# Alkali/Surfactant Improved Low-Salinity Waterflooding

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Abstract Extensive laboratory studies have shown that oil recovery from water flooding is dependent on the salinity and composition of the injected water. The potential of low-salinity waterflooding (LSWF) has been observed in field trials, with relatively good agreement with the measured laboratory data. However, the incremental recovery from LSWF is relatively modest (2-10 % OOIP) compared to other water-based EOR methods such as chemical methods, particularly when applied in tertiary mode. In this paper, we investigate low-salinity flooding combined with alkali to improve the incremental recovery. The recoveries are also compared with low-salinity brine combined with surfactant. This is studied in a system, which is first shown to be responsive to low salinity. The low-salinity recovery result is used as a baseline for comparison. A clay-rich core from a sandstone reservoir and crude oil were used. The flooding experiments were performed by successive injection of high-salinity formation brine and low-salinity water or low-salinity water combined with a surfactant or alkali (SDS/NaOH). Based on the results, without adding alkali or surfactant, low-salinity flooding recovered  $\sim 4\%$  additional oil over the recovery from high-salinity injection. However, when combined with 1 wt% alkali/surfactant, the oil recovery increased to 7-17 % OOIP. Minor formation damage was observed in all experiments. Interfacial tension (IFT) reduction (capillary desaturation) in each combined method is envisaged to be the driving mechanism for the enhancement of oil recovery. Interfacial tension reduction decreases capillary pressure, thereby decreasing trapping or re-trapping of the mobilized oil by low-salinity flooding. Comparison of the recovery from surfactant-improved low salinity and alkali-improved low salinity indicates that higher oil recovery can be achieved with surfactant than with alkali. Higher efficiency with surfactant can be attributed to the lower attainable IFT with surfactant than alkali (higher capillary numbers). Nevertheless, due to lower costs, alkali is more cost effective than surfactant and is advantageous because it reduces adsorption of in-situ generated petroleum surfactant. The results of the study emphasize the benefits of hybrid methods for the improvement of oil recovery. Particularly where a reservoir is responsive

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to low salinity, recovery can be enhanced by the addition of a small amount of alkali or surfactant.

## List of Symbols

TAN	Total acid number
TBN	Total base number
dFW 0.1	Formation water diluted 10 times
dFW0.01	Formation water diluted 100 times
DP	Differential pressure
DW	Distilled water
FW	Formation water
HS	High salinity
IFT	Interfacial tension
Κ	Absolute (brine) permeability of core in each flooding step
Kinit	Initial absolute (brine) permeability of core
LS	Low salinity
LSWF	Low-salinity water flooding
LSWF-A	Low-salinity water with alkali
LSWF-S	Low-salinity water with surfactant
OOIP	Oil originally in place
PV	Pore volume
ROS	Remaining oil saturation
$S_{ m wi}$	Initial water saturation
Sor	Residual oil saturation
SDS	Sodium dodecyl sulfate
TDS	Total dissolved solid
$v_{ m w}$	Displacement velocity
$\mu_{ m w}$	Viscosity of displacing phase
$\sigma_{ m ow}$	Oil/brine interfacial tension (IFT)

# **1** Introduction

Numerous laboratory and field studies, some of the earliest back in 1920s, have reported the benefits of adding chemicals or surfactants to injection water as enhanced oil recovery (EOR) methods. Surfactant injection improves oil recovery by lowering the oil–water interfacial tension (IFT), thereby preventing capillary trapping of oil and/or remobilizing the trapped oil. However, the efficiency of the process could be reduced due to surfactant loss by adsorption and reduction of interfacial tension between water and oil (oleic phase), which ultimately renders the process technically unviable. Studies have shown that surfactant retention increases with increasing salinity of the aqueous phase (Friedman 1986; Alagic and Skauge 2010; Alagic et al. 2011). In particular, when multivalent ions are present in the water, surfactant solubility may be hindered via specific mechanisms, which can be dependent on temperature. The presence of divalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) in high-salinity water may

cause precipitation and retardation of surfactant in porous media. Combining surfactant with low-salinity water containing low concentration of divalent ions improves the performance of surfactant flooding (Hirasaki et al. 1983; Stournas 1984; Mannhardt and Jha 1994).

The idea of injecting low-salinity water as an oil recovery mechanism (alone) was introduced in 1960s by Bernard (1967), who demonstrated that injection of fresh water or low salt (NaCl) containing brine could increase oil recovery both in secondary and tertiary modes. Extensive research studies about 30 years later (Jadhunandan and Morrow 1995; Yildiz and Morrow 1996; Tang and Morrow 1999; Zhang and Morrow 2006) revived the idea again. The research efforts of Webb et al. (2005), Lager et al. (2006), and Lager et al. (2007) confirmed the low-salinity effect by conducting reservoir conditions coreflood experiments. The laboratory results were validated by field trials including log-inject-log, single-well chemical tracer, and interwell tests (Webb et al. 2004; McGuire et al. 2005; Lager et al. 2008; Vledder et al. 2010; Mahani et al. 2011). The efforts in the past two decades have been devoted to understanding the underlying mechanisms of oil recovery by low-salinity waterflooding (LSWF). What is mainly agreed upon is that this process induces wettability alteration of rock surface, from more oil wetting to more water wetting (Mahani et al. 2014). However, there is not yet consensus on the mechanism. In 2009, Ligthelm et al. proposed the LSWF mechanism to be the expansion of the electrical double layers that surround the clay and oil particles and increase the level of zeta potential. It was suggested that a decrease in the ionic strength by lowering the salinity in the brine would increase the electrostatic repulsion between the clay particle and the oil. Once the repulsive forces exceed the binding forces via the multivalent cation bridges, the oil is desorbed from the clay surfaces, which will lead to a change in wetting phase toward increased water wetness. If the electrolyte concentration is reduced further, the electrostatic forces within the clay minerals will start to exceed binding forces, which may lead to the formation damage. Other mechanisms suggested in the literature include multicomponent-ion exchange (MIE) (Lager et al. 2006), formation damage and fine migration (Tang and Morrow 1999), pH-induced oil mobilization (pH increase) (Austad et al. 2010a, b), mineral dissolution, and other mechanisms, a review of which can be found in (Hughes et al. 2010).

Given that low-salinity flooding and surfactant/alkali flooding are each proven IOR/EOR processes, in this paper, the focus is placed on recent advances made in their application by combining the methods that can boost recovery and make it easier to deploy to field.

Alagic and Skauge (2010) proposed a hybrid EOR process combining the effect of lowsalinity water injection and surfactant flooding in a low-salinity surfactant (LSWF-S) injection process. The idea is that a more efficient oil recovery process can be achieved by combining destabilization of oil layers during a LSWF with a low IFT environment that prevents re-trapping of these oil layers. Several experiments were conducted on Berea core plugs. The highest recovery was obtained by a tertiary oil recovery of 94.4 % of OOIP by LSWF-S injection. A change in S<sub>or</sub> from 0.30 (LSWF) to less than 0.05 (LSWF-S) was observed. In addition, a significantly higher oil recovery was achieved when surfactant solution was introduced into a pre-established LS environment compared to a high-salinity environment.

Riisøen (2012) studied the effect of combined low-salinity water and surfactant injection on oil recovery in aged Bentheimer cores at different temperatures. The results showed that the combination of low salinity and surfactant injection results in a significant increase in oil recovery (additional 26 % OOIP). However, an increase of temperature to 90 °C lowered the recovery factor. A reduction in pH was also observed, suggesting hydrolysis of the surfactant at elevated temperature. Despite the insignificant response to low-salinity brine, combination with a surfactant can be more beneficial than low-salinity brine injection or surfactant flooding alone, since it increases oil recovery, and therefore can be more attractive economically.

Nevertheless, in the above-mentioned studies, the main motivation behind combining lowsalinity water and surfactant (LSWF-S) was to alleviate the operational challenges associated with surfactant flooding such as surfactant adsorption, scaling, and oil trapping in porous media. While addressing these issues are still relevant and important, in this paper, we introduce a hybrid EOR method based on addition of an alkali to low-salinity brine (LSWF-A). This combination has not been explored in this context in the literature and offers the benefit of both low-salinity effect and alkali flooding simultaneously. We apply the method in cores which are responsive to low salinity and compare its performance to low-salinity waterflooding (LSWF) alone and low-salinity flooding with surfactant (LSWF-S). We apply the mixture (LSWF-A or LSWF-S) immediately after HS injection without preflushing the core with LSW to establish low salinity. This is not critical and necessary to the success of the combined method. This study also utilizes reservoir core material (with complex mineralogy and low permeability) rather than outcrop material (Berea or Bentheimer, which typically have high permeability), as used in most studies. These make this study different from the previously published papers.

In the following sections, the details of core flooding experiments are presented and the results are analyzed. The coreflooding tests consist of (1) low salinity-only coreflooding (on reservoir core material), (2) combined low salinity and surfactant, and (3) combined low salinity and alkali. The experiments are designed such that first responsiveness of the system (oil–brine–rock) to low salinity is established. Then, on that basis, surfactant and alkali are combined and the recovery factors are compared.

## 2 Material and Methods

#### 2.1 Core Material

Core materials from a sandstone reservoir in the Middle East were used in the laboratory experiments. The porosity of the core materials, determined by the weighing difference method, was 14–17 %, and the brine permeability was 20–23 mD. The core properties are summarized in Table 1. Rock mineral composition of the cores was determined by XRD and is given in Table 2. The cores were mainly composed of quartz, albite, clay minerals (Kaolinite and Muscovite), and trace amount of calcite and dolomite. Clay minerals are widely accepted as a key parameter for low-salinity water flooding (Tang and Morrow 1999; Mahani et al. 2014).

Core ID	Length (cm)	Diameter (cm)	Porosity %	Brine permeability (mD)	Swi %	Aging time (days)
C1	5	3.79	15.63	22.8	27.9	30
C2	4.84	3.8	14.62	21.0	25.4	30
C3	4.9	3.8	14.91	21.1	24.5	30
C4	4.9	3.8	17.41	27.4	24.1	30
C5	5	3.8	14.98	20.6	25.6	30

 Table 1
 Core dimensions, properties, initial saturations, and aging times

Table 2         Mineral composition of sandstone cores (wt%)	Quartz	Albite	Calcite	Calcite	Dolomite	Kaolinite	Muscovite
	67	21	4	4	2	4	2
Table 3         Composition of           formation water         Image: Composition of the second secon	Concen	tration (r	ng/l)				Components
	63,204						Na <sup>+</sup> & K <sup>+</sup>
	13,600						Ca <sup>2+</sup>
	2,673						Mg <sup>2+</sup>
	127,436						Cl-
	500						$SO_{4}^{2-}$
	2,440						$HCO_3^-$
	209,853						TDS (ppm)
Table 4         Basic properties of test oils	Oil sample	Density 70 °C	/ (g/cm <sup>3</sup> )		cosity (cp) 0°C	TAN/TBN (mg KOH/	g oil)
	A	0.9203		4.2	7	2.683/0.42	(±0.01/0.1)
	В	0.8549		3.1	5	0.842/0.21	$(\pm 0.01/0.1)$

## 2.2 Brines

Synthetic formation brine similar to the reservoir formation brine was prepared by dissolving salts in distilled water (DW). The composition of the formation brine is summarized in Table 3. The formation brine contains both monovalent and divalent ions. Formation brine is used for initialization of the cores and in the first step of the flooding experiments. Low-salinity brines were prepared by diluting the formation brine with distilled water (DW) in pre-specified volume ratios, 0.1 and 0.01. The following terminology is used: dFW0.1—formation brine diluted 10 times, and dFW0.01—formation brine diluted 100 times.

## 2.3 Oils

Two types of crude oil were used for saturating the cores: (a) Oil A, with acid number (TAN) 2.683 mg KOH/g oil and base number (TBN) of 0.24 mg KOH/g oil; and (b) Oil B, with acid number (TAN) of 0.842 mg KOH/g oil and base number (TBN) of 0.21 mg KOH/g oil. The oils were centrifuged and filtered through a 5-micrometer Millipore. The acid and base numbers (TAN and TBN) of the test oils were measured in the laboratory according to the modified ASTM D664 and ASTM D2896 methods, respectively. The oil properties are summarized in Table 4. The acid number of both crudes is relatively high, which makes them suitable (i.e., good potential for in-situ surfactant generation) for combined low-salinity alkali flooding.

## 2.4 Alkali

Sodium hydroxide (NaOH) supplied by Merck Company is used. Alkaline solution was prepared by mixing 1 wt% of alkali with low-salinity water (dFW0.01).

Brine	pH @ ambient	IFT (mN/m) @ 70 °C	IFT (mN/m) @ 70 °C		
	conditions	Crude A—Brine	Crude B—Brine		
FW	6.5	7.04	5.40		
d0.1FW	6.3	6.93	5.31		
d0.01FW	6.1	6.78	5.16		
d0.01FW + 1 wt% Surf.	7.6	2.5	-		
d0.01FW + 1 wt% Alk.	12.8	3.44	_		

 Table 5
 Brine pH and interfacial tension (IFT)

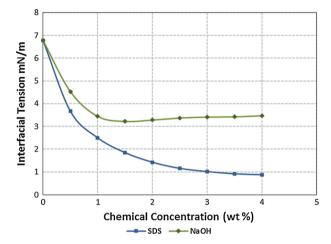


Fig. 1 IFT values between oil A and chemical solution versus chemical concentration in dFW0.01

# 2.5 Surfactant

Sodium dodecyl sulfate (SDS) (which is an anionic surfactant), supplied by Merck Company, was used. The surfactant solution was prepared by mixing 1 wt% of surfactant with low-salinity water (dFW0.01). No co-surfactant or co-solvent was used.

# 2.6 IFT Measurements

The IFT measurements between the crude oil and the surfactant/alkali brine solutions were performed at 70 °C by spinning drop interfacial tensiometer. The IFT measurements were performed using diluted synthetic formation water (dFW0.01) with different surfactant/alkali concentrations. The IFT data with FW, diluted FW and with chemicals, as used in the core-flooding experiments, are presented in Table 5. IFT curves with the concentration of the added chemical are shown in Figure 1.

# 2.7 Core Handling

The cores were cleaned by Soxhlet extraction technique using toluene and methanol at 115 °C. After drying at 60 °C to a constant weight, the core was saturated with the for-

Exp. #	1st Flood	2nd Flood	Core ID	Temp (°C)	Test oil
Exp. 1	FW	dFW0.1	C1	70	А
Exp. 2	FW	dFW0.01	C2	70	А
Exp. 3	FW	dFW0.01+1 wt% SDS	C3	70	А
Exp .4	FW	dFW0.01+1 wt% NaOH	C4	70	А
Exp. 5	FW	dFW0.01	C5	70	В

Table 6 Layout of core displacement experiments

mation brine to determine the pore volume. The core was aged with 100 % formation brine for 15 days at 70 °C to establish ionic equilibrium between the rock surface and the formation brine.

The brine permeability was measured at different flow rates in the core holder. The initial water saturation ( $S_{wi}$ ) was established by flooding the core with the test oil in the coreholder to the irreducible water saturation. The core was then removed from the coreholder and aged in the test oil in a sealed Pyrex jar at 70 °C for 30 days.

## 2.8 Coreflooding

A coreholder apparatus was used in the flooding experiments. The core was placed in the coreholder with a confining pressure of 140 bar to mimic reservoir stress conditions.<sup>1</sup> Identical flooding conditions, i.e., temperature, gravity stable displacement, and 1 ft/day (0.035 cc/min) nominal flooding rate, were applied in all floods. Further, a backpressure of 5 bar was applied to avoid formation of gas by light ends in the crude oil. The pressure drop across the core was carefully monitored in all experiments. Two floods were performed on each core. The first flood was a continuous injection of formation water (high-salinity brine) to remaining oil saturation, while the second flood was low salinity/combined low salinity and chemicals. Remaining oil saturation after waterflooding was considered to be obtained when water cut values were high and stable over time. Following this, the low salinity/combined low salinity and chemicals were then initiated and run by continuous injection until stable water cut was obtained. The produced oil was collected using a fractional collector, and the oil recovery was determined as a percentage of original oil in place (OOIP). The set-up was equipped with several valves, which enabled us to change the injection fluid from one transfer vessel to other without disturbing the pressure equilibrium of the system. The effluent samples were collected regularly, and pH was measured and recorded. Table 6 shows experimental layout for core displacement experiments.

## **3 Low-Salinity Flooding Results**

In this section, we will present the coreflooding results. For the sake of brevity, we will not present all studied cases in which we used another core and showed consistent results with those presented here.

<sup>&</sup>lt;sup>1</sup> Since the core samples are well consolidated and stress competent, the confining pressure has negligible influence on the permeability and porosity of the samples.

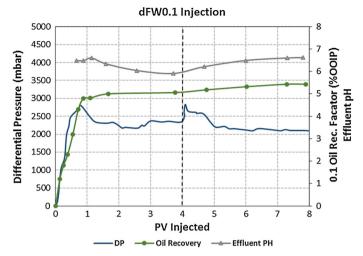


Fig. 2 Oil recovery, effluent pH and pressure drop versus pore volume injected in FW  $\rightarrow$  dFW0.1 flooding (core C1)

## 3.1 Experiment 1 (FW-dFW0.1)

Core C1 was flooded with formation brine (FW) at the rate of 1 ft/day at 70 °C. The oil production after injection of 4PV formation brine was stabilized, yielding about 50 % OOIP recovery. When switched to low-salinity water (dFW 0.1), the recovery increased by 4.3 % of OOIP. The pressure drop across the core and recovery were monitored continuously. Figure 2 shows the oil recovery profiles, variation in the differential pressure, and pH of the effluent versus the pore volume injected.

3.2 Experiment 2 (FW-dFW0.01)

Similar to experiment 1, core C2 was initially flooded with formation brine (FW) and the oil recovery of 49 % of OOIP was achieved after 4 PVs (consistent with C1). The core was then flooded with dFW0.01 brine, which resulted in 9 % OOIP additional recovery. The results are shown in Fig. 3. Considering the test conditions to be the same as in experiment 1, the additional production highlights the effect of brine salinity reduction on the oil recovery. The oil recovery with dFW0.01 was almost doubled compared to dFW0.1.

3.3 Experiment 3 (FW-dFW0.01 with crude type B)

To investigate sensitivity of the effect to types of crude oil, core C5 saturated and aged with another crude B. This crude oil has lower acid number (three times lower) than crude A and different physical properties. FW injection in secondary recovery mode resulted in 51.5 % OOIP recovery and, after switching to dFW0.01, 5.6 % more oil recovered in tertiary recovery mode. Oil recovery, pressure drop, and pH of effluent water are shown in Fig. 4.

3.4 Experiment 4 (FW-dFW0.01+Surf.)

Core C3 was flooded with successive injection of formation brine and then low-salinity brine plus surfactant (dFW 0.01+1 wt% SDS). During formation brine injection, the oil

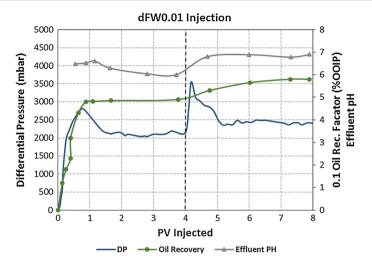


Fig. 3 Oil recovery, effluent pH, and pressure drop versus pore volume injected in FW  $\rightarrow$  dFW0.01 flooding (core C2)

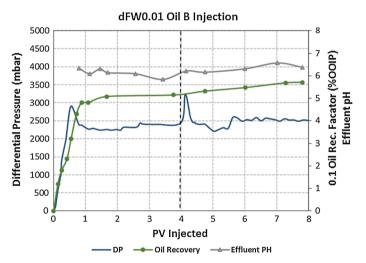


Fig. 4 Oil recovery, water effluent pH, and pressure drop evolution during FW  $\rightarrow$  dFW0.01 injection into core C5 saturated with oil B

recovery and pressure stabilized at 4 PVs, and a recovery factor of 51% OOIP was achieved. Switching to surfactant-improved low-salinity water resulted in 22% additional oil recovery. The ultimate oil recovery at the plateau was 73% OOIP. The results are shown in Fig. 5.

#### 3.5 Experiment 5 (FW-dFW0.01+Alkali)

Core C4 was used to investigate the effect of adding alkali to low-salinity water on oil recovery. FW was first injected for about 4 PVs to stable production, reaching 50% OOIP plateau recovery. The experiment was switched to low-salinity water with 0.01FW salinity and 1 wt% NaOH. Flooding with 1 wt% alkali increased oil recovery from 50 to 62.3 %

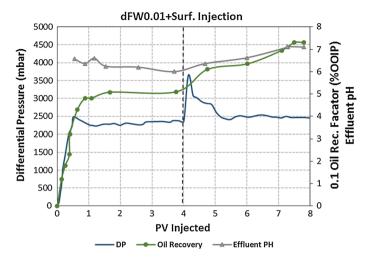


Fig. 5 Oil recovery, effluent pH, and pressure drop versus pore volume injected in  $FW \rightarrow dFW0.01 + Surf.$  flooding (core C3)

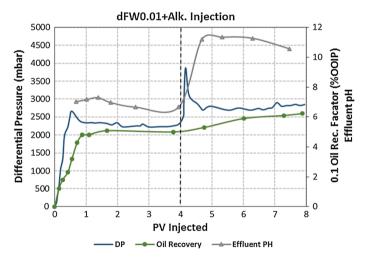


Fig. 6 Oil recovery, effluent pH, and pressure drop versus pore volume injected in FW  $\rightarrow$  dFW0.01+Alk. Flooding (core C4)

equivalent to 12.3 % improvement in oil recovery. Figure 6 shows oil recovery, pressure drop, and pH of effluent water through the core versus the injected pore volume.

Figure 7 compares the oil recoveries from all flooding studies. In all cases, the HS flooding experiment is reproducible, and the results are consistent in all samples, with recovery values between 49–51.5 % OOIP and breakthrough time of 0.39–0.42 PVI.

## 4 Discussion

The main purpose of the study was the examination of the low-salinity water (LSW) effect and the improvement it brought about. The target saturation was the remaining oil saturation

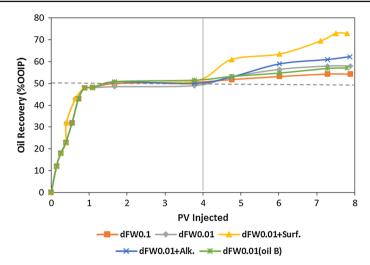


Fig. 7 Comparison of oil recovery versus PV injected for all core flooding experiments

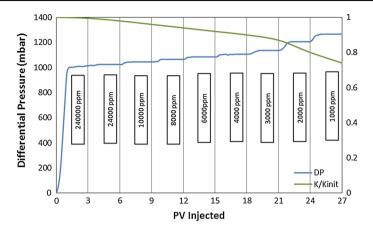
(not necessarily the residual oil saturation) remaining after flooding with high-salinity formation water. Low-salinity flooding improves process economics as (1) it is operationally cheaper than most EOR methods and (2) it can delay water breakthrough time and accelerate oil recovery compared to conventional waterflooding, normally with high-salinity water. Nevertheless, low-salinity waterflood experiments (Tang and Morrow 1997; McGuire et al. 2005; Lager et al. 2006; Boussour et al. 2009; RezaeiDoust et al. 2010; Rivet and Lake 2010; Nasralla et al. 2011) often show modestly improved oil recovery compared to, for instance, chemical EOR methods. The relatively low recoveries by low salinity could be related to

- (i) the initial wettability of the samples (more initially oil-wetting cores yield potentially higher oil recovery by low salinity);
- (ii) clay type, their content, and distribution in core (clay type, content, and distribution are not favorable in some cases i.e., kaolinite vs. montmorillonite);
- (iii) timing of low-salinity injection (secondary versus tertiary mode); tertiary mode gives often lower recoveries; and
- (iv) trapping of the mobilized oil by low salinity in water-wet pores or smaller pores.

We therefore conducted additional experiments where low-salinity water was combined with alkali and surfactant to generate a hybrid EOR method and to reach maximum possible oil recovery with low salinity. This is particularly important for field applications of the process where the incremental recovery obtained from coreflooding is often jeopardized by reservoir heterogeneity and layering, in-situ mixing of high salinity and low salinity, and sub-optimal well placement. These operational considerations necessitate optimization of the low-salinity process. Further optimization of the process is achievable by the addition of polymer to low-salinity brine, in which case the mobility ratio and sweep efficiency can be improved.

4.1 Brine Compatibility and Formation Damage

It is known that ionic composition and concentration of present ions in injected brine can affect interactions with rock matrix and may influence differential pressure (DP) during



**Fig. 8** Brine compatibility and formation damage experiment for a clean core (initially 100 % brine saturated). Salinity is reduced in steps from 240,000 ppm down to 1,000 ppm. At the end of each salinity step, stable pressure is reached

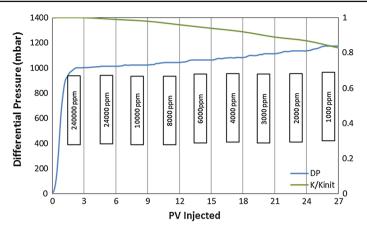
waterflood (Pu et al. 2008; Alotaibi and Nasr-El-Din 2009). It has been reported (Morrow 1998; Pu et al. 2008) that flooding with low-salinity water may initiate detrimental rock/fluid interactions, causing formation damage (i.e., swelling of clays and/or detachment of fine particles, reduction in permeability and consequent reduction in injectivity). The major challenge is, therefore, to discern whether irregular pressure profiles observed in coreflooding are due to clay layers expansion (swelling), fine release (e.g. clay deflocculation), or simply an indication of wettability state and relative permeability effect.

It is noted that during LSWF floods, after a period of injection, the differential pressure (DP) increased to a maximum value, followed by a relatively sharp decrease—but not in all cases. In cases where the increase in pressure drop was observed, no fine particle was detected in the sampling tubes. Nevertheless, this does not necessarily mean that fine migration did not take place in the core given their low permeability.

To better understand the pressure behavior during LSWF and get clarity and certainty on the clay stability and formation damage, we performed two additional sequential flooding experiments: in one experiment, a core 100 % brine saturated (no oil) is used (Fig. 8) and in another one, core is at  $S_{or}$  (Fig. 9). The goal was to determine the effect of injection brine salinity on core permeability and pressure increase over core, also when oil is present at  $S_{or}$ . The latter experiment is more realistic and indicates whether formation damage is minor or major when oil is present in the sample and clays are protected.

In Table 7, the results of permeability variation versus brine salinity, ranging from 240,000 ppm going down in steps to 1,000 ppm, are presented. According to the results, reduction of injection water salinity could cause some degree of permeability impairment in core, 100 % saturated with brine. For the low-salinity brine (~2,000 ppm) used in the study, the impairment ( $K/K_{init}$ ) is ~16%. In the other case where core was saturated with oil at  $S_{or}$  (Fig. 9), the reduction of permeability impairment in the presence of oil is likely due to coating of the clays by oil, which shields them from swelling and migration. It is expected that at higher oil saturations (as experienced in our coreflooding), the permeability impairment would be even less—similar results were reported by Mungan (1968) and Clementz (1977). For further verification, on three core samples from the flooding experiments (C2, C3, and C4), the (brine) permeability was measured after the experiment (see Table 8), which showed

**Table 7**Compatibility andformation damage experiments



**Fig. 9** Brine compatibility and formation damage experiment for a core at  $S_{or}$ . Salinity is reduced in steps from 240,000 ppm down to 1,000 ppm. At the end of each salinity step, stable pressure is reached

Salinity (ppm)	$\Delta P$ (mbar)	<i>K</i> / <i>K</i> <sub>init</sub>	Pressure increase (%)
I-Compatibility ex	periment (100 % b	rine saturated)	
240,000	1,010	0.997	_
24,000	1,025	0.98	1.5
10,000	1,045	0.96	3.3
8,000	1,065	0.94	5.2
6,000	1,085	0.92	6.9
4,000	1,106	0.9	8.7
3,000	1,136	0.87	11.1
2,000	1,206	0.8	16.3
1,000	1,266	0.74	20.2
II-Compatibility ex	xperiment (core @	Sor)	
240,000	1,004	0.996	_
24,000	1,014	0.99	1.0
10,000	1,024	0.98	2.0
8,000	1,044	0.96	3.8
6,000	1,064	0.94	5.6
4,000	1,084	0.92	7.4
3,000	1,114	0.89	9.9
2,000	1,136	0.87	11.6
1,000	1,176	0.83	14.6

4.8–9.9 % permeability reduction. The results of these experiments suggest that formation damage was minor in the floodings, while noting that the main clay type is kaolinite, which is not prone to swelling.

Another point is that when clay swelling and fine migration are significant, it is more likely that a notable and monotonically increasing pressure build-up across the core will be

<b>Table 8</b> (Brine) permeabilitypre- and post-experiment	Core ID (experiment)	Brine perm	neability (mD)	)
		Pre-test	Post-test	% Permeability decrease
	C2 (d0.01FW)	20.98	18.9	9.9
	C3 (d0.01FW+Surf.)	21.11	20.1	4.8
	C4 (d0.01FW+Alk.)	27.4	25.1	8.4

observed. The pressure profile obtained from the floodings showed close to regular behavior. The overall pressure during the LSWF-A and LSWF-S was slightly higher than with LSFW, simply because of higher viscosity of low salinity with alkali or surfactant. The pressure peak observed at early time during the LSWF, LSWF-A, and LSWF-S could be explained by pressure transient effect and total mobility effect caused by release of extra oil (oil bank formation) in the core. Oil bank has a lower mobility than the displacing brine. When the oil bank is produced, the pressure starts declining again.

#### 4.2 Capillary End Effect Contribution

Capillary end effects in coreflood experiments can, in some cases, significantly influence the computation of final saturation levels. Capillary end effects arise from the discontinuity of capillarity in the wetting phase at the outlet end of the core sample.

Our flooding rate was 1ft/day and was chosen to mimic actual reservoir flow conditions. However, it is known that coreflooding experiments at low rate and short core may suffer from capillary end effects where the swept oil is accumulated at the outlet of the core and cannot be produced due to negative capillary pressure gradient at the outlet. This effect is stronger for high permeability (contrary to what is commonly assumed, see for instance Masalmeh 2012) and more oil-wet samples. Therefore, oil recovery may be underestimated in the FW flooding step, and thus corrections are required. Unfortunately, many of the existing data on low-salinity flooding effect in the literature do not explicitly address (correct) this, and as a result in some cases, the reported low-salinity recoveries are overestimated. In particular, once surfactant or alkali is added to the injected low-salinity water, the IFT is reduced, which suppresses the capillary pressure. Hence, the capillary end effect is (significantly) suppressed and that leads to higher oil recovery. This is purely an experimental artifact, and the extra benefit in this case is unrealistic, since no capillary end effect is experienced in the field.

To get certainty on the recoveries obtained during low salinity with/without alkali or surfactant, one should clearly determine the capillary end effect contribution to the additional recovery. We therefore performed complementary experiments to determine the amount of oil held up in the sample by the capillary end effect during the flooding with FW at low rates (1 ft/day). An aged core of similar (brine) permeability and porosity to those used in the flooding experiments, saturated with oil and brine at connate water, was flooded sequentially with formation brine at multiple rates: 1, 2, 5, 8, and 10 ft/day—each for about 4 PVs to reach stable production. The differential pressure and oil recovery results in each step are shown in Table 9. As seen in this table, about 5.5 % OOIP of additional oil can be recovered by bumping injection rate ten times. This means the actual oil recovery with high-salinity FW is 5.5 % higher than reported in Table 10. Once the experiment is switched to low salinity, this unrecovered oil due to the capillary end effect can be produced. Assuming that low salinity (with surfactant or alkali) may have recovered most of the oil from the end effect due to the reduction of capillary pressure (via lowering IFT), a 5.5 % correction is applied on oil recoveries.

<b>Table 9</b> Capillary end effect           experiment: differential pressure	Capillary end effect experiment	nt	
(DP) and additional oil recovery versus injection rate	Additional oil recovery %	$\Delta P$ (mbar)	Injection rate (ft/day)
	0 (reference case)	2000	1
	2.5	3,000	2
	1	4,100	5
	1	5,200	8
	1	6,800	10

In low-salinity injection experiments (0.01FW) without any additional chemical, the pressure drop was overall only 260 mbar higher than the high-salinity formation brine step. According to Table 9, about 1,000 mbar pressure increase at 2 ft/day can recover 2.5 % additional oil. Therefore, the slight pressure build-up during low salinity is not enough to recover any substantial oil from the capillary end effect. This means that the oil recovery yielded from low-salinity brine cannot be attributed to formation damage, but to wettability alteration in the whole sample (more water wetness), leading to reduction of remaining oil saturation (ROS), plus a contribution from suppression of the capillary end effect. Nevertheless, due to the uncertain contribution of the end effect, we assume that 5.5 % correction is applied to all cases (bearing in mind that this is an upper limit for correction). A history matching study is required to determine the exact correction. Even with this assumption, we still arrive at a clear low-salinity effect (at least 3.5 % additional oil) for 0.01FW. For 0.1FW, we observe a low-salinity effect, which cannot be ignored, but since it is in the range of 5.5 % (estimated for capillary end effect), this correction makes the exact quantity doubtful. Therefore, for the 0.1FW case, we assume 'no significant' low-salinity effect.

#### 4.3 Further Analysis of the Core Flooding Experiments

The oil recovery obtained in the experiments occurred mainly in the first 2–3 pore volumes injected. The relevant observations during these experiments are discussed in the following:

## 4.3.1 pH Change

With the exception of the low salinity with alkali experiment, a minor increase in effluent pH was noted. While the effluent pH appears to be influenced by the presence of acidic crude oil, ion exchange with clay minerals, and the presence of calcite (4 wt%), dolomite (2 wt%), and albite (21 %) (which generally tend to create an alkaline solution at low-salinity conditions), the overall magnitude of the pH change is not enough to drive oil mobilization (by the mechanism suggested by Austad et al. (2010b)). Moreover, since the formation damage was small ( $\sim$ 5–10 % permeability reduction) in our experiments, it cannot also be the prime recovery mechanism, while small contributions ( $\sim$ 0.05–0.1%, calculated based on 5–10% permeability impairment) cannot be excluded. On the other hand, since electric charges and ion distribution around oil and clay are strongly affected by brine salinity, as shown from zeta potential data in Nasralla et al. (2011) and RezaeiDoust et al. (2011), other mechanisms related to the expansion of electric double layers (Ligthelm et al. 2009; RezaeiDoust et al. 2011; Abdulrazag et al. 2012; Mahani et al. 2014 and ion exchange processes with clay could account for the effect.

Table TO OILLOC	оvегу, <i>ப</i> т, ш <u></u> дп-заш.	table 10 On ICCOVERY, D1, ingu-saminty, and IOW-saminty Viscosity and capitaly number in Inording experiments	viscusity and capill	ary mumber in moo	ung experiments			
Case	HS flood rec.	LS flood rec. (without correction)	HS breakthrough $\Delta P$ @ End time (PVI) of HS (mbar)		ΔP @ End of LS (mbar)	Viscosity of HS (cp) @ 70°C	Viscosity of HS Viscosity of (cp) @ 70°C LS/LS+Alk./LS +Surf. (cp) @ 70°C	HS Viscosity of Capillary number C LS/LS+Alk./LS $(\mu_w v_w / \sigma_{ow})$ +Surf. (cp) @ $70^{\circ}$ C
d0.1FW	50	54.3	0.39	2,340	2,096	0.498	0.498	2.54E-07
d0.01FW	49	58	0.40	2,145	2,405	0.498	0.497	2.59E-07
d0.01FW + Surf.	51	73	0.42	2,360	2,455	0.498	0.57	8.04E-07
d0.01FW + Alk.	50	62.3	0.40	2,310	2,850	0.498	0.68	6.97E-07
d0.01FW (Crude B) 51.5	B) 51.5	57.6	0.42	2,452	2,511	0.498	0.497	3.4E-07

Table 10 Oil recovery, DP, high-salinity, and low-salinity viscosity and capillary number in flooding experiments

Note that the gradual increase in pH of the effluent observed during LSWF-S is due to the alkaline property of the surfactant solutions (pH = 7.6 at ambient conditions). The incremental increase in pH during a transient period is related to the propagation of surfactant solution through the cores.

#### 4.3.2 Effect of Chemical Properties of Oil

It is generally accepted that adsorption of polar compounds onto the rock surface has a significant effect on the wettability of reservoirs (Morrow 1990; Zou 1997; Tie and Morrow 2005; Zhang and Austad 2005; Fogden 2009; Hamouda and Chukwudeme 2009). In other words, the wettability of hydrocarbon reservoirs depends on the specific interactions in the oil/rock/brine systems. Naphthenic acids are the products of extensive oxidation of crude oil and play an important role in wettability control of reservoirs. Carboxylic groups in naphthenic acids from the crude oil are the most strongly adsorbed material onto the rock surface, and they may act as "anchor" molecules for other surface-active components present in the crude oil. However, there is only limited knowledge of the influence of organic acids on the three-phase system of oil/brine/rock.

Different reservoirs contain crude oils of widely varying TANs and TBNs, and hence they exhibit different interactions between the fluids and the rock minerals. Skauge et al. (1999) showed that the acidic and basic components also play a major role for wettability alteration. Denekas et al. (1959), Crocker and Marchin (1988), and Dubey (1993) have also studied the implications of acid/base content on wettability alteration of different surfaces, where crudes with higher acid number generated more oil-wetting cores; however, this is not generally valid, as low acid number crudes also produced oil-wet conditions depending on brine salinity and divalent compositions.

In our study, in order to establish a wide range of initial wetting conditions, two types of crude oil with different concentrations of polar components (TAN and TBN) were used: (a) oil A with TAN = 2.683 mg of KOH/g and TBN = 0.42 mg of KOH/g, and (b) oil B with TAN = 0.842 mg of KOH/g and TBN = 0.21 mg of KOH/g. The crude oil designated B has a lower ratio of TAN/TBN and has been used for investigation of the influence of type of crude oil on low-salinity effect. The low-salinity effect was observed for both crudes, 9.5 and 5.6 % for crude oil A and B, respectively. Lower recovery for crude B may be because of lower acid number/base number ratio and is in line with the findings of Hadia et al. (2012), which showed that production behavior during low-salinity flooding indicated that the different oil variants established different wetting conditions.

While the presence of acidic components (higher TAN/TBN ratio) seems to provide a more favorable environment for low-salinity tertiary flooding, TAN and TBN are not properly descriptive of crude oil polar components. Therefore, other types of analysis are required to understand which polar oil components are responsible for low-salinity effect.

#### 4.3.3 Comparison of Alkali- and Surfactant-Improved Low-Salinity Waterflooding

The motivation to combine alkali with low salinity as a new hybrid method was to achieve higher oil recoveries in low-salinity flooding, while remaining cost effective. That is why small quantities (1 wt%) of chemical are used.

The main mechanism of oil recovery in alkali flooding has been reported to be related to IFT reduction by means of in-situ formation of petroleum surfactant (soap) through reaction of alkali and crude oil (Hawkins et al. 1994; Fadili et al. 2009). The combined alkali/low

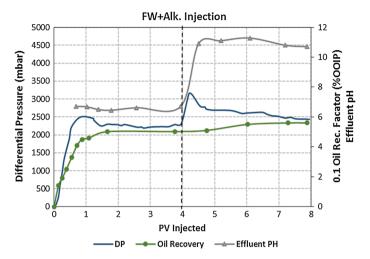


Fig. 10 Oil recovery, effluent pH, and pressure drop versus pore volume injected in  $FW \rightarrow FW + Alk$ . flooding

salinity thus has the benefit of mobilizing more oil both by low-salinity effect and wettability alteration on one hand, and by reducing capillary trapping or re-trapping because of lower IFT provided by alkali on the other hand. Lower IFT can potentially destabilize the oilbrine interface and reduce re-trapping of the mobilized oil by low salinity. Re-trapping of oil can occur in water-wet and smaller pores where capillary pressure is stronger. Our data indicate that addition of 1 wt% NaOH to d0.01FW brine reduced IFT about 2 times and increased capillary number about 2.7 times (see Table 10—capillary numbers). This explains the increase in oil recovery and suggests that small quantities of alkali can be effective. Further investigation by mixing the same amount of alkali (1 wt%) with FW and injection in tertiary mode after FW indicated that the process is not as effective. The recovery curve is depicted in Fig. 10. The FW recovery is 50.2 % OOIP, and total recovery by FW + Alk. is 56 % OOIP. The low recovery in this case is because (1) low-salinity effect is not produced with FW, (2) above-optimum salinity results in large IFT, and (3) there is the possibility of high adsorption of the generated surfactant at high salinity.

The experiment performed with surfactant (LSWF-S) confirms the effect observed by Alagic and Skauge (2010) as a low-salinity flooding enhancer. However, in our study, the combined low-salinity water and chemical was applied immediately after FW without preflush. When surfactant was combined with FW and injected after FW, it yielded considerably lower recovery (see Fig. 11). In this case, the recovery with FW was 50.5 % OOIP and with FW+Surf. was 60 % OOIP, which is about 12 % less than that achieved with dFW0.01 + Surf. Lower recovery can be explained by similar arguments, as in the case of FW+Alk.

Comparison of the recoveries from LSWF-A and LSWF-S shows higher improvement with surfactant than with alkali. According to Fig. 1 and Table 5, this is conceivable because of larger reduction of IFT (and larger capillary number by surfactant than with alkali), and therefore producing a better effect. What still makes alkali/low-salinity flood attractive is the lower costs of alkali, since surfactants are typically expensive.

#### 4.3.4 Other Considerations in LSWF-A

An important consideration in alkali flooding is related to the alkali reaction with clay minerals. This reaction depends on brine salinity and the presence of (adsorbed) divalent cations

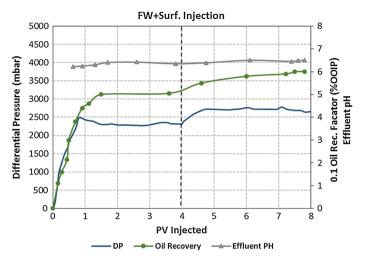


Fig. 11 Oil recovery, effluent pH, and pressure drop versus pore volume injected in  $FW \rightarrow FW + Surf.$  flooding

such as  $Ca^{2+}$  and  $Mg^{2+}$  on the clays. When divalents exist, alkali reaction with rock results in precipitation. Reaction with divalents on the clays consumes the alkaline solution as it moves through the reservoir. Besides, there exist other complications such as ion exchange and hydrolysis, congruent and incongruent dissolution reactions, and insoluble salt formation by reaction with hardness ions in the pore fluids (Sheng 2011). These phenomena (reactions, precipitation) can cause pressure increase in the core (formation damage). These effects could be significantly reduced in a low-salinity environment, as used in this study.

Nevertheless, if the concentrations of alkali and brine salinity/composition are designed properly and according to the oil chemistry, the alkali flooding could result in favorable recovery. Our promising results on combining low salinity and alkali flooding processes, therefore, call for further investigation and optimization.

#### 5 Summary and Concluding Remarks

- (1) Low-salinity brine, obtained by dilution of formation brine 10 and 100 times, resulted in additional oil recovery of about 1–4 % OOIP in tertiary mode flooding. Complementary tests suggested minor damage to the core, thus no major contribution to oil recovery from this mechanism.
- (2) Without evaluation of the capillary end effect (either by dedicated experiments like ours or by multi-rate injections during each flooding process), EOR recovery factors could be overestimated. In this study, the end effect contribution was estimated to be  $\sim$ 5.5 % OOIP. Based on our analysis, this can be an upper limit, although it still resulted in clear low-salinity recovery.
- (3) Usage of two types of crude oils with different acid/base numbers showed that smaller recoveries are obtained with the oil having lower TAN/TBN ratio. Clearly, the existence of polar oil components (e.g., acid groups) is important in this process and affects the rock wettability. Nevertheless, TAN/TBN alone is not descriptive of oil composition and does not indicate which polar groups are responsible for the effect. Further study is required to understand this.

- (4) No major pH change was observed in the flooding experiments with low salinity (except with those containing surfactant/alkali, which is expected). The pH change was within one pH unit, which is not sufficient to desorb polar groups or mobilize oil via mechanisms similar to the effect of alkali flooding or saponification. Nevertheless, in our opinion, the pH change is an effect of the low-salinity mechanism, not necessarily the cause.
- (5) Combining low-salinity water with alkali, improved oil recovery by ~7 % OOIP compared to ~3.5 % OOIP (both corrected) with low-salinity flooding alone. The additional recovery is attributed to IFT reduction via in-situ soap generation and makes LSWF-A a promising hybrid EOR concept. Besides, the low-salinity environment in the core reduces adsorption of in-situ generated surfactant.
- (6) Comparison of alkali and surfactant recoveries, 7 % versus 17 %, respectively, indicates that surfactant is more effective (i.e., resulting in lower remaining oil saturation) than alkali, potentially achieving a lower IFT for the addition of an equal amount of alkali or surfactant to brine (higher capillary number with surfactant). Nevertheless, surfactant is more expensive than alkali to apply.
- (7) Since the main objective of the paper was to investigate possible improvements of 'low salinity process,' while limiting the consumption of chemicals, we did not aim to investigate low/ultra-low IFT cases as often considered in ASP or surfactant flooding. Further improvements are possible by applying the process in secondary mode to achieve higher recoveries, viscosifying brine by adding polymer, optimizing alkali/surfactant type and concentration, and manipulating brine salinity and composition to optimize IFT.

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