

1 Evidence, Mechanisms and Improved Understanding of Controlled Salinity  
2 Waterflooding Part 1: Sandstones

3

4 Jackson, M.D.<sup>1</sup>, Vinogradov, J.<sup>1,2</sup>, Hamon, G.<sup>3</sup> and Chamerois, M.<sup>3</sup>

5 1. Department of Earth Science and Engineering, Imperial College London, UK

6 2. Now at the School of Engineering, University of Aberdeen, UK

7 3. TOTAL Research, Pau, France.

8

9 **Abstract**

10 It is widely accepted that oil recovery during waterflooding can be improved by modifying the  
11 composition of the injected brine, typically by lowering the total salinity to less than 5,000ppm.  
12 Numerous laboratory experiments and field tests, in both clastic and carbonate rock samples  
13 and reservoirs, have demonstrated this ‘low salinity effect’ (LSE). However, despite a plethora  
14 of studies and data, the LSE remains poorly understood. Evidence to support the widely held  
15 view that improved recovery is conditional on the presence of clay minerals in sandstones,  
16 multivalent ions in the formation brine, and significant dilution of the injection brine, is  
17 surprisingly scarce. Moreover, there is no method to determine the optimum injection brine  
18 composition for a given crude-oil-brine-rock (COBR) system. Many studies have reported the  
19 successful application of controlled salinity water injection. However, many others (and more  
20 unpublished) observed no benefit, and the available data are often inconsistent and  
21 contradictory.

22 This review collects and summarizes the available data for the first time and discusses the pore-  
23 to mineral-surface-scale mechanisms that have been proposed to explain the LSE. Based on  
24 this, it outlines an integrated experimental programme that could be used to identify the optimal  
25 injection brine composition for a given COBR system. The available evidence suggests that  
26 the LSE is real, and is caused by one or more pore- to mineral-surface-scale mechanism(s)  
27 which facilitate improved oil recovery at the core- to reservoir-scale. These mechanisms occur  
28 at COBR interfaces, and are multi-ion exchange (MIE), local increase in pH ( $\Delta\text{pH}$ ) and double  
29 layer expansion (DLE). However, the available evidence is not sufficient to unambiguously  
30 identify which, if any, of these mechanisms are essential. Other proposed mechanisms, such  
31 as clay swelling and fines migration, formation of natural surfactants at elevated pH, reduction  
32 in oil/brine interfacial tension, and increased solubility of polar oil compounds in brine, may  
33 occur in some cases but do not appear to be necessary to observe improved oil recovery.  
34 Understanding is hampered by a lack of common experimental conditions across length-scales.  
35 Core-scale measurements are often obtained at reservoir conditions of pressure, temperature,  
36 brine salinity and crude oil composition. In contrast, pore- and mineral-surface-scale  
37 measurements such as atomic force or scanning electron microscopy, contact angle and wetting  
38 surface, adsorption and adhesion, are often obtained at laboratory temperature and pressure,

39 lower brine salinity and simplified crude composition. These contrasting experimental  
40 conditions may explain the contradictory data obtained to date.

41 A common feature of all three proposed mechanisms for the LSE is that they lead to changes  
42 in zeta potential at mineral surfaces, either through changes in mineral surface charge (MIE,  
43  $\Delta\text{pH}$ ) or changes in the thickness of the double layer (DLE). Thus they change the magnitude  
44 of the electrostatic forces acting between mineral surfaces and polar organic species.  
45 Experiments that can probe this effect at conditions appropriate to reservoir displacements,  
46 whilst also measuring oil recovery, oil and brine composition and pH, and (if possible) the *in-*  
47 *situ* distribution of the fluids, are required to understand the LSE and predict the optimum  
48 injection brine composition for a given COBR system.

49

## 50 **Introduction**

51 It is now widely accepted that oil recovery during secondary or tertiary waterflooding can be  
52 improved by modifying the composition of the injected brine, typically by lowering the total  
53 salinity to less than 5,000ppm (for comparison, seawater salinity is c. 35,000ppm and many  
54 formation brines have salinities in excess of 200,000ppm; e.g. Barth, 1990). Numerous  
55 laboratory experiments and field tests, in both clastic and carbonate rock samples and  
56 reservoirs, have demonstrated this 'low salinity effect' (LSE) (e.g. Tang and Morrow, 1999a;  
57 1999b; Webb et al., 2004; 2005; McGuire et al., 2005; Lager et al., 2008a; 2008b; Seccombe  
58 et al., 2008; 2010; Ligthelm et al., 2009; Vledder et al., 2010; Yousef et al., 2010; 2012a;  
59 2012b; 2012c). Modification of injected brine composition was first suggested as an IOR  
60 method in clastic reservoirs in the late 1950s by Martin (1959) and again in the 1960s by  
61 Bernard (1967). However, the approach did not gain traction until the 1990s and 2000s, when  
62 Morrow and co-workers published a series of papers that demonstrated the LSE in coreflooding  
63 experiments on outcrop and reservoir sandstones (Jadhunandan and Morrow, 1995; Yildiz and  
64 Morrow, 1996; Tang and Morrow, 1997; 1999a,b; 2002; Morrow et al., 1998; Zhang and  
65 Morrow, 2006). Shortly after, BP published the results of a 'log-inject-log' field trial which  
66 showed that injection of low salinity brine (<3,000ppm) in a clastic reservoir reduced the  
67 residual oil saturation relative to the injection of seawater or high salinity formation brine (c.  
68 220,000ppm; Webb et al., 2004).

69 Since these early studies, a large and increasing number of papers have been published on  
70 controlled salinity waterflooding. These have demonstrated its successful application in other  
71 laboratory experiments and field trials (e.g. Loaharjo et al., 2007; Lager et al., 2008a; 2008b;  
72 Patil et al., 2008; Alotaibi et al., 2010; Cissokho et al., 2010; see, for example, Figure 1a,b) and  
73 in carbonate as well as clastic rocks and reservoirs (e.g. Yousef et al., 2011a; 2011b; 2012a;  
74 2012b; 2012c). Increases in oil recovery of up to 35% compared to re-injection of formation  
75 brine have been observed in laboratory coreflooding experiments (e.g. McGuire et al., 2005;  
76 Ligthelm et al., 2009; Austad et al., 2010), and field tests have demonstrated decreases in  
77 residual oil saturation of 50% compared to conventional water injection (e.g. Webb et al., 2004;  
78 Seccombe et al., 2010). Moreover, there has been increasing focus on the collection of

79 laboratory data to explain the LSE, including contact angles (e.g. Alotaibi et al., 2011), oil-  
80 brine interfacial tension (e.g. Gupta et al., 2011), coreflood effluent brine composition and pH  
81 (e.g. Lager et al., 2008a), zeta potential of mineral surfaces (e.g. Nasralla and Nasr-El-Din,  
82 2014), cation-exchange-capacity (CEC) (e.g. Pingo-Almada et al., 2013), adhesion maps (e.g.  
83 Buckley et al., 1989; Buckley and Morrow, 1990), adsorption studies (e.g. Austad et al., 2010),  
84 and imaging of mineral surfaces at a variety of lengthscales (e.g. Berg et al., 2010; Wideroe et  
85 al., 2010; Fogden, 2011). However, despite this plethora of new studies and data, the LSE  
86 remains poorly understood. Many published studies have reported the successful application  
87 of controlled salinity water injection (e.g. Tang and Morrow, 1999a; 1999b; Webb et al., 2004;  
88 2005; McGuire et al., 2005; Lager et al., 2008a; 2008b; Seccombe et al., 2008; 2010; Ligthelm  
89 et al., 2009; Vledder et al., 2010), but there are also many other published experiments (and  
90 many more unpublished), in which no benefit was observed (e.g. Sharma and Filoco, 2000;  
91 Zhang and Morrow, 2006; Pu et al., 2008; Boussour et al., 2009; Alotaibi et al., 2010; Cissokho  
92 et al., 2010; Rivet et al., 2010; RezaeiDoust et al., 2010; Skrettingland et al., 2011; Shiran and  
93 Skauge, 2012; Nasralla and Nasr-El-Din, 2014; see, for example, Figure 1c,d). Moreover,  
94 many studies report data that support a particular hypothesis but contradict, or are inconsistent  
95 with, the results of other studies. Other studies fail to obtain, or report, data other than those  
96 required to test a given hypothesis, so the results cannot be cross-compared (see Al-Adasani et  
97 al., 2012 for an overview and also Table 1).

98 The aim of this review is to facilitate such a comparison where possible and, in other cases, to  
99 collect and summarize the available data. The objectives of the review are fivefold: (i) to  
100 summarize the evidence that supports the LSE; (ii) to identify the key mechanisms that have  
101 been proposed for the LSE and the evidence to support these, (iii) to identify where evidence  
102 for a particular mechanism contradicts, or is inconsistent with, the results of other studies, (iv)  
103 to highlight the key issues that must be resolved before the LSE can be properly explained, and  
104 (v) to suggest approaches to resolve these. Three recent summaries provide good but relatively  
105 brief introductions to the topic (Morrow and Buckley, 2011; Skauge, 2013; Sheng, 2014); this  
106 review explores the data and mechanisms in rather more depth. We do not discuss numerical  
107 simulation of the LSE (see Sheng 2014 for an overview). We focus here on sandstone rock  
108 samples and reservoirs; controlled salinity waterflooding in carbonates will be discussed in a  
109 companion paper.

110

## 111 **Evidence to support the low salinity effect**

112 Much of the evidence to support the LSE, defined here as an increase in oil recovery with  
113 decreased injection brine salinity or altered brine composition, comes from laboratory  
114 coreflood experiments, either in secondary or tertiary mode. Coreflood data are often  
115 supplemented by spontaneous imbibition (SI) experiments. We focus here on the results of  
116 coreflooding experiments, and also on a number of field tests which report data consistent with  
117 the LSE. SI experiments can quantify wettability changes associated with the LSE, but  
118 increases in oil recovery in SI experiments are often poorly correlated with improved oil  
119 recovery in corefloods (e.g. Skauge, 2013; Masalmeh et al., 2014; Sorop et al., 2015).

120 The earliest evidence of the LSE came from coreflood experiments using synthetic cores  
121 containing sand and montmorillonite, Berea cores, and outcrop cores from Wyoming. In these  
122 experiments, injecting brine containing <10,000ppm NaCl yielded higher recovery of Soltrol  
123 in both secondary and tertiary waterfloods compared to brine containing up to 150,000ppm  
124 NaCl (Bernard et al., 1967). Improved oil recovery was associated with a significant increase  
125 in pressure drop across the samples at the residual oil saturation. All cores were clay bearing,  
126 although the Berea samples contained only trace amounts (Table 1). Further indirect evidence  
127 of the LSE in sandstones was provided by Yildiz and Morrow (1996), who investigated the  
128 impact of mono- and divalent ions on waterflooding using simple synthetic brines. Tang and  
129 Morrow (1997) investigated the impact on oil recovery of aging and displacement temperature,  
130 oil composition, and initial and invading brine salinity. The LSE was not specifically identified  
131 in these studies; indeed, reducing the invading brine salinity was reported to yield only modest  
132 recovery increases. Reducing the initial brine salinity was observed to have a much more  
133 significant effect. The first comprehensive study of the LSE in sandstones was undertaken by  
134 Morrow et al. (1998) and Tang and Morrow (1999a,b) who demonstrated that injection of low  
135 salinity brine increased oil recovery in both secondary and tertiary mode.

136 Since then, numerous studies have demonstrated the LSE in sandstone coreflooding  
137 experiments, and have investigated various aspects of the experimental method, rock and fluid  
138 materials, and initial and flooding conditions (see Table 1 for a summary). A number of field  
139 tests have also reported data consistent with the LSE. Webb et al. (2004) observed reduced  
140 residual oil saturation in log-inject-log tests after low salinity water injection in secondary  
141 mode, while single-well-chemical-tracer-tests (SWCTT) have demonstrated reduced residual  
142 oil saturation and improved oil recovery following secondary and tertiary low salinity water  
143 injection in sandstone (McGuire et al., 2005; Seccombe et al., 2008) and carbonate (Yousef et  
144 al., 2012c) reservoirs. Inter-well tests have provided evidence of the LSE at the reservoir scale  
145 (Lager et al., 2008b; Seccombe et al., 2010), as has some historical field data (Robertson et al.,  
146 2007; Batias et al., 2009; Vledder et al., 2010).

147

### 148 **Necessary conditions for the low salinity effect**

149 It is widely accepted that the following conditions are necessary for the LSE to be observed in  
150 sandstones (see also Tang and Morrow, 1999a; Morrow and Buckley, 2011):

- 151 1. Significant clay fraction.
- 152 2. Presence of formation water.
- 153 3. Exposure to crude oil containing acid or basic polar components to create mixed- or  
154 oil-wet initial conditions.
- 155 4. Significant reduction in salinity of injection brine.
- 156 5. Presence of multivalent ions in the connate water.

157 These necessary conditions are qualitative; they are not sufficient to quantitatively predict the  
158 LSE. Moreover, in some cases they appear to be necessary but not sufficient, because  
159 experimental studies have been published that appear to meet these conditions but in which the

160 LSE was not observed. Thus they cannot be used to screen candidate reservoirs for low salinity  
161 water injection. The supporting evidence for these conditions is discussed briefly in the  
162 following sections.

163

#### 164 **Presence and type of clay minerals**

165 It is widely agreed that clay minerals are required to observe the LSE effect in sandstones. The  
166 importance of clay minerals was initially highlighted by Bernard (1967) and further  
167 investigated by Tang and Morrow (1999a), who claimed that the LSE was not observed in  
168 clean sandstones, or sandstones in which clay minerals had been stabilised by firing and  
169 acidizing. However, only one low salinity coreflood was reported in a clean sandstone, and  
170 this contained an iron oxide coating which was interpreted to significantly modify the quartz  
171 surface properties; moreover, firing and acidizing modifies crude oil-brine-rock (COBR)  
172 interactions beyond stabilizing clay fines. Thus the presence of clays as a necessary condition  
173 for the LSE was not supported by abundant evidence. Subsequent papers by Morrow and co-  
174 workers assumed clays were necessary, and experiments investigating the LSE were almost all  
175 conducted on clay-bearing sandstone samples (e.g. Tang and Morrow 1999b; Zhang and  
176 Morrow, 2006; Loahardjo et al., 2007, 2010; Zhang et al, 2007).

177 The importance of clay minerals was also emphasized by Lager et al. (2007) and Seccombe et  
178 al. (2008), who published a correlation suggesting the LSE increases with increasing kaolinite  
179 content. However, the correlation was based on only four data points and the lowest kaolinite  
180 content investigated was c. 4.5 wt%. Lebedeva et al. (2011) observed the LSE in sandpacks  
181 with kaolinite-coated sand, but not in pure quartz sand. Zhang and Morrow (2006) further  
182 claimed that the type of clay mineral was important, attributing the lack of LSE in some Berea  
183 sandstone samples to the presence of chlorite. Later studies have argued that the LSE should  
184 be favoured by clay minerals with high CEC (e.g. Austad et al. 2010), although this criterion  
185 alone would not rule out chlorite, and suggests kaolinite is suboptimal (Table 2). The LSE has  
186 been demonstrated with clay mineral types other than kaolinite (e.g. Cissokho et al., 2010).  
187 Recent studies have argued that clay minerals are important because they are more susceptible  
188 to wettability alteration in the presence of multivalent ions such as  $Ca^{2+}$  (e.g. Mugele et al.,  
189 2015). However, shortly after the pioneering work of Tang and Morrow (1999a), the presence  
190 of clay minerals as a necessary condition for the LSE became widely accepted and, as a result,  
191 very few studies have investigated the LSE in clay-free sandstones (although not all report the  
192 clay content; see Table 1). Some studies have observed the LSE in clay-free sandstones and  
193 sandpacks, and at quartz mineral surfaces (e.g. Pu et al., 2008, 2010; Hassenkam et al., 2011,  
194 2012; Suman et al., 2014). It has also been suggested that organic material adsorbed onto the  
195 surface of quartz grains may enhance the LSE (Mathiesen et al., 2014; Hilner et al., 2015). The  
196 published evidence supporting the presence of clay minerals as a necessary condition is  
197 therefore far from overwhelming.

198

#### 199 **Wettability alteration and the LSE**

200 It is also widely agreed that the LSE effect in sandstones is observed when (i) the initial wetting  
201 state has changed from strongly water-wet towards mixed-wet after aging, and (ii) the  
202 wettability of the mineral surfaces changes to become more water-wet when low salinity brine  
203 enters the pore-space.

204 A number of mechanisms have been proposed to facilitate wettability alteration of silicate  
205 mineral surfaces following primary drainage. These include (i) surface precipitation, observed  
206 when the oil is a poor solvent for polar organic compounds, (ii) direct adsorption of polar  
207 organic compounds onto oppositely charged mineral surface sites following collapse of the  
208 water film at low pH and/or high salinity, and (iii) multivalent cation bridging to allow polar  
209 organic compounds to adsorb onto mineral surfaces with the same polarity (e.g. Buckley et al.,  
210 1989, 1997, 1998). Wettability alteration therefore depends upon the properties of the oil (polar  
211 compounds and solvency), the properties of the mineral surfaces (CEC, surface groups and  
212 electrical charge) and the composition and pH of the formation brine that initially wets the  
213 surfaces (e.g. Drummond and Israelachvili, 2004; Suijkerbuijk et al., 2012). It is widely agreed  
214 that the LSE is observed only if one or more of these mechanisms caused wettability alteration  
215 prior to low salinity brine injection.

216 The majority of the evidence to support wettability alteration towards more water-wet  
217 conditions when low salinity brine enters the pore-space has been obtained from core-scale SI  
218 experiments. These have yielded higher imbibition rate and total oil production with decreased  
219 salinity of the invading brine in both secondary and tertiary mode (e.g. Fig. 2a). Measurements  
220 of contact angle and/or oil wetting area at oil-brine-mineral interfaces have also shown a  
221 decrease with decreasing salinity, consistent with a change to more water-wet conditions (e.g.  
222 Alotaibi et al., 2011; Suijkerbruik et al., 2013; Mahani et al., 2013; Fig. 2b). However, we note  
223 that nano-scale imaging of the pore-scale distribution of oil and water in natural sandstone  
224 using cryogenic broad ion-beam polishing in combination with scanning electron microscopy  
225 (cryo-BIB-SEM) is casting doubt on the utility of contact-angle measurements to characterize  
226 wettability (Schmatz et al., 2015). Some evidence for wettability change is also provided by  
227 Nuclear Magnetic Resonance (NMR) analysis, which has suggested a more water-wetting state  
228 following low salinity brine injection in intact sandstone samples (Chen et al., 2010; Wideroe  
229 et al. 2010). At the mineral-surface scale, direct imaging of clay-coated surfaces using optical  
230 microscopy (Berg et al., 2010; Cense et al., 2011; Fig. 2c) and SEM (Fogden et al., 2011) has  
231 suggested that oil droplets can be detached by low salinity brine to expose more water-wet  
232 surfaces, consistent with a change to a more water-wetting state. However, in the study by  
233 Fogden et al. (2011), it was argued that increased adhesion of polar oil components to clay  
234 minerals at low salinity (discussed further below) caused clay particles to be detached and  
235 mobilized with the oil; the clay minerals became less water-wet with decreasing salinity, but  
236 their mobilisation revealed more water-wet surfaces. A similar mechanism may also have  
237 operated in the study by Berg and co-workers (Berg et al., 2010; Cense et al., 2011).

238 Atomic Force Mapping (AFM) at the molecular scale has, in contrast, suggested decreased  
239 rather than increased adhesion of both polar and non-polar oil components to silica and natural  
240 quartz surfaces at low salinity (Hassenkam et al., 2011, 2012; Mathieson et al., 2014; Hilner et  
241 al., 2015). However, illite clay and mica were less sensitive than pure silica, which is

242 inconsistent with the view that clay minerals play an important role (Hassenkam et al., 2011,  
243 2012). SEM imaging has also suggested that aged glass surfaces can become more water-wet  
244 (or have the advancing contact modified to mimic water-wet behaviour) when in contact with  
245 low salinity brine at moderate to high pH (Fogden, 2011). Indirect evidence of the importance  
246 of wettability alteration is also suggested by the temperature dependence of the LSE observed  
247 in some studies, although the evidence is contradictory: some studies suggest secondary  
248 recovery increases with increasing temperature (Cissokho et al., 2010; Robertson, 2010) and  
249 others suggest the opposite (Gamage and Thyne, 2011), while tertiary recovery appears to be  
250 maximized at intermediate temperature (Cissokho et al., 2010; Gamage and Thyne, 2011).  
251 Wettability change is known to be temperature dependent (e.g. Jadhunandan and Morrow;  
252 1995; Liu and Buckley, 1997; Tang and Morrow, 1997).

253 Despite the broad consensus that the LSE is associated with a change to more water-wetting  
254 conditions, the evidence is still contradictory. At the core-scale, Ashraf et al. (2010)  
255 determined initial wettability after aging using the Amott-Harvey method and correlated this  
256 with the LSE; low salinity corefloods yielded the highest incremental recovery for the samples  
257 which were initially most water-wet, not mixed-wet (Fig. 2d). Sandegen et al. (2011) history  
258 matched successful low salinity corefloods and obtained the best match for lower imbibition  
259 capillary pressure curves, consistent with a change to more oil-wet conditions; however, the  
260 results were uncertain owing to a lack of constraining experimental data. At the mineral-  
261 surface scale, adhesion measurements by Buckley and co-workers (Buckley et al., 1989,  
262 Buckley and Morrow, 1990) for various crude oils on glass surfaces have demonstrated that  
263 adhesion is pH-dependent at low salinity, consistent with the Derjaguin-Landau-Verwey-  
264 Overbeek (DLVO) theory that describes the relative contribution of electrostatic and van-der-  
265 Waals forces dictating colloidal stability (e.g. Evans and Wennerstrom, 1999). However, a  
266 transition from no adhesion to adhesion was typically observed with decreasing salinity at fixed  
267 pH (e.g. Fig. 2e), inconsistent with the wettability changes described above. The trend could  
268 be reversed at elevated temperature for some crude oils (Buckley and Morrow, 1990).  
269 Similarly, Drummond and Israelachvili (2002, 2004) recorded an increase in the static contact  
270 angle of mica surfaces with decreasing salinity at moderate pH, inconsistent with increasingly  
271 water-wet behaviour (e.g. Fig. 2f). However, the brines in these studies did not contain any  
272 divalent cations such as  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . Lebedeva and co-workers (Lebedeva and Fogden, 2010;  
273 Lebedeva et al., 2010) found that adhesion (characterised via the hysteresis of advancing and  
274 receding contact angles) of crude oil to kaolinite increased with decreasing pH and salinity of  
275 both NaCl and  $\text{CaCl}_2$  brines. Adsorption of polar oil components onto silicate mineral surfaces  
276 has also been shown to be strongly pH dependent (e.g. Austad et al. 2010; RezaiDoust et al.,  
277 2011; Aksulu et al., 2012; see Fig. 3a,b); changes in pH are often associated with the LSE (e.g.  
278 Fig. 3c).

279 Wettability change is a *consequence*, not a *cause*, of the processes underlying the LSE, and  
280 several mechanisms have been proposed that relate wettability changes to the injection of low  
281 salinity brine (see next section). Optimum oil recovery is usually observed in mixed-wet  
282 conditions, which yield relatively low water relative permeability and residual oil saturation

283 (e.g. Jadhunandan and Morrow, 1995). Thus a shift to more water-wet conditions during low  
284 salinity waterflooding should not favour increased recovery (Li, 2011).

285 During injection of high salinity brine into an initially mixed-wet system, in which the larger  
286 pores are preferentially oil-wet, the invading brine first displaces oil from the water-wet pores  
287 in the order smallest to largest. It then displaces oil from the oil-wet pores from largest to  
288 smallest, until the capillary entry pressure exceeds the driving pressure, leaving oil trapped on  
289 oil-wet surfaces and in the intermediate-sized pores. This process yields higher recovery than  
290 waterflooding a water-wet system, in which the invading brine displaces oil from the pores in  
291 the order smallest to largest, leaving oil trapped in the largest pores (Jadhunandan and Morrow,  
292 1995). Sorbie et al. (2010) suggested that injecting low salinity brine into the same system  
293 decreases the contact angle and therefore the capillary entry pressure of the oil-wet pores, thus  
294 allowing low salinity brine to displace oil from smaller pores for the same driving pressure and  
295 reducing the residual oil saturation. This hypothesis has not been confirmed by pore-scale  
296 imaging or modelling, although advances in nano-scale imaging may make this possible (e.g.  
297 Cissokho et al., 2011; Fogden et al., 2011; Schmatz et al., 2015). Such imaging techniques  
298 have shown that a non-wetting oil phase may be separated from quartz mineral surfaces by a  
299 thin brine film, but there can be direct points of contact between oil and mineral at asperities  
300 and clay aggregates. Such contact points act as pinning points and cause discontinuous motion  
301 of the oil-water-solid contact line. The LSE may involve the de-pinning of these contact lines  
302 rather than wholesale wettability alteration of mineral surfaces (Schmatz et al., 2015).

303

#### 304 **Reduction in injection brine salinity**

305 Tang and Morrow (1999a) observed the LSE effect with injection of 10 and 100 times diluted  
306 formation brine (c. 24,000ppm TDS, yielding injection brine salinities of c. 2,400 and 240ppm  
307 TDS); higher injection brine salinities were not tested. Improved recovery was observed with  
308 dilution of injection brine, and also formation plus injection brine (see also Yildiz and Morrow,  
309 1996; Tang and Morrow, 2002; Zhang and Morrow, 2006). Lager, Webb and co-workers found  
310 no LSE with injection of seawater into cores containing higher salinity formation brine, but a  
311 significant LSE in the same system when injecting 1,000ppm brine (Fig. 4a); they suggested,  
312 based on experience from (mostly unreported) coreflooding experiments, that the LSE is  
313 observed only for injection brine salinities below c. 5000ppm (Webb et al., 2004, 2005; Lager  
314 et al., 2007). Subsequent studies have almost all used low salinity brines with concentrations  
315 below 5000ppm (see Table 1). Cissokho et al. (2010) reported a clear threshold in injected  
316 brine ( $\text{NaCl}+\text{CaCl}_2$ ) salinity of 1000ppm below which the LSE was observed (Fig. 4b).

317 However, no model is available to predict this threshold value for a given COBR system.  
318 Moreover, numerous studies have demonstrated that simply reducing the injected brine salinity  
319 below a threshold value is not sufficient for the LSE to be observed (e.g. Sharma and Filoco,  
320 2000; Zhang and Morrow, 2006; Pu et al., 2008; Alotaibi et al., 2010; Cissokho et al., 2010;  
321 Rivet et al., 2010; RezaeiDoust et al., 2010; Skrettingland et al., 2011; Nasralla and Nasr-El-  
322 Din, 2014; Fig. 1c,d). In some cases, improved recovery has been observed by increasing the



323 injection brine salinity relative to the formation brine (e.g. Tang and Morrow, 1997; Sharma  
324 and Filocco, 2000; Fig. 1e). RezaeiDoust et al. (2011) observed a modest increase in recovery  
325 when injecting NaCl brine of higher salinity, but the same ionic strength, into a core containing  
326 crude oil and CaCl<sub>2</sub> brine (Fig. 1f). Thus the evidence that improved recovery is necessarily  
327 associated with a significant reduction in brine salinity is not conclusive. Rather, it appears that  
328 recovery can be improved by modifying the injection brine salinity (composition) in some  
329 controlled way that has not yet been identified.

330

### 331 **Initial water saturation and presence of multivalent ions in the formation brine**

332 Most oil reservoirs initially contain some formation water containing multivalent ions (e.g.  
333 Barth, 1990); thus these necessary conditions are normally satisfied. Tang and Morrow (1999a)  
334 observed no LSE in cores aged in crude oil with no formation brine, while Lager et al. (2008a)  
335 observed no LSE in cores from which multivalent ions had been flushed from the mineral  
336 surfaces, prior to aging in crude oil and brine containing no multivalent ions. They argued that  
337 multivalent ions must be initially present to promote wettability alteration of clay mineral  
338 surfaces through bridging mechanisms specifically involving these cations (see also Anderson,  
339 1986 and references therein). As discussed above, the presence of formation water, and of  
340 multivalent ions in the formation water, appears to be related to the initial mixed-wetting state  
341 required for the LSE.

342 However, the LSE has been reported in cores aged in crude oil and brine containing no  
343 multivalent ions other than those initially adsorbed onto mineral surfaces (Agbalaka et al.,  
344 2008). Moreover, Li (2011) observed the highest incremental oil recovery during tertiary low  
345 salinity waterflooding in a weakly water-wet Berea sandstone sample aged with crude oil  
346 without initial water present. Numerous studies have demonstrated that formation brine  
347 containing multivalent ions is not sufficient for the LSE to be observed (e.g. Sharma and Filoco,  
348 2000; Zhang and Morrow, 2006; Alotaibi et al., 2010; Cissokho et al., 2010; Rivet et al., 2010;  
349 RezaeiDoust et al., 2010; Skrettingland et al., 2011; Nasralla and Nasr-El-Din, 2014). Aksulu  
350 et al. (2012) argued that the initial pH is also important, with low pH (c. 5) promoting  
351 adsorption of polar oil compounds (e.g. Fig 3a,b). However, numerous studies have observed  
352 the LSE at higher initial pH (e.g. Morrow et al., 1998; Maas et al., 2001; McGuire et al., 2005;  
353 Lager et al., 2008a; Cissokho et al., 2010; Fjelde et al., 2012; see Table 1). As yet, no model  
354 or dataset is available that allows the optimal initial brine saturation, composition or pH to be  
355 predicted.

356

### 357 **Summary**

358 Evidence to support the widely accepted necessary conditions for the LSE to be observed in  
359 sandstones is surprisingly sparse, despite the large number of published studies. Formation  
360 water is invariably present so this condition is naturally met; however, evidence supporting the  
361 necessary presence of clay minerals and multivalent ions, initially mixed-wet conditions, and

362 a significant reduction in injection brine salinity, is far from overwhelming. To properly  
363 predict the necessary conditions for the LSE to be observed requires an understanding of the  
364 underlying mechanisms; these are reviewed in the next section.

365

## 366 **Proposed mechanisms for the low salinity effect in sandstones**

### 367 **Clay swelling and fines migration**

368 *Mechanism:* Early studies of the LSE suggested that improved recovery is associated with clay  
369 swelling and fines migration (Bernard, 1967; Tang and Morrow, 1999a) which are known to  
370 be promoted at low salinity (e.g. Lever and Dawe, 1984). Bernard (1967) suggested that the  
371 LSE is associated with swelling clays such as montmorillonite. Tang and Morrow (1999a)  
372 suggested that the LSE results from (i) adsorption of polar components from crude oil onto  
373 fines-coated mineral surfaces through one of the mechanisms discussed previously (Fig. 5a),  
374 (ii) stripping of the mixed-wet fines during low salinity water injection, and (iii) accumulation  
375 of the oil-bearing fines at the oil-water interface (Fig. 5b). In their model, the LSE results from  
376 the mobilization of oil attached to the fines, with exposure of the water-wet surfaces beneath  
377 the stripped fines yielding more water-wet behaviour (Fig. 5c).

378 *Supporting evidence:* Bernard (1967) observed improved recovery in coreflooding experiments  
379 only when associated with an increase in pressure drop (at constant rate) consistent with  
380 formation damage (e.g. Krueger, 1986). Elution of fines was not reported. Tang and Morrow  
381 (1999a) observed increased oil recovery (e.g. Fig. 6a), an increase in pH, and an increase in  
382 pressure drop associated with production of fines (e.g. Fig. 6b), when dilute formation brine  
383 (<1550 ppm TDS) was injected in secondary and tertiary mode into sandstone cores containing  
384 kaolinite. The LSE ceased after firing of the cores (compare Fig. 6c,d), injection of  $\text{Ca}^{2+}$  ions  
385 during successful low salinity waterfloods (e.g. Fig. 6a), reduction of the initial water saturation  
386 to zero (Fig. 6e), and with the use of refined oil. Tang and Morrow (1999a) argued that each  
387 of these actions stabilized or removed the fines, which is why the LSE effect ceased. A number  
388 of subsequent studies have also observed evidence of fines migration associated with the LSE,  
389 either through elution of fines (e.g. Loaharjo et al., 2007; Agbalaka et al., 2008; Boussour et  
390 al., 2009) or by SEM imaging of the pore-space (e.g. Cissokho et al. 2011; Fogden et al., 2011).

391 *Contrary evidence:* Numerous studies have observed the LSE without production of fines (e.g.  
392 Zhang and Morrow, 2006; Zhang et al., 2007; Lager et al., 2008a; 2008b; Alagic and Skauge,  
393 2010; Ligthelm et al., 2009; Cissokho et al., 2010; Alotaibi et al., 2010; Rivet et al., 2010;  
394 RezaeiDoust et al., 2011); others have observed modest or no reduction in permeability (e.g.  
395 Zhang et al., 2007; Lager et al., 2008a,b; Ligthelm et al., 2009; Alotaibi et al., 2010; Rivet et  
396 al., 2010; Pu et al., 2010; Robertson et al., 2010; RezaeiDoust et al., 2011). Several studies  
397 have observed fines production and/or permeability decrease with no LSE (e.g. Boussour et  
398 al., 2009; Cissokho et al., 2010; 2012; Nasralla and Nasr-El-Din 2014). This suggests that  
399 fines migration and associated permeability changes are not always associated with the LSE  
400 and *vice-versa*. Moreover, it is clear that clay swelling and/or fines migration cannot explain  
401 the LSE observed in carbonates (e.g. PART 2).

402 *Summary:* Clay swelling and fines migration may be the underlying mechanism that causes the  
403 LSE in some cases, but the LSE is not conditional on the occurrence of clay swelling and fines  
404 migration.

405

#### 406 **pH increase and surfactant generation**

407 *Mechanism:* McGuire et al. (2005) suggested that the increase in pH observed in some low  
408 salinity corefloods (e.g. Fig. 3c) leads to the generation of surfactants from the residual oil.  
409 These reduce the oil-water interfacial tension (IFT), and also the oil-water contact angle to  
410 yield more water-wet conditions. When crude oil is contacted by the low salinity water with  
411 elevated pH, the acid components in the oil are saponified. McGuire et al. (2005) argued that  
412 this leads to improved oil recovery in a process analogous to alkaline surfactant flooding. They  
413 further argued that the reduction in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in low salinity brine inhibits  
414 the precipitation of surfactants observed in high salinity systems. Thus the injection of low  
415 salinity brine both causes surfactants to be generated, and allows them to function more  
416 efficiently to increase oil recovery.

417 *Supporting evidence:* pH increases associated with the LSE have been reported by a number of  
418 authors (e.g. Fig. 3c). McGuire et al. (2005) suggested that the sensitivity of surfactant  
419 precipitation to  $\text{Ca}^{2+}$  is responsible for the effect observed by Tang and Morrow (1999a) in  
420 which injection of  $\text{Ca}^{2+}$  ions during a successful low salinity waterflood terminated the LSE  
421 (e.g. Fig. 6a).

422 *Contrary evidence:* Although effluent oil-brine IFT has been observed to decrease (from c.  
423 25mN/m to c. 18mN/m) with a concomitant increase in pH during successful low salinity  
424 corefloods, the few reported values remain too high for saponification to have occurred (Tang  
425 and Morrow, 2002). The saponification reaction requires high acid number, yet the LSE has  
426 been observed with lower AN crudes (e.g. Zhang and Morrow, 2006; Loaharjo et al., 2007;  
427 Zhang et al., 2007; Boussour et al., 2009; Pu et al., 2010; RezaeiDoust et al., 2011). No  
428 correlation between the LSE and AN has been observed (Fig. 7; Lager et al., 2008a). Moreover,  
429 it has been suggested that the pH required for saponification ( $\text{pH}>9$ ) is unlikely to be observed  
430 at reservoir conditions, owing to the presence of  $\text{CO}_2$  and other pH buffers. A number of  
431 studies have demonstrated the LSE in unbuffered systems with  $\text{pH}<9$  suggesting saponification  
432 did not occur (e.g. Fig. 3d; see also Table 1). Zhang et al. (2007) found no relationship between  
433 effluent pH and the LSE.

434 *Summary:* If sufficiently high pH ( $>9$ ) is reached with high acid number oils ( $>0.2$  mgKOH/g),  
435 then saponification may occur, but this seems unlikely in many reservoir settings and the LSE  
436 is not conditional on saponification.

437

#### 438 **Multi-ion exchange (MIE)**

439 *Mechanism:* Lager et al. (2008a) were the first to measure effluent brine composition during  
440 coreflooding experiments and noted that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations initially fell below those  
441 in the low salinity injection brine (Fig. 8). They suggested that this ‘stripping’ of multivalent  
442 ions is associated with ion exchange between the low salinity brine and clay minerals. In their  
443 model, adsorption of multivalent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  onto clay mineral surfaces is  
444 promoted at low concentration, in exchange for directly adsorbed polar oil compounds. Thus  
445 MIE releases oil previously adsorbed onto clay mineral surfaces and makes these surfaces more  
446 water-wet (Fig. 9). For the LSE to be observed, the model predicts that clay minerals must be  
447 present along with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations in the formation brine; moreover, polar oil  
448 compounds must have been adsorbed directly onto the clay mineral surfaces following primary  
449 drainage.

450 *Supporting evidence:* MIE has been observed when fresher groundwater invades a more saline  
451 sandstone aquifer containing clay minerals (or other ion exchangers) and multivalent ions (e.g.  
452 Valocchi et al., 1981; Appelo et al., 1994), and also in clay-bearing sandstone corefloods at the  
453 residual oil saturation (Pingo-Almada et al., 2013). Lager et al. (2008a) tested the link between  
454 MIE and the LSE by removing all  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the clay mineral surfaces in a sandstone  
455 core and then flooding with high and then low salinity NaCl brine; the low salinity brine yielded  
456 no additional recovery. Subsequent addition of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to the low salinity brine also  
457 yielded no additional recovery. When  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were initially present in the same  
458 plug, low salinity flooding (with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present) yielded an additional 5% recovery.  
459 Lager et al. (2008a) further argued that the absence of a LSE observed by Tang and Morrow  
460 (1999a) after firing of their Berea sample was because ion exchange with the clay minerals was  
461 prevented. Alagic and Skauge (2010) found that  $\text{Mg}^{2+}$  was retained in aged samples during  
462 successful LSE corefloods, which is consistent with MIE if  $\text{Mg}^{2+}$  present in the initial brine  
463 was adsorbed onto clay mineral surfaces after injection of low salinity NaCl brine.  $\text{Ca}^{2+}$  was  
464 eluted, but this was ascribed to calcite dissolution.

465 *Contrary evidence:* Adsorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at low salinity is inconsistent with the  
466 increased pH observed in many studies if this reflects cation exchange with protons in response  
467 to low salinity injection as discussed in the next section (e.g. Austad et al. 2010); however, pH  
468 increase may also reflect the presence and dissolution of small amounts of carbonate material  
469 (e.g. Tang and Morrow, 1999a; McGuire et al., 2005; Lager et al., 2008a; Pu et al., 2008; 2010).  
470 Lager et al. (2008a) argue that clay minerals act as ion exchangers, suggesting those with high  
471 CEC are optimal, yet kaolinite has been closely associated with the LSE despite its relatively  
472 low CEC (Table 2; Lager et al. 2007; Secombe et al. 2008). Evidence to link MIE and the  
473 LSE is sparse: only two papers report effluent cation depletion below that of the injected lower  
474 salinity brine in association with a significant LSE (Lager et al. 2008a,b; see Fig. 8a,b); a third  
475 claimed effluent cation depletion but the reported data are insufficient to confirm this and the  
476 observed LSE was in any case very small (Wideroe et al., 2010).

477 *Summary:* MIE has been observed in field and laboratory experiments and is known in the  
478 water resources literature. However, MIE alone is not enough to cause the LSE: an additional  
479 requirement is the presence of crude oil containing polar components initially adsorbed directly  
480 onto clay mineral surfaces that can exchange with divalent cations in the brine. No optimum

481 clay type, crude oil or injection brine composition, or method for predicting these, has been  
482 derived from the MIE model. Moreover, published evidence to directly link MIE with the LSE  
483 is sparse. The MIE mechanism alone does not explain the numerous coreflooding experiments  
484 where the conditions for MIE were met but no LSE was observed.

485

#### 486 **Local increase in pH ( $\Delta\text{pH}$ )**

487 *Mechanism:* Austad and co-workers (Austad et al. 2010; RezaeiDoust et al., 2009, 2011; Aksulu  
488 et al., 2012) proposed a model that also invokes ion exchange but, in contrast to the MIE model  
489 of Lager et al. (2008a), they suggested that injection of low salinity brine leads to desorption  
490 of surface-active cations from clay mineral surfaces and replacement by protons. This causes  
491 a concomitant increase in local pH, which is sufficient to release previously adsorbed acidic  
492 and basic organic materials (Fig. 10). For the LSE to be observed, the model requires clay  
493 minerals to be present, along with surface-active cations in the formation brine (particularly  
494  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), and polar oil compounds initially adsorbed directly onto the clay mineral  
495 surfaces following primary drainage (similar to the MIE model). Moreover, adsorption of polar  
496 oil compounds must be strongly pH dependent.

497 *Supporting evidence:* Austad and co-workers noted that many unbuffered laboratory  
498 coreflooding experiments show an increase in pH following the injection of low salinity brine  
499 (e.g. Fig. 3c); moreover, RezaeiDoust et al. (2011) found that pH increase depended upon the  
500 prevalent cation affinity to clay mineral surfaces, with low salinity NaCl brines showing the  
501 largest pH increase consistent with the low affinity of  $\text{Na}^+$ . Austad and co-workers also  
502 reported adsorption tests that show a strong pH dependence of both acidic and basic organic  
503 adsorption on clay minerals (Austad et al. 2010; RezaeiDoust et al., 2011; Aksulu et al., 2012),  
504 consistent with the requirements of their model (e.g. Fig. 3a,b). The composition of the  
505 injection brine is predicted to be relatively unimportant so long as it is dilute enough to yield  
506 significant desorption of surface-active cations. However, the removal of  $\text{Ca}^{2+}$  from the  
507 injection brine is argued to be particularly favourable, because pH increase is then more  
508 significant, consistent with a number of studies that show the LSE with injection of dilute NaCl  
509 brine, although not all of these observed the expected increase in pH (Loahardjo et al., 2007;  
510 Alagic and Skauge, 2010; Boussour et al., 2009; Ligthelm et al., 2009; RezaeiDoust et al.,  
511 2011; Nasralla and Nasr-El-Din, 2014). Tang and Morrow (1999a) found that increasing the  
512  $\text{Ca}^{2+}$  concentration terminated the LSE, but there was no consistent decrease in pH (e.g. Figs.  
513 6a,b). RezaeiDoust et al. (2011) reported modest increases in oil recovery when injecting  
514 higher salinity NaCl brine into a core containing crude oil and  $\text{CaCl}_2$  brine, and argued that  
515 this reflected the differing affinities of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations toward clay mineral surfaces,  
516 consistent with the model predictions. Ion exchange leading to pH increase has been observed  
517 and modelled in other studies relating to formation damage, although these studies considered  
518 only monovalent ions in single phase flow (e.g. Vaidya and Fogler, 1990; Souto and Bazin,  
519 1993).

520 *Contrary evidence:* Several unbuffered experimental studies report little or no change in  
521 effluent pH associated with the LSE (e.g. Fig. 3d); moreover, in the reservoir, such a global pH  
522 change is unlikely to occur owing to the presence of pH buffers such as CO<sub>2</sub>. Nevertheless,  
523 Austad and co-workers argue that local increases in pH adjacent to the clay mineral surfaces  
524 are sufficient to cause desorption of organic materials. Several studies have observed effluent  
525 pH increases in unbuffered experiments but no associated LSE (e.g. Cissokho et al., 2010;  
526 RezaeiDoust et al. 2010; Wideroe et al., 2010). Austad et al. (2010) suggested that the decrease  
527 in Ca<sup>2+</sup> and Mg<sup>2+</sup> observed in the laboratory experiments of Lager et al. (2008a) resulted from  
528 deposition of Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> rather than MIE, but Ca(OH)<sub>2</sub> deposition was predicted  
529 to occur only at pH > 11; such high pH was not observed. Austad et al. (2010) also suggested  
530 that the ΔpH model explains the field test data of Lager et al (2008b) (Fig. 8b), ascribing the  
531 initial increase in Mg<sup>2+</sup> at the producer well to desorption of Mg<sup>2+</sup> on contact with low salinity  
532 injected water. The subsequent decrease in Mg<sup>2+</sup>, which Lager et al (2008b) ascribed to MIE,  
533 was suggested to reflect Mg(OH)<sub>2</sub> precipitation at pH > 9. However, such high pH was not  
534 observed at the production well. Alagic and Skaug (2010) found that Mg<sup>2+</sup> was retained in  
535 aged samples during successful LSE corefloods, which is inconsistent with desorption. Similar  
536 to Lager et al (2008a), Austad et al. (2010) suggest that clay minerals with high CEC are  
537 optimal, yet kaolinite is closely associated with the LSE and has relatively low CEC (Table 2).

538 *Summary:* Adsorption of organic polar compounds is pH dependent (along with many other  
539 factors) so pH change is likely to lead to desorption. However, not all unbuffered experiments  
540 that show the LSE display effluent brine pH increases, and pH increases in buffered reservoirs  
541 will be limited. Local pH increase at mineral surfaces is difficult to prove. Desorption of  
542 multivalent cations at low salinity has yet to be satisfactorily reconciled with the depletion  
543 observed in aquifers and coreflooding experiments; there is no evidence of brine compositional  
544 changes consistent with multivalent cation desorption. No model capable of quantitatively  
545 predicting the dilution required to ensure desorption and associated LSE has been published.  
546 The ΔpH model does not explain those coreflooding experiments where pH change was  
547 recorded and the other LSE requirements were met, but no LSE was observed.

548

#### 549 **Double layer expansion (DLE)**

550 *Mechanism:* Ligthelm et al. (2009) suggested that expansion of the electrical double layer at  
551 mineral-brine interfaces, as a result of low salinity brine injection, is the primary mechanism  
552 leading to the LSE. It is well known that at low to moderate salinity, the thickness of the diffuse  
553 part of the electrical double layer at mineral-brine interfaces increases with decreasing ionic  
554 strength. Likewise, the zeta potential, which is a measure of the electrical potential at the so-  
555 called shear plane where the electrical charges are mobile (see Fig. 11), also increases with  
556 decreasing ionic strength (e.g. Fig. 12a,b; see also Vinogradov et al., 2010). The ionic strength  
557 of an electrolyte is related to concentration and valency by (Hunter, 1981)

558

559 
$$I = \frac{1}{2} \sum_j C_j z_j^2 \tag{1}$$

560

561 where  $C$  is the molar concentration (or molarity, in mol·L<sup>-1</sup> or M) and  $z$  is the valency of ionic  
 562 species  $j$  (Fig. 12d). Note that the ionic strength can be increased either by increasing the  
 563 concentration at constant valency, or by increasing the valency at constant concentration. At  
 564 low concentration (< 0.1M) the double layer thickness (as measured by the Debye length) is  
 565 related to the ionic strength by (Hunter, 1981)

566

567 
$$\lambda = \left( \frac{\varepsilon k_B T}{1000 e^2 N_A I} \right)^{\frac{1}{2}} \tag{2}$$

568

569 where  $k_B$  is Boltzmann's constant (= 1.3806488 × 10<sup>-23</sup> J·K<sup>-1</sup>),  $T$  is temperature (K),  $\varepsilon$  is the  
 570 permittivity of vacuum (=8.854 187 817 × 10<sup>-12</sup> F·m<sup>-1</sup>),  $N_A$  is Avogadro's number (=  
 571 6.02214129 × 10<sup>23</sup> mol<sup>-1</sup>), and  $e$  is the charge on an electron (= 1.60217657 × 10<sup>-19</sup> C).  
 572 Ligthelm et al. (2009) argued that injection of low salinity brine causes the electrical double  
 573 layer to expand according to equation (2), resulting in increased electrostatic repulsion between  
 574 charged mineral surfaces and adsorbed polar oil components. When this repulsion exceeds the  
 575 binding forces, the polar oil components desorb yielding more water-wet mineral surfaces,  
 576 consistent with DLVO theory and some previous studies of wettability alteration (Evans and  
 577 Wennerstrom, 1999; Anderson, 1986 and references therein; Buckley et al., 1989, 1998) and  
 578 AFM (Siretanu et al., 2014; Hilner et al, 2015). If the brine concentration is further reduced,  
 579 DLE then causes clay particles to also detach, leading to fines migration and formation damage  
 580 as outlined above. Thus there is an optimum injection brine salinity which is low enough to  
 581 cause desorption of oil and wettability alteration, but not fines release and formation damage  
 582 (see also Pingo-Almada et al., 2013). Ligthelm et al. (2009) further argued that although MIE  
 583 may occur, it is not the primary mechanism of wettability alteration or the LSE; rather, it is a  
 584 secondary effect that further decreases the ionic strength by reducing the multivalent cation  
 585 concentration (see below).

586 *Supporting evidence:* The available evidence and models suggest that DLE, and a  
 587 commensurate increase in zeta potential, occurs when the ionic strength of the brine is reduced,  
 588 so long as the ionic strength is not too high and the pH is not close to the isoelectric point at  
 589 which the zeta potential is zero (see Revil et al., 1999; Vinogradov et al., 2010 and also Fig  
 590 12c-f). Hilner et al. (2015) observed a significant decrease in adhesion between non-polar oil  
 591 molecules and natural quartz surfaces at a similar threshold salinity to that at which the LSE is  
 592 typically observed, and argued that DLE will always play a role in the LSE even if other  
 593 mechanisms also contribute. Ligthelm et al. (2009) suggested that the composition of the  
 594 injected brine is not critical, so long as the salinity is low enough for DLE to cause desorption  
 595 of oil from mineral surfaces. The ΔpH model also makes this prediction which, as discussed

596 in the previous section, is supported by a number of experimental studies. Note that equations  
597 (1) and (2) show that increasing the valency of the ions can have a similar effect on DLE as  
598 increasing the concentration (Fig. 12b); thus the common practise of reporting concentration  
599 as TDS in ppm when brines contain multivalent ions is misleading. All natural brines contain  
600 multivalent ions, so concentration should be reported as ionic strength. Tang and Morrow  
601 (1999a) and Nasralla and Nasr-El-Din (2014) both showed that the LSE was inhibited by  
602 injection of  $\text{CaCl}_2$  as compared to NaCl brine, consistent with reduced DLE expansion owing  
603 to the presence of divalent cations.

604 *Contrary evidence:* The DLE model assumes that electrostatic forces play an important role in  
605 controlling wettability; in particular, that the polar oil components of interest and/or the  
606 brine/oil interface have the same polarity as the mineral surfaces at reservoir pH, so will be  
607 repelled as the salinity decreases yielding desorption and more water-wetting behaviour. This  
608 is inconsistent with mineral-surface-scale adhesion tests that suggest increased adhesion of oil  
609 as salinity decreases at fixed pH (e.g. Buckley et al., 1989, Buckley and Morrow, 1990;  
610 Drummond and Israelachvili 2002, 2004; Lebedeva and Fogden 2010; Lebedeva et al., 2010),  
611 but is consistent with many plug scale measurements of wettability as a function of brine  
612 salinity (e.g. Anderson, 1986 and references therein; Lighthelm et al., 2009; Fig. 13a) and also  
613 AFM data (Siretanu et al., 2014; Hilner et al., 2015). Furthermore, DLE fails to explain why  
614 the LSE effect is not always observed with reduced ionic strength. Basic data are still lacking  
615 to confirm DLE does occur at the conditions of interest: most measurements of zeta potential  
616 are obtained at relatively low salinity and temperature, on powdered samples, and in the  
617 absence of crude oil (e.g. Fig. 12). Models of the double layer (as used in the DLVO model  
618 and surface complexation models; see, for example, Brady and Krumhansl, 2012) are valid  
619 only at low ionic strength ( $<0.1\text{M}$ ) when it is reasonable to assume the ions behave as point  
620 charges and ion interactions can be neglected (e.g. Hunter, 1981). This salinity is much lower  
621 than seawater (c.  $0.5\text{M}$ ) and most formation brines. Vinogradov et al. (2010) showed that the  
622 zeta potential at quartz surfaces in contact with NaCl brine becomes constant at concentrations  
623 of c.  $0.5\text{M}$  and higher (Fig. 12a) and argued that the thickness of the double layer is comparable  
624 to the radius of a hydrated  $\text{Na}^+$  ion at this concentration; further increasing the concentration  
625 cannot further reduce the double layer thickness owing to the finite size of the ions. At  
626 concentrations above a threshold value, equation 2 is therefore no longer valid and the double  
627 layer thickness is controlled by the radius of the dominant ionic species rather than the ionic  
628 strength. Thus DLE will not occur until the brine concentration is reduced below a threshold  
629 value specific to a given brine ionic composition, and the double layer thickness at higher  
630 concentration will depend upon ion species and size.

631 *Summary:* Further data are required to determine whether DLE does occur at reservoir  
632 conditions and is associated with wettability alteration and the LSE. In particular,  
633 measurements of zeta potential at appropriate conditions of temperature, salinity, intact  
634 samples, wetting and presence of crude oil. Additional data are also required to resolve the  
635 discrepancy between some adhesion tests and DLVO theory.

636



637 **Discussion**

638 The key mechanisms underlying the LSE have yet to be determined, but the available evidence  
639 suggests that the LSE is the macroscopic (core- to reservoir-scale) manifestation of  
640 microscopic (mineral-surface to pore-scale) changes following injection of low salinity brine  
641 (or brine of controlled composition). These microscopic changes may include wettability  
642 alteration (manifested by a change in contact angle, contact angle hysteresis, or wetting surface  
643 area), a reduction in IFT, and/or an increase in the solubility of polar oil compounds in the  
644 brine. Such changes affect the efficiency with which brine displaces oil, by releasing oil  
645 previously adsorbed to mineral surfaces, allowing water to invade oil-filled pores that would  
646 be otherwise bypassed, or reducing oil trapped by snap-off. A common factor across three of  
647 the key mineral-surface scale mechanisms that have been invoked to explain the LSE is a  
648 change in the magnitude of electrostatic interactions between charged mineral surfaces and  
649 polar organic compounds: the zeta potential will change in response to (i) multi-ion exchange  
650 (MIE), because adsorption or desorption of ions changes the surface charge, (ii) local pH  
651 increase ( $\Delta\text{pH}$ ), because this also changes the surface charge (see Fig. 12), and (iii) a decrease  
652 in ionic strength because this causes double layer expansion (DLE) (see Fig. 12). However,  
653 the relationship between MIE,  $\Delta\text{pH}$ , ionic strength and the zeta potential is still poorly  
654 understood owing to a lack of data acquired at the relevant conditions, despite the efforts of  
655 groups such as those at Texas A & M (e.g. Alotaibi et al. 2010; 2011; Nasralla and Nasr-El-  
656 Din, 2014) and Shell (e.g. Suijkerbuik et al. 2014). Thus the contribution of electrostatic forces  
657 remains poorly understood. For example, modest increases in oil recovery have been observed  
658 when injecting higher salinity NaCl brine into a core containing crude oil and CaCl<sub>2</sub> brine of  
659 the same ionic strength (RezaeiDoust et al., 2011); this may reflect (i) a change in surface  
660 charge owing to the differing affinities of Na<sup>+</sup> and Ca<sup>2+</sup> cations toward clay minerals (e.g.  
661 Mugele et al., 2015), (ii) local pH change and/or (iii) a change in the double layer thickness.  
662 However, as surface charge was not measured, the mechanism cannot be determined.

663 At present, the  $\Delta\text{pH}$  and MIE mechanisms are difficult to reconcile, as the former requires  
664 desorption of multivalent cations at low concentration and exchange with protons to increase  
665 pH, whereas the latter requires the opposite: adsorption of multivalent cations at low  
666 concentration and exchange with polar oil compounds, accompanied by little or no change in  
667 pH. In both cases, pH change recorded in effluent brine may be dominated by the presence of  
668 buffers such as CO<sub>2</sub>, or by dissolution of small amounts of carbonate material, so may not be  
669 diagnostic of mechanisms occurring at the mineral-surface scale. McGuire et al. (2005)  
670 calculated that dissolution of just 7.2g of calcite (<0.1wt% of core sample material) over 15  
671 pore-volumes (PV) of waterflooding of a North Sea core increased effluent pH by 2 pH units;  
672 even trace amounts of carbonate material or other soluble minerals in natural samples can  
673 influence pH. There is still a need for carefully designed coreflooding experiments to allow  
674 individual mechanisms to be isolated and identified; this will likely require the use of synthetic  
675 core materials in the first instance, so mineralogy can be precisely controlled, allowing  
676 processes such as carbonate mineral dissolution to be eliminated or quantified. Moreover,  
677 studies are required that report a broad range of data types and measurements, to facilitate

678 cross-comparison of results and allow the underlying mechanisms to be identified or eliminated  
679 (e.g. Table 3).

680 Of the other proposed mechanisms, the available evidence suggests that fines migration or  
681 saponification may be responsible for the LSE only in some specific cases with (in the former  
682 mechanism) swelling clays, very low salinity brine, high brine pH and (in the latter mechanism)  
683 high AN crude. However, it is worth noting that several studies have reported a link between  
684 IFT and salinity, with IFT generally decreasing with decreasing salinity (e.g. Badakshan and  
685 Bakes, 1990; Ikeda et al., 1992; Cai et al., 1996); some studies have also found that the IFT  
686 drops to a minimum at a critical salinity (Fig. 13b). For example, Moeini et al. (2014) observed  
687 a minimum of c. 13mN/m at a salinity of c. 30,000 ppm NaCl or CaCl<sub>2</sub> brine, although this is  
688 higher than the injection brine salinity typically associated with the LSE. A salinity-dependent  
689 decrease in IFT reduces the capillary entry pressure, consistent with the pore-scale LSE  
690 proposed by Sorbie et al. (2010). Moreover, it is well known that the solubility of polar organic  
691 compounds in brine increases with decreasing salinity; adjusting the solubility by varying the  
692 salt concentration is a process termed 'salting in/out' (RezaeiDoust et al., 2009). This  
693 mechanism has been suggested to contribute to the LSE, although it has been largely ignored  
694 and remains comparatively under investigated (RezaeiDoust et al., 2009, 2011).

695 Many of the proposed mechanisms underlying the LSE occur at mineral surfaces;  
696 consequently, rather than the bulk rock properties, it is the surface properties that are of interest  
697 and how these are affected by the presence of crude oil, formation brine, and low salinity brine  
698 (Suijkerbuijk et al., 2013; Mathieson et al., 2014; Mugele et al., 2015; Hilner et al., 2015). For  
699 example, extremely small volumes of clay or organic matter may be present in a sample but if  
700 this material coats the mineral surfaces then it will dominate the surface interactions.  
701 Characterisation of surface properties can include imaging of clay mineral distribution,  
702 measurements of zeta potential, contact angle, adhesion and adsorption, AFM, SEM, and  
703 NMR. However, where required, it is essential that these measurements are conducted at  
704 reservoir conditions of salinity, temperature and pressure, and in the presence of crude oil;  
705 otherwise the resulting data cannot directly be applied to interpret the LSE. Ensuring consistent  
706 experimental conditions may help to reconcile the differences observed in wetting behaviour  
707 as a function of salinity at different scales.

708 For example, several mineral-surface-scale studies have observed a decrease in adhesion of  
709 crude oil to mineral surfaces with increasing salinity (e.g. Buckley et al., 1989, Buckley and  
710 Morrow, 1990; Drummond and Israelachvili, 2002, 2004; Lebedeva and Fogden, 2010;  
711 Lebedeva et al., 2010), yet plug-scale measurements of wettability suggest the opposite (e.g.  
712 Anderson, 1986 and references therein; Lighthelm et al., 2009; compare Figs. 2e,f and Fig.  
713 13a). The difference may relate to the experimental conditions such as temperature (e.g.  
714 Buckley and Morrow 1990) and the presence of multivalent cations (for example, Brown and  
715 Neustadter 1980). Similarly, adsorption tests on polar compounds and clay minerals have  
716 demonstrated strong pH dependence at room temperature, but it is not clear whether the results  
717 apply at elevated temperature and pressure (e.g. Fig. 3a,b). Measurements of zeta potential are  
718 typically obtained at relatively low ionic strength and temperature; few data are available at  
719 seawater salinity and above (e.g. Fig. 12). Furthermore, surface properties that may control

720 the LSE, such as electrical charge, reaction sites and CEC, may be affected by the history of  
721 the rock samples, including any previous experiments, cleaning, and storage, yet surface  
722 properties are rarely measured prior to coreflooding experiments. Initial surface conditions  
723 may vary, even though bulk properties are similar. This may explain why repeat corefloods on  
724 the same sample can yield different results, and why outcrop and reservoir cores often behave  
725 differently (e.g. Loardarjho et al., 2010; Winoto et al., 2012). Finally, reaction kinetics likely  
726 play a role in dictating the mechanisms underlying the LSE, including the rate of adsorption  
727 and desorption of ions and polar organic compounds (e.g. Mahani et al., 2013; Suijkerbuijk et  
728 al., 2013). If the timescales of ion exchange and/or wettability alteration are longer than the  
729 duration of an experiment, then no LSE will be observed.

730 Identification of the underlying mechanism(s) is essential to allow prediction of the optimum  
731 conditions to observe the LSE. At present, no model can predict these conditions *a-priori*, or  
732 even whether the LSE will be observed; there are still no criteria that can be used with  
733 confidence to screen candidate reservoirs for low salinity water injection prior to conducting  
734 laboratory tests. The necessary conditions outlined earlier in this paper relate partly to the  
735 initial conditions, and partly to the secondary or tertiary low salinity flooding conditions; a  
736 useful step to elucidate the underlying mechanism(s) may be to separate these initial and  
737 flooding conditions. The evidence reviewed here suggests that the initial conditions may  
738 include a change from water- to mixed-wettability for the LSE to be observed, which requires  
739 specific formation brine and crude oil composition, brine pH, mineralogy (including the  
740 presence of clay minerals) and aging temperature and duration. All of these should be  
741 replicated in laboratory experiments, but in many studies they are not (for example, the initial  
742 pH is too high, failing to account for pH buffers at reservoir conditions); in others, the initial  
743 conditions are not reported or measured. In these cases, a failure to observe the LSE cannot be  
744 properly diagnosed, because it cannot be determined whether the flooding conditions were at  
745 fault, or the initial conditions failed to create the necessary wetting state.

746 A key requirement of any mechanism is that it can explain (and predict) those cases where the  
747 LSE is not observed, as well as those cases where it is observed. Most studies concentrate on  
748 the latter. The laboratory and field experiments reported by Skrettingland et al. (2011) provide  
749 a key test in this respect: (i) the COBR system apparently met all of the necessary conditions  
750 (Amott Index of aged samples indicated initially mixed- to weakly water-wet conditions, crude  
751 contained polar components, sandstone contained clay minerals including kaolinite and  
752 chlorite, formation brine contained multivalent cations including  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), (ii) the  
753 salinity of the injection brine was significantly reduced, (iii) experiments were conducted at  
754 reservoir conditions, (iv) there was an increase in effluent brine pH in some coreflooding  
755 experiments to  $\text{pH} > 12$  when alkaline low salinity brine was injected, and (v) an associated  
756 increase in pressure drop associated with formation damage. Yet no LSE was observed. None  
757 of the proposed mechanisms can explain this. Aksulu et al. (2012) suggested the initial  
758 reservoir pH was too high (at c. 7) for significant adsorption of organic components to have  
759 occurred (cf. Fig. 3a,b), which suggests the failure lay with the initial rather than the flooding  
760 conditions, but this is inconsistent with the measured initial wettability, and also the numerous  
761 studies in which the LSE has been observed at comparable initial pH. Another key test is to

762 explain the contradictory evidence concerning the temperature dependence of the LSE  
763 discussed previously. As yet, little or no data are available to determine or predict the  
764 temperature dependence of the proposed MIE,  $\Delta\text{pH}$  or DLE mechanisms. Finally, an important  
765 issue is that of capillary effects in coreflooding experiments: during low salinity water  
766 injection, changes in wettability, permeability (owing to formation damage) or IFT change the  
767 relative importance of capillary forces in fixed-rate corefloods, so recovery may be affected by  
768 changes in capillary end effects (e.g. Skauge, 2013; Masalmeh et al., 2014). While some  
769 studies have recognized this, many have not.

770

## 771 **Conclusions**

772 The LSE is real, but the necessary conditions for improved oil recovery have not yet been  
773 identified and may require a controlled change in brine composition rather than a simple  
774 salinity reduction. The currently available criteria reviewed here are insufficient to even screen  
775 potential candidate reservoirs, let alone identify the optimal injection brine composition for a  
776 given reservoir. Furthermore, the available evidence supporting many of the conditions  
777 currently believed to be necessary is not compelling.

778 The outstanding research question now is to identify the pore- and mineral-scale mechanism(s)  
779 which facilitate improved oil recovery at the core- to reservoir-scale by controlling the injection  
780 brine composition. The most likely mechanisms identified to date occur at COBR interfaces  
781 and are multi-ion exchange (MIE), local increase in pH ( $\Delta\text{pH}$ ) and double layer expansion  
782 (DLE). Other mechanisms, such as clay swelling and fines migration, formation of natural  
783 surfactants at elevated pH, reduction in oil/brine interfacial tension, and increased solubility of  
784 polar oil compounds in brine, may occur in some cases but do not appear to be necessary to  
785 observe improved oil recovery.

786 However, the available evidence is not sufficient to unambiguously identify which, if any, of  
787 these mechanisms are essential. Moreover, understanding is hampered by a lack of common  
788 experimental conditions across length-scales; core-scale measurements are often obtained at  
789 reservoir pressure, temperature, brine salinity, crude oil composition and other conditions, but  
790 pore- and mineral-surface-scale measurements such as AFM, SEM, contact angle and wetting  
791 surface, adsorption and adhesion, are often obtained at laboratory temperature and pressure,  
792 for lower brine salinity and simplified crude composition. Contrasting experimental conditions  
793 may explain the contradictory data obtained to date.

794 A common feature of all three proposed mechanisms is that they will lead to changes in zeta  
795 potential at mineral surfaces, either through changes in mineral surface charge (MIE,  $\Delta\text{pH}$ ) or  
796 changes in the thickness of the double layer (DLE). Thus they will change the magnitude of  
797 electrostatic forces acting between mineral surfaces and polar organic species. Measurements  
798 of zeta potential at the appropriate conditions are urgently required to determine the  
799 commonality and significance of changes in surface charge during controlled salinity  
800 waterflooding and whether these are associated with improved recovery.

801 **Acknowledgements**

802 TOTAL are thanked for partial supporting Jackson through the TOTAL Chairs programme at  
803 Imperial College London, for supporting Vinogradov through the TOTAL Laboratory for  
804 Reservoir Physics at Imperial College London, and for granting permission to publish this  
805 work.

806 **References**

- 807 1. Abass, E., Abdalla, A. A., & Alawad, F. A. 2013. Experimental Investigation of Low  
808 Salinity Hot Water Injection to Enhance the Recovery of Heavy Oil Reservoirs. Society  
809 of Petroleum Engineers. doi:10.2118/164768-MS.
- 810 2. Agbalaka C. C., Dandekar A. Y., Patil S. L., Khataniar S. and Hemsath J. H. 2008.  
811 Coreflooding studies to evaluate the impact of salinity and wettability on oil recovery  
812 efficiency. *Transp. Porous Media* 76 77–94. doi: 10.1007/s11242-008-9235-7.
- 813 3. Aksulu, H., Hamsø, D., Strand, S., Puntervold, T., and T.Austad. 2012. Evaluation of  
814 Low-Salinity Enhanced Oil Recovery Effects in Sandstone: Effects of the Temperature  
815 and pH Gradient. *Energy Fuels*, 2012, 26 (6), pp 3497–3503. doi:10.1021/ef300162n.
- 816 4. Al-Adasani, A., Bai, B., and Wu, Y.-S. 2012. Investigating Low-Salinity Waterflooding  
817 Recovery Mechanisms in Sandstone Reservoirs. Society of Petroleum Engineers.  
818 doi:10.2118/152997-MS.
- 819 5. Alagic, E. and Skauge, A. 2010. Combined Low Salinity Brine Injection and Surfactant  
820 Flooding in Mixed-Wet Sandstone Cores. *Energy & Fuels* 24 (6): 3551–3559.  
821 doi:10.1021/ef1000908.
- 822 6. Alotaibi, M. B., Azmy, R., & Nasr-El-Din, H. A. 2010. A Comprehensive EOR Study  
823 Using Low Salinity Water in Sandstone Reservoirs. Society of Petroleum Engineers.  
824 doi:10.2118/129976-MS.
- 825 7. Alotaibi, M. B., Nasralla, R. A., & Nasr-El-Din, H. A. 2011. Wettability Studies Using  
826 Low-Salinity Water in Sandstone Reservoirs. Society of Petroleum Engineers.  
827 doi:10.2118/149942-PA.
- 828 8. Amashukeli, X., Grunthaner, F.J., Patrick, S.B. and Yung, P.T. 2008. Subcritical water  
829 extractor for Mars analog soil analysis, *Astrobiology*, 8 597–604.
- 830 9. Anderson, W.G., 1986, Wettability Literature Survey- Part 1: Rock/Oil/Brine  
831 Interactions and the Effects of Core Handling on Wettability, *Journal of Petroleum*  
832 *Technology*, October, 1125-1144.
- 833 10. Appelo, C. A. J. 1994. Cation and proton exchange, pH variations, and carbonate  
834 reactions in a freshening aquifer. *Water Resources Research*, 30(10), pp. 2793-2805.  
835 doi: 10.1029/94WR01048.
- 836 11. Ashraf, A., Hadia, N.J., Torsæter, O., and Tweheyo, M.T. 2010. Laboratory investigation  
837 of low salinity waterflooding as secondary recovery process: effect of wettability. Paper  
838 SPE 129012 presented at the SPE Oil and Gas India Conference and Exhibition, Mumbai,  
839 India, 20–22 January. doi: 10.2118/129012-MS.
- 840 12. Aubrey, A.D., Chalmers, J.H., Bada, J.L., Grunthaner, F.J., Amashukeli, X., Willis, P.,  
841 Skelley, A.M., Mathies, R.A., Quinn, R.C., Zent, A.P., Ehrenfreund, P., Amundson, R.,  
842 Glavin, D.P., Botta, O., Barron, L., Blaney, D.L., Clark, B.C., Coleman, M., Hofmann,

- 843 B.A., Josset, J-L., Rettberg, P., Ride, S., Robert, F., Sephton, M.A. and Yen, A. 2008.  
844 *Astrobiology*, 8: 583-595. doi:10.1089/ast.2007.0169.
- 845 13. Austad, T., RezaeiDoust, A., & Puntervold, T. 2010. Chemical Mechanism of Low  
846 Salinity Water Flooding in Sandstone Reservoirs. Society of Petroleum Engineers.  
847 doi:10.2118/129767-MS.
- 848 14. Badakshan, A., and Bakes, P., 1990. The Influence of Temperature and Surfactant  
849 Concentration on Interfacial Tension of Saline Water and Hydrocarbon Systems in  
850 Relation to Enhanced Oil Recovery by Chemical Flooding, SPE Paper.
- 851 15. Barth, T. 1991. Organic acids and inorganic ions in waters from petroleum reservoirs,  
852 Norwegian continental shelf: a multivariate statistical analysis and comparison with  
853 American reservoir formation waters. *Applied Geochemistry*, Volume 6, Issue 1, Pages  
854 1-15, ISSN 0883-2927. doi:10.1016/0883-2927(91)90059-X.
- 855 16. Batias, J., Hamon, G., Lalanne, B., and Romero, C. 2009. Field and Laboratory  
856 Observations of Remaining Oil Saturations in a Light Oil Reservoir Flooded by a Low  
857 Salinity Aquifer. Paper SCA2009-01 presented at the 23rd International Symposium of  
858 the Society of Core Analysts, Noordwijk aan Zee, The Netherlands, 27–30 September.
- 859 17. Berg, S., Cense, A. W., Jansen, E., and Bakker, K. 2010. Direct Experimental Evidence  
860 of Wettability Modification By Low Salinity. Society of Petrophysicists and Well-Log  
861 Analysts.
- 862 18. Bernard, G. G. 1967. Effect of Floodwater Salinity on Recovery of Oil from Cores  
863 Containing Clays. Society of Petroleum Engineers. doi:10.2118/1725-MS.
- 864 19. Boussour, S., Cissokho, M., Cordier, P., Bertin, H. J., and Hamon, G. 2009. Oil Recovery  
865 by Low-Salinity Brine Injection: Laboratory Results on Outcrop and Reservoir Cores.  
866 Society of Petroleum Engineers. doi:10.2118/124277-MS.
- 867 20. Brady, P.V. and Krumhansl, J.L., 2012, A surface complexation model of oil-brine-  
868 sandstone interfaces at 100°C: Low salinity waterflooding, *Journal of Petroleum Science*  
869 and Engineering 81, 171-176.
- 870 21. Brown, C.E. and Neustadter, E.L., 1980, The Wettability of Oil/Water/Silica Systems  
871 With Reference to Oil Recovery, *J. Cdn. Pet. Tech.*, 19, 100-110.
- 872 22. Buckley, J. S., and Morrow, N. R. 1990. Characterization of Crude Oil Wetting Behavior  
873 by Adhesion Tests. Society of Petroleum Engineers. doi:10.2118/20263-MS.
- 874 23. Buckley, J. S., Liu, Y., and Monsterleet, S. 1998. Mechanisms of Wetting Alteration by  
875 Crude Oils. Society of Petroleum Engineers. doi:10.2118/37230-PA.
- 876 24. Buckley, J. S., Liu, Y., Xie, X., and Morrow, N. R. 1997. Asphaltenes and Crude Oil  
877 Wetting - The Effect of Oil Composition. Society of Petroleum Engineers.  
878 doi:10.2118/35366-PA.
- 879 25. Buckley, J. S., Takamura, K., and Morrow, N. R. 1989. Influence of Electrical Surface  
880 Charges on the Wetting Properties of Crude Oils. Society of Petroleum Engineers.  
881 doi:10.2118/16964-PA.
- 882 26. Burgos, W. D., Pisutpaisal, N., Mazzaresse, M. C. and Chorover, J. 2002. Adsorption of  
883 Quinoline to Kaolinite and Montmorillonite. *Environmental Engineering Science*. 19(2):  
884 59-68. doi:10.1089/10928750252953697.
- 885 27. Carroll, D. 1959. Ion exchange in clays and other minerals. *Geological Society of*  
886 *America Bulletin* 70 (6): 749-780. doi:10.1130/0016-7606

- 887 28. Cai, B.-Y., Yang, J.-T., Guo, T.-M., 1996, *J. Chem. Eng. Data* 41, 493-496.
- 888 29. Cense, A.W., Berg, S., Jansen, E. and Bakker, K. 2011. Direct Visualization of Designer  
889 Waterflooding in Model Experiments, SPE paper 144936 presented at the SPE Enhanced  
890 Oil Recovery Conference.
- 891 30. Chassagne, C., Mietta, F. and Winterwerp, J.C. 2009. Electrokinetic study of kaolinite  
892 suspensions. *Journal of Colloid and Interface Science*, Volume 336, Issue 1, Pages 352-  
893 359, ISSN 0021-9797, doi:10.1016/j.jcis.2009.02.052.
- 894 31. Chen, Q., Mercer, D., and Webb, K. 2010. NMR Study on Pore Occupancy and  
895 Wettability Modification during Low Salinity Waterflooding. Paper SCA 2010-27  
896 presented at the 24th International Symposium of Core Analysts, Halifax, Canada, 4-7  
897 October.
- 898 32. Cissokho, M., Ahmadi, A., Bertin, H., Omari, A., and Hamon, G. 2012. Some  
899 investigations on the role of microparticles on the low salinity process. Paper SCA2012-  
900 15 presented at the International Symposium of the Society of Core Analysts, Aberdeen,  
901 Scotland, UK, 27-30 August, 2012.
- 902 33. Cissokho, M., Bertin, H., and Hamon, H. 2011. Low salinity waterflooding in sandstones  
903 pore scale observations. *Flows and mechanics in natural porous media from pore to field  
904 scale. Pore2Field. 16-18 November 2011, IFP Energies nouvelles (France).*
- 905 34. Cissokho, M., Bertin, H., Boussour, S., Cordier, P., and Hamon, G. 2010. Low Salinity  
906 Oil Recovery On Clayey Sandstone: Experimental Study. *Petrophysics*, 51, 5, 305-313.
- 907 35. Drever, J.I., 1982, *The Geochemistry of Natural Waters*, Prentice-Hall, Englewood  
908 Cliffs, 388pp.
- 909 36. Drummond, C. and Israelachvili, J. 2004. Fundamental studies of crude oil-surface water  
910 interactions and its relationship to reservoir wettability. *Journal of Petroleum Science and  
911 Engineering*, Volume 45, Issues 1-2, Pages 61-81, ISSN 0920-4105.  
912 doi:10.1016/j.petrol.2004.04.007.
- 913 37. Duman, O. and Tunç, S. 2009. Electrokinetic and rheological properties of Na-bentonite  
914 in some electrolyte solutions. *Microporous and Mesoporous Materials*, Volume 117,  
915 Issues 1-2, Pages 331-338, ISSN 1387-1811, doi:10.1016/j.micromeso.2008.07.007.
- 916 38. Durán, J.D.G., Ramos-Tejada, M.M., Arroyo, F.J. and González-Caballero, F. 2000.  
917 Rheological and Electrokinetic Properties of Sodium Montmorillonite Suspensions: I.  
918 Rheological Properties and Interparticle Energy of Interaction. *Journal of Colloid and  
919 Interface Science*, 229, 107-117, doi:10.1006/jcis.2000.6956.
- 920 39. Evans and Wennerstrom, 1999. *The Colloidal Domain: Where Physics, Chemistry,  
921 Biology and Technology Meet.*
- 922 40. Fjelde, I., Asen, S. M., and Omekeh, A. V. 2012. Low Salinity Water Flooding  
923 Experiments and Interpretation by Simulations. *Society of Petroleum Engineers.*  
924 doi:10.2118/154142-MS.
- 925 41. Fogden, A. 2011. Effect of water salinity and pH on the wettability of a model substrate,  
926 *Energy and Fuels*, 25, 5113-5125, doi: 10.1021/ef200920s.
- 927 42. Fogden, A., Kumar, M., Morrow, N., and Buckley, J. 2011, Mobilization of fine particles  
928 during flooding of sandstones and possible relations to enhanced oil recovery. *Energy  
929 and Fuels*, 25, 1605-1616. doi: 10.1021/ef101572n.

- 930 43. Gamage, P. and Thyne, G. 2011. Systematic Investigation of the Effect of Temperature  
931 During Aging and Low Salinity Flooding of Berea Sandstone and Minn. 16th European  
932 Symposium on Improved Oil Recovery, Cambridge, UK, 12-14 April, 2011.
- 933 44. Glover P. W.J. and Jackson M.D. 2010, Borehole electrokinetics. *The Leading Edge*, 29,  
934 724-728. doi: 10.1190/1.3447786.
- 935 45. Gupta, R., Smith, G. G., Hu, L., Willingham, T., Lo Cascio, M., Shyeh, J. J., and Harris,  
936 C. R. 2011. Enhanced Waterflood for Carbonate Reservoirs - Impact of Injection Water  
937 Composition. Society of Petroleum Engineers. doi:10.2118/142668-MS.
- 938 46. Hassenkam, T., Mitchell, A.C., Pedersen, C.S., Skovbjerg, L.L., Bovet, N., and Stipp,  
939 S.L.S. 2012. The low salinity effect observed on sandstone model surfaces. *Colloids Surf.*  
940 *A Physicochem. Eng. Aspects*, 403, 79–86. doi: 10.1016/j.colsurfa.2012.03.058.
- 941 47. Hassenkam, T., Pedersen, C.S., Dalby, K., Austad, T., and Stipp, S.L.S. 2011. Pore-scale  
942 observation of low salinity effects on outcrop and oil reservoir sandstone. *Colloids Surf.*  
943 *A Physicochem. Eng. Aspects*, 490, 179–88. doi: 10.1016/j.colsurfa.2011.09.025.
- 944 48. Hilner, E., Andersson, M.P., Hassenkam, T., Matthiesen, J., Salino P.A. and Stipp, S.L.S.  
945 2015. The effect of ionic strength on oil adhesion in sandstone – the search for the low  
946 salinity mechanism. *Scientific Reports* 5, 9933. doi: 10.1038/srep09933
- 947 49. Hunter, R. J. 1981. *Zeta Potential in Colloid Science*, Academic Press, New York.
- 948 50. Jadhunandan, P. P., and Morrow, N. R. 1995. Effect of Wettability on Waterflood  
949 Recovery for Crude-Oil/Brine/Rock Systems. Society of Petroleum Engineers.  
950 doi:10.2118/22597-PA.
- 951 51. Ikeda, N., Aratono, M., Motomura, J., 1992, *J. Colloid Interface Sci.*, 149, 208-215.
- 952 52. Kosmulski, M. and Dahlsten, P. 2006. High ionic strength electrokinetics of clay  
953 minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 291, 212-  
954 218, doi:10.1016/j.colsurfa.2006.06.037.
- 955 53. Krueger, R. F. 1986. An Overview of Formation Damage and Well Productivity in  
956 Oilfield Operations. Society of Petroleum Engineers. doi:10.2118/10029-PA.
- 957 54. Lebedeva, E.V. and Fogden, A., 2010. Adhesion of Oil to Kaolinite in Water, *Environ.*  
958 *Sci. Technol.*, 44, 9470-9475, doi: 10.1021/es102041b.
- 959 55. Lebedeva, E.V., Fogden, A., Senden, T.J and Knackstadt, M.A., 2010, Kaolinite  
960 wettability – the effect of salinity, pH and calcium, Society of Core Analysts paper  
961 SCA2010-11.
- 962 56. Lebedeva, E.V. and Fogden, A., 2011, Micro-CT and Wettability Analysis of Oil  
963 Recovery from Sand Packs and the Effect of Waterflood Salinity and Kaolinite, *Energy*  
964 *and Fuels*, 25, 5683-5694, doi: 10.1021/ef201242s.
- 965 57. Lager A., K.J. Webb and C.J.J. Black. 2007. Impact of Brine Chemistry on Oil Recovery.  
966 Paper A24 presented at the 14th European Symposium on Improved Oil Recovery.
- 967 58. Lager, A., Webb, K. J., Black, C. J. J., Singleton, M. & Sorbie, K. S. 2008a. Low salinity  
968 oil recovery - An experimental investigation. *Petrophysics*, 49, 1, 28-35.
- 969 59. Lager, A., Webb, K.J., Collins, I.R., and Richmond, D.M. 2008b. LoSal™ Enhanced Oil  
970 Recovery: Evidence of Enhanced Oil Recovery at the Reservoir Scale. Paper SPE 113976  
971 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19–23 April. doi:  
972 10.2118/113976-MS.



- 973 60. Lever A., and R.A. Dowe. 1984. Water sensitivity and migration of fines in the Hopeman  
974 sandstone. *J. Pet. Geology*, 7(1), 97-108. doi: 10.1111/j.1747-5457.1984.tb00165.x.
- 975 61. Li, Y., 2011. Oil Recovery by Low Salinity Water Injection into a Reservoir: A New  
976 Study of Tertiary Oil Recovery Mechanism. *Transport in Porous Media*, Volume 90,  
977 Issue 2, pp 333-362. doi: 10.1007/s11242-011-9788-8.
- 978 62. Liegthelm, D.J., Gronsveld, J., Hofman, J.P., Brussee, N., Marcelis, F., and van der  
979 Linde, H.A. 2009. Novel Waterflooding Strategy by Manipulation of Injection Brine  
980 Composition. Paper SPE 119835 presented at the EUROPEC/EAGE Annual Conference  
981 and Exhibition, Amsterdam, 8–11 June. doi: 10.2118/119835-MS.
- 982 63. Liu, Y. and Buckley, J. S. 1997. Evolution of Wetting Alteration by Adsorption From  
983 Crude Oil. Society of Petroleum Engineers. doi:10.2118/28970-PA.
- 984 64. Loahardjo, N., Xie, X., and Morrow, N.R. 2010. Oil Recovery by Sequential  
985 Waterflooding of Mixed-Wet Sandstone and Limestone. *Energy & Fuels* 24 (9): 5073–  
986 5080. doi:10.1021/ef100729b.
- 987 65. Loahardjo, N., Xie, X., Yin, P., and Morrow, N.R. 2007. Low Salinity Waterflooding of  
988 a Reservoir Rock. Paper SCA 2007-29 presented at the 2007 SCA International  
989 Symposium, Calgary, 10–12 September.
- 990 66. Maas, J.G., Wit, K., and Morrow, N.R. 2001. Enhanced Oil Recovery by Dilution of  
991 Injection Brine: Further Interpretation of Experimental Results. Paper SCA 2001-13  
992 presented at the 2001 International Symposium of the Society of Core Analysts,  
993 Edinburgh, UK, 17–19 September.
- 994 67. Madsen, L., and Lind, I. 1998. Adsorption of Carboxylic Acids on Reservoir Minerals  
995 From Organic and Aqueous Phase. Society of Petroleum Engineers. doi:10.2118/37292-  
996 PA.
- 997 68. Mahani, H., Berg, S., Bartels, W.-B., Joekar-Niasar, V., and Ilic, D. 2013. Kinetics of the  
998 Low Salinity Waterflooding Effect Studied in a Model System. Society of Petroleum  
999 Engineers paper SPE165255MS. doi:10.2118/165255-MS.
- 1000 69. Martin, J. C. 1959. The Effects of Clay on the Displacement of Heavy Oil by Water.  
1001 Society of Petroleum Engineers. doi:10.2118/1411-G.
- 1002 70. Martinez, R. E., Sharma, P. and Kappler, A. 2010. Surface binding site analysis of Ca<sup>2+</sup>-  
1003 homoionized clay–humic acid complexes, *Journal of Colloid and Interface Science*,  
1004 Volume 352, Issue 2, Pages 526-534, ISSN 0021-9797, doi:10.1016/j.jcis.2010.08.082.
- 1005 71. Masalmeh, S. K., Sorop, T.G., Suijkerbuijk, B.M.J.M, Vermolen, E.C.M., Douma, S.,  
1006 van del Linde, H.A. and Pieterse, S.G.J., 2014. Low Salinity Flooding: Experimental  
1007 Evaluation and Numerical Interpretation. International Petroleum Technology  
1008 Conference. doi: 10.2523/17558-MS.
- 1009 72. Matthiesen, J., Bovet, N., Hilner, E., Andersson, M.P., Schmidt, D.A., Webb, K.J.,  
1010 Dalby, K.N., Hassenkam, T., Crouch, J., Collins, I.R. and Stipp, S.L.S. 2014. *Energy*  
1011 *Fuels*, 28, 4849–4858. doi: 10.1021/ef500218x.
- 1012 73. McGuire, P. L., Chatham, J. R., Paskvan, F. K., Sommer, D. M., and Carini, F. H. 2005.  
1013 Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska’s North  
1014 Slope. Society of Petroleum Engineers. doi:10.2118/93903-MS.
- 1015 74. Morrow, N., and Buckley, J. 2011. Improved Oil Recovery by Low-Salinity  
1016 Waterflooding. Society of Petroleum Engineers. doi:10.2118/129421-JPT.

- 1017 75. Morrow, N.R., Tang, G., Valat, M., Xie, X., 1998. Prospects of improved oil recovery  
1018 related to wettability and brine composition. *Journal of Petroleum Science and*  
1019 *Engineering*, 20, 267–276. doi: 10.1016/S0920-4105(98)00030-8.
- 1020 76. Mugele, F., Bera, B., Cavalli, A., Siretanu, I., Maestro, A., Duits, M., Cohen-Stuart, M.,  
1021 van den Ende, D., Stocker I. and Collins, I., 2015, Ion adsorption-induced wetting  
1022 transition in oil-water-mineral systems. *Sci. Rep.* 5, 10519; doi: 10.1038/srep10519.
- 1023 77. Nasralla, R. A., and Nasr-El-Din, H. A. 2014. Double-Layer Expansion: Is It a Primary  
1024 Mechanism of Improved Oil Recovery by Low-Salinity Waterflooding? *Society of*  
1025 *Petroleum Engineers*. doi:10.2118/154334-PA.
- 1026 78. Patil, S. B., Dandekar, A. Y., Patil, S., and Khataniar, S. 2008. Low Salinity Brine  
1027 Injection for EOR on Alaska North Slope (ANS). *International Petroleum Technology*  
1028 *Conference*. doi:10.2523/12004-MS.
- 1029 79. Pingo Almada, M. B., Pieterse, S. G. J., Marcelis, A. H. M., van Haasterecht, M. J. T.,  
1030 Brussee, N. J., and van der Linde, H. A. 2013. Experimental Investigation on the Effects  
1031 of Very Low Salinity on Middle Eastern Sandstone Corefloods. *Society of Petroleum*  
1032 *Engineers*. doi:10.2118/165180-MS.
- 1033 80. Pu, H., Xie, X., Yin, P., and Morrow, N.R. 2010. Low Salinity Waterflooding and  
1034 Mineral Dissolution. Paper SPE 134042 presented at the SPE Annual Technical  
1035 Conference and Exhibition, Florence, Italy, 19–22 September. doi: 10.2118/134042-MS.
- 1036 81. Pu, H.; Xie, X.; Yin, P.; Morrow, N. R., 2008. Application of coalbed methane water to  
1037 oil recovery by low salinity waterflooding. Paper SPE 113410 presented at the 2008 SPE  
1038 Improved Oil Recovery Symposium, Tulsa, OK, USA, April 19-23, 2008.  
1039 doi:10.2118/113410-MS.
- 1040 82. Revil, A., P. A. Pezard, and P. W. J. Glover. 1999. Streaming potential in porous media:  
1041 1. Theory of the zeta potential, *J. Geophys. Res.*, 104(B9), 20021–20031.  
1042 doi: 10.1029/1999JB900089.
- 1043 83. RezaeiDoust, A., Puntervold, T., Strand, S. & Austad, T., 2009, Smart Water as  
1044 Wettability Modifier in Carbonate and Sandstone: A Discussion of  
1045 Similarities/Differences in the Chemical Mechanisms, *Energy Fuels* 23, 4479–4485.  
1046 doi:10.1021/ef900185q.
- 1047 84. RezaeiDoust, A., Puntervold, T., & Austad, T. 2010. A Discussion of the Low-Salinity  
1048 EOR Potential for a North Sea Sandstone Field. *Society of Petroleum Engineers*.  
1049 doi:10.2118/134459-MS.
- 1050 85. RezaeiDoust, A., T. Puntervold, and T. Austad. 2011. Chemical verification of the EOR  
1051 mechanism by using low saline/smart water in sandstone. *Energy & Fuels*, 25, 2151-  
1052 2162, doi:10.1021/ef200215y.
- 1053 86. Rivet, S.M., Lake, L.W., and Pope, G.A. 2010. A Coreflood Investigation of Low-  
1054 Salinity Enhanced Oil Recovery. Paper SPE 134297 presented at the SPE Annual  
1055 Technical Conference and Exhibition, Florence, Italy, 19–22 September.  
1056 doi:10.2118/134297-MS.
- 1057 87. Robertson, E.P. 2007. Low-Salinity Waterflooding to Improve Oil Recovery—Historical  
1058 Field Evidence. Paper SPE 109965 paper presented at the Annual Technical Conf. and  
1059 Exhibition, Anaheim, California, USA, 11–14 November. doi: 10.2118/109965-MS.

- 1060 88. Robertson, E.P. 2010. Oil Recovery Increases by Low-Salinity Flooding: Minnelusa and  
1061 Green River Formations. Paper SPE 132154 presented at the SPE Annual Technical  
1062 Conference and Exhibition, Florence, Italy, 19–22 September. doi: 10.2118/132154-MS.
- 1063 89. Robertson, E.P., Thomas, C.P., Zhang, Y. and Morrow, N.R. 2003. Improved  
1064 Waterflooding through Injection-Brine Modification. Technical Report, INEEL/EXT-  
1065 02-01591.
- 1066 90. Sandengen , K., Tweheyo, M.T., Rphaug, M., Kjølhamar, A., Crescente, C. and Kippe,  
1067 V. 2011. Experimental evidence of low salinity water flooding yielding a more oil-wet  
1068 behaviour. SCA2011-16. Presented at the International Symposium of the Society of  
1069 Core Analysts held in Austin, Texas, USA 18-21 September, 2011.
- 1070 91. Schmatz, J., Urai, J.L., Berg, S. and Ott, H. 2015. Nanoscale imaging of pore-scale fluid-  
1071 fluid-solid contacts in sandstone, *Geophys. Res. Lett.*, 42, 2189–2195,  
1072 doi:10.1002/2015GL063354.
- 1073 92. Secombe, J. C., Lager, A., Webb, K. J., Jerauld, G., and Fueg, E. 2008. Improving  
1074 Wateflood Recovery: LoSal™ EOR Field Evaluation. Society of Petroleum Engineers.  
1075 doi:10.2118/113480-MS.
- 1076 93. Secombe, J., Lager, A., Jerauld, G., Jhaveri, B., Buikema, T., Bassler, S., Denis, J.,  
1077 Webb, K., Cockin, A., and Fueg, E. 2010. Demonstration of Low-Salinity EOR at  
1078 Interwell Scale, Endicott Field, Alaska. Society of Petroleum Engineers.  
1079 doi:10.2118/129692-MS.
- 1080 94. Shaker Shiran, B. and Skauge, A. 2012. Wettability and Oil Recovery by Low Salinity  
1081 Injection. Society of Petroleum Engineers. doi:10.2118/155651-MS.
- 1082 95. Sharma, M.M. and Filoco, P.R. 2000. Effect of Brine Salinity and Crude-Oil Properties  
1083 on Oil Recovery and Residual Saturations. *SPE J.* 5, 293–300. doi: 10.2118/65402-PA.
- 1084 96. Siretanu, I., Ebeling, D., Andersson, M.P., Stipp, S.L.S., Philipse, A., Stuart, M.C., van  
1085 den Ende, D. and Mugele, F. 2014. Direct observation of ionic structure at solid-liquid  
1086 interfaces: a deep look into the Stern Layer. *Sci. Rep.* 4, 4956. doi::10.1038/srep04956.
- 1087 97. Sorop, T.G., Masalmeh, S.K., Suijkerbuijk, B.M.J.M., van der Linde, H.A., Mahani, H.,  
1088 Brussee, N.J., Marcelis, F.A.H.M. and Coom, A. 2015. Relative Permeability  
1089 Measurments to Quantify the Low Salinity Waterflooding Effect at Field Scale, SPE  
1090 paper 177856, presented at the Abu Dhabi International Petroleum Exhibition and  
1091 Conference.
- 1092 98. Skauge A. 2013. Low Salinity Flooding - A Critical Review. IOR 2013 - From  
1093 Fundamental Science to Deployment.
- 1094 99. Skrettingland, K., Holt, T., Tweheyo, M. T., & Skjevraak, I. 2011. Snorre Low-Salinity-  
1095 Water Injection--Coreflooding Experiments and Single-Well Field Pilot. Society of  
1096 Petroleum Engineers. doi:10.2118/129877-PA.
- 1097 100. Sondi, I., Bišćan, J. and Pravdić, V. 1996. Electrokinetics of Pure Clay Minerals  
1098 Revisited. *Journal of Colloid and Interface Science*, Volume 178, Issue 2, Pages 514-  
1099 522, ISSN 0021-9797, doi:10.1006/jcis.1996.0146.
- 1100 101. Sorbie, K.S. and Collins, I.R. 2010. A Proposed Pore-Scale Mechanism for How Low  
1101 Salinity Waterflooding Works. Paper SPE 129833 presented at the SPE Improved Oil  
1102 Recovery Symposium, Tulsa, 24–28 April. doi: 10.2118/129833-MS.

- 1103 102. Souto, E. and Bazin, B., 1993, Ion Exchange Between Hydrogen and Homoionic Brines  
1104 Related to Permeability Reduction, SPE paper SPE25203.
- 1105 103. Suijkerbuijk, B., Hofman, J., Ligthelm, D. J., Romanuka, J., Brussee, N., van der Linde,  
1106 H., and Marcelis, F. 2012. Fundamental Investigations into Wettability and Low Salinity  
1107 Flooding by Parameter Isolation. Society of Petroleum Engineers. doi:10.2118/154204-  
1108 MS.
- 1109 104. Suijkerbuijk, M.J.M., H.P.C.E. Kuipers, C.P.J.W. van Kruijsdijk, S. Berg, J.F. van  
1110 Winden, D.J. Ligthelm, H. Mahani, M. Pingo Almada, E. Van den Pol, V. Joeekar Niasar,  
1111 J. Romanuka, E.C.M. Vermolen, I.S.M. Al-Qarshubi. 2013. The Development of a  
1112 Workflow to Improve Predictive Capability of Low Salinity Response. 6th International  
1113 Petroleum Technology Conference. doi:10.2523/17157-MS.
- 1114 105. Suman, Y., E. Shirif, H. Ibrahim and A. Ala-Ktiwi. 2014. Evaluation of Low Saline  
1115 “Smart Water” Enhanced Oil Recovery in Light Oil Reservoirs. World Journal of  
1116 Engineering and Technology, Vol. 2 No. 1, pp. 13-22. doi: 10.4236/wjet.2014.21002.
- 1117 106. Tang, G. and Morrow, N.R. 2002. In: Injection of dilute brine and crude oil/brine/rock  
1118 interactions. American Geophysical Union, Washington D.C.. 129: 9. doi:  
1119 10.1029/129GM16.
- 1120 107. Tang, G. Q. and Morrow, N. R. 1997. Salinity, temperature, oil composition, and oil  
1121 recovery by waterflooding. SPE Reservoir Engineering, 12, 4, 269-276.  
1122 doi:10.2118/36680-PA.
- 1123 108. Tang, G.-Q. and Morrow, N. R. 1999a. Influence of brine composition and fines  
1124 migration on crude oil brine rock interactions and oil recovery. Journal of Petroleum  
1125 Science & Engineering, vol.24, p. 99–111. doi: 10.1016/S0920-4105(99)00034-0.
- 1126 109. Tang, G.-Q. and Morrow, N.R. 1999b. Oil Recovery by Waterflooding and Imbibition –  
1127 Invading Brine Cation Valency and Salinity. Paper SCA-9911 presented at the 1999  
1128 International Symposium of the Society of Core Analysts, Golden, Colorado, USA, 1–4  
1129 August.
- 1130 110. Vaidya, R.N. and Fogler, H.S., 1990, Fines Migration and Formation Damage: Influence  
1131 of pH and Ion Exchange, SPE paper SPE19413.
- 1132 111. Valocchi A.J., Street, R. L., and Roberts, P. V. 1981. Transport of ion exchanging solutes  
1133 in groundwater: Chromatographic theory and field simulation. Water Resources  
1134 Research, 17(5), pp. 1517-1527. doi: 10.1029/WR017i005p01517.
- 1135 112. van Olphen, H. and Fripiat, J.J., 1979, Data Handbook for Clay Minerals and other Non-  
1136 Metallic Minerals, Pergamon Press, New York, 346pp.
- 1137 113. Vledder, P., Gonzalez, I. E., Carrera Fonseca, J. C., Wells, T., and Ligthelm, D. J. 2010.  
1138 Low Salinity Water Flooding: Proof Of Wettability Alteration On A Field Wide Scale.  
1139 Society of Petroleum Engineers. doi:10.2118/129564-MS.
- 1140 114. Wainippee, W., Cuadros, J., Sephton, M. A., Unsworth, C., Gill, M. G., Strekopytov, S.  
1141 and Weiss, D. J. 2013. The effects of oil on As(V) adsorption on illite, kaolinite,  
1142 montmorillonite and chlorite. Geochimica et Cosmochimica Acta, Volume 121, Pages  
1143 487-502, ISSN 0016-7037, doi:10.1016/j.gca.2013.07.018.
- 1144 115. Webb, K. J., Black, C. J. J., and Al-Ajeel, H. 2004. Low Salinity Oil Recovery - Log-  
1145 Inject-Log. Society of Petroleum Engineers. doi:10.2118/89379-MS.

- 1146 116. Webb, K.J., C.J.J. Black and I.J. Edmonds. 2005. Low Salinity Oil Recovery – The Role  
1147 of Reservoir Condition Corefloods. 13th European Symposium on Improved Oil  
1148 Recovery.
- 1149 117. Wideroe, H.C., Rueslaatten, H., Boassen, T., Crescente, C.M., Røphaug, M., Soerland,  
1150 G.H., and Urkedal, H. 2010. Investigation of Low Salinity Water Flooding by NMR and  
1151 CRYOEM. Paper SCA 2010-26 presented at the 24th International Symposium of  
1152 Core Analysts, Halifax, Canada, 4–7 October.
- 1153 118. Winoto, W., Loahardjo, N., Xie, S. X., Yin, P., and Morrow, N. R. 2012. Secondary and  
1154 Tertiary Recovery of Crude Oil from Outcrop and Reservoir Rocks by Low Salinity  
1155 Waterflooding. Society of Petroleum Engineers. doi:10.2118/154209-MS.
- 1156 119. Yildiz H. O., and Norman R. Morrow, 1996. Effect of brine composition on recovery of  
1157 Moutray crude oil by waterflooding. *Journal of Petroleum Science and Engineering*,  
1158 Volume 14, Issues 3–4, Pages 159–168. doi: 10.1016/0920-4105(95)00041-0.
- 1159 120. Yin, X., Yan, L., Liu, J., Xu, Z. and Miller, J. D. 2013. Anisotropic surface charging of  
1160 chlorite surfaces. *Clays and Clay Minerals*, 61(2):152-164, doi:  
1161 10.1346/CCMN.2013.0610212.
- 1162 121. Yousef, A. A., Al-Saleh, S. H., Al-Kaabi, A., and Al-Jawfi, M. S. 2011a. Laboratory  
1163 Investigation of the Impact of Injection-Water Salinity and Ionic Content on Oil  
1164 Recovery From Carbonate Reservoirs. Society of Petroleum Engineers.  
1165 doi:10.2118/137634-PA.
- 1166 122. Yousef, A. A., Al-Saleh, S., Al-Kaabi, A. U., and Al-Jawfi, M. S. 2010. Laboratory  
1167 Investigation of Novel Oil Recovery Method for Carbonate Reservoirs. Society of  
1168 Petroleum Engineers. doi:10.2118/137634-MS.
- 1169 123. Yousef, A. A., Al-Saleh, S., and Al-Jawfi, M. S. 2012a. Improved/Enhanced Oil  
1170 Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic  
1171 Content. Society of Petroleum Engineers. doi:10.2118/154076-MS.
- 1172 124. Yousef, A. A., Al-Saleh, S., and Al-Jawfi, M. S. 2012b. The Impact of the Injection  
1173 Water Chemistry on Oil Recovery from Carbonate Reservoirs. Society of Petroleum  
1174 Engineers. doi:10.2118/154077-MS.
- 1175 125. Yousef, A. A., Al-Salehsalah, S. H., and Al-Jawfi, M. S. 2011b. New Recovery Method  
1176 for Carbonate Reservoirs through Tuning the Injection Water Salinity: Smart  
1177 WaterFlooding. Society of Petroleum Engineers. doi:10.2118/143550-MS.
- 1178 126. Yousef, A. A., Liu, J. S., Blanchard, G. W., Al-Saleh, S., Al-Zahrani, T., Al-zahrani  
1179 Rashad Madees, Tammar, H. I. and Al-mulhim Nayef. 2012c. Smart Waterflooding:  
1180 Industry's First Field Test in Carbonate Reservoirs. Society of Petroleum Engineers.  
1181 doi:10.2118/159526-MS.
- 1182 127. Zhang, Y. and Morrow, N.R. 2006. Comparison of Secondary and Tertiary Recovery  
1183 With Change in Injection Brine Composition for Crude Oil/Sandstone Combinations.  
1184 Paper SPE 99757 presented at the SPE/DOE Symposium on Improved Oil Recovery,  
1185 Tulsa, 22–26 April. doi: 10.2118/99757-MS.
- 1186 128. Zhang, Y., Xie, X., and Morrow, N.R. 2007. Waterflood performance by injection of  
1187 brine with different salinity for reservoir cores. Paper SPE 109849 presented at the SPE  
1188 Annual Technical Conference and Exhibition, Anaheim, California, USA, 11–14  
1189 November. doi: 10.2118/109849-MS.

1190

## 1191 **Acknowledgements**

1192 Jackson was funded by the TOTAL Chairs Programme at Imperial College London, and  
1193 Vinogradov through the TOTAL Laboratory for Reservoir Physics at Imperial College  
1194 London. TOTAL are also thanked for granting permission to publish.

1195

## 1196 **Figure Captions**

1197 Figure 1. Examples of (a, b) successful low salinity waterfloods, and (c, d) unsuccessful low  
1198 salinity waterfloods in sandstones in (a, c) secondary mode, and (b, d) tertiary mode. (a) data  
1199 from Ashraf et al. (2010), for details refer to PID 5 in Table 1; (b) RezaeiDoust et al. (2011),  
1200 for details see PID 24 in Table 1, top row for the lower curve and bottom row for the upper  
1201 curve; (c) Tang and Morrow (1997), for details see the DG brine experiments in PID 31 in  
1202 Table 1; (d) Nasralla and Nasr-El-Din (2014), for details see the top row of PID 20 in Table 1.  
1203 Also shown are examples where injecting brine of higher salinity yielded increased recovery  
1204 (plot (e), data from Tang and Morrow, (1997), for details see the top row of PID 31 in Table  
1205 1) and where injecting brine of the same ionic strength but containing no divalent ions yielded  
1206 increased recovery (plot (f), data from RezaeiDoust et al. (2011), for details see PID 24 in Table  
1207 1). Secondary mode refers to injection of low salinity brine into rock saturated with oil and  
1208 connate brine of higher salinity at the irreducible saturation; tertiary mode refers to the injection  
1209 of low salinity brine into rock containing oil and brine of some higher salinity (such as  
1210 seawater, aquifer brine or formation brine) which has been used to displace the oil in a  
1211 preceding waterflood.

1212

1213 Figure 2. Evidence for a link between wettability alteration and brine salinity. (a) Spontaneous  
1214 imbibition data from aged Berea sandstone initially saturated with crude oil and high salinity  
1215 formation brine, for a variety of dilute invading brine salinities (Morrow et al., 1998). Several  
1216 studies have reported similar results (e.g. Tang and Morrow, 1999b; Maas et al., 2001;  
1217 Robertson et al., 2003; Zhang and Morrow, 2006; Zhang et al., 2007; Ligthelm et al., 2009;  
1218 Chen et al., 2010; Wickramathilaka et al., 2010; Wideroe et al., 2010; Suijkerbuijk et al. 2012);  
1219 (b) Contact angle and contact surface diameter as a function of salinity: the North Sea crude  
1220 oil droplets were used on Montmorillonite patches when high salinity brine was displaced by  
1221 the same brine diluted 8 fold (Mahani et al., 2013). (c) Mobilization of oil droplets when low  
1222 salinity brine flows past a model montmorillonite-quartz substrate (Berg et al., 2010; Cense et  
1223 al., 2011, Mahani et al., 2013). (d) Incremental oil recovery from low salinity corefloods as a  
1224 function of initial sample wettability (Ashraf et al., 2010). (e) Adhesion map for crude oil-  
1225 brine-glass as a function of salinity and pH at ambient temperature (Buckley and Morrow,  
1226 1990). Adhesion is a measure of the surface wettability; when the oil droplet adheres, the  
1227 surface is oil-wet (Buckley and Morrow, 1990). (f) Wettability map for crude oil on mica in

1228 NaCl solutions. Static contact angle measurements show that three wettability regimes can be  
1229 distinguished (Drummond and Israelachvili, 2004)

1230

1231 Figure 3. Evidence for a link between pH and the LSE. (a,b) Impact of pH on adsorption of  
1232 polar oil compounds on clay mineral surfaces, and (c,d) observed pH changes during successful  
1233 LSE corefloods. Plots (a – Madsen and Lind, 1998; 0.1M NaCl) and (b – Burgos et al., 2002)  
1234 show adsorption of acid (4-tetr-benzoic-acid PTBBA) and basic (Quinoline) polar organic  
1235 compounds respectively onto kaolinite as a function of pH. Plot (c) shows an example of  
1236 increased effluent brine pH associated with the LSE (Cissokho et al., 2012: for details see PID  
1237 10 in Table 1); similar pH increases have been observed in a number of studies (e.g. Tang and  
1238 Morrow, 1999a; Maas et al., 2001; McGuire et al., 2005; Loaharjo et al., 2007; Austad et al.  
1239 2010; Alotaibi et al., 2010; Cissokho et al. 2010; RezaeiDoust et al., 2011). Plot (d) shows an  
1240 example of approximately constant effluent brine pH associated with the LSE (Loaharjo et al.,  
1241 2007: for details see PID 15 in Table 1); a similar lack of pH change has been observed in a  
1242 number of studies (e.g. Zhang et al., 2007; Loaharjo et al., 2007; Lager et al., 2008a,b; Austad  
1243 et al. 2010; Alotaibi et al., 2010; RezaeiDoust et al., 2011; Nasralla and Nasr-El-Din, 2014).

1244

1245 Figure 4. Impact of injection brine salinity on the LSE. (a) Comparison of secondary  
1246 coreflooding with seawater and 1,000ppm dilute brine (Webb et al., 2005; for details see PID  
1247 33 in Table 1). (b) Incremental recovery as a function of injection brine salinity during tertiary  
1248 waterflooding (Cissokho et al., 2010; for details see the top row of PID 9 in Table 1).

1249

1250 Figure 5. Fines migration as a mechanism for the LSE (Tang and Morrow, 1999a).

1251

1252 Figure 6. Impact of low salinity brine injection on (a) oil recovery from a kaolinite-bearing CS  
1253 sandstone reservoir sample in tertiary mode; curves 1-3 denote sequential waterfloods on the  
1254 same plug after cleaning and restoration; note also the cessation of the LSE on injecting  $\text{Ca}^{2+}$   
1255 ions; (b) pressure drop and pH associated with the same corefloods as in (a); note fines elution  
1256 progressively decreased from flood 1 to flood 3; (c) oil recovery from a Berea sandstone sample  
1257 in secondary mode, and (d) a fired and acidized Berea sample; (e) Berea sandstone sample in  
1258 secondary mode with  $S_{wi}=0$ . From Tang and Morrow (1999a); for more details see PID 31 in  
1259 Table 1.

1260

1261 Figure 7. Compilation of data relating the LSE and acid number (AN) of the crude oil.

1262

1263 Figure 8.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in produced brine during low salinity brine injection in  
1264 (a) a coreflooding experiment (Lager et al., 2008a) and (b) a production well test (Lager et al.,

1265 2008b; solid lines represent the concentration of the cations in the initial formation brine,  
1266 dashed lines denote concentration of the cations in the injected low salinity brine). Both tests  
1267 (a) and (b) showed increased oil recovery.

1268

1269 Figure 9. Proposed mechanisms for adsorption of polar compounds onto clay mineral surfaces  
1270 associated with MIE (Lager et al. 2008b). During low salinity waterflooding, the organic polar  
1271 compounds or organo-metallic complexes of oil that are directly attached to clay minerals via  
1272 cation exchange or cation/ligand/water bridging are replaced with uncomplexed cations from  
1273 low salinity brine.

1274

1275 Figure 10.  $\Delta$ pH mechanism at clay mineral surfaces (Austad et al., 2010). During low salinity  
1276 waterflooding, basic (plots a-c) or acidic (plots d-f) components of oil are desorbed from clay  
1277 mineral surfaces via exchange with protons, leading to an increase in pH.

1278

1279 Figure 11. Charge distribution at the quartz mineral – brine interface, from Glover and  
1280 Jackson (2010).

1281

1282 Figure 12. Effect of brine ionic strength on (a) zeta potential measured in sandstones saturated  
1283 with NaCl brine (Vinogradov et al., 2010); note the constant zeta potential at high ionic  
1284 strength, and (b) the Debye length, a measure of the thickness of the diffuse part of the double  
1285 layer; note that the same double layer thickness can be observed for varying concentration and  
1286 valency. Also shown is the pH dependence of the zeta potential of (c) kaolinite, (d) illite, (e)  
1287 chlorite and (f) montmorillonite in brines of various composition and ionic strength ((1) - Duran  
1288 et al., 2000; (2) - Kosmulsi and Dahlsten, 2006; (3) - Duman and Tunc, 2009; (4) - Chassagne  
1289 et al., 2009; (5) - Martinez et al., 2010; (6) - Wainipee et al., 2013; (7) - Sondi et al., 1996; (8)  
1290 - Yin et al., 2013; (9) - Alotaibi et al. 2011).

1291

1292 Figure 13. (a) Wettability index of intact samples as a function of initial brine salinity (from  
1293 Ligthelm et al., 1989). Samples become increasingly oil-wet with increasing salinity,  
1294 consistent with DVLO theory. Wetting layer collapse and cation bridging are promoted at high  
1295 salinity owing to the decrease in thickness of the electrical double layers. (b) IFT as a function  
1296 of salinity for NaCl and CaCl<sub>2</sub> brine, from Moeini et al. (2014).

1297

1298



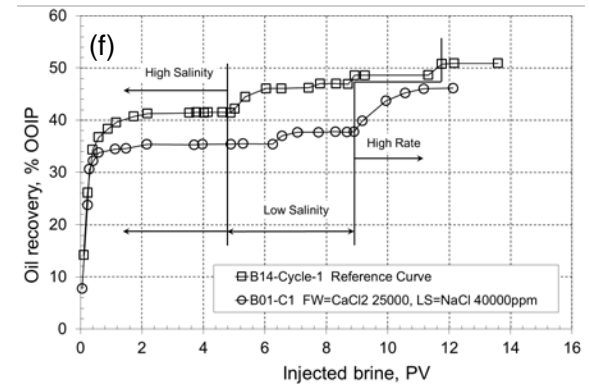
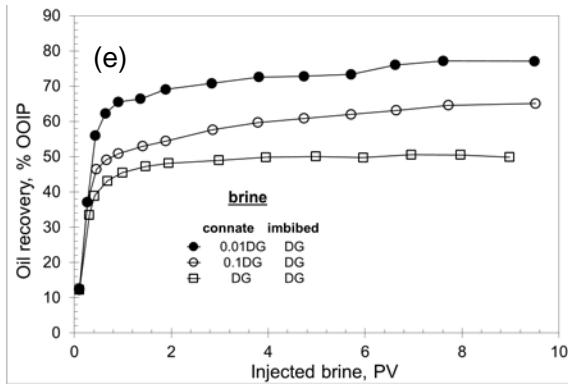
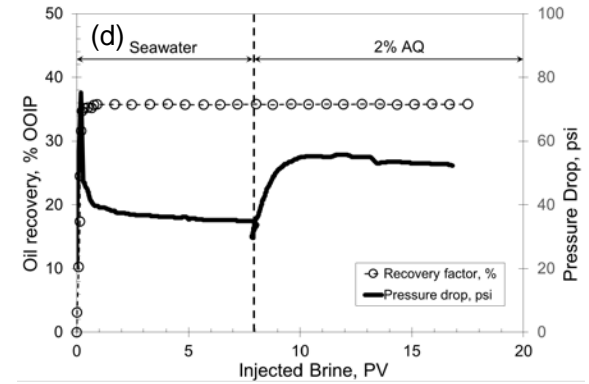
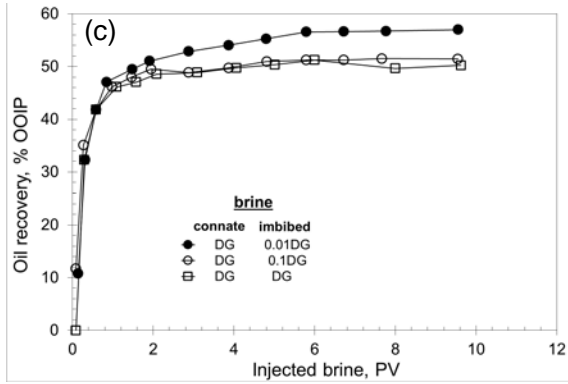
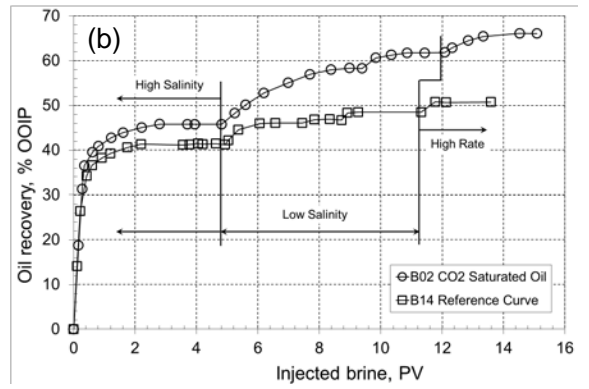
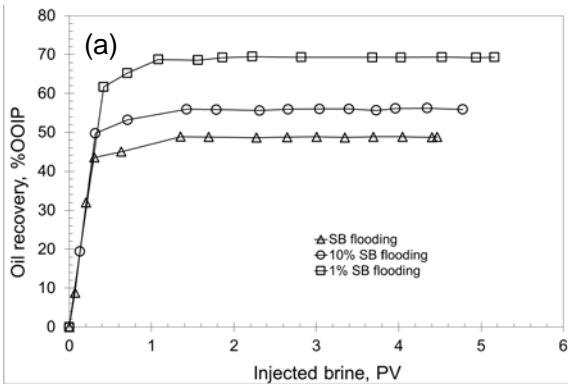
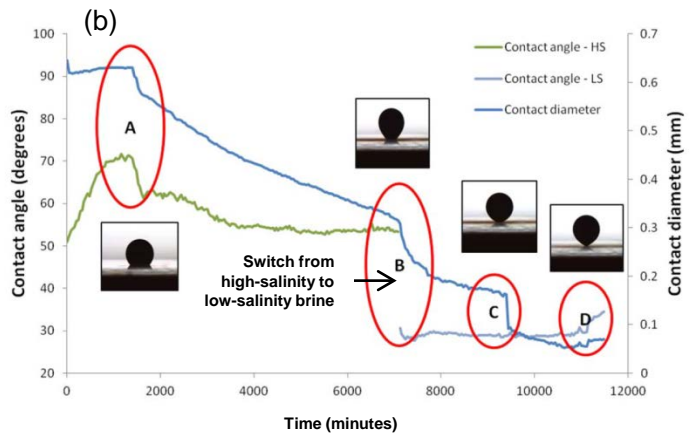
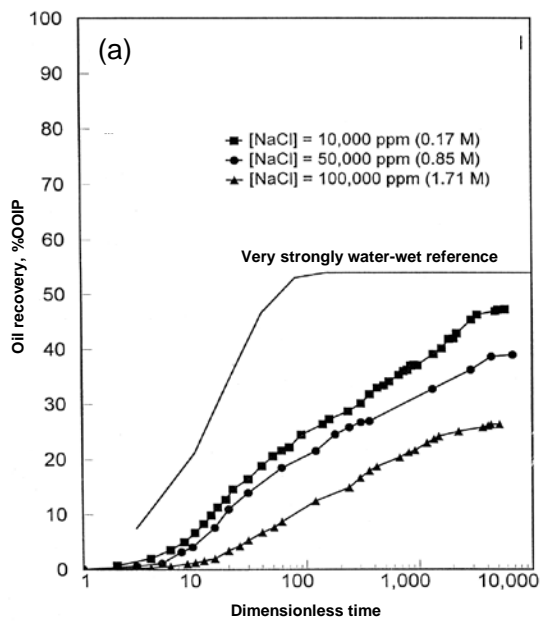


Figure 1



(c)

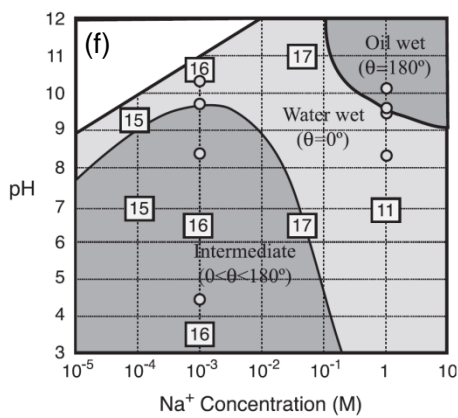
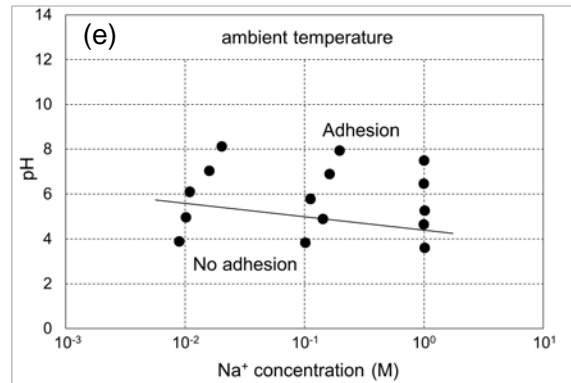
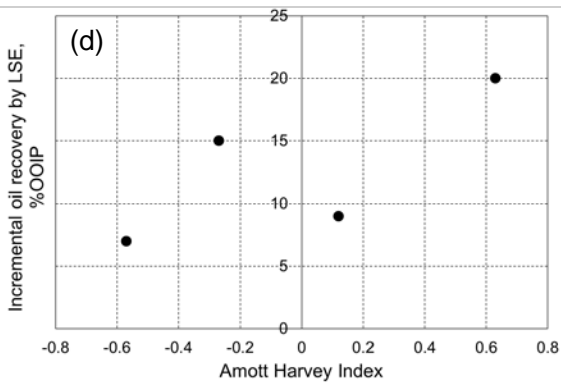
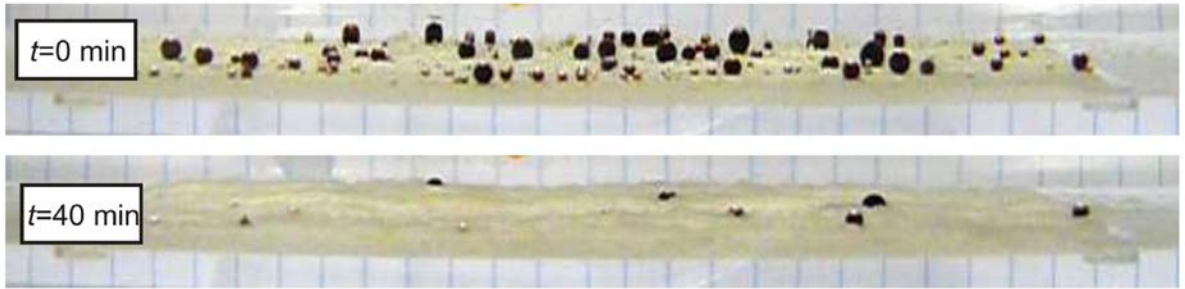


Figure 2

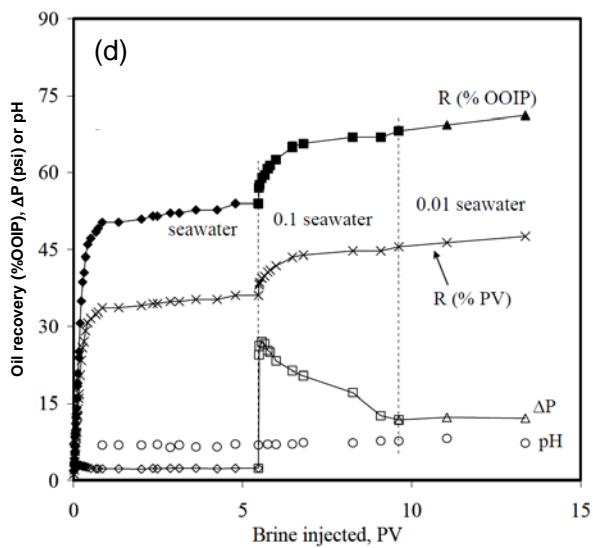
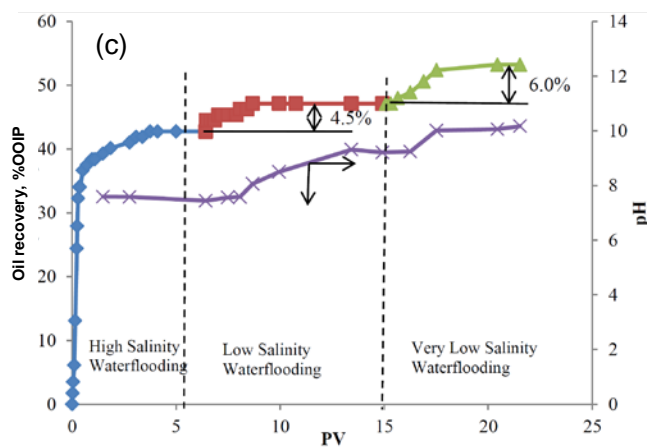
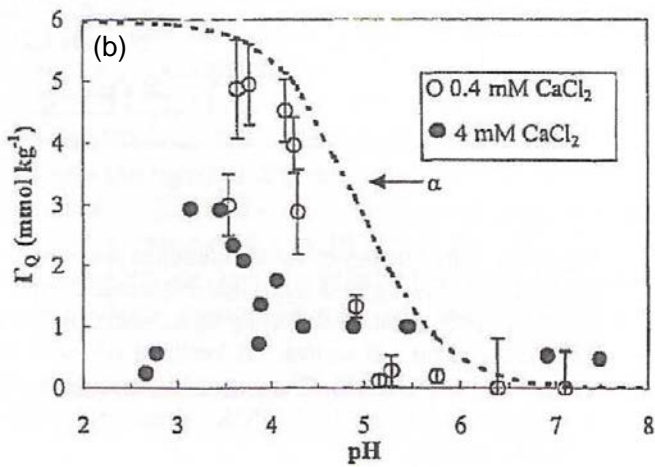
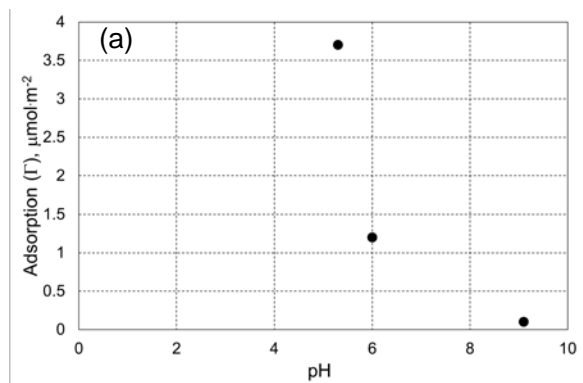


Figure 3

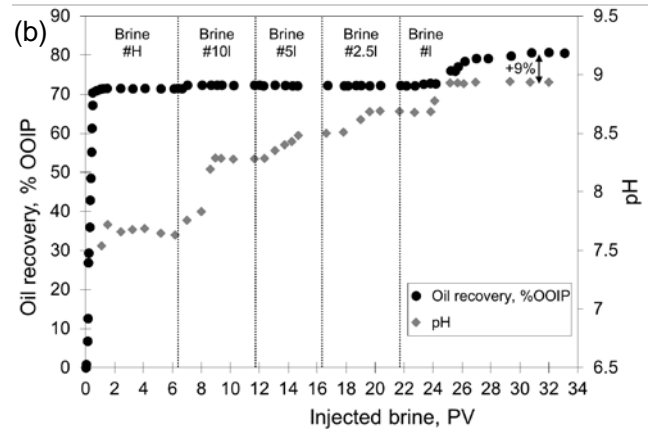
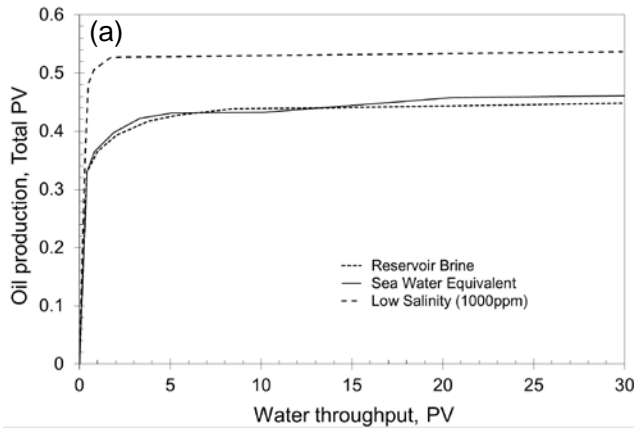
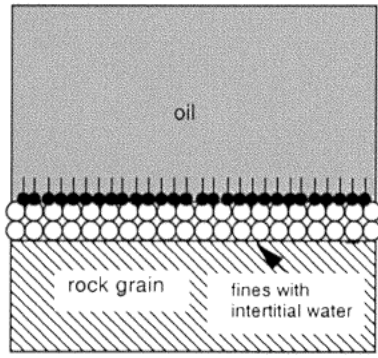
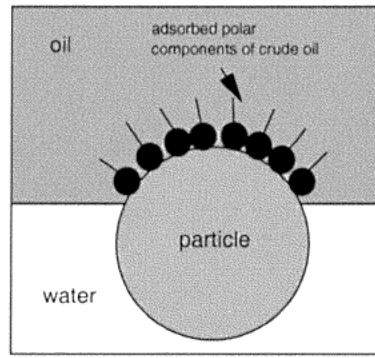


Figure 4

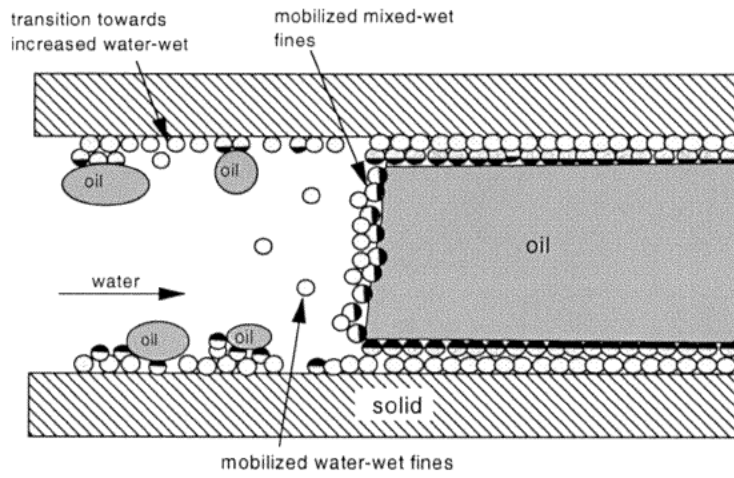


adsorption onto potentially mobile fines at low initial water saturation

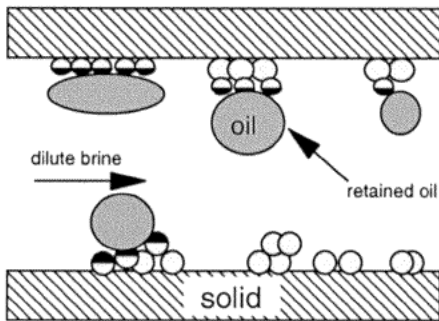


mobilized particle at oil-water interface

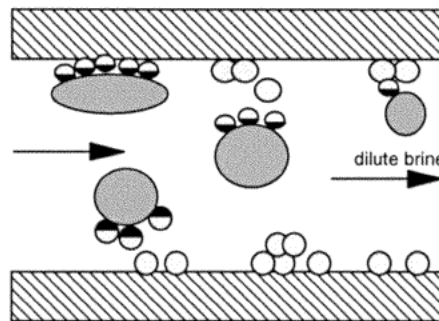
a. Adsorption of Polar Components from Crude Oil to Form Mixed-wet Fines



b. Partial Stripping of Mixed-wet Fines from Pore Walls during Waterflooding



retained oil before injection of dilute brine



partial mobilization of residual oil through detachment of fines

c. Mobilization of Trapped Oil

Figure 5

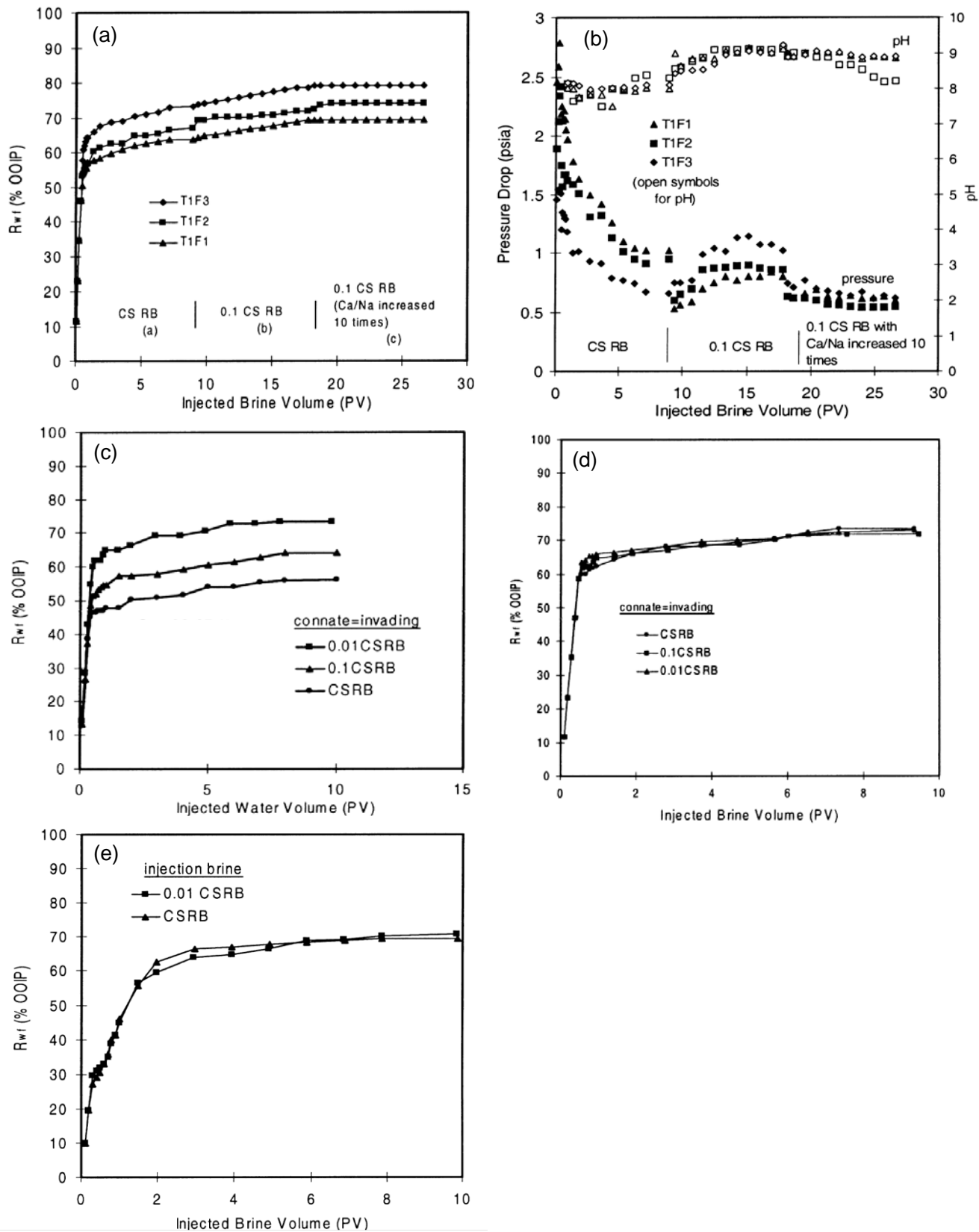


Figure 6

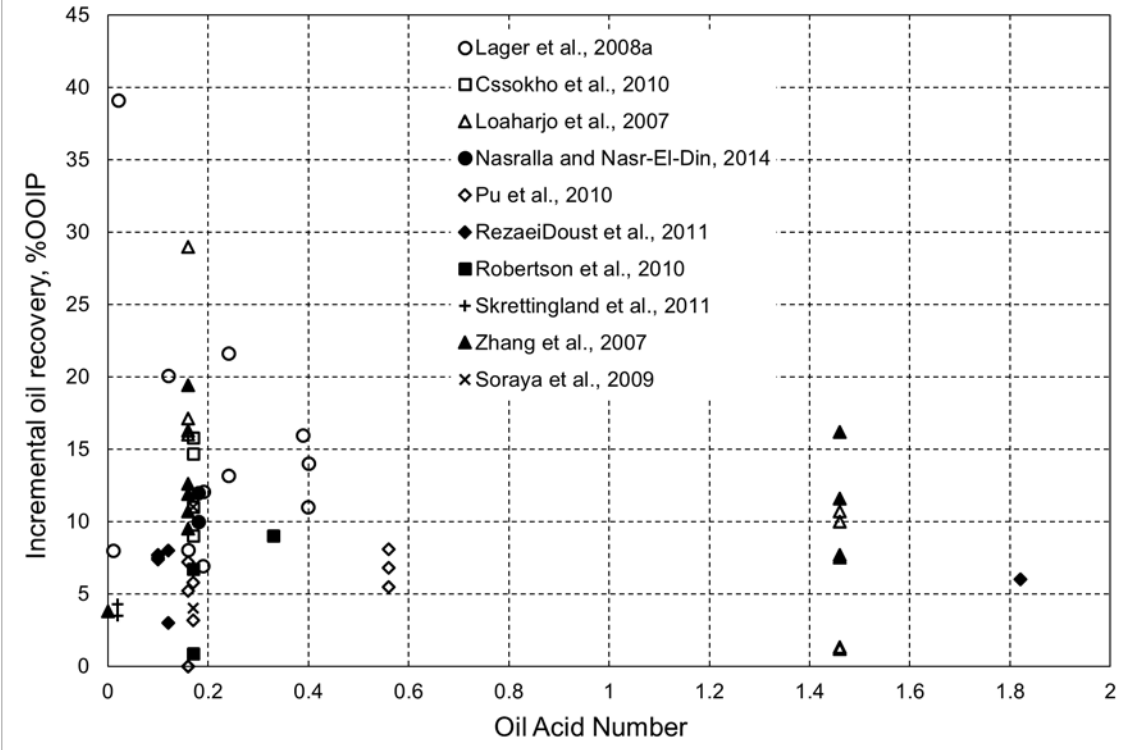


Figure 7

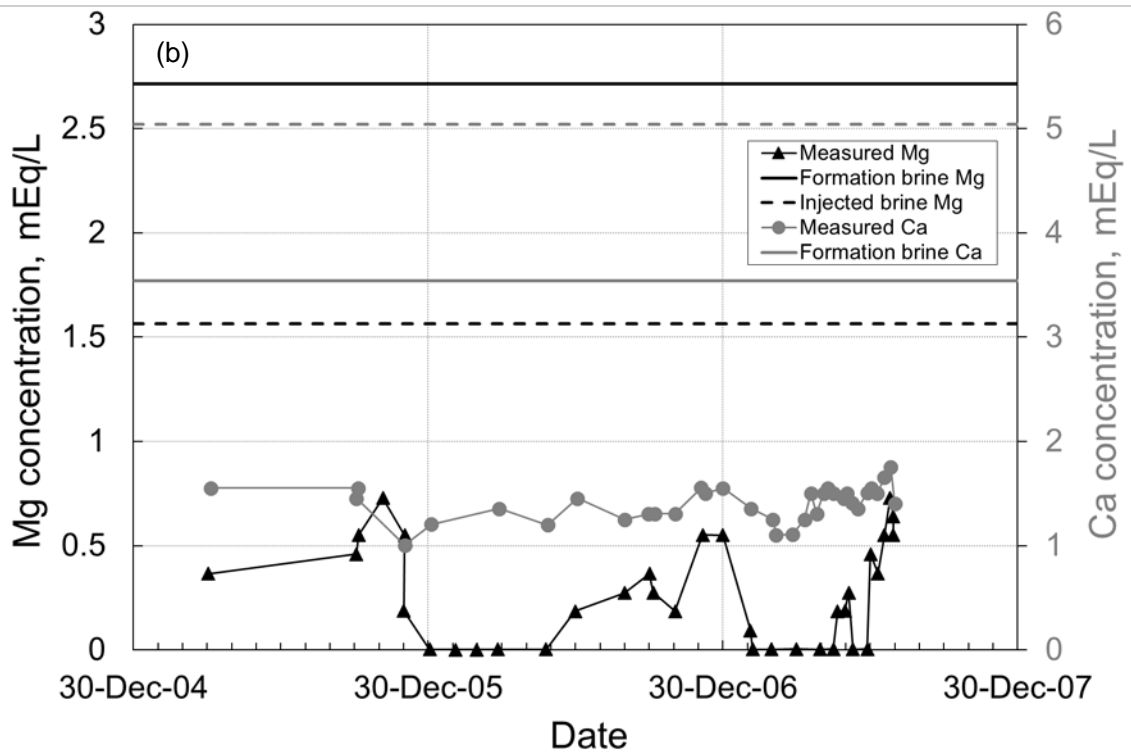
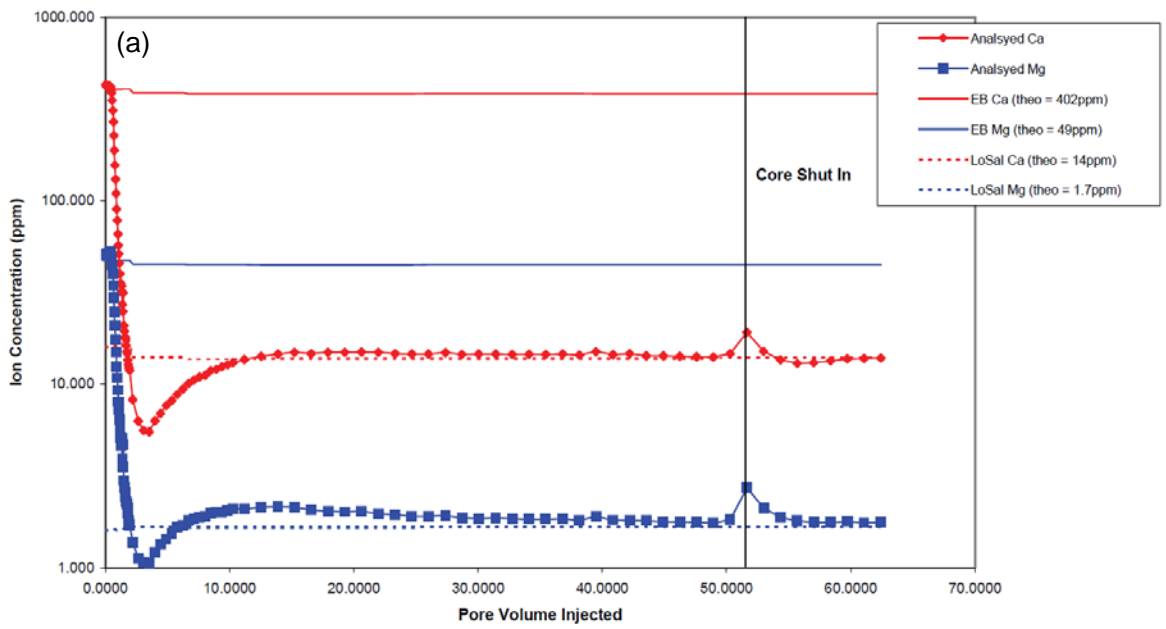


Figure 8



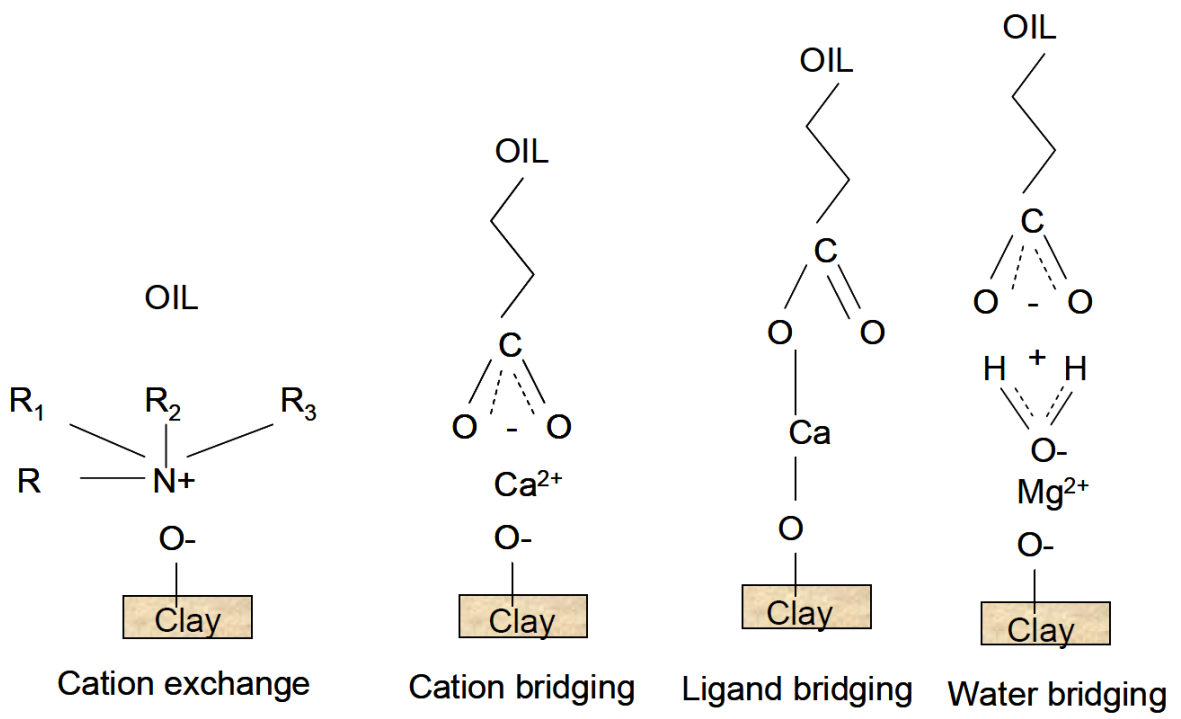


Figure 9

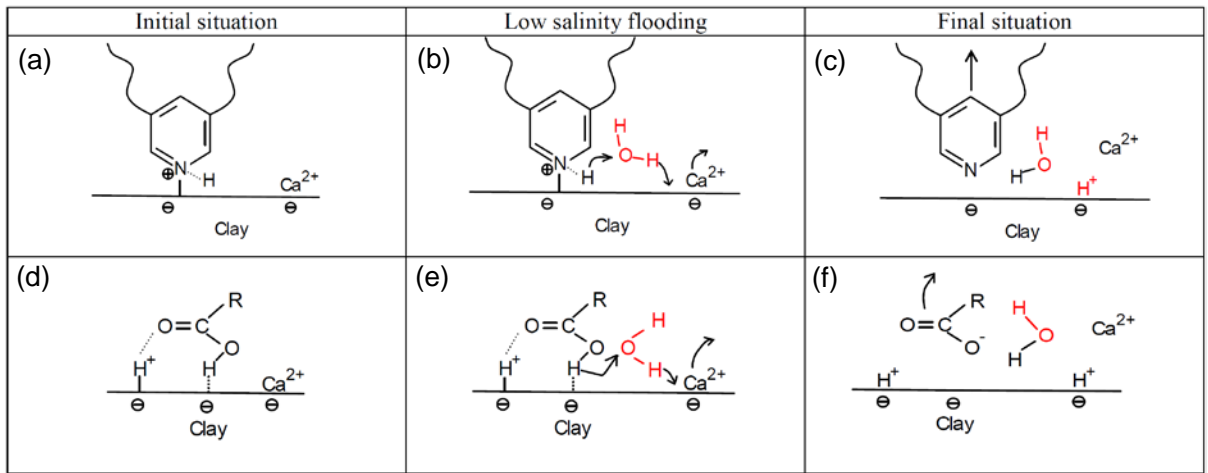


Figure 10

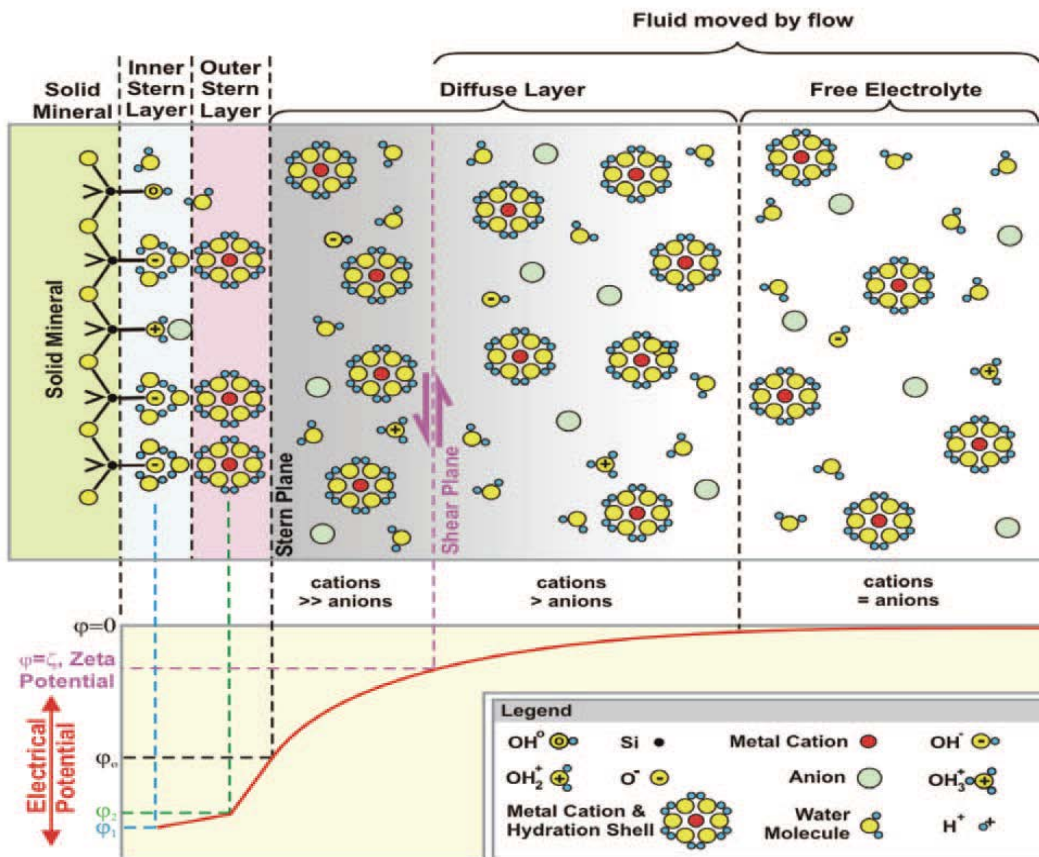


Figure 11

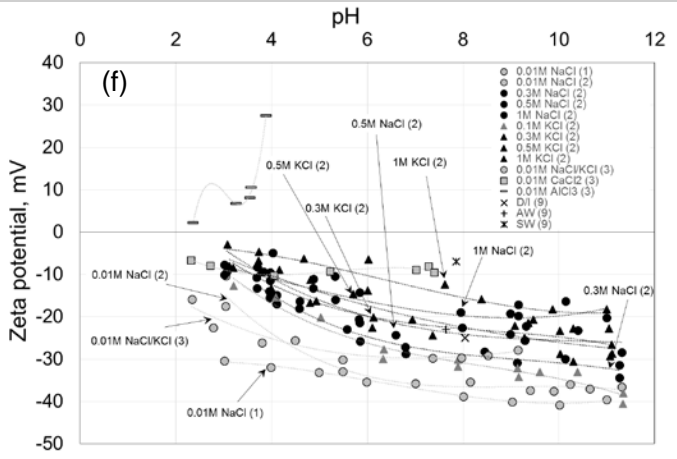
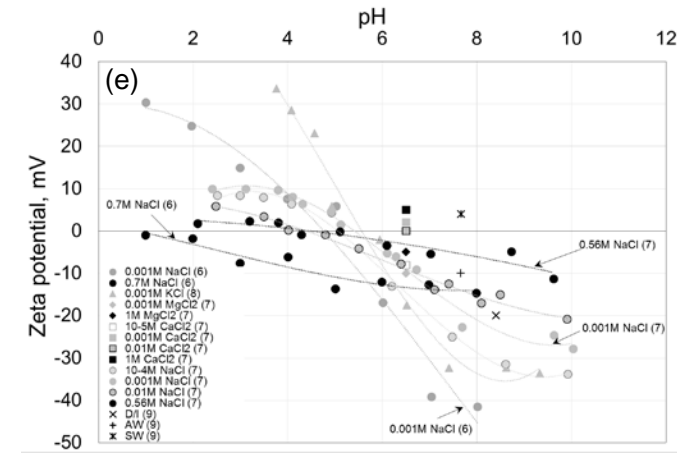
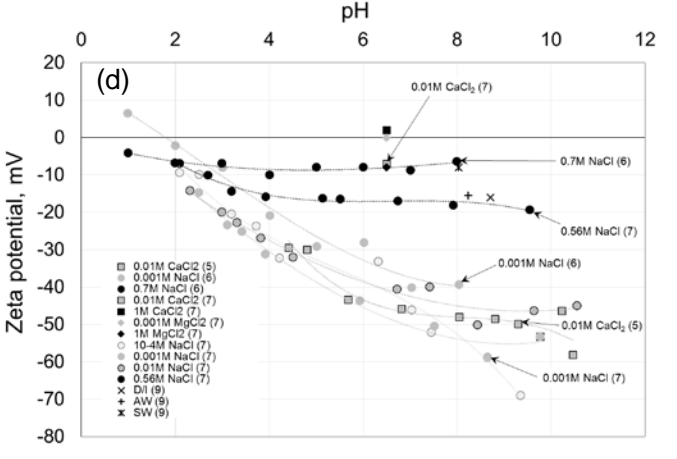
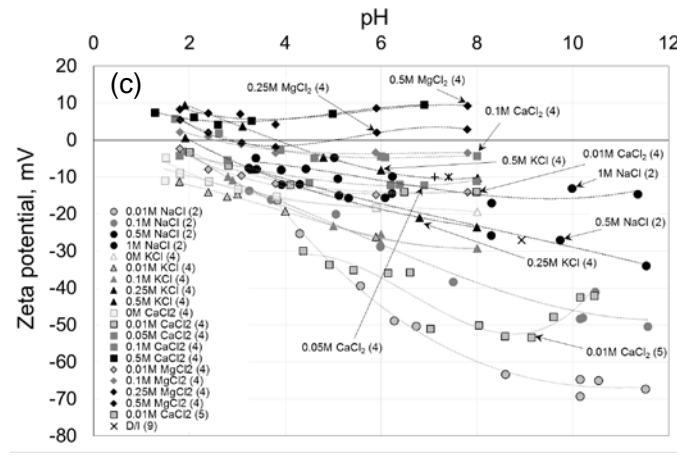
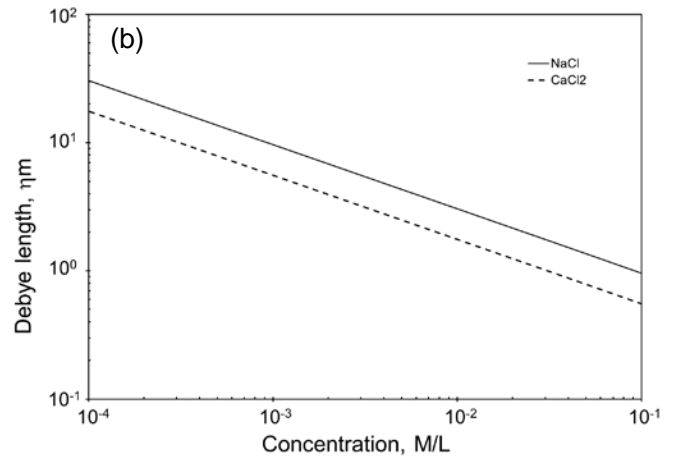
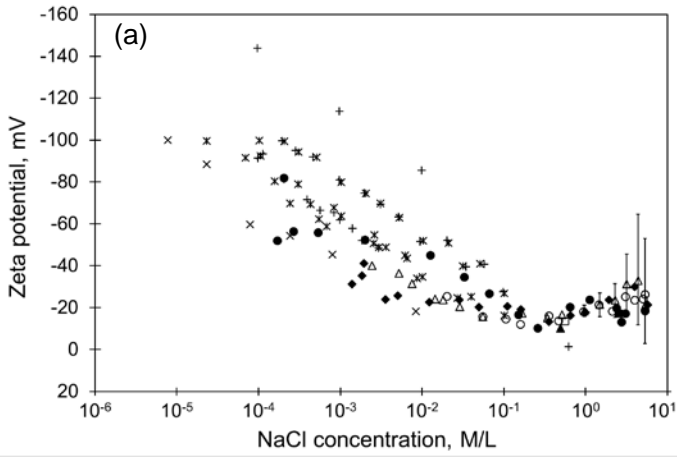


Figure 12

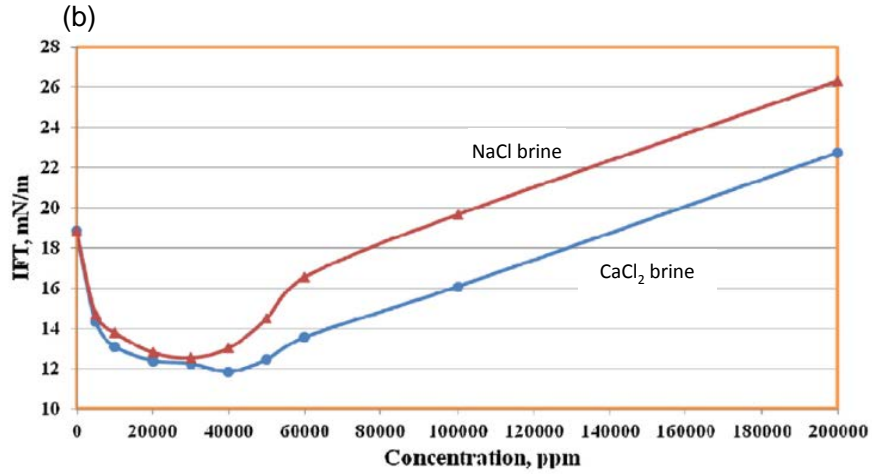
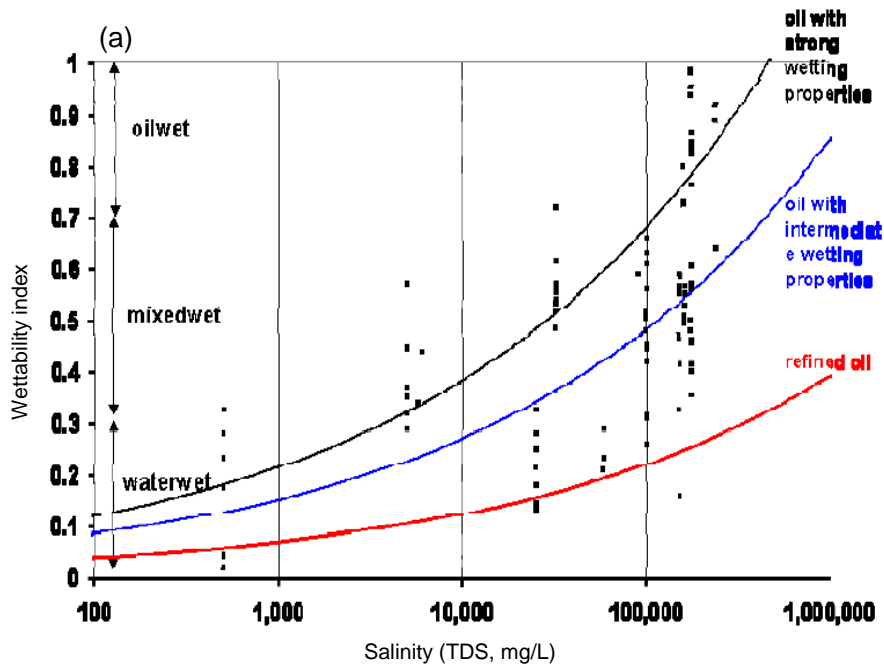


Figure 13