure to LS brine

Thin liquid films in improved oil recovery from low-salinity brine

Philip C. Myint^{a,b}, Abbas Firoozabadi^{a,c,*}

^a*Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, USA*

^b*Lawrence Livermore National Laboratory, Livermore, California, USA*

^c*Reservoir Engineering Research Institute, Palo Alto, California, USA*

Abstract

Low-salinity waterflooding is a relatively new method for improved oil recovery that has generated much interest. It is generally believed that low-salinity brine alters the wettability of oil reservoir rocks towards a wetting state that is optimal for recovery. The mechanism(s) by which the wettability alteration occurs is currently an unsettled issue. This paper reviews recent studies on wettability alteration mechanisms that affect the interactions between the brine/oil and brine/rock interfaces of thin brine films that wet the surface of reservoir rocks. Of these mechanisms, we pay particular attention to double-layer expansion, which is closely tied to an increase in the thickness and stability of the thin brine films. Our review examines studies on both sandstones and carbonate rocks. We conclude that the thin-brine-film mechanisms provide a good qualitative, though incomplete, picture of this very complicated problem. We give suggestions for future studies that may help provide a more quantitative and complete understanding of low-salinity waterflooding.

1. Introduction

Despite society's best efforts toward developing renewable energy sources, more than 70% of the global energy consumption in the coming decades is expected to come from fossil fuels [1]. To meet this high demand, the petroleum research community has continually strived to develop innovative methods for improved oil recovery. One such method that has gained much attention in the past two decades is low-salinity waterflooding (LSW). The improved recovery from LSW is referred to in the literature as the low-salinity effect (LSE). LSW has attracted great interest partly because of its deceptively simple nature. As its name implies, LSW involves the injection of only low-salinity brine. No additional chemicals, which may be costly to the operation, are necessary to observe the LSE, although there have been recent efforts to couple LSW with polymer flooding [2]. Improved recovery has been observed for both secondary-mode LSW, which involves injection of brine into rock saturated with oil, and tertiary-mode LSW, which involves injection of low-salinity brine after the rock has already been flooded in secondary mode with brine of a different composition.

Studies on LSW date back to at least the 1940s, although most of the modern work on this topic began in the 1990s [3, 4]. Since then, the number of papers on LSW has rapidly increased, especially in the past several years. Based on these studies, it is generally believed that LSE occurs because LSW alters the wettability of oil reservoir rocks towards a state more favorable to oil recovery [4, 5]. Other processes, such as an increase in the elasticity of brine/oil interfaces that

*Corresponding author: abbas.firoozabadi@yale.edu

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4 we discuss briefly in Section 4, may also contribute to the improved oil recovery from LSW, but
5 wettability alteration is currently thought to be a major factor. To understand the wettability
6 alteration, it is important to note that the pores of rock saturated with oil are wetted by a residual
7 thin brine film, with oil occupying the rest of the pores. Saturating rock with the oil may cause the
8 rock to become more oil-wet through a variety of brine/oil/rock interactions [6]. LSW studies on
9 sandstones conclude that a high oil recovery is observed in rocks that are weakly water-wet [3, 7].
10 LSW alters the wettability of the sandstones from an oil-wet state towards an optimum weakly
11 water-wet state, thereby leading to an improved recovery. The LSW literature can be classified
12 into studies on sandstones and studies on carbonates. This is a natural choice of division because
13 the surface charge and the chemical reactivity of the two rock types, which consequently affect their
14 wetting behavior, can be very different under the same reservoir conditions [8, 6], [9]*. In fact, until
15 the recent work of Yousef *et al.*, LSE was not even observed in carbonates [10], [11]*. Yousef *et*
16 *al.* report that LSW alters the wettability towards more water-wet conditions, and the maximum
17 LSE is observed for rocks that are weakly water-wet. In summary, LSW in both sandstones and
18 carbonates may alter the wettability towards an optimum state that lies in the weakly-wet region
19 of the spectrum. A glaring question that remains is how does this alteration occur?

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23 The mechanism(s) by which the wettability alteration occurs is currently a major topic of
24 debate in the LSW literature. Various mechanisms have been proposed, but none of them have
25 definitively been shown to be the primary one [12]. This is due to the complex nature of the
26 brine/oil/rock interactions, and is further complicated by a number of conflicting observations
27 from experimental studies [4]. The low-salinity effect likely results from a combination of more
28 than one mechanism. This review focuses on mechanisms which change the stability of thin brine
29 films that wet the surface of oil reservoir rocks. We pay particular attention to the so-called
30 double-layer expansion (DLE) [13], [14]**, [15]*. DLE is described by classical Derjaguin-Landau-
31 Verwey-Overbeek (DLVO) theory. In DLE, injection of low-salinity brine increases the electrostatic
32 repulsion between the film's brine/oil and brine/rock interfaces via the expansion of two electrical
33 double layers, one formed at each of the two interfaces. Consequently, the film becomes thicker
34 and more stable, resulting in a more water-wet rock. Our review also includes studies on chemical
35 mechanisms in low-salinity brine which affect the non-DLVO interactions between the brine/oil and
36 brine/rock interfaces. For example, wettability alteration may occur because of multicomponent
37 ionic exchange (MIE) involving divalent cations near the clay surfaces of sandstones [16]*. Crude
38 oil forms organometallic complexes with divalent cations adsorbed on the clay surface. In LSW,
39 MIE occurs so that the complexed cations are replaced with uncomplexed cations from the brine
40 film, leading to release of the organometallic complexes and oil recovery.

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45 Section 2 discusses in detail recent (published 2009 or later) studies which show that DLE and
46 the chemical mechanisms, which we refer to collectively as thin-brine-film mechanisms, can play an
47 important role in low-salinity wettability alteration of sandstones. Section 3 discusses studies on
48 thin-brine-film mechanisms in carbonates. We conclude with some closing remarks and suggestions
49 for future studies in Section 4.
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52 **2. Wettability alteration involving thin brine films on sandstones**

53 *2.1. Chemical composition of sandstones*

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55 Sandstones are primarily composed of quartz, which has the same chemical formula as silica
56 (SiO_2), but may also contain other minerals (e.g., feldspars, anhydrite, mica, calcite) as well as
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4 various clays (kaolinite, illite, chlorite, montmorillonite). The clays are particularly important for
5 LSW because they are commonly found along the surfaces of the pores in which the oil and brine
6 reside. Silica has an isoelectric point at a pH value of 2, and its surface becomes more negatively
7 charged as the pH increases above this value [8, 6]. Reservoir brines are typically at pH values above
8 the isoelectric point. Clays are also negatively charged on their faces. As a result, sandstones are
9 negatively charged along the surface of the pores. These negative charges play a central role in the
10 wettability alteration mechanisms described in Section 2.2.
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13 *2.2. Double-layer expansion (DLE) and two chemical mechanisms*

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15 The wettability of the reservoir rock depicted in Figure 1 depends on the stability of the thin
16 brine film that wets its surface. The film’s stability is influenced by interactions between its brine/oil
17 and brine/rock interfaces. In sandstones, these interactions include: 1) electrostatic interactions
18 between charged groups on the oil surface of the brine/oil interface and charges on the rock surface
19 of the brine/rock interface; 2) hydrogen bonding between polar functional groups in the crude oil,
20 such as those present in asphaltenes, and polar groups on the rock surface; 3) Lewis acid/base
21 interactions between charged basic groups (e.g., NH_4^+) on the oil surface and negatively-charged
22 groups on the rock surface; 4) formation of organometallic complexes between charged acidic groups
23 (e.g., COO^-) on the oil surface and divalent cations (usually Ca^{2+} and Mg^{2+}) adsorbed on the rock
24 surface. The first interaction is described by classical DLVO theory, while the last three, which are
25 depicted in Figure 1(b), can be thought of as non-DLVO interactions between the brine film’s two
26 interfaces [17]*, [16]*, [18]**. All of these interactions contribute to the disjoining pressure $\Pi(h)$
27 in the film, a quantity that depends on its thickness h . The average thickness of the wetting brine
28 films is thought to be less than 10 nm, and may be much smaller than that value [8, 19]. Attractive
29 interactions between the two interfaces produce negative contributions to Π that cause the film to
30 collapse, decreasing h . Repulsive interactions produce positive contributions to Π that stabilize
31 the film and increase h . Stable, thick brine films are indicative of a water-wet state. The LSW
32 mechanisms described in this section either weaken attractive interactions or strengthen repulsive
33 interactions, thereby resulting in a more stable, thicker brine film and a transition from an oil-wet
34 state to a more water-wet state that results in improved oil recovery.
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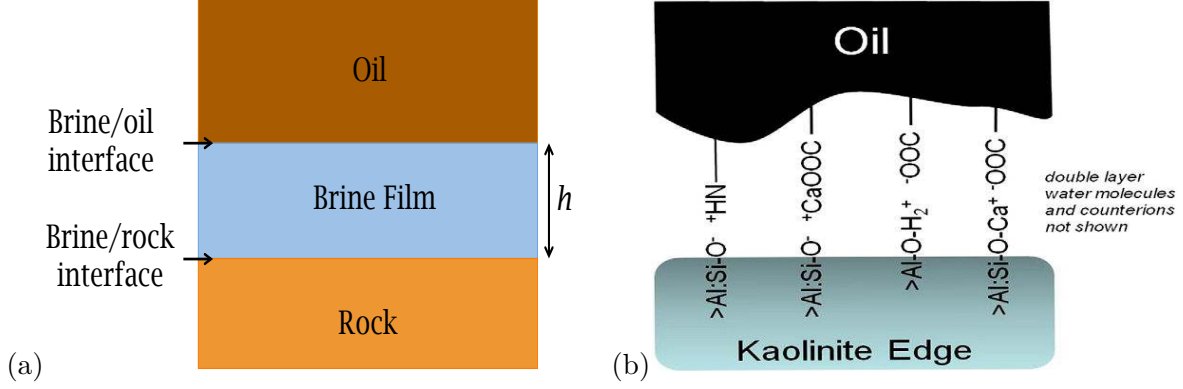


Figure 1: (a) The wettability of oil reservoir rocks is influenced by interactions between the brine/oil and brine/rock interfaces of thin brine films that wet the surfaces of the pores in which the fluids reside. Repulsive interactions produce a positive contribution to the disjoining pressure Π in the film that increases the film's thickness h and leads to a more water-wet state. The average thickness of these wetting films is thought to be less than 10 nm, and may be much smaller than that value [8, 19]. (b) is a schematic of non-DLVO interactions between brine/oil and brine/clay (kaolinite) interfaces, and is adapted from Figure 6 of [20]*, with permission.

One of the most simple, yet effective ways in which low-salinity brine may alter the wettability is double-layer expansion [15]*. Counterions in the brine film adsorb to the negatively-charged brine/oil and brine/rock interfaces, whose electrostatic potentials we represent by ψ_1 and ψ_2 , respectively. The counterions form an electrical double layer at each interface and screen the repulsion between the two negatively-charged interfaces [Figure 2(a)]. A characteristic length of this screening is the Debye length κ^{-1} given by

$$\kappa^{-1} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I} \right)^{1/2}, \quad (1)$$

where ϵ_r is the relative permittivity (dielectric constant) of the brine, ϵ_0 is the permittivity of free space, k_B is the Boltzmann constant, T is the temperature, N_A is Avogadro's number, e is the charge of an electron, and the ionic strength I is

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2, \quad (2)$$

where n is the number of ionic species, c_i is the molar concentration of i , and z_i is the charge of i [21]. When the brine salinity is lowered, the Debye length increases since the ionic strength decreases. Both of the double layers expand to become more diffuse and the screening becomes weaker. As a result, the two interfaces experience a greater electrostatic repulsion [Figure 2(b)]. In other words, the electrostatic contribution Π^{els} to the disjoining pressure becomes more positive. This last point is clear from the following approximation [19] to Π^{els} that is valid for a brine film where the thickness obeys $h\kappa > 1$ and is composed of a symmetric electrolyte (i.e., contains only cations and anions with the same magnitude z of their charge) with molar concentration c :

$$\Pi^{els}(h) \approx 64cN_A k_B T \tanh\left(\frac{ze\psi_1}{4k_B T}\right) \tanh\left(\frac{ze\psi_2}{4k_B T}\right) \exp(-h\kappa). \quad (3)$$

Based on the properties of the hyperbolic tangent function, Π^{els} is positive if both ψ_1 and ψ_2 are negative, and Π^{els} increases in magnitude as the potentials become more negative. The end result of

decreasing the salinity is a more stable, thicker brine film and a more water-wet state [Figure 2(c)]. We note that rather than working directly with ψ_1 and ψ_2 , these potentials are often estimated by the zeta potentials ζ_1 and ζ_2 , respectively, which are experimentally easier to measure.

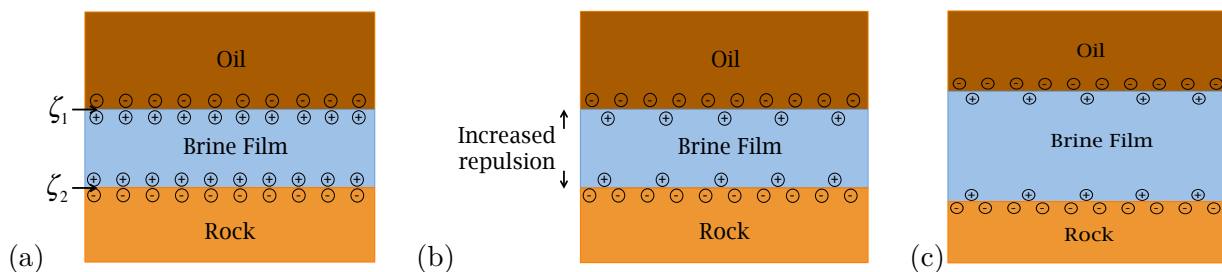


Figure 2: (a) Counterions in the thin brine film adsorb to the negatively-charged brine/oil and brine/rock interfaces to form an electrical double layer at each interface. The potentials at the two interfaces are estimated by the zeta potentials ζ_1 and ζ_2 . (b) When the brine salinity is decreased, the screening from the counterions becomes weaker because the diffuse part of both double layers expand. Consequently, there is more repulsion between the two interfaces, which is reflected in the zeta potentials ζ_1 and ζ_2 becoming more negative. (c) The double-layer expansion (DLE) appears as a thicker brine film that is indicative of a more water-wet state.

In addition to DLE, the stability of the brine film may be affected by two chemical mechanisms: 1) multicomponent ionic exchange (MIE) [16]* and 2) the Austad *et al.* mechanism [22]*, [23]. These mechanisms weaken the attractive non-DLVO interactions described earlier in this section and illustrated in Figure 1(b) [16]*, [9]*, [18]**. A recent thermodynamic model has found that weakening these interactions can be important in LSW [20]*. For example, in MIE, divalent cations adsorbed on clay surfaces of sandstones and bridged with oil molecules to form organometallic complexes are exchanged with uncomplexed cations from the brine film [16]*. MIE improves oil recovery because it removes the bridging interactions between the brine/oil and brine/rock interfaces of the film, leading to a more water-wet state. The uncomplexed cations can be divalents not bridged to oil or they can be monovalent cations, which are unable to form organometallic complexes even though they may adsorb to the clay surfaces. As evidence of MIE, Lager *et al.* have performed coreflooding studies which show no LSE from tertiary-mode LSW where divalents have been flushed out from the connate brine present in the core [16]*. In the absence of divalent cations, MIE does not improve oil recovery because there are no organometallic complexes.

Austad *et al.* have proposed a chemical mechanism on clay surfaces in which the clay acts as a cation exchanger (Figure 3) [22]*. When the salinity decreases, the equilibrium between the adsorbed cations and their desorbed counterparts in the brine is disturbed because the concentration of cations in the brine is lowered. To counteract this disturbance, there is a net desorption of cations, especially Ca^{2+} . The desorbed cations are exchanged with protons produced from the hydrolysis of nearby water molecules, which creates a local increase in the pH [Figures 3(b) and 3(e)]. The local increase in pH induces acid/base reactions that result in the release of basic [Figure 3(c)] and acidic [Figure 3(f)] groups in oil from the clay surface. The net result is wettability alteration and oil release due to breakage of non-DLVO interactions (acid/base interactions, hydrogen bonds) between the brine/oil and brine/clay interfaces. In addition, the Austad *et al.* mechanism alters the brine/clay electrostatic potential because substitution of an adsorbed divalent cation with H^+ makes the clay surface even more negatively charged. This enhances the double-layer expansion.

Both MIE and the Austad *et al.* mechanism have been proposed to occur only on clay surfaces. Presumably this is because it has been thought that clay, especially kaolinite, must be present

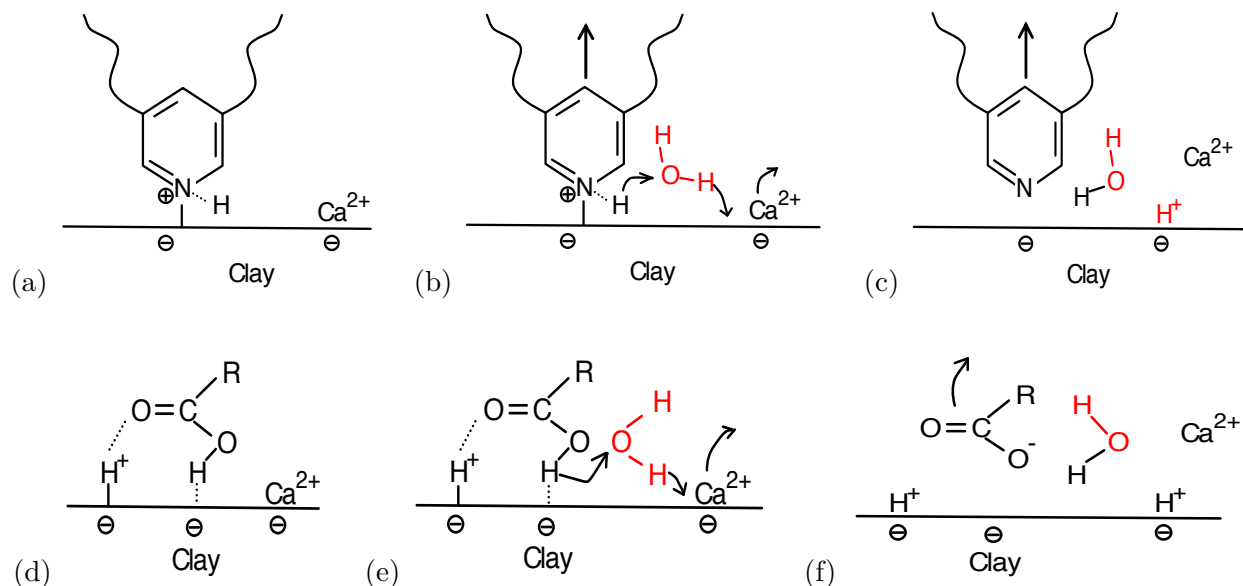


Figure 3: (a)–(c) Mechanism proposed by Austad *et al.* for detachment of basic groups in oil, where (a) shows the initial situation before LSW, (b) the chemical reactions occurring in low-salinity brine, and (c) the final situation after LSW. (d)–(f) illustrate their mechanism for detachment of acidic groups in oil. The chemical reactions break the brine/oil and brine/rock interactions depicted in (a) and (d), and they also enhance the double-layer expansion by increasing the net negative potential along the clay surface. Adapted from Figure 1 of [22]*, with permission.

for LSE to be observed [3]. However, more recent studies have observed LSE in kaolinite-free sandstones [24] and in sandstones that do not contain significant amounts of any type of clay [25]. Furthermore, silica can undergo cation exchange processes. A recent paper reports that negatively-charged surfactants are able to adsorb onto silica surfaces as long as divalent (Ca^{2+}) cations are present to bridge the surfactants to the negatively-charged silica [26]*. No such adsorption is detected when the brine is changed to NaCl, because sodium is unable to participate in bridging interactions. The adsorption is pH-dependent, indicating that there is cation exchange with H^+ as well. Other studies have confirmed that the presence of Ca^{2+} and Mg^{2+} are important for the adsorption of asphaltenes on quartz [27, 28]. Thus it is plausible that the two chemical mechanisms can also occur on quartz surfaces, not just on clays, and may be responsible for part of the LSE observed in the clay-free rocks. In the next few sections, we describe recent studies which show that DLE and the two chemical mechanisms can be important for wettability alteration in LSW.

2.3. Visualization of DLE and DLE-induced wettability alteration

Direct evidence of DLE and the chemical mechanisms in low-salinity brine comes from the work of Lee *et al.* [14]**. They have created dispersions of sand-like (silica) or clay-like particles in a mixture of *n*-heptane with aerosol-OT, an anionic model surfactant. There is a thin brine film surrounding the particles because they are first placed in a brine solution before being transferred to the oil. If the brine film contains divalent cations, organometallic complexes can form as described in Section 2.2. Lee *et al.* use small angle neutron scattering to measure the thickness of these films as a function of brine composition and salinity. Although the estimated uncertainty in the measurements are relatively large, some interesting trends are apparent in Figure 4. As expected, decreasing the salinity increases the thickness (i.e., makes the particles more water-wet) due to DLE

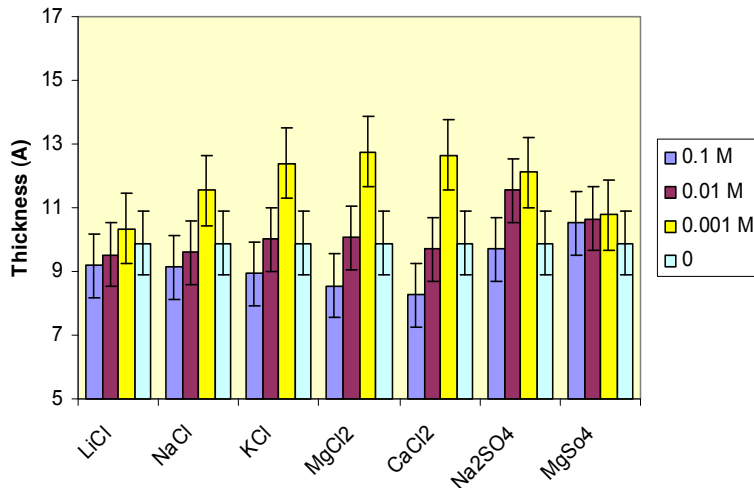


Figure 4: Thickness of thin brine films surrounding sand-like particles dispersed in a mixture of *n*-heptane and anionic surfactant. The thickness and the salinity are reported in ångströms and molarity, respectively. Error bars are also shown. Adapted from Figure 12 of [14]**, with permission.

and the chemical mechanisms. Interestingly, the thickness seems to reach a maximum at low salt concentrations; the films are not the thickest in deionized water. Comparing results for LiCl, NaCl, and KCl, we see that the thickness of brine films with larger monovalent cations are more sensitive to salinity. This trend is presented from another perspective in Section 2.4, where we examine the zeta potential of silica particles in solutions of NaCl, KCl, and CsCl. Another topic we discuss in the next section is divalent cations vs. monovalent cations. Figure 4 shows that the thickness of films with divalent cations are more sensitive to salinity. There are at least two reasons for this behavior. First, because monovalent cations cannot form organometallic complexes, MIE will not affect the thickness of films made of brines like NaCl. Only DLE and the Austad *et al.* mechanism may occur in these films. In contrast, when the salinity of brine films with divalent cations is decreased, all three mechanisms (DLE, MIE, Austad *et al.*) can occur. Second, divalent cations are said to be specifically adsorbed to certain surfaces, like silica (see [29] and the references cited therein). Divalent cations adsorb directly to these surfaces to form inner-sphere complexes, whereas monovalent cations form outer-sphere complexes, where there is at least one water molecule lying between the surface and the cation [17]*, [29], [9]*. For these reasons, one can expect the thickness of brine films with divalent cations to be more sensitive to the salinity.

Berg *et al.* have monitored the effect of low-salinity brine on crude oil droplets attached to clay particles adhered to a glass substrate that is placed in a transparent flow cell [30]. High-salinity brine is flowed into the cell at a steady speed to remove loosely-attached droplets. Afterwards, low-salinity brine is entered at the same speed, resulting in detachment of oil from the clay particles. Many trials with different low-salinity brines are conducted. Images recorded by a digital camera are analyzed to quantify the amount of oil release. For trials with very low-salinity brine (2.0 g/L NaCl), an average of 66% of the oil is released, but there is significant production of fines (small fragments) due to de-flocculation of clay from the substrate. Fines production, which we briefly discuss in Section 2.6, is sometimes undesirable in field-scale operations because it may damage the well productivity. Berg *et al.* report that high-salinity brine diluted four times (≈ 6.5 g/L in dissolved salts) leads to a 59% recovery of the oil, and there is no significant fines production. They conclude

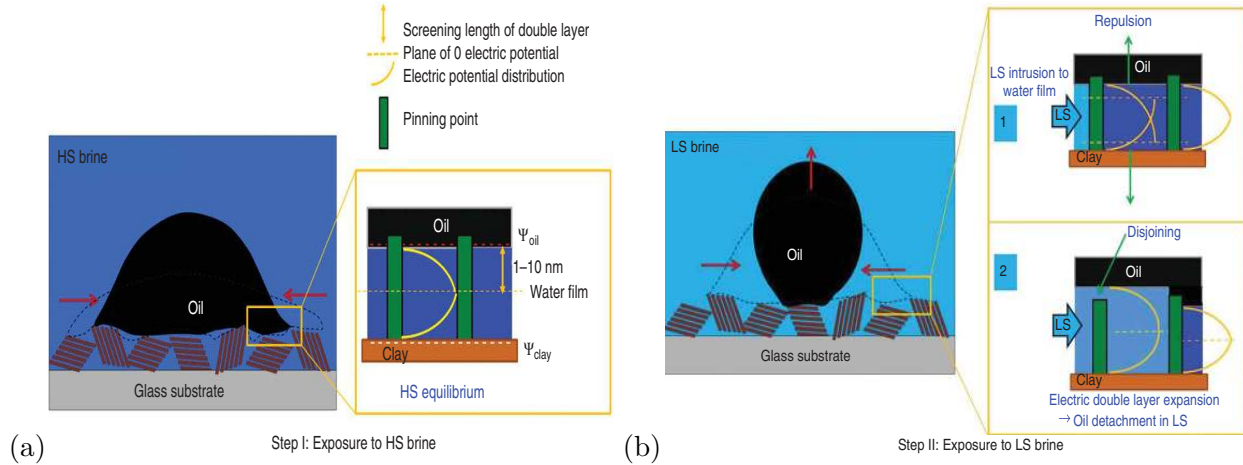


Figure 5: Low-salinity wettability alteration on clay surfaces envisioned by Mahani *et al* [18]**. Oil adhesion is dictated by the stability of the thin brine film between oil and clay shown in (a). The stability depends in part on non-DLVO interactions between the brine/oil and brine/clay interfaces, which act as discrete pinning points between oil and clay. (b) Low-salinity brine gradually displaces high-salinity brine in the brine film. This results in DLE and breakage of the pinning points, leading to release of the oil. Adapted from Figure 14 of [18]**, with permission.

that in low-salinity brine, the adhesion forces that attach the oil droplets to the clays are weakened due to DLE and the chemical mechanisms. The oil droplets are released as a result.

Mahani *et al.* use a similar setup as Berg *et al.*, except that low-salinity brine is slowly introduced so as to not hydrodynamically disturb the oil [18]**. Instead, the low-salinity brine diffuses into the narrow space between the oil and clay previously occupied by the high-salinity brine film (Figure 5). In addition to theoretically modeling this diffusion process, Mahani *et al.* also experimentally monitor the recession of the three-phase brine/oil/clay contact line and the change in the oil droplet’s contact angle as high-salinity brine is displaced by low-salinity brine. The contact angle decreases over time, indicating a transition towards a more water-wet state, until it reaches a critical value of between 40–50° where oil droplets start to detach from the clay. The contact angle, however, does not always decrease in a smooth, gradual manner. Periods of gradual decrease are punctuated by sudden, step-like drops. Mahani *et al.* interpret the results of their experimental measurements and their diffusion model with the picture illustrated in Figure 5. Oil is attached to the clay surface due to electrostatic screening from ions in the brine film, as well as the non-DLVO interactions described in Section 2.2, which serve as discrete pinning points between oil and clay [Figure 5(a)]. In low-salinity brine, DLE and the chemical mechanisms weaken the attraction between brine/oil and brine/clay interfaces, and the step-like drops in the contact angle may correspond to breakage of the discrete pinning points [Figure 5(b)].

2.4. Zeta potential, contact angle, oil recovery, and AFM measurements

Rather than directly visualizing DLE, some studies have provided evidence for it through a combination of zeta potential, contact angle, and oil recovery measurements. Alotaibi *et al.* have measured the contact angle of oil droplets placed on a flat sheet of Berea sandstone that is immersed in one of three different brines [31]. In order of decreasing salinity, the brines are formation water, seawater, and aquifer water. Experiments are conducted at 50 °C and 90 °C. For both temperatures, they find that the rock becomes more water-wet as the salinity decreases. The wettability alteration is especially pronounced for aquifer water, which has a salinity roughly ten times less than that of

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4 seawater. Alotaibi *et al.* have also measured the zeta potential of brine/Berea and a few different
5 brine/clay dispersions. For all dispersions, the zeta potential becomes more negative (there is more
6 double-layer expansion) at lower salinities. Nasralla *et al.* have observed similar results for a more
7 diverse variety of systems [32]. In addition to the same three brines studied by Alotaibi *et al.*,
8 Nasralla *et al.* have also examined aquifer water diluted by a factor of ten and deionized water.
9 They have measured the zeta potential of both brine/oil and brine/rock dispersions. Except for a
10 few issues that we discuss in Section 2.6, their results are in agreement with what we would expect
11 if DLE is a major mechanism of wettability alteration. That is, decreasing the salinity leads to
12 more negative zeta potentials at both interfaces of the thin brine films, which results in a more
13 water-wet state and improved oil recovery. In their experiments, deionized water has the most
14 negative brine/oil and brine/rock zeta potentials, the highest water-wet contact angle, and the
15 greatest secondary-mode oil recovery.

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18 The extent of the double-layer expansion is affected by the composition of the brine (e.g.,
19 whether the brine contains divalent or monovalent cations) and the pH of brine. As we alluded to
20 in our discussion of the film thickness measurements by Lee *et al.* [14]**, DLE is more sensitive
21 to salinity in brines with larger monovalent cations. Similar results are obtained by Dishon *et al.*
22 *et al.*, who have measured the brine/silica zeta potential for three different brines (NaCl, KCl, and
23 CsCl) at two different concentrations, 10 millimolar (mM) and 1 mM [33]. The zeta potentials at
24 10 mM are -22 mV, -20 mV, and -16 mV for NaCl, KCl, and CsCl, respectively. At 1 mM, the
25 zeta potential for all three brine/silica dispersions is -33 mV so that the change with salinity is
26 more pronounced for the larger cations. At the same concentration, the brine/rock and brine/oil
27 zeta potentials tend to be more negative if the brine contains monovalent cations as opposed to
28 divalent cations [29, 32, 27]. This may be because divalents have a stronger influence on the ionic
29 strength and electrostatic screening as evident in Equation (2), and because as we discussed in
30 Section 2.3, divalents adsorb more strongly to charged surfaces than do monovalents. Farooq *et al.*
31 have measured the zeta potential of dispersions containing different sandstone minerals and rocks,
32 including silica, kaolinite, reservoir rocks, and two types of outcrop rocks (Berea and Bentheimer)
33 that mimic reservoir rocks [29]. The dispersions are formed using one of five different solutions:
34 deionized water, brine solutions of pure NaCl, CaCl₂, MgCl₂, and a mixed brine that is composed
35 mainly of NaCl but also contains small amounts of divalents. All the brines are at the same
36 concentration of 1500 parts-per-million (ppm). It is found that for kaolinite at a pH of 6, the zeta
37 potentials are approximately -75 mV, -30 mV, -15 mV, -10 mV, and -7 mV in deionized water,
38 NaCl, mixed brine, CaCl₂, and MgCl₂, respectively. The other minerals and rocks exhibit similar
39 trends with respect to the relative magnitude of the zeta potentials.

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42 Nasralla *et al.* have compared the brine/oil zeta potential for two crude oils and three types of
43 brines (NaCl, CaCl₂, MgCl₂) with each brine type at three different weight fractions of salt [34].
44 At the same weight fraction, NaCl displays the most negative zeta potential with both oils. Conse-
45 quently, the thin brine film with NaCl undergoes the most DLE, and Nasralla *et al.* find that NaCl
46 provides greater secondary-mode improved oil recovery than CaCl₂ and MgCl₂. The differences
47 among the three types of brines would be even more disparate if they were compared at the same
48 mole fraction, rather than weight fraction. Finally, as the pH of the brine increases, the interfaces
49 of the brine film become more negative. The brine/rock zeta potentials of silica and various other
50 sandstone minerals become more negative with increasing pH [33, 29]. The same is also true for
51 the brine/oil zeta potential [34], [15]*. The enhanced double-layer expansion at higher pH values
52 is reflected in oil recovery measurements. For example, Nasralla *et al.* report that a low-salinity
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4 diluted aquifer water solution at a pH of 4.8 leads to a secondary-mode recovery of 37% of the
5 original oil-in-place (OOIP) in a Berea sandstone core at 100 °C and 34 bar, while the same brine
6 at the same conditions but at a pH of 7.3 yields a recovery of 47% OOIP [15]*.

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8 Double-layer expansion is related to force measurements from atomic force microscopy (AFM).
9 AFM can be used to measure the adhesion, as a function of salinity, between quartz grains removed
10 from sandstone cores and AFM tips functionalized with oil, both of which are submerged in brine.
11 The adhesion is an indication of the attractive interactions between the brine/oil and brine/quartz
12 interfaces of thin brine films in reservoir rocks. Diluting the brine makes the quartz surface more
13 water-wet and reduces the adhesion to oil [35]. The experimentally measured adhesion force as a
14 function of salinity can be fitted well with force predictions from DLVO theory [36]*. This result
15 implies that DLE, which is based on DLVO theory, can be a major mechanism for the improved oil
16 recovery from low-salinity brine.
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19 20 2.5. DLE vs. MIE

21 At low salinities, DLE and the two chemical mechanisms discussed in Section 2.2 occur together
22 to enhance the wetting of thin brine films and improve the oil recovery. Two studies have done
23 coreflooding experiments to determine whether DLE plays a more dominant role than MIE, one of
24 the two chemical mechanisms, in causing the low-salinity effect. Ligthelm *et al.* have injected a high-
25 salinity formation brine, which contains both monovalent and divalent cations, into a sandstone
26 core in secondary mode to recover an oil volume equivalent to about 28% of the total pore volume
27 of the core [13]. They then inject a high-salinity NaCl solution in tertiary mode to recover an
28 additional 3% of the pore volume in oil. This recovery is rather small and may be partly a result of
29 experimental artifacts, such as a change in the flow rate between the secondary- and tertiary-mode
30 injections. The high-salinity NaCl is continually injected until divalent cations are no longer present
31 in the effluent brine. The NaCl has roughly the same ionic strength as the formation brine, so there
32 is expected to be little DLE, but MIE occurs since sodium can exchange with the complexed divalent
33 cations. Ligthelm *et al.* follow the high-salinity NaCl injection with injection of a low-salinity NaCl
34 solution, which recovers about 6% of the pore volume in oil. During the low-salinity NaCl injection,
35 there is significant DLE, but no MIE because all the divalent cations have been effectively flushed
36 out. Since the recovery is larger when there is DLE, Ligthelm *et al.* conclude that DLE is more
37 important than MIE in their system. Xie *et al.* have performed similar experiments and also report
38 that DLE is more significant than MIE in their system [37]. Their oil recovery measurements are
39 supported by disjoining pressure calculations and zeta potential measurements.
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45 2.6. Limitations of DLE and the chemical mechanisms

46 The studies described in Sections 2.3–2.5 have verified from multiple perspectives that DLE and
47 the chemical mechanisms can be important in LSW. They provide a qualitative picture, and even a
48 quantitative explanation in certain cases [36]*, of low-salinity wettability alteration. However, they
49 cannot explain all of the results. The purpose of this section is to discuss these limitations in order
50 to stress that more careful studies are needed and to agree with the assessment in the literature
51 that no one mechanism can explain all of the results [38, 12].
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53 First, we note that if the brine salinity is reduced, the wettability does not always change in
54 a consistent manner. In Section 2.4, we described a study by Alotaibi *et al.* who report that the
55 brine/rock zeta potential of Berea sandstone becomes more negative with decreasing salinity, as
56 expected [31]. The brine/rock zeta potential of Scioto sandstone in their study also exhibits the
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4 same behavior, but the contact angle of oil droplets on Scioto does not change as expected. Con-
5 tact angle measurements suggest that Scioto is more oil-wet (less water-wet) in low-salinity aquifer
6 water than in high-salinity seawater. Similarly, Nasralla *et al.* find that even though seawater's
7 salinity is significantly lower than that of formation brine, it produces a more oil-wet state and
8 yields less secondary-mode oil recovery than formation brine [32]. An important, but unresolved
9 issue is whether low-salinity brine is more efficient than deionized water for LSW. The film thickness
10 measurements in Figure 4 suggest that deionized water is not the optimal choice because it does
11 not lead to the most double-layer expansion. However, recent zeta potential and oil recovery mea-
12 surements that we have discussed show that deionized water may be most effective [32, 29], [15]*.
13 A similar discrepancy exists for the effect of monovalent vs. divalent cations. Figure 4 suggests
14 that double-layer expansion may be greater in brine films with CaCl_2 rather than NaCl , while
15 zeta potential and oil recovery measurements have found that NaCl may be more effective for
16 LSW [34, 29], [15]*. These results show that LSW involves very complicated phenomena that
17 depend on the specific systems (rocks, brines, crude oils) and conditions under study. It is difficult
18 to make broad, sweeping generalizations that apply to all systems under all conditions.

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20 Even if deionized water yields the largest recovery, it may not be an ideal choice in field-scale
21 LSW operations because it could damage oil well productivity through fines migration. It is known
22 that below a critical salt concentration, clays may de-flocculate from sandstone surfaces and migrate
23 through the pores as fines [39, 30]. Despite the potential damage caused by the fines, they may
24 improve the recovery because the fines carry attached oil droplets, and they allow for greater sweep
25 efficiency of the brine through the formation. Although fines migration is no longer thought to
26 be a major mechanism for LSW wettability alteration [16]*, [38, 24, 5], it may be important in
27 certain cases. In a few laboratory experiments, LSE is observed only in cores where there is fines
28 migration [25, 40]. It is unclear why in these studies, DLE and the chemical mechanisms do not
29 improve the oil recovery unless fines are also produced. Pu *et al.* do report, however, that fines
30 migration in their study is associated with dissolution of anhydrite (CaSO_4) in the sandstone, which
31 produces sulfate ions [25]. This may be related to a chemical mechanism in carbonates that we
32 discuss in Section 3.

39 **3. Wettability alteration involving thin brine films on carbonates**

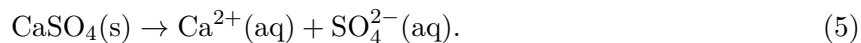
40 *3.1. Chemical composition and reactivity of carbonates*

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42 Carbonates are primarily composed of calcite, which is a common mineral form of calcium
43 carbonate (CaCO_3). Carbonates may also contain other minerals like aragonite (another form of
44 CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], and anhydrite (CaSO_4). Two common types of rocks found in
45 carbonate oil reservoirs are dolostone, which mainly contains dolomite, and limestone (e.g., chalk).
46 The isoelectric points of these carbonate minerals and rocks are well above the isoelectric point of
47 quartz ($\text{pH} = 2$) [41]*. For example, the isoelectric point of calcite in pure water lies in the pH
48 range of 7 to 12 (depending on the conditions [41]*), with the exact value often quoted as being
49 the midpoint of this range, a pH of 9.5 [8, 6]. Based on this fact alone, one may conclude that
50 carbonate surfaces have a much stronger tendency to be positively charged than sandstone surfaces.
51 Unlike quartz, however, calcite is chemically reactive and can dissolve in brine to produce Ca^{2+} ,
52 CO_3^{2-} , HCO_3^- , and H_2CO_3 [29], [9]*. Furthermore, the presence of Mg^{2+} and SO_4^{2-} in the brine or
53 in the rocks, such as those found in dolomite and anhydrite, can lead to more reactions near the
54 brine/carbonate interface, including substitution of calcium with magnesium on the rock surface,
55 mineral dissolution, precipitation, and adsorption.

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4 The chemical reactivity of carbonates affects the charge along the brine/carbonate interface.
5 The dissolution of calcite, which may be expressed as
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9 increases the pH [9]*, [42]. The increase in pH drives the zeta potential of the brine/carbonate
10 interface towards the negative direction [41]*. Ions created during mineral dissolution or already
11 present in the brine can adsorb to the carbonate surface to further alter the charge. An important
12 ion for LSW in carbonates is the sulfate ion (SO_4^{2-}), which is produced by anhydrite dissolution:
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17 The adsorption of SO_4^{2-} created by anhydrite dissolution places negative charges near the carbonate
18 surface.
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20 21 *3.2. Double-layer expansion and a chemical mechanism proposed by Austad et al.*

22 The chemical reactions described in Section 3.1 underlie two LSW mechanisms that affect the
23 stability of wetting thin brine films on carbonates: 1) double-layer expansion, and 2) a chem-
24 ical mechanism proposed by Austad *et al.* involving SO_4^{2-} produced by anhydrite dissolution
25 [43]*, [44]*. Injection of low-salinity brine in carbonate reservoirs disturbs the thermodynamic
26 equilibrium established among the ions dissolved in the brine film, the ions adsorbed to the rock
27 surface, and the species incorporated into the rock matrix [41]*. This disturbance induces the
28 dissolution of minerals like calcite and anhydrite to counteract the decrease in the concentration of
29 dissolved ions. As discussed above, the dissolution of calcite and anhydrite increases the pH and
30 produces sulfate ions, respectively. Both reactions cause the brine/carbonate interface to become
31 more negatively charged and repelled by the negatively-charged brine/oil interface. The decreased
32 ionic strength in the brine film expands the two electrical double layers (one at each of the film's two
33 interfaces) and thereby reduces the screening of the repulsion. As a result, the film becomes thicker
34 because the positive electrostatic contribution to the disjoining pressure Π increases. The carbonate
35 consequently becomes more water-wet. A recent study has attempted to demonstrate wettability
36 alteration on both calcite and quartz surfaces through disjoining pressure calculations [45]*.
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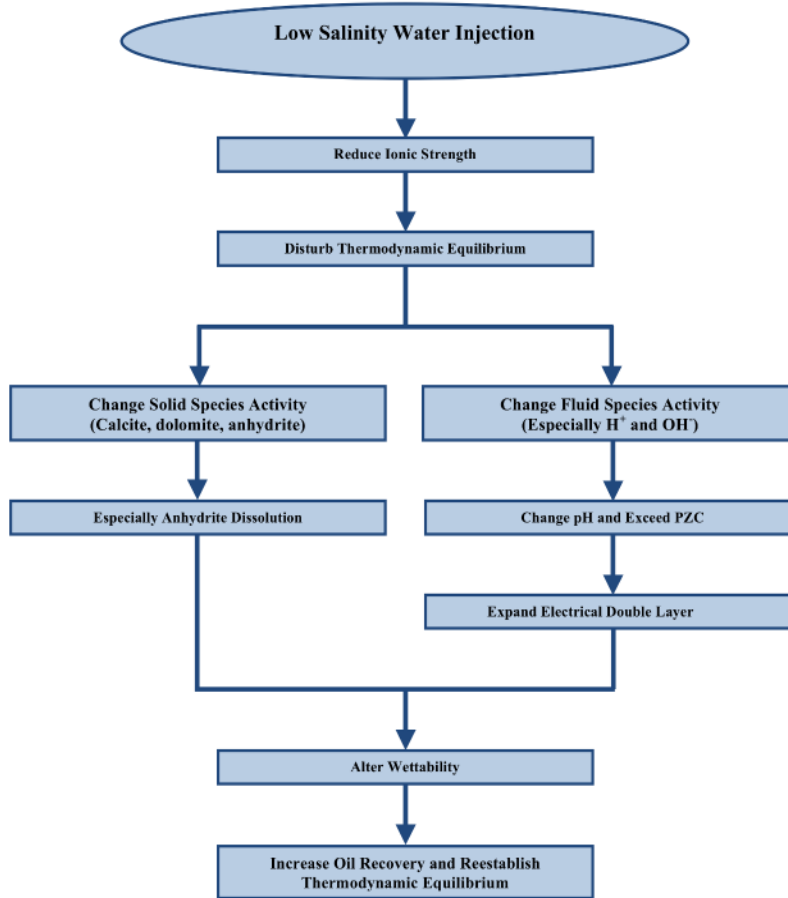


Figure 6: Flowchart of LSW mechanisms in carbonates. Injection of low-salinity brine disturbs the thermodynamic equilibrium, which leads to dissolution of minerals like anhydrite and an increase in the pH. Sulfate ions produced by anhydrite dissolution induces a chemical mechanism proposed by Austad *et al.* [43]* in which chemical bonds between the brine/oil and brine/carbonate interfaces of thin brine films are broken. The pH increase lowers the positive charge of the brine/carbonate interface. If the pH exceeds the rock's point of zero charge (PZC), which has a similar meaning to its isoelectric point, the surface becomes negatively charged and double-layer expansion (i.e., an increase in the film thickness) occurs. Both double-layer expansion and the chemical mechanism alter the wettability towards a more water-wet state favorable to oil recovery. Adapted from Figure 19 of [41]*, with permission.

Anhydrite dissolution may improve oil recovery by increasing the connectivity of the pores so that the reservoir becomes more permeable to flow [10], [11]*. Furthermore, anhydrite dissolution is a key feature of a LSW chemical mechanism proposed by Austad *et al.* [43]*. This mechanism is adapted from one that they proposed earlier to explain how seawater enhances the stability of thin brine films on chalk surfaces [44]*. According to this mechanism, sulfate ions produced by anhydrite dissolution in LSW adsorbs to the carbonate surface. This leads to co-adsorption of Ca^{2+} and Mg^{2+} onto the rock. The Ca^{2+} ions can then react with carboxylic groups in oil that are bonded to the carbonate surface. The reaction with Ca^{2+} breaks the bonds between the brine/oil and brine/carbonate interfaces and causes release of the carboxylic groups, leading to improved oil recovery. At sufficiently high temperatures, Mg^{2+} can substitute Ca^{2+} on the carbonate surface and thereby displace Ca^{2+} ions on the surface that are bridged to carboxylic groups. In this manner, the Ca/Mg substitution further improves oil recovery. The aforementioned chemical mechanism

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4 for carbonates resembles the two chemical mechanisms for sandstones detailed in Section 2.2 since
5 all three involve breaking attractive interactions between the brine/oil and brine/rock interfaces
6 of thin brine films, causing the film to become more wetting. The two LSW mechanisms for
7 carbonates (double-layer expansion and the chemical mechanism induced by anhydrite dissolution)
8 are summarized in the flowchart of Figure 6. In the rest of this section, we discuss experimental
9 and theoretical studies on these mechanisms, as well as their implications for improved oil recovery.

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11 The low-salinity effect in carbonates was first observed by Yousef *et al.* They have injected
12 six different brines into cores obtained from a carbonate reservoir whose composition is roughly
13 80% calcite, 13% dolomite, and 6% anhydrite [10]. In order of decreasing salinity, the brines are
14 formation water, seawater, seawater diluted two times, 10 times, 20 times, and 100 times. They re-
15 port improved oil recovery from tertiary-mode LSW, although the recovery from 100 times diluted
16 seawater is negligible compared to that from 20 times diluted seawater. The oil recovery measure-
17 ments are consistent with their contact angle measurements of oil droplets on flat carbonate rock
18 plates. Over the six different brines, the contact angle decreases from 88–92° in the formation brine
19 to 58–62° in 100 times diluted seawater. They define the contact angle so that its decrease at lower
20 salinities indicates a transition to a more water-wet state. The difference in the average contact
21 angle between the two lowest-salinity brines is small (roughly 2°). Nuclear magnetic resonance
22 (NMR) results obtained by Yousef *et al.* suggest that the wettability alteration could be due to
23 anhydrite dissolution, which is consistent with the Austad *et al.* mechanism, or to a change in the
24 surface charge of the carbonate, which is consistent with double-layer expansion [10], [11]*.

25
26 The occurrence of double-layer expansion during LSW in carbonates is supported by zeta po-
27 tential measurements. Yousef *et al.* have found that the brine/carbonate zeta potentials in seawater
28 diluted two times, 10 times, 20 times, and 100 times become increasingly negative with decreasing
29 salinity [11]*. The zeta potentials are more negative at 60 °C than at 40 °C, which suggests that
30 DLE is more pronounced at the higher temperature. These findings are consistent with the results
31 of Alotaibi *et al.*, who have measured zeta potentials of limestone and dolomite particles in different
32 brines at two different temperatures (25 °C and 50 °C) [46]. The experimental trend with respect
33 to temperature agrees with the assertion of Austad *et al.* that LSW is most effective at an opti-
34 mum temperature of between 90–110 °C [43]*. The zeta potential behavior with respect to brine
35 composition and pH is more complicated and highly dependent on the specific conditions under
36 study. Just as we described in Section 2 for sandstones, divalent cations (Ca^{2+} and Mg^{2+}) can
37 adsorb strongly to calcite surfaces. The adsorption is sufficiently strong that Farooq *et al.* report
38 the brine/calcite zeta potential to be positive (varying between about 5 to 20 mV) throughout the
39 entire pH range of 2 to 11 for CaCl_2 and MgCl_2 solutions at 1500 ppm [29]. However, carbonate
40 rocks are not always positively charged in the presence of CaCl_2 and MgCl_2 . Chen *et al.* have
41 measured the zeta potential of TP powder, which is 82% calcite but also contains some quartz and
42 clays, in 0.1 weight percent CaCl_2 over a pH range of 5 to 11. They find that the zeta potential
43 monotonically decreases from about 5 mV at pH = 5 to -23 mV at pH = 11 [47]. They have also
44 measured the zeta potential of TP powder in three different pure brines (NaCl , CaCl_2 , MgCl_2)
45 over a concentration range of 0 to 10 weight percent. In all three brines, the zeta potential of the
46 powder becomes more negative with decreasing salinity, which is consistent with DLE as a LSW
47 mechanism. At the same weight percent of brine, TP powder dispersions in NaCl have the most
48 negative zeta potential, followed by dispersions in MgCl_2 , then CaCl_2 . The zeta potential of the
49 powder in NaCl is negative throughout the entire concentration range, while it is negative below
50 a certain concentration in the other two brines (approximately 2 and 7 weight percent for CaCl_2
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4 and MgCl_2 , respectively). The presence of sulfate ions in the brine can significantly lower the zeta
5 potentials of calcite and dolomite surfaces toward negative values [9]*, [46].

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7 Austad *et al.* devised their chemical mechanism based on their earlier studies of seawater in chalk
8 cores [44]* and on the observation that no LSE is obtained in their anhydrite-free cores [43]*. Their
9 mechanism has been theoretically corroborated with density functional theory (DFT) simulations
10 by Sánchez and Miranda, who have studied the adsorption of propionic acid (this compound mimics
11 the acidic components of oil) on a calcite surface [48]*. The DFT simulations show that substitution
12 of calcium with magnesium on the calcite surface, which is one feature of the Austad *et al.* chemical
13 mechanism, is thermodynamically favorable to release of the adsorbed acid. The simulations place
14 a monolayer of water molecules on the calcite surface and employ a continuum solvent model with a
15 dielectric constant, which may represent the aqueous brine film environment. Sánchez and Miranda
16 show that increasing the dielectric constant of the brine, which is associated with decreasing the
17 salinity, is favorable to the release of the acid (and therefore also oil) on Mg-substituted calcite.

18
19 In a recent study, Al-Shalabi *et al.* use a geochemical/thermodynamic model to find that the
20 observed wettability alteration in the experiments of Yousef *et al.* [10], [11]* is more strongly corre-
21 lated with a change in surface charge from the pH increase as opposed to anhydrite dissolution [41]*.
22 They caution that this conclusion applies only to the specific system in their study, not necessarily
23 to all carbonate systems. This agrees with our assertion in Section 2.6 that due to the complex
24 nature of brine/oil/rock interactions, it is difficult to state generalizations that apply to all systems
25 under all conditions. This difficulty is exemplified by the results of Zahid *et al.*, who have obtained
26 substantial tertiary-mode oil recovery in carbonate cores at 90 °C from diluted seawater injection,
27 but no significant recovery in chalk cores [49]. Improved recovery is not observed in their chalk
28 cores even though Ca/Mg substitution on the surface occurs. For the carbonate cores, their ex-
29 perimental results reveal no evidence for either of the two mechanisms that we have focused on in
30 this section. Their NMR results do not show a change in the surface charge, which suggests that
31 DLE is not prominent in their cores. The cores are also anhydrite-free, so they cannot undergo the
32 Austad *et al.* chemical mechanism. Instead Zahid *et al.* suggest dissolution of other minerals besides
33 anhydrite, coupled with fines migration, as a possible explanation for the wettability alteration.

34 35 36 37 38 39 **4. Conclusions**

40
41 We have reviewed experimental and theoretical studies on mechanisms that affect the wetting
42 behavior of thin brine films on the surfaces of oil reservoir rocks. These mechanisms have been
43 used to explain how injection of low-salinity brine alters the wettability of the rocks towards a state
44 that is more optimal for oil recovery. Our review is divided into studies on sandstones and studies
45 on carbonates. For both rock types, we have primarily focused on double-layer expansion. In this
46 mechanism, injection of low-salinity brine expands the two electrical double layers in the film and
47 increases the electrostatic repulsion between the film's brine/oil and brine/rock interfaces. As a
48 result, the film becomes thicker. We have also reviewed studies on three chemical mechanisms, two
49 in sandstones and one in carbonates, that affect the attractive interactions (e.g., organometallic
50 bridges, hydrogen bonding, acid/base interactions) between the thin brine film's two interfaces. We
51 have shown from multiple perspectives that double-layer expansion and the chemical mechanisms
52 can play an important role in low-salinity waterflooding. They paint a clear qualitative picture of
53 low-salinity wettability alteration. Yet, we have noted that they cannot explain all of the observed
54 results. Despite over two decades of study, a complete and quantitative understanding of low-
55 salinity waterflooding remains elusive. The underlying reason is because it involves many complex
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4 brine/oil/rock interactions manifested over a wide range of length scales. This inherent difficulty
5 makes it very challenging to isolate certain effects and obtain consistent, repeatable results.

6 We suggest the following studies be conducted in order to gain a more complete understand-
7 ing of the physicochemical phenomena behind low-salinity waterflooding. First, more brine film
8 thickness measurements are needed to better understand the effect of brine salinity, composition,
9 pH, and temperature on double-layer expansion. The thickness measurements may be compared to
10 zeta potential measurements, which are relatively more common in the literature. Only one study
11 has measured film thicknesses on sandstones in the context of low-salinity waterflooding [14]**.
12 No thickness measurements on carbonates have been done. Molecular simulations, similar to those
13 carried out in [48]*, provide valuable information about the brine/oil/rock interactions at a funda-
14 mental level. To the best of our knowledge, molecular simulations have not been directly applied
15 to thin liquid films in low-salinity waterflooding, but they have been used to study the formation
16 of thin liquid films on the surfaces of gas hydrates [50]*. The simulations can compute the film
17 thickness, the charge density along the film's interfaces, and potentially also the disjoining pressure
18 in the film. Furthermore, experimental variables that are difficult to control in real laboratory set-
19 tings tend to be easier to control in simulations. The molecular simulations can be complemented
20 with thermodynamic models [20]*, [41]* that provide information about brine/oil/rock interac-
21 tions at a more macroscopic level. Finally, other processes besides wettability alteration may also
22 contribute to the improved oil recovery from low-salinity brine. One promising topic involves the
23 viscoelasticity of the brine/oil interface. Recent studies have shown that this fluid/fluid interface
24 becomes more elastic as the salinity is reduced [51]. The increased elasticity hinders snap-off of
25 the oil into small droplets dispersed in the brine. As a result, the oil phase is more continuous and
26 mobile (easier to extract) in low-salinity waterflooding than in high-salinity waterflooding. Com-
27 bining these suggested studies with the extensive work that has already been done will improve
28 our understanding of low-salinity waterflooding and help unlock its potentially enormous benefits
29 to society.
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36 **Acknowledgments**

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42 Research Institute.
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26 This paper gives a clear explanation of how the chemical reactivity of calcite exposed
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41 The authors of this work are among the first to have reported improved oil recovery
42 from low-salinity brine in carbonates. Their paper presents a set of experimental measure-
43 ments (oil recoveries, zeta potentials, contact angles, NMR) whose results support the two
44 wettability alteration mechanisms in carbonates that we have focused on in our paper.
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10 This is the only study so far that has measured thicknesses of thin brine films in the
11 context of low-salinity waterflooding. The thickness measurements provide direct evidence for
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4 The authors of this work have developed a thermodynamic model that provides theo-
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7 able to the release of propionic acid adsorbed on a flat calcite surface. The propionic acid
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