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

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Abstract

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 However, many others (and more unpublished) observed no benefit, and the available data are often inconsistent and contradictory.

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

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

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

Introduction

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

Since these early studies, a large and increasing number of papers have been published on controlled salinity waterflooding. These have demonstrated its successful application in other laboratory experiments and field trials (e.g. Loaharjo et al., 2007; Lager et al., 2008a; 2008b; Patil et al., 2008; Alotaibi et al., 2010; Cissokho et al., 2010; see, for example, Figure 1a,b) and in carbonate as well as clastic rocks and reservoirs (e.g. Yousef et al., 2011a; 2011b; 2012a; 2012b; 2012c). Increases in oil recovery of up to 35% compared to re-injection of formation brine have been observed in laboratory coreflooding experiments (e.g. McGuire et al., 2005; Ligthelm et al., 2009; Austad et al., 2010), and field tests have demonstrated decreases in residual oil saturation of 50% compared to conventional water injection (e.g. Webb et al., 2004; Seccombe et al., 2010). Moreover, there has been increasing focus on the collection of laboratory data to explain the LSE, including contact angles (e.g. Alotaibi et al., 2011), oil-brine interfacial tension (e.g. Gupta et al., 2011), coreflood effluent brine composition and pH (e.g. Lager et al., 2008a), zeta potential of mineral surfaces (e.g. Nasralla and Nasr-El-Din, 2014), cation-exchange-capacity (CEC) (e.g. Pingo-Almada et al., 2013), adhesion maps (e.g. Buckley et al., 1989; Buckley and Morrow, 1990), adsorption studies (e.g. Austad et al., 2010), and imaging of mineral surfaces at a variety of lengthscales (e.g. Berg et al., 2010; Wideroe et al., 2010; Fogden, 2011). However, despite this plethora of new studies and data, the LSE remains poorly understood. Many published studies have reported the successful application of controlled salinity water injection (e.g. Tang and Morrow, 1999a; 1999b; Webb et al., 2004; 2005; McGuire et al., 2005; Lager et al., 2008a; 2008b; Seccombe et al., 2008; 2010; Ligthelm et al., 2009; Vledder et al., 2010), but there are also many other published experiments (and many more unpublished), in which no benefit was observed (e.g. Sharma and Filoco, 2000; Zhang and Morrow, 2006; Pu et al., 2008; Boussour et al., 2009; Alotaibi et al., 2010; Cissokho et al., 2010; Rivet et al., 2010; RezaeiDoust et al., 2010; Skrettingland et al., 2011; Shiran and Skauge, 2012; Nasralla and Nasr-El-Din, 2014; see, for example, Figure 1c,d). Moreover, many studies report data that support a particular hypothesis but contradict, or are inconsistent with, the results of other studies. Other studies fail to obtain, or report, data other than those required to test a given hypothesis, so the results cannot be cross-compared (see Al-Adasani et al., 2012 for an overview and also Table 1).

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

Evidence to support the low salinity effect

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

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

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

Necessary conditions for the low salinity effect

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

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

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

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

Presence and type of clay minerals

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

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

Wettability alteration and the LSE

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

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

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

Atomic Force Mapping (AFM) at the molecular scale has, in contrast, suggested decreased rather than increased adhesion of both polar and non-polar oil components to silica and natural quartz surfaces at low salinity (Hassenkam et al., 2011, 2012; Mathieson et al., 2014; Hilner et al., 2015). However, illite clay and mica were less sensitive than pure silica, which is inconsistent with the view that clay minerals play an important role (Hassenkam et al., 2011, 2012). SEM imaging has also suggested that aged glass surfaces can become more water-wet (or have the advancing contact modified to mimic water-wet behaviour) when in contact with low salinity brine at moderate to high pH (Fogden, 2011). Indirect evidence of the importance of wettability alteration is also suggested by the temperature dependence of the LSE observed in some studies, although the evidence is contradictory: some studies suggest secondary recovery increases with increasing temperature (Cissokho et al., 2010; Robertson, 2010) and others suggest the opposite (Gamage and Thyne, 2011), while tertiary recovery appears to be maximized at intermediate temperature (Cissokho et al., 2010; Gamage and Thyne, 2011). Wettability change is known to be temperature dependent (e.g. Jadhunandan and Morrow; 1995; Liu and Buckley, 1997; Tang and Morrow, 1997).

Despite the broad consensus that the LSE is associated with a change to more water-wetting conditions, the evidence is still contradictory. At the core-scale, Ashraf et al. (2010) determined initial wettability after aging using the Amott-Harvey method and correlated this with the LSE; low salinity corefloods yielded the highest incremental recovery for the samples which were initially most water-wet, not mixed-wet (Fig. 2d). Sandegen et al. (2011) history matched successful low salinity corefloods and obtained the best match for lower imbibition capillary pressure curves, consistent with a change to more oil-wet conditions; however, the results were uncertain owing to a lack of constraining experimental data. At the mineral-surface scale, adhesion measurements by Buckley and co-workers (Buckley et al., 1989, Buckley and Morrow, 1990) for various crude oils on glass surfaces have demonstrated that adhesion is pH-dependent at low salinity, consistent with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory that describes the relative contribution of electrostatic and van-der-Waals forces dictating colloidal stability (e.g. Evans and Wennerstrom, 1999). However, a transition from no adhesion to adhesion was typically observed with decreasing salinity at fixed pH (e.g. Fig. 2e), inconsistent with the wettability changes described above. The trend could be reversed at elevated temperature for some crude oils (Buckley and Morrow, 1990). Similarly, Drummond and Israelachvili (2002, 2004) recorded an increase in the static contact angle of mica surfaces with decreasing salinity at moderate pH, inconsistent with increasingly water-wet behaviour (e.g. Fig. 2f). However, the brines in these studies did not contain any divalent cations such as Ca^{2+} or Mg^{2+}. Lebedeva and co-workers (Lebedeva and Fogden, 2010; Lebedeva et al., 2010) found that adhesion (characterised via the hysteresis of advancing and receding contact angles) of crude oil to kaolinite increased with decreasing pH and salinity of both NaCl and $CaCl_2$ brines. Adsorption of polar oil components onto silicate mineral surfaces has also been shown to be strongly pH dependent (e.g. Austad et al. 2010; RezaiDoust et al., 2011; Aksulu et al., 2012; see Fig. 3a,b); changes in pH are often associated with the LSE (e.g. Fig. 3c).

Wettability change is a *consequence*, not a *cause*, of the processes underlying the LSE, and several mechanisms have been proposed that relate wettability changes to the injection of low salinity brine (see next section). Optimum oil recovery is usually observed in mixed-wet conditions, which yield relatively low water relative permeability and residual oil saturation (e.g. Jadhunandan and Morrow, 1995). Thus a shift to more water-wet conditions during low salinity waterflooding should not favour increased recovery (Li, 2011).

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

Reduction in injection brine salinity

Tang and Morrow (1999a) observed the LSE effect with injection of 10 and 100 times diluted formation brine (c. 24,000ppm TDS, yielding injection brine salinities of c. 2,400 and 240ppm TDS); higher injection brine salinities were not tested. Improved recovery was observed with dilution of injection brine, and also formation plus injection brine (see also Yildiz and Morrow, 1996; Tang and Morrow, 2002; Zhang and Morrow, 2006). Lager, Webb and co-workers found no LSE with injection of seawater into cores containing higher salinity formation brine, but a significant LSE in the same system when injecting 1,000ppm brine (Fig. 4a); they suggested, based on experience from (mostly unreported) coreflooding experiments, that the LSE is observed only for injection brine salinities below c. 5000ppm (Webb et al., 2004, 2005; Lager et al., 2007). Subsequent studies have almost all used low salinity brines with concentrations below 5000ppm (see Table 1). Cissokho et al. (2010) reported a clear threshold in injected brine ($NaCl+CaCl_2$) salinity of 1000ppm below which the LSE was observed (Fig. 4b).

However, no model is available to predict this threshold value for a given COBR system. Moreover, numerous studies have demonstrated that simply reducing the injected brine salinity below a threshold value is not sufficient for the LSE to be observed (e.g. Sharma and Filoco, 2000; Zhang and Morrow, 2006; Pu et al., 2008; Alotaibi et al., 2010; Cissokho et al., 2010; Rivet et al., 2010; RezaeiDoust et al., 2010; Skrettingland et al., 2011; Nasralla and Nasr-El-Din, 2014; Fig. 1c,d). In some cases, improved recovery has been observed by increasing the injection brine salinity relative to the formation brine (e.g. Tang and Morrow, 1997; Sharma and Filocco, 2000; Fig. 1e). RezaeiDoust et al. (2011) observed a modest increase in recovery when injecting NaCl brine of higher salinity, but the same ionic strength, into a core containing crude oil and $CaCl_2$ brine (Fig. 1f). Thus the evidence that improved recovery is necessarily associated with a significant reduction in brine salinity is not conclusive. Rather, it appears that recovery can be improved by modifying the injection brine salinity (composition) in some controlled way that has not yet been identified.

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

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

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

Summary

Evidence to support the widely accepted necessary conditions for the LSE to be observed in sandstones is surprisingly sparse, despite the large number of published studies. Formation water is invariably present so this condition is naturally met; however, evidence supporting the necessary presence of clay minerals and multivalent ions, initially mixed-wet conditions, and a significant reduction in injection brine salinity, is far from overwhelming. To properly predict the necessary conditions for the LSE to be observed requires an understanding of the underlying mechanisms; these are reviewed in the next section.

Proposed mechanisms for the low salinity effect in sandstones

Clay swelling and fines migration

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

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

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

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

pH increase and surfactant generation

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

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

Contrary evidence: Although effluent oil-brine IFT has been observed to decrease (from c. 25mN/m to c. 18mN/m) with a concomitant increase in pH during successful low salinity corefloods, the few reported values remain too high for saponification to have occurred (Tang and Morrow, 2002). The saponification reaction requires high acid number, yet the LSE has been observed with lower AN crudes (e.g. Zhang and Morrow, 2006; Loaharjo et al., 2007; Zhang et al., 2007; Boussour et al., 2009; Pu et al., 2010; RezaeiDoust et al., 2011). No correlation between the LSE and AN has been observed (Fig. 7; Lager et al., 2008a). Moreover, it has been suggested that the pH required for saponification (pH>9) is unlikely to be observed at reservoir conditions, owing to the presence of CO_2 and other pH buffers. A number of studies have demonstrated the LSE in unbuffered systems with pH<9 suggesting saponification did not occur (e.g. Fig. 3d; see also Table 1). Zhang et al. (2007) found no relationship between effluent pH and the LSE.

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

Multi-ion exchange (MIE)

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

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

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

Summary: MIE has been observed in field and laboratory experiments and is known in the water resources literature. However, MIE alone is not enough to cause the LSE: an additional requirement is the presence of crude oil containing polar components initially adsorbed directly onto clay mineral surfaces that can exchange with divalent cations in the brine. No optimum clay type, crude oil or injection brine composition, or method for predicting these, has been derived from the MIE model. Moreover, published evidence to directly link MIE with the LSE is sparse. The MIE mechanism alone does not explain the numerous coreflooding experiments where the conditions for MIE were met but no LSE was observed.

Local increase in pH (ΔpH)

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

Supporting evidence: Austad and co-workers noted that many unbuffered laboratory coreflooding experiments show an increase in pH following the injection of low salinity brine (e.g. Fig. 3c); moreover, RezaiDoust et al. (2011) found that pH increase depended upon the prevalent cation affinity to clay mineral surfaces, with low salinity NaCl brines showing the largest pH increase consistent with the low affinity of Na^{+}. Austad and co-workers also reported adsorption tests that show a strong pH dependence of both acidic and basic organic adsorption on clay minerals (Austad et al. 2010; RezaiDoust et al., 2011; Aksulu et al., 2012), consistent with the requirements of their model (e.g. Fig. 3a,b). The composition of the injection brine is predicted to be relatively unimportant so long as it is dilute enough to yield significant desorption of surface-active cations. However, the removal of Ca^{2+} from the injection brine is argued to be particularly favourable, because pH increase is then more significant, consistent with a number of studies that show the LSE with injection of dilute NaCl brine, although not all of these observed the expected increase in pH (Loahardjo et al., 2007; Alagic and Skauge, 2010; Boussour et al., 2009; Ligthelm et al., 2009; RezaeiDoust et al., 2011; Nasralla and Nasr-El-Din, 2014). Tang and Morrow (1999a) found that increasing the Ca^{2+} concentration terminated the LSE, but there was no consistent decrease in pH (e.g. Figs. 6a,b). RezaeiDoust et al. (2011) reported modest increases in oil recovery when injecting higher salinity NaCl brine into a core containing crude oil and $CaCl_2$ brine, and argued that this reflected the differing affinities of Na^{+} and Ca^{2+} cations toward clay mineral surfaces, consistent with the model predictions. Ion exchange leading to pH increase has been observed and modelled in other studies relating to formation damage, although these studies considered only monovalent ions in single phase flow (e.g. Vaidya and Fogler, 1990; Souto and Bazin, 1993).

Contrary evidence: Several unbuffered experimental studies report little or no change in effluent pH associated with the LSE (e.g. Fig. 3d); moreover, in the reservoir, such a global pH change is unlikely to occur owing to the presence of pH buffers such as CO_2. Nevertheless, Austad and co-workers argue that local increases in pH adjacent to the clay mineral surfaces are sufficient to cause desorption of organic materials. Several studies have observed effluent pH increases in unbuffered experiments but no associated LSE (e.g. Cissokho et al., 2010; RezaeiDoust et al. 2010; Wideroe et al., 2010). Austad et al. (2010) suggested that the decrease in Ca^{2+} and Mg^{2+} observed in the laboratory experiments of Lager et al. (2008a) resulted from deposition of $Mg(OH)_2$ and $Ca(OH)_2$ rather than MIE, but $Ca(OH)_2$ deposition was predicted to occur only at pH > 11; such high pH was not observed. Austad et al. (2010) also suggested that the ΔpH model explains the field test data of Lager et al (2008b) (Fig. 8b), ascribing the initial increase in Mg^{2+} at the producer well to desorption of Mg^{2+} on contact with low salinity injected water. The subsequent decrease in Mg^{2+}, which Lager et al (2008b) ascribed to MIE, was suggested to reflect $Mg(OH)_2$ precipitation at pH > 9. However, such high pH was not observed at the production well. Alagic and Skauge (2010) found that Mg^{2+} was retained in aged samples during successful LSE corefloods, which is inconsistent with desorption. Similar to Lager et al (2008a), Austad et al. (2010) suggest that clay minerals with high CEC are optimal, yet kaolinite is closely associated with the LSE and has relatively low CEC (Table 2).

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

Double layer expansion (DLE)

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

$$I = \frac{1}{2}\sum_{j} C_j z_j^2 \qquad (1)$$

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

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

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

Supporting evidence: The available evidence and models suggest that DLE, and a commensurate increase in zeta potential, occurs when the ionic strength of the brine is reduced, so long as the ionic strength is not too high and the pH is not close to the isoelectric point at which the zeta potential is zero (see Revil et al., 1999; Vinogradov et al., 2010 and also Fig 12c-f). Hilner et al. (2015) observed a significant decrease in adhesion between non-polar oil molecules and natural quartz surfaces at a similar threshold salinity to that at which the LSE is typically observed, and argued that DLE will always play a role in the LSE even if other mechanisms also contribute. Ligthelm et al. (2009) suggested that the composition of the injected brine is not critical, so long as the salinity is low enough for DLE to cause desorption of oil from mineral surfaces. The ΔpH model also makes this prediction which, as discussed in the previous section, is supported by a number of experimental studies. Note that equations (1) and (2) show that increasing the valency of the ions can have a similar effect on DLE as increasing the concentration (Fig. 12b); thus the common practise of reporting concentration as TDS in ppm when brines contain multivalent ions is misleading. All natural brines contain multivalent ions, so concentration should be reported as ionic strength. Tang and Morrow (1999a) and Nasralla and Nasr-El-Din (2014) both showed that the LSE was inhibited by injection of $CaCl_2$ as compared to NaCl brine, consistent with reduced DLE expansion owing to the presence of divalent cations.

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

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

Discussion

The key mechanisms underlying the LSE have yet to be determined, but the available evidence suggests that the LSE is the macroscopic (core- to reservoir-scale) manifestation of microscopic (mineral-surface to pore-scale) changes following injection of low salinity brine (or brine of controlled composition). These microscopic changes may include wettability alteration (manifested by a change in contact angle, contact angle hysteresis, or wetting surface area), a reduction in IFT, and/or an increase in the solubility of polar oil compounds in the brine. Such changes affect the efficiency with which brine displaces oil, by releasing oil previously adsorbed to mineral surfaces, allowing water to invade oil-filled pores that would be otherwise bypassed, or reducing oil trapped by snap-off. A common factor across three of the key mineral-surface scale mechanisms that have been invoked to explain the LSE is a change in the magnitude of electrostatic interactions between charged mineral surfaces and polar organic compounds: the zeta potential will change in response to (i) multi-ion exchange (MIE), because adsorption or desorption of ions changes the surface charge, (ii) local pH increase (ΔpH), because this also changes the surface charge (see Fig. 12), and (iii) a decrease in ionic strength because this causes double layer expansion (DLE) (see Fig. 12). However, the relationship between MIE, ΔpH, ionic strength and the zeta potential is still poorly understood owing to a lack of data acquired at the relevant conditions, despite the efforts of groups such as those at Texas A & M (e.g. Alotaibi et al. 2010; 2011; Nasralla and Nasr-El-Din, 2014) and Shell (e.g. Suijkerbuik et al. 2014). Thus the contribution of electrostatic forces remains poorly understood. For example, modest increases in oil recovery have been observed when injecting higher salinity NaCl brine into a core containing crude oil and $CaCl_2$ brine of the same ionic strength (RezaeiDoust et al., 2011); this may reflect (i) a change in surface charge owing to the differing affinities of Na^+ and Ca^{2+} cations toward clay minerals (e.g. Mugele et al., 2015), (ii) local pH change and/or (iii) a change in the double layer thickness. However, as surface charge was not measured, the mechanism cannot be determined.

At present, the ΔpH and MIE mechanisms are difficult to reconcile, as the former requires desorption of multivalent cations at low concentration and exchange with protons to increase pH, whereas the latter requires the opposite: adsorption of multivalent cations at low concentration and exchange with polar oil compounds, accompanied by little or no change in pH. In both cases, pH change recorded in effluent brine may be dominated by the presence of buffers such as CO_2, or by dissolution of small amounts of carbonate material, so may not be diagnostic of mechanisms occurring at the mineral-surface scale. McGuire et al. (2005) calculated that dissolution of just 7.2g of calcite (<0.1wt% of core sample material) over 15 pore-volumes (PV) of waterflooding of a North Sea core increased effluent pH by 2 pH units; even trace amounts of carbonate material or other soluble minerals in natural samples can influence pH. There is still a need for carefully designed coreflooding experiments to allow individual mechanisms to be isolated and identified; this will likely require the use of synthetic core materials in the first instance, so mineralogy can be precisely controlled, allowing processes such as carbonate mineral dissolution to be eliminated or quantified. Moreover, studies are required that report a broad range of data types and measurements, to facilitate cross-comparison of results and allow the underlying mechanisms to be identified or eliminated (e.g. Table 3).

Of the other proposed mechanisms, the available evidence suggests that fines migration or saponification may be responsible for the LSE only in some specific cases with (in the former mechanism) swelling clays, very low salinity brine, high brine pH and (in the latter mechanism) high AN crude. However, it is worth noting that several studies have reported a link between IFT and salinity, with IFT generally decreasing with decreasing salinity (e.g. Badakshan and Bakes, 1990; Ikeda et al., 1992; Cai et al., 1996); some studies have also found that the IFT drops to a minimum at a critical salinity (Fig. 13b). For example, Moeini et al. (2014) observed a minimum of c. 13mN/m at a salinity of c. 30,000 ppm NaCl or $CaCl_2$ brine, although this is higher than the injection brine salinity typically associated with the LSE. A salinity-dependent decrease in IFT reduces the capillary entry pressure, consistent with the pore-scale LSE proposed by Sorbie et al. (2010). Moreover, it is well known that the solubility of polar organic compounds in brine increases with decreasing salinity; adjusting the solubility by varying the salt concentration is a process termed ‘salting in/out’ (RezaeiDoust et al., 2009). This mechanism has been suggested to contribute to the LSE, although it has been largely ignored and remains comparatively under investigated (RezaeiDoust et al., 2009, 2011).

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

For example, several mineral-surface-scale studies have observed a decrease in adhesion of crude oil to mineral surfaces with increasing salinity (e.g. Buckley et al., 1989, Buckley and Morrow, 1990; Drummond and Israelachvili, 2002, 2004; Lebedeva and Fogden, 2010; Lebedeva et al., 2010), yet plug-scale measurements of wettability suggest the opposite (e.g. Anderson, 1986 and references therein; Lighthelm et al., 2009; compare Figs. 2e,f and Fig. 13a). The difference may relate to the experimental conditions such as temperature (e.g. Buckley and Morrow 1990) and the presence of multivalent cations (for example, Brown and Neustadter 1980). Similarly, adsorption tests on polar compounds and clay minerals have demonstrated strong pH dependence at room temperature, but it is not clear whether the results apply at elevated temperature and pressure (e.g. Fig. 3a,b). Measurements of zeta potential are typically obtained at relatively low ionic strength and temperature; few data are available at seawater salinity and above (e.g. Fig. 12). Furthermore, surface properties that may control the LSE, such as electrical charge, reaction sites and CEC, may be affected by the history of the rock samples, including any previous experiments, cleaning, and storage, yet surface properties are rarely measured prior to coreflooding experiments. Initial surface conditions may vary, even though bulk properties are similar. This may explain why repeat corefloods on the same sample can yield different results, and why outcrop and reservoir cores often behave differently (e.g. Loardarjho et al., 2010; Winoto et al., 2012). Finally, reaction kinetics likely play a role in dictating the mechanisms underlying the LSE, including the rate of adsorption and desorption of ions and polar organic compounds (e.g. Mahani et al., 2013; Suijkerbuijk et al., 2013). If the timescales of ion exchange and/or wettability alteration are longer than the duration of an experiment, then no LSE will be observed.

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

A key requirement of any mechanism is that it can explain (and predict) those cases where the LSE is not observed, as well as those cases where it is observed. Most studies concentrate on the latter. The laboratory and field experiments reported by Skrettingland et al. (2011) provide a key test in this respect: (i) the COBR system apparently met all of the necessary conditions (Amott Index of aged samples indicated initially mixed- to weakly water-wet conditions, crude contained polar components, sandstone contained clay minerals including kaolinite and chlorite, formation brine contained multivalent cations including Ca^{2+} and Mg^{2+}), (ii) the salinity of the injection brine was significantly reduced, (iii) experiments were conducted at reservoir conditions, (iv) there was an increase in effluent brine pH in some coreflooding experiments to pH > 12 when alkaline low salinity brine was injected, and (v) an associated increase in pressure drop associated with formation damage. Yet no LSE was observed. None of the proposed mechanisms can explain this. Aksulu et al. (2012) suggested the initial reservoir pH was too high (at c. 7) for significant adsorption of organic components to have occurred (cf. Fig. 3a,b), which suggests the failure lay with the initial rather than the flooding conditions, but this is inconsistent with the measured initial wettability, and also the numerous studies in which the LSE has been observed at comparable initial pH. Another key test is to explain the contradictory evidence concerning the temperature dependence of the LSE discussed previously. As yet, little or no data are available to determine or predict the temperature dependence of the proposed MIE, ΔpH or DLE mechanisms. Finally, an important issue is that of capillary effects in coreflooding experiments: during low salinity water injection, changes in wettability, permeability (owing to formation damage) or IFT change the relative importance of capillary forces in fixed-rate corefloods, so recovery may be affected by changes in capillary end effects (e.g. Skauge, 2013; Masalmeh et al., 2014). While some studies have recognized this, many have not.

Conclusions

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

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

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

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

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Figure Captions

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Figure 13. (a) Wettability index of intact samples as a function of initial brine salinity (from Ligthelm et al., 1989). Samples become increasingly oil-wet with increasing salinity, consistent with DVLO theory. Wetting layer collapse and cation bridging are promoted at high salinity owing to the decrease in thickness of the electrical double layers. (b) IFT as a function of salinity for NaCl and $CaCl_2$ brine, from Moeini et al. (2014).

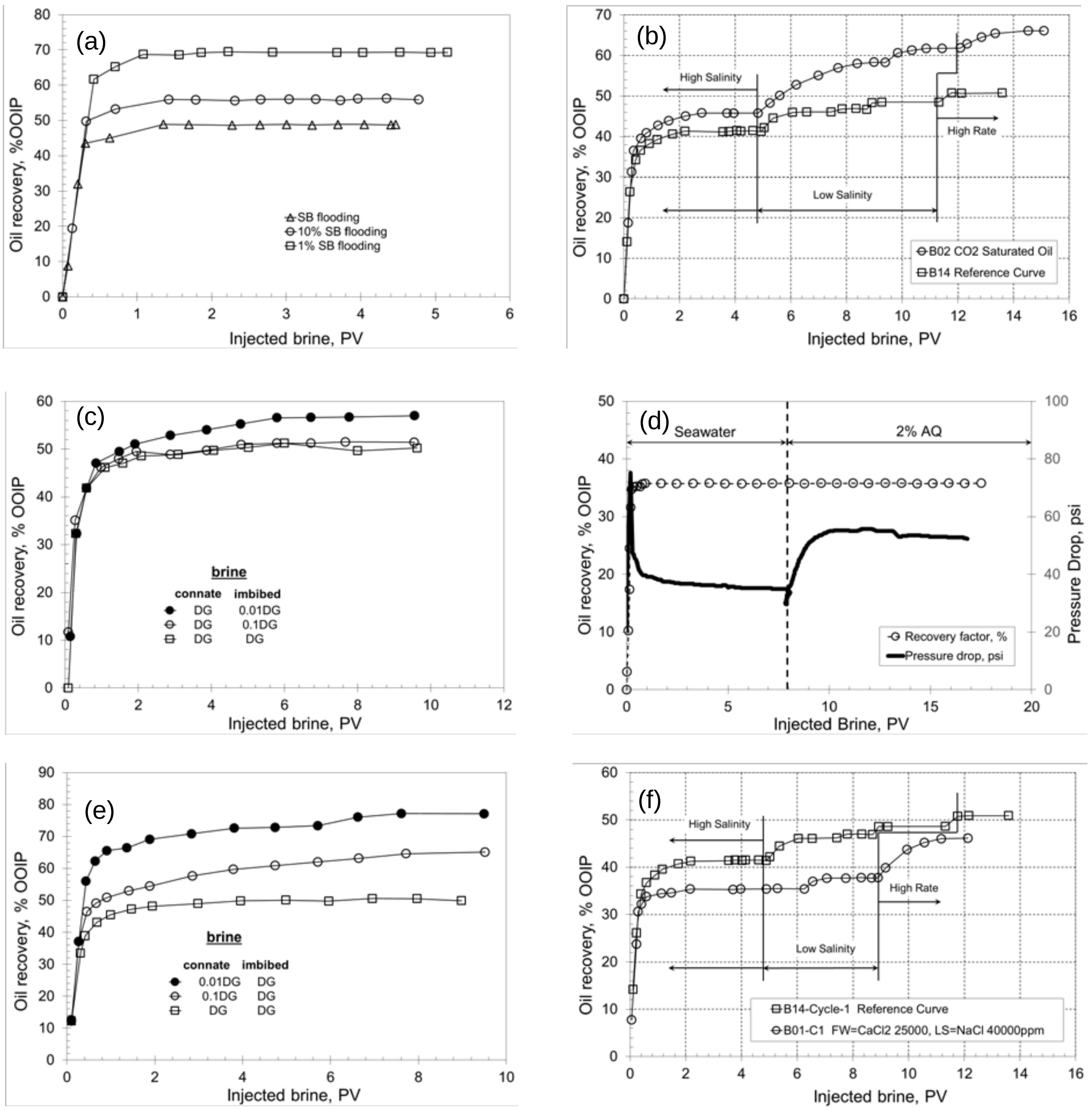

(a)
Oil recovery, %OOIP
Injected brine, PV
SB flooding
10% SB flooding
1% SB flooding
(b)
Oil recovery, % OOIP
Injected brine, PV
High Salinity
Low Salinity
High Rate
B02 CO2 Saturated Oil
B14 Reference Curve
(c)
Oil recovery, % OOIP
Injected brine, PV
brine
connate imbibed
DG 0.01DG
DG 0.1DG
DG DG
(d)
Seawater
2% AQ
Oil recovery, % OOIP
Pressure Drop, psi
Injected Brine, PV
Recovery factor, %
Pressure drop, psi
(e)
Oil recovery, % OOIP
Injected brine, PV
brine
connate imbibed
0.01DG DG
0.1DG DG
DG DG
(f)
Oil recovery, % OOIP
Injected brine, PV
High Salinity
Low Salinity
High Rate
B14-Cycle-1 Reference Curve
B01-C1 FW=CaCl2 25000, LS=NaCl 40000ppm

Figure 1

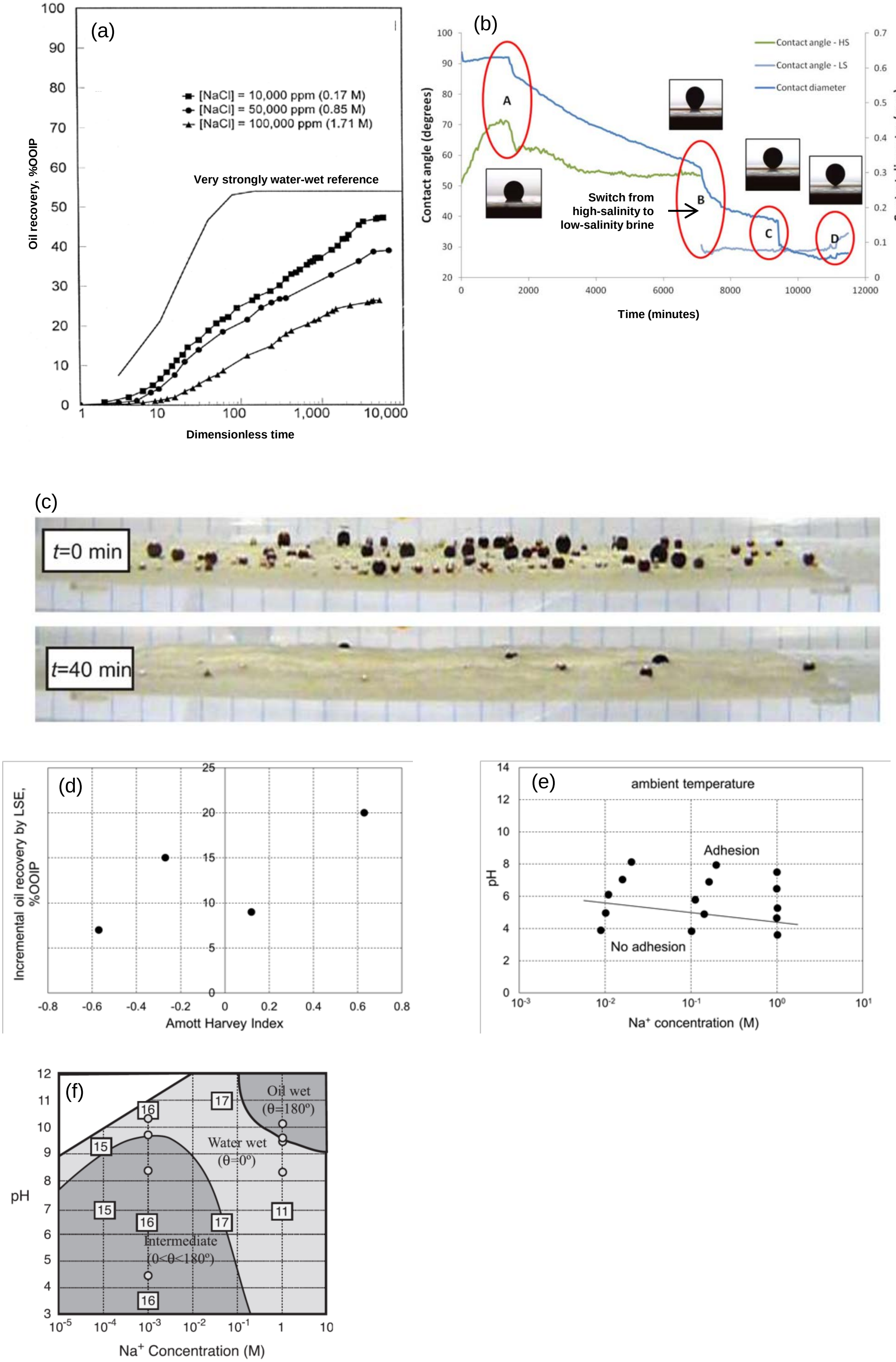

(a)
Oil recovery, %OOIP
100
90
80
70
60
50
40
30
20
10
0
1
10
100
1,000
10,000
Dimensionless time
[NaCl] = 10,000 ppm (0.17 M)
[NaCl] = 50,000 ppm (0.85 M)
[NaCl] = 100,000 ppm (1.71 M)
Very strongly water-wet reference
(b)
Contact angle (degrees)
Contact diameter (mm)
Time (minutes)
Contact angle - HS
Contact angle - LS
Contact diameter
A
B
C
D
Switch from high-salinity to low-salinity brine
0
2000
4000
6000
8000
10000
12000
(c)
t=0 min
t=40 min
(d)
Incremental oil recovery by LSE, %OOIP
Amott Harvey Index
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
25
20
15
10
5
(e)
ambient temperature
pH
Na+ concentration (M)
Adhesion
No adhesion
14
12
10
8
6
4
2
0
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
(f)
pH
Na+ Concentration (M)
Oil wet (θ=180º)
Water wet (θ=0º)
Intermediate (0<θ<180º)
15
16
17
11
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10

Figure 2

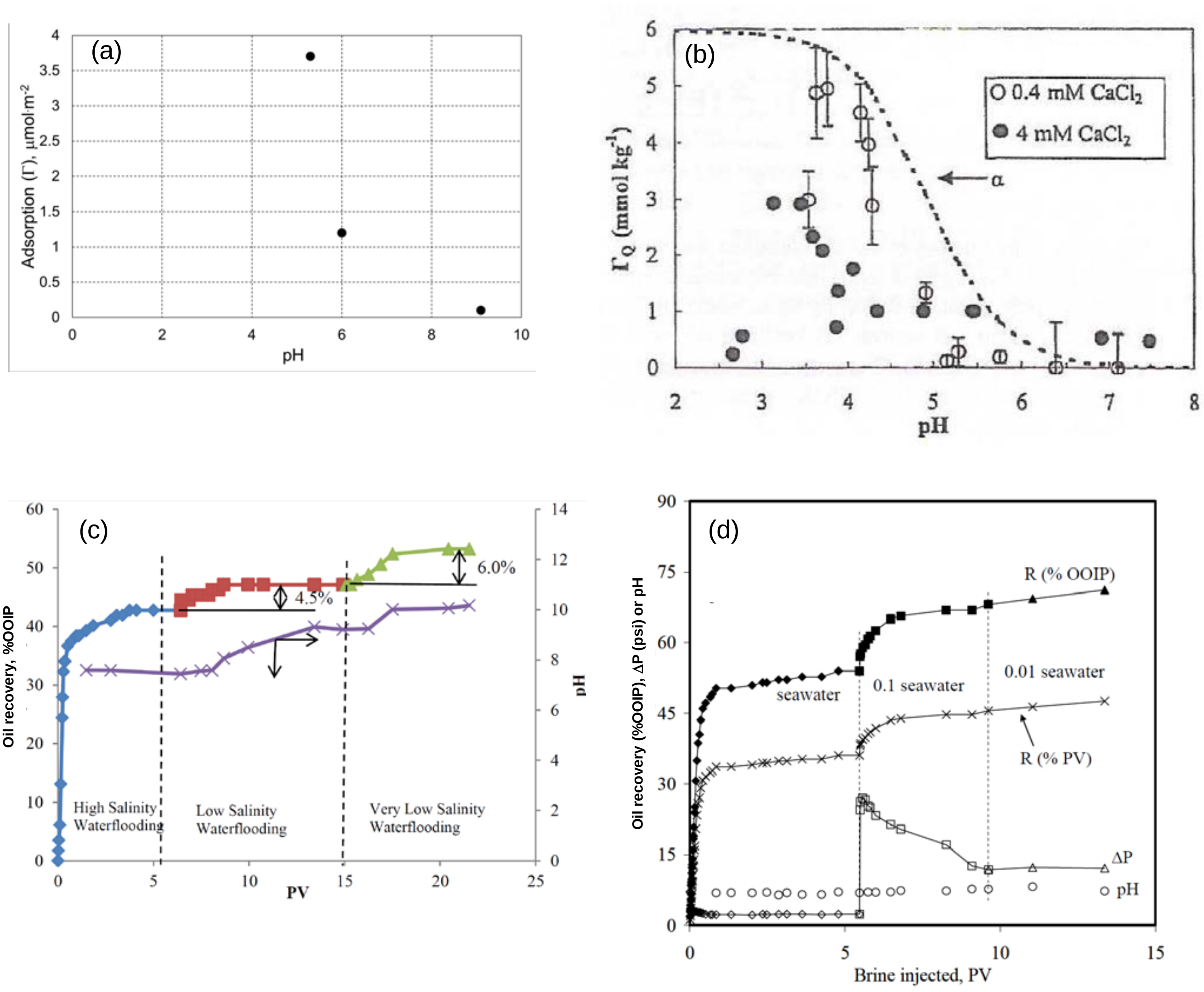

(a)
Adsorption (Γ), µmol·m⁻²
pH
0
0.5
1
1.5
2
2.5
3
3.5
4
0
2
4
6
8
10
(b)
Γ_Q (mmol kg⁻¹)
pH
O 0.4 mM CaCl₂
● 4 mM CaCl₂
α
0
1
2
3
4
5
6
2
3
4
5
6
7
8
(c)
Oil recovery, %OOIP
pH
PV
4.5%
6.0%
High Salinity Waterflooding
Low Salinity Waterflooding
Very Low Salinity Waterflooding
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
0
5
10
15
20
25
(d)
Oil recovery (%OOIP), ΔP (psi) or pH
Brine injected, PV
R (% OOIP)
seawater
0.1 seawater
0.01 seawater
R (% PV)
ΔP
pH
0
15
30
45
60
75
90
0
5
10
15

Figure 3

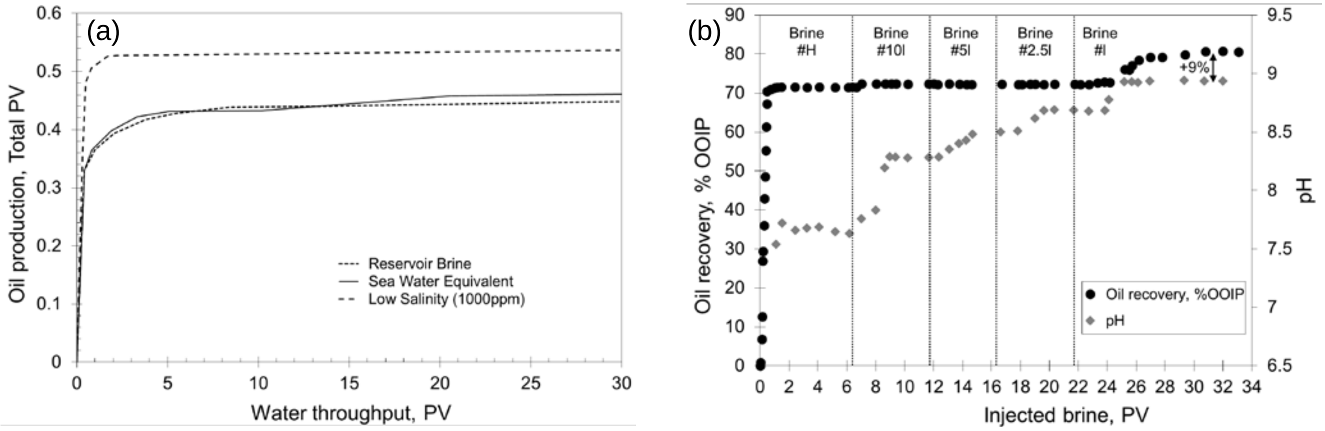
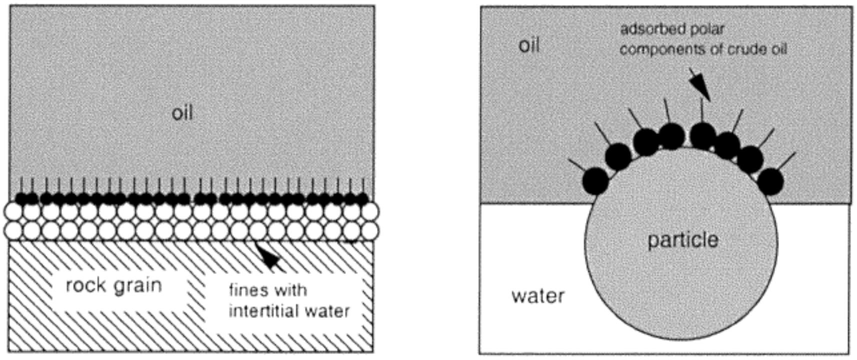

(a)
Oil production, Total PV
Water throughput, PV
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
Reservoir Brine
Sea Water Equivalent
Low Salinity (1000ppm)
(b)
Oil recovery, % OOIP
pH
Injected brine, PV
Brine #H
Brine #10l
Brine #5l
Brine #2.5l
Brine #l
+9%
Oil recovery, %OOIP
pH
90
80
70
60
50
40
30
20
10
0
9.5
9
8.5
8
7.5
7
6.5
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34

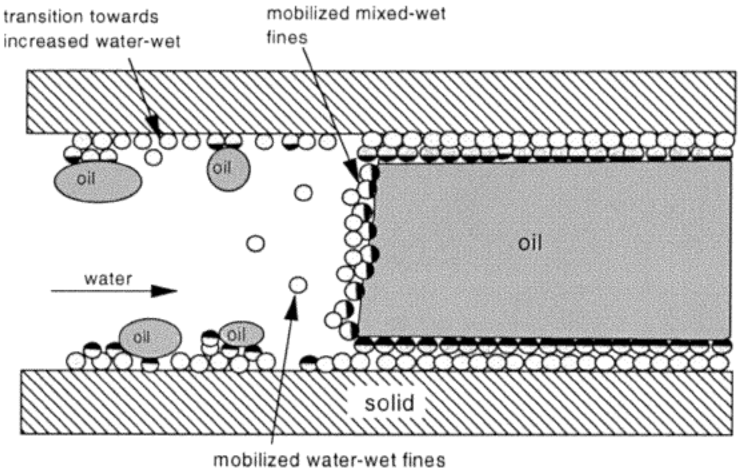
Figure 4



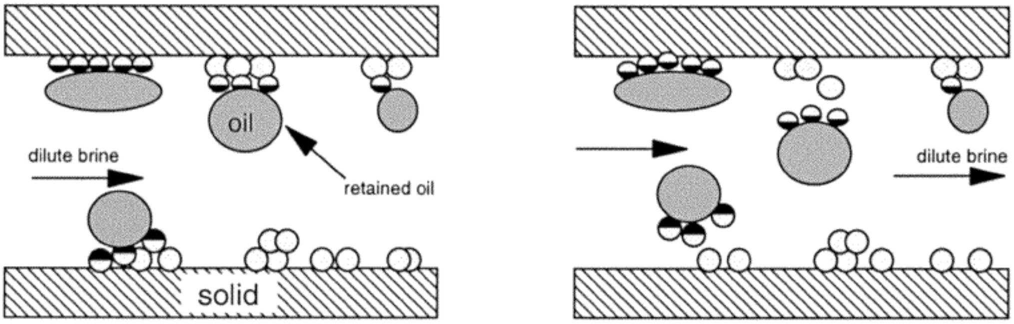
adsorption onto potentially mobile fines at low initial water saturation

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

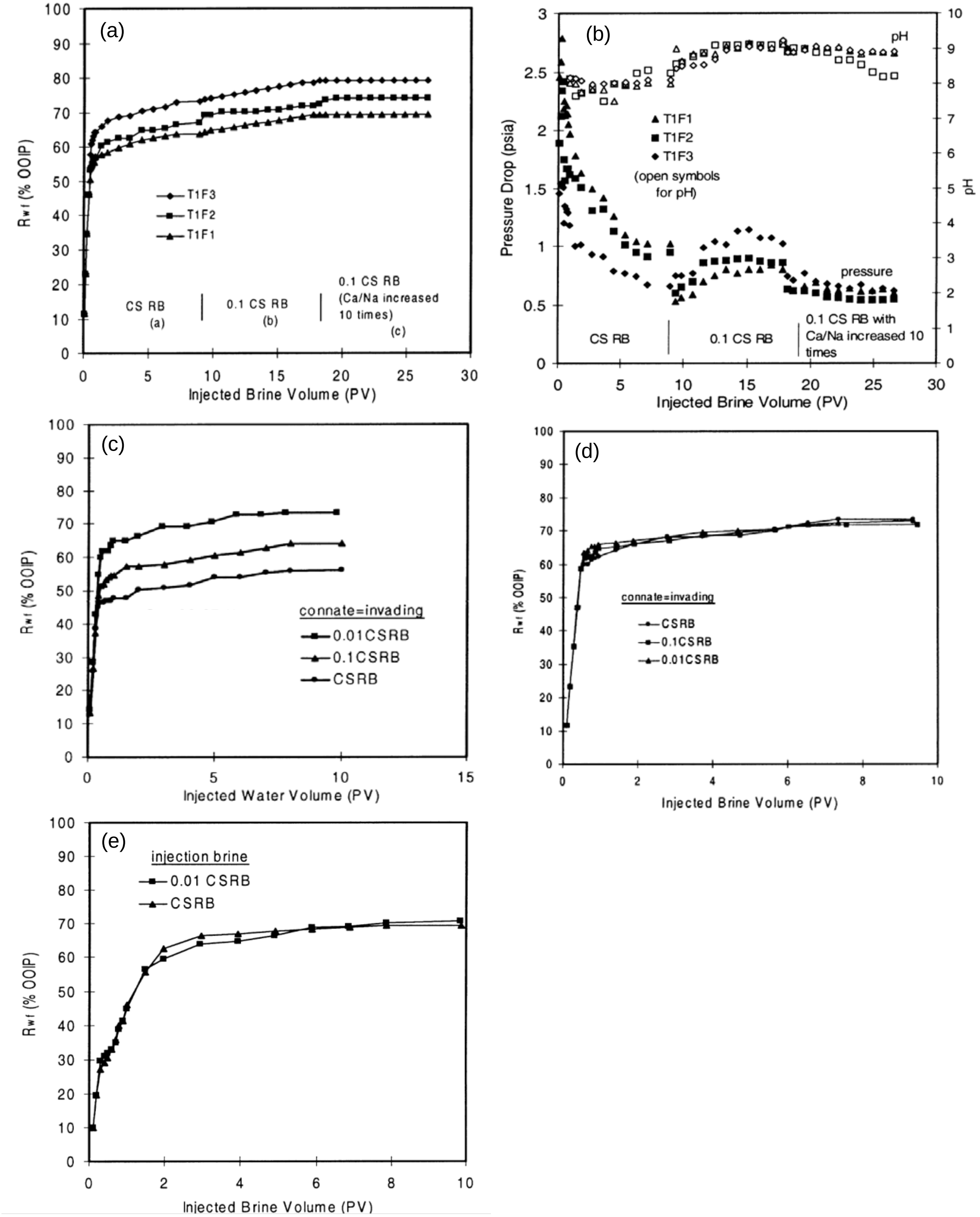
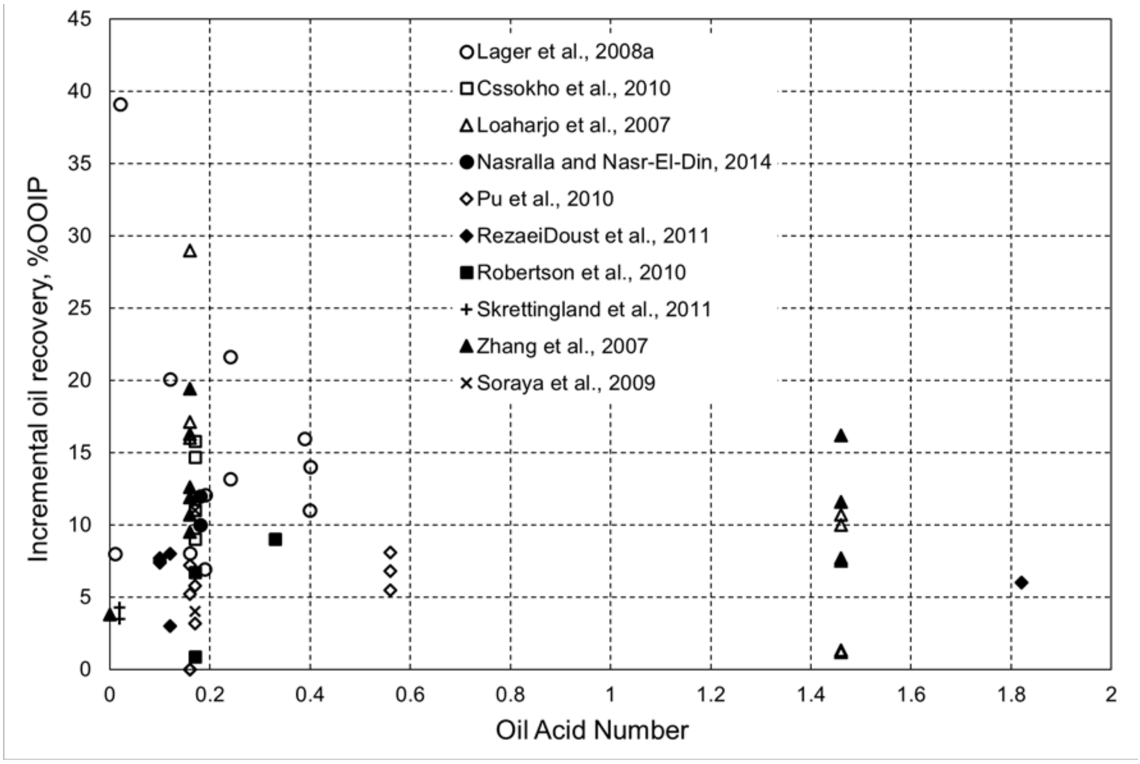

(a)
Rwf (% OOIP)
T1F3
T1F2
T1F1
CS RB
(a)
0.1 CS RB
(b)
0.1 CS RB
(Ca/Na increased
10 times)
(c)
Injected Brine Volume (PV)
(b)
Pressure Drop (psia)
pH
T1F1
T1F2
T1F3
(open symbols
for pH)
pressure
CS RB
0.1 CS RB
0.1 CS RB with
Ca/Na increased 10
times
Injected Brine Volume (PV)
(c)
Rwf (% OOIP)
connate=invading
0.01CSRB
0.1CSRB
CSRB
Injected Water Volume (PV)
(d)
Rwf (% OOIP)
connate=invading
CSRB
0.1CSRB
0.01CSRB
Injected Brine Volume (PV)
(e)
Rwf (% OOIP)
injection brine
0.01 CSRB
CSRB
Injected Brine Volume (PV)

Figure 6



45
40
35
30
25
20
15
10
5
0
Incremental oil recovery, %OOIP
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Oil Acid Number
○ Lager et al., 2008a
□ Cssokho et al., 2010
△ Loaharjo et al., 2007
● Nasralla and Nasr-El-Din, 2014
◇ Pu et al., 2010
◆ RezaeiDoust et al., 2011
■ Robertson et al., 2010
+ Skrettingland et al., 2011
▲ Zhang et al., 2007
× Soraya et al., 2009

Figure 7

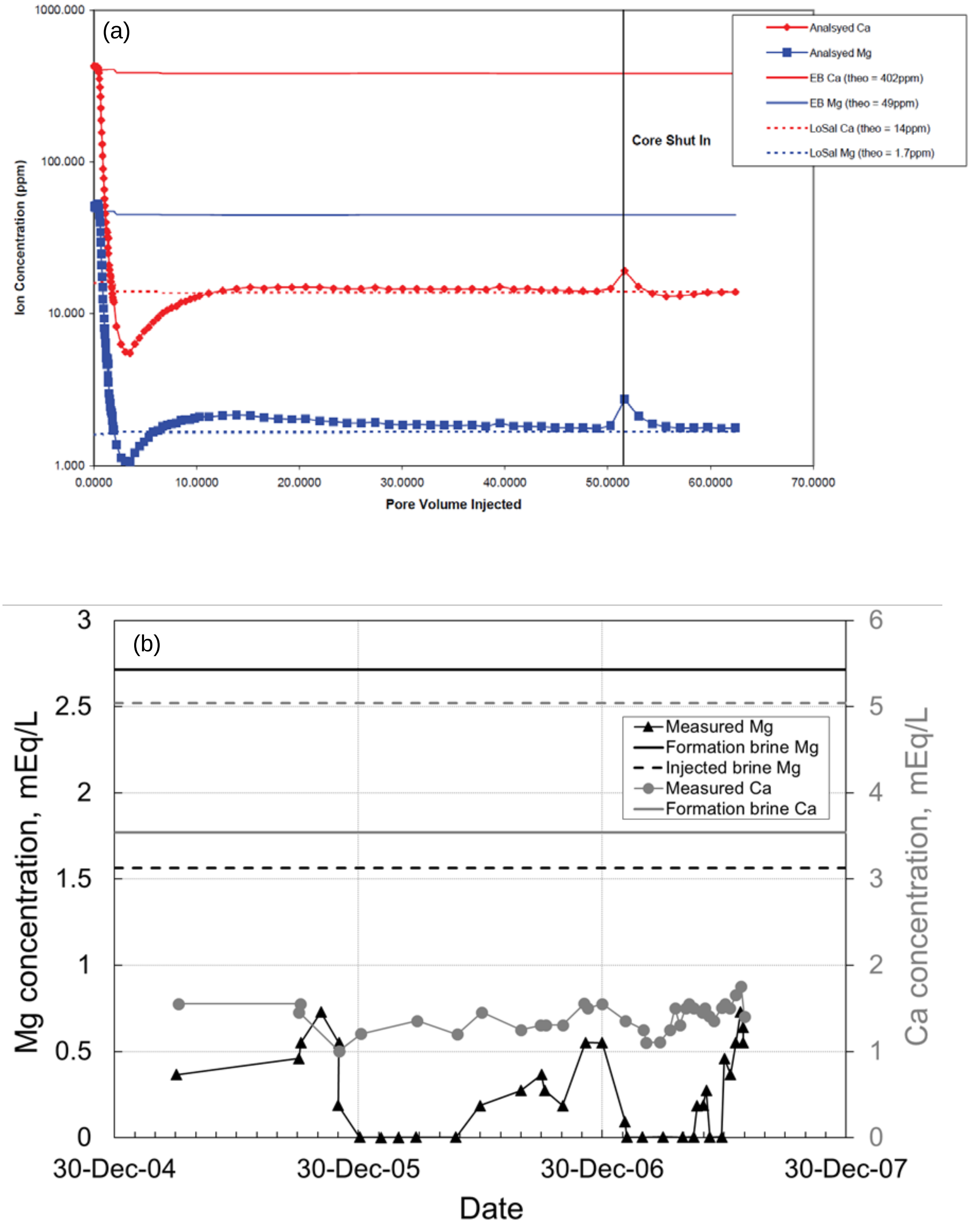
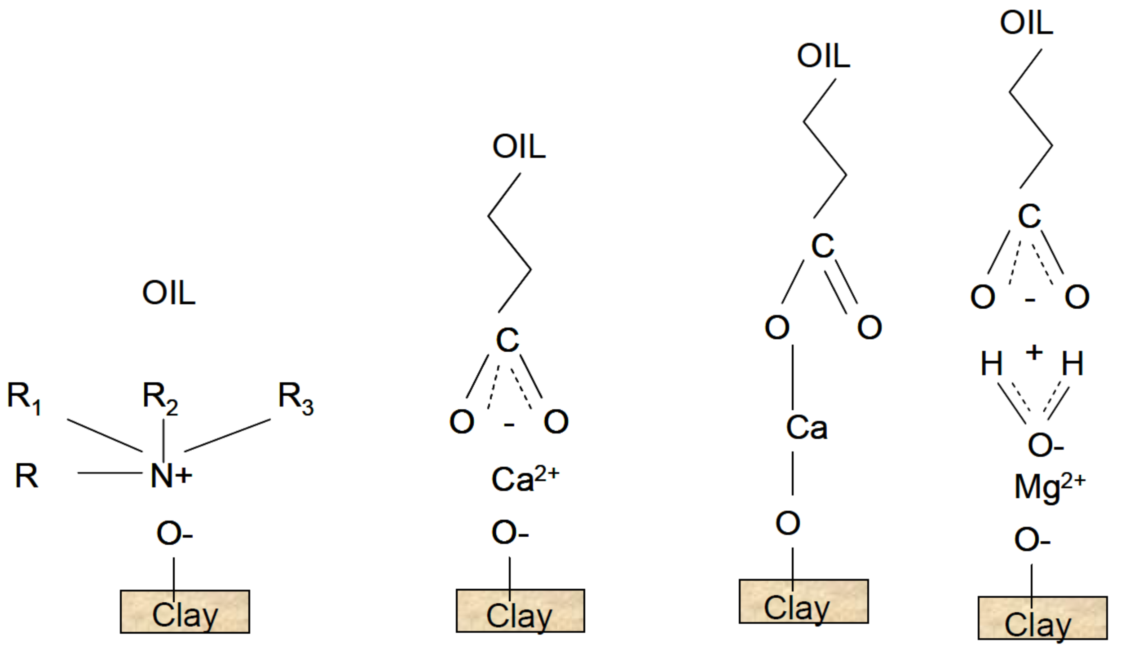

(a)
Ion Concentration (ppm)
1000.000
100.000
10.000
1.000
0.0000
10.0000
20.0000
30.0000
40.0000
50.0000
60.0000
70.0000
Pore Volume Injected
Core Shut In
Analsyed Ca
Analsyed Mg
EB Ca (theo = 402ppm)
EB Mg (theo = 49ppm)
LoSal Ca (theo = 14ppm)
LoSal Mg (theo = 1.7ppm)
(b)
Mg concentration, mEq/L
3
2.5
2
1.5
1
0.5
0
Ca concentration, mEq/L
6
5
4
3
2
1
0
30-Dec-04
30-Dec-05
30-Dec-06
30-Dec-07
Date
Measured Mg
Formation brine Mg
Injected brine Mg
Measured Ca
Formation brine Ca

Figure 8



Cation exchange

Cation bridging

Ligand bridging

Water bridging

Figure 9

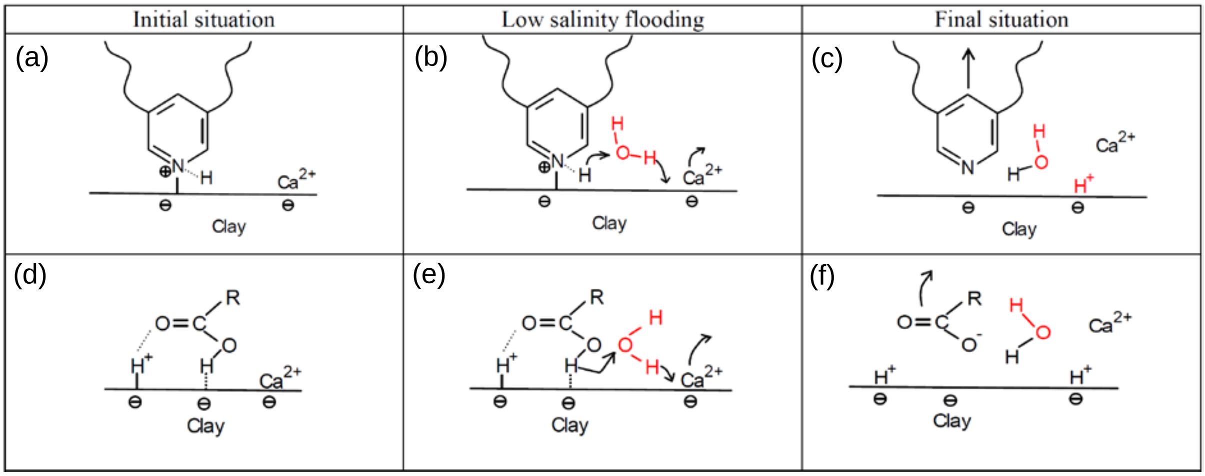

Initial situation
Low salinity flooding
Final situation
(a)
(b)
(c)
(d)
(e)
(f)
N
H
O
R
C
Ca^{2+}
H^{+}
⊕
⊖
Clay

Figure 10

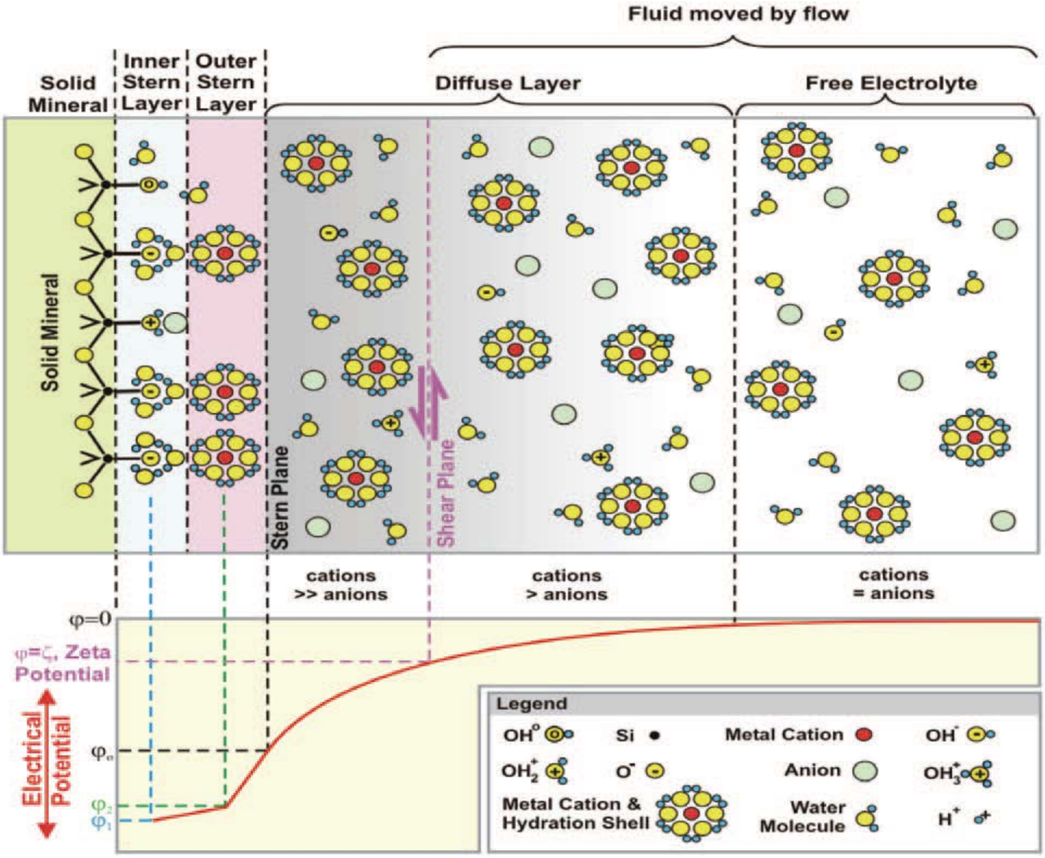
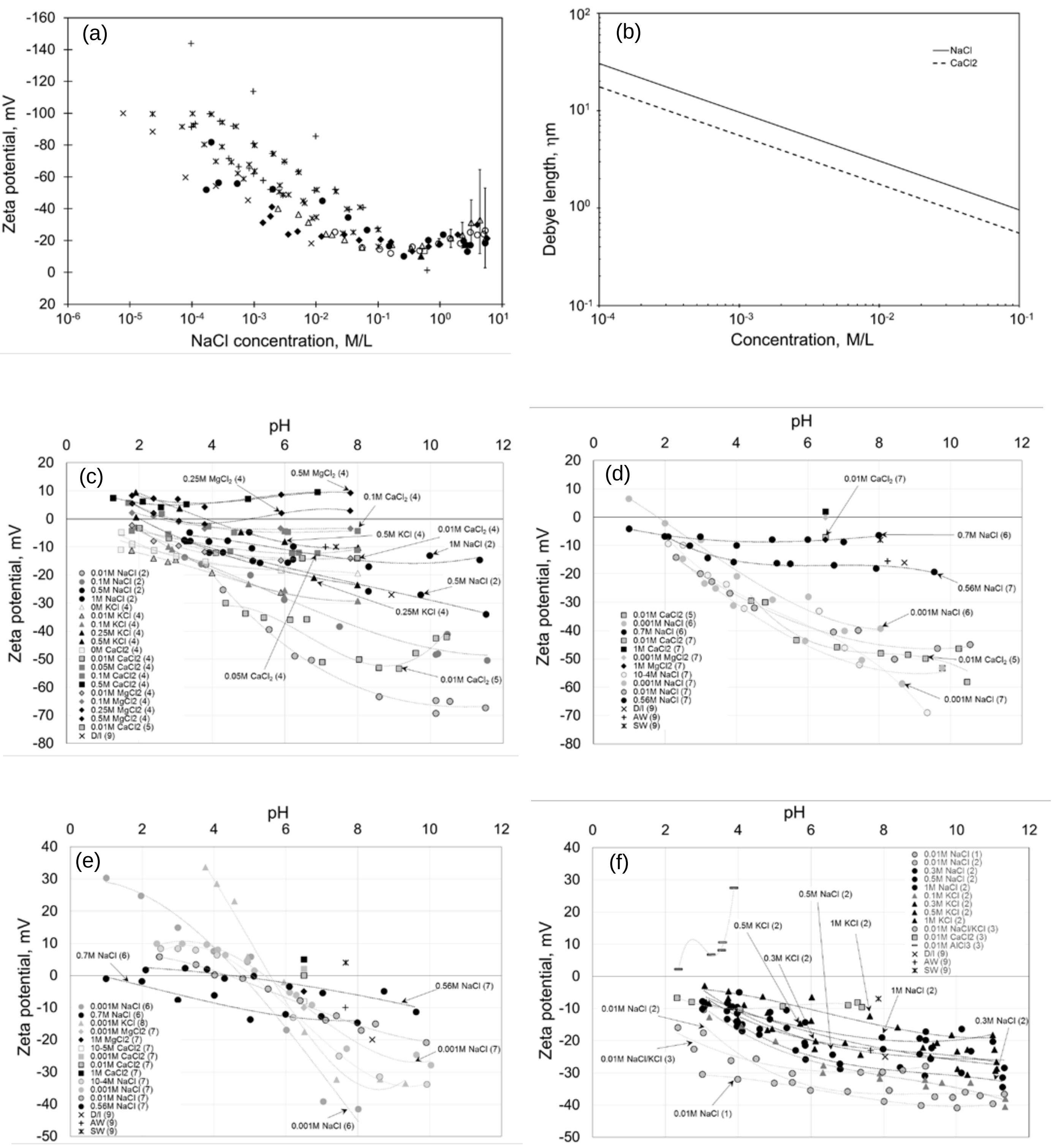

Fluid moved by flow
Solid Mineral
Inner Stern Layer
Outer Stern Layer
Diffuse Layer
Free Electrolyte
Solid Mineral
Stern Plane
Shear Plane
cations >> anions
cations > anions
cations = anions
φ=0
φ=ζ, Zeta Potential
Electrical Potential
φ₀
φ₂
φ₁
Legend
OH°
Si
Metal Cation
OH⁻
OH₂⁺
O⁻
Anion
OH₃⁺
Metal Cation & Hydration Shell
Water Molecule
H⁺

Figure 11



(a)
Zeta potential, mV
-160
-140
-120
-100
-80
-60
-40
-20
0
20
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
NaCl concentration, M/L
(b)
NaCl
CaCl2
Debye length, ηm
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Concentration, M/L
(c)
pH
0
2
4
6
8
10
12
Zeta potential, mV
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
0.25M MgCl$_2$ (4)
0.5M MgCl$_2$ (4)
0.1M CaCl$_2$ (4)
0.01M CaCl$_2$ (4)
0.5M KCl (4)
1M NaCl (2)
0.5M NaCl (2)
0.25M KCl (4)
0.05M CaCl$_2$ (4)
0.01M CaCl$_2$ (5)
0.01M NaCl (2)
0.1M NaCl (2)
0.5M NaCl (2)
1M NaCl (2)
0M KCl (4)
0.01M KCl (4)
0.1M KCl (4)
0.25M KCl (4)
0.5M KCl (4)
0M CaCl2 (4)
0.01M CaCl2 (4)
0.05M CaCl2 (4)
0.1M CaCl2 (4)
0.5M CaCl2 (4)
0.01M MgCl2 (4)
0.1M MgCl2 (4)
0.25M MgCl2 (4)
0.5M MgCl2 (4)
0.01M CaCl2 (5)
D/I (9)
(d)
pH
0
2
4
6
8
10
12
Zeta potential, mV
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
0.01M CaCl$_2$ (7)
0.7M NaCl (6)
0.56M NaCl (7)
0.001M NaCl (6)
0.01M CaCl$_2$ (5)
0.001M NaCl (7)
0.01M CaCl2 (5)
0.001M NaCl (6)
0.7M NaCl (6)
0.01M CaCl2 (7)
1M CaCl2 (7)
0.001M MgCl2 (7)
1M MgCl2 (7)
10-4M NaCl (7)
0.001M NaCl (7)
0.01M NaCl (7)
0.56M NaCl (7)
D/I (9)
AW (9)
SW (9)
(e)
pH
0
2
4
6
8
10
12
Zeta potential, mV
40
30
20
10
0
-10
-20
-30
-40
-50
0.7M NaCl (6)
0.56M NaCl (7)
0.001M NaCl (7)
0.001M NaCl (6)
0.001M NaCl (6)
0.7M NaCl (6)
0.001M KCl (8)
0.001M MgCl2 (7)
1M MgCl2 (7)
10-5M CaCl2 (7)
0.001M CaCl2 (7)
0.01M CaCl2 (7)
1M CaCl2 (7)
10-4M NaCl (7)
0.001M NaCl (7)
0.01M NaCl (7)
0.56M NaCl (7)
D/I (9)
AW (9)
SW (9)
(f)
pH
0
2
4
6
8
10
12
Zeta potential, mV
40
30
20
10
0
-10
-20
-30
-40
-50
0.01M NaCl (1)
0.01M NaCl (2)
0.3M NaCl (2)
0.5M NaCl (2)
1M NaCl (2)
0.1M KCl (2)
0.3M KCl (2)
0.5M KCl (2)
1M KCl (2)
0.01M NaCl/KCl (3)
0.01M CaCl2 (3)
0.01M AlCl3 (3)
D/I (9)
AW (9)
SW (9)
0.5M NaCl (2)
0.5M KCl (2)
1M KCl (2)
0.3M KCl (2)
1M NaCl (2)
0.01M NaCl (2)
0.3M NaCl (2)
0.01M NaCl/KCl (3)
0.01M NaCl (1)

Figure 12

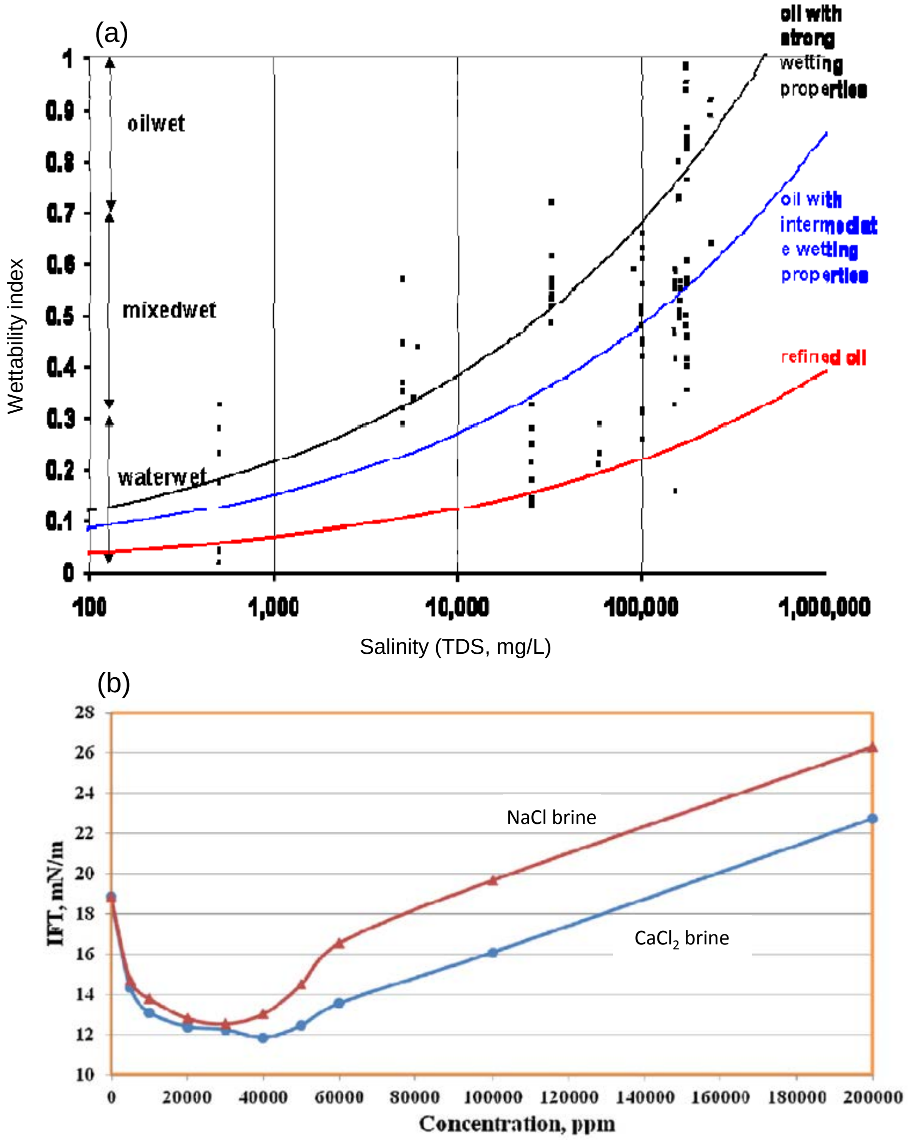

(a)
oil with strong wetting properties
oil with intermediate wetting properties
refined oil
oilwet
mixedwet
waterwet
Wettability index
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
1,000
10,000
100,000
1,000,000
Salinity (TDS, mg/L)
(b)
NaCl brine
$CaCl_2$ brine
IFT, mN/m
28
26
24
22
20
18
16
14
12
10
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
200000
Concentration, ppm

Figure 13