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Effect of crude oil ageing on low salinity and low salinity surfactant flooding

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ABSTRACT

Injection of brine with lower salinity than the connate brine has proven to give a moderate increase in oil recovery in sandstones. Recent research has shown that this process will significantly benefit from introducing surfactant optimised for low salinity environment.

The mechanisms underlying increased recovery by low salinity brine injection are not yet fully understood. However, research to date suggests that they are related to complex crude oil/brine/rock interactions. With this in mind, the present paper investigates primarily how the extent of oil recovery from Berea sandstones subjected to long term exposure of crude oil is influenced by (1) low salinity water injection and (2) combined process low salinity water injection with surfactant flooding.

Core displacement tests were conducted on four Berea cores (30 cm), two in a natural state and two that had been subject to extensive crude oil ageing at high temperature. Results obtained from different flooding steps are discussed in terms of oil recovery and effluent properties including turbidity, pH- and ion analysis (Na^+, Mg^{2+}, Ca^{2+}). The results effectively illustrate that oil recoveries from the aged cores are higher during both low salinity water injection and low salinity water injection combined with surfactant flooding. An assessment of how tertiary oil recovery in aged and unaged cores varies with surfactant concentration is also presented.

Effluent ion analysis from low salinity water floods showed that Mg^{2+} ions were strongly retained in the aged core while Ca^{2+} ions were being produced from both aged and unaged cores. The latter was attributed mainly to calcite dissolution. Results obtained from pressure profiles, effluent ion analysis and turbidity tests suggest higher production and elution of fine particles from the unaged core.

1. Introduction

In recent years, low salinity water flooding has received considerable attention as a new EOR method (Tang and Morrow, 1997; Morrow et al., 1998; Sharma and Filoco, 2000; Lager et al., 2006; Zhang et al., 2007; Webb et al., 2008). In general, recovery is reported to be higher for low salinity brine injection compared to injection of sea water or high salinity produced water. Results from about 30 core floods performed in BP's laboratories show incremental recoveries ranging from 5 to 40% OOIP (Webb et al., 2008). Also, the potential of low salinity water injection into oil fields has also been tested by SWCTT (Lager et al., 2008; Skrettingland et al., 2010). A number of hypotheses as to why injection of low salinity water should give an increase in recovery have been put forward. This includes multi-component ion exchange, wettability alteration, fines migration and increasing pH. Evidence in the literature goes against either fines migration or increasing pH as being the only mechanisms since they are features associated with some, but not all, successful low salinity floods (see Lager et al., 2006, and references cited therein).

Several authors have reported on the effect of wettability on oil recovery (see e.g., Craig, 1971; Anderson, 1987a; Jadhunandan and Morrow, 1991). With respect to waterflood recovery, a water-wet system is characterised by no oil production after water breakthrough (WBT). An oil-wet system typically displays early water breakthrough, with significant production after WBT. Further, a maximum in oil recovery has been found at near neutral wettability (Morrow et al., 1986; Anderson, 1987b; Zhou et al., 1995, 2000; Yildiz and Morrow, 1996; Tang and Morrow, 1997). Tang and Morrow (1997) and Morrow et al. (1998) showed an increase in the amount of spontaneous water imbibition and total waterflood recovery with decreasing brine salinity for Berea sandstone cores. The cores had been aged in reservoir crude oils, and reservoir brines and dilutions of these were used during waterflooding. Based on these results, increased oil recovery by low salinity flooding appears to be correlated to the system becoming more water-wet.

In the pH ranges typically encountered in sandstone reservoirs, both the crude oil/brine and the rock/brine interfaces are negatively charged. One would therefore expect repulsion between the crude oil–brine and rock–brine interfaces (see e.g. Anderson, 1986; Buckley et al., 1989). However, multivalent ions in the brine such as Ca^{2+} and

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Mg^{2+} can act as bridges between the negatively charged crude oil–brine and rock–brine surfaces, leading to crude oil adsorption and decreased water-wetness (Buckley et al., 1997; Liu and Buckley, 1997; Buckley et al., 1998).

If clays are contacted by a water phase with which they are not in ionic equilibrium, such as when brine with a salinity that differs from the connate brine salinity is injected, ions are exchanged between them until a new equilibrium is established. This process is referred to as ion exchange or multi-component ion exchange. This can lead to (1) detachment of clay particles from pores leading to fines migration and/or (2) destabilisation of oil layers adsorbed to the pore walls. Cation exchange between mineral surface and the invading brine can be studied by analysing the effluent brine composition during low salinity waterfloods. Based on such analyses, Lager et al. (2006) concluded that cation exchange between the mineral surface and the invading brine is the primary mechanism underlying the improved waterflood recovery seen by low salinity brine injection.

Surfactant injection is a well-known method for obtaining increased oil recovery. Surfactant injection improves oil recovery by lowering the oil–water interfacial tension (IFT), and thus prevents oil from becoming capillary trapped and/or remobilises the trapped oil. Success criteria for a chemical injection process include high incremental oil recovery and low retention of surfactant. High recoveries are expected for flow at high capillary number, i.e. at low IFT (see f. ex. Lake, 1989 and references cited therein). Surfactants that give low IFT at low salinities are more readily available and less expensive than those that are efficient in high salinity brine. In addition, surfactant retention increases with increasing salinity (Friedmann, 1986).

Based on the positive results from low salinity waterflooding, and the possibility of further increasing the efficiency of this process by adding surfactant, Alagic and Skauge (2010) presented a hybrid EOR process combining the effect of low salinity (LS) brine and surfactant injection in a combined low salinity brine and surfactant (LS-S) injection process. The idea is that a more efficient oil recovery process can be obtained by combining destabilisation of oil layers during a LS water injection with a low IFT environment that prevents re-trapping of the mobilised oil.

The present study compares the effect of combined low salinity and surfactant injection on oil recovery in aged and unaged Berea cores. Attention is also given to effluent ion analysis to detect differences, if any, between effluent composition during LS injection in aged and unaged cores. Further, long cores, which minimise capillary end-effects, were used to confirm the results found by Alagic and Skauge (2010) on short core plugs.

2. Materials and methods

2.1. Fluids

Sea water (SW) with the composition given in Table 1 was used initially to saturate the cores and represents the high salinity water. The low salinity brine (LS) contained 0.5 wt.% NaCl. An internal olefin sulfonate (Enordet O242L, Shell Chemicals) was the surfactant formulation used in this study. The composition of injection solution during low salinity surfactant flooding was 0.50 wt.% NaCl mixed with surfactant and co-solvent (iso-amyl alcohol) added in a 1:1 weight ratio. Two sets of surfactant concentrations, i.e., 0.4 wt.% and 1.0 wt.%, were used to obtain objectives of this work.

Table 1
Composition of high salinity brine (SW).

	Conc. (ppm)
Na^{+}	11,159
Ca^{2+}	471
Mg^{2+}	1329
Cl^{-}	20,130
HCO_3^{-}	142
SO_4^{2-}	2740
K^{+}	349

Table 2
Physical properties of Berea cores.

Core ID	L (cm)	D (cm)	ϕ (%)	PV (ml)
B1	26.0	3.73	20.4	58.15
B2	24.0	3.73	20.0	52.58
B3	29.2	3.76	18.5	59.93
B4	29.7	3.76	18.5	63.25

2.2. Dynamic displacement experiments

Four long Berea cores, B1 through B4, have been used in this work. Their physical properties are reported in Table 2. During preparatory work, all cores were dried at 70 °C to constant weight. Afterwards, they were mounted in long core holders with 30 bars confining pressure, saturated with sea water (SW), and equilibrated for three days at ambient temperature. Initial water saturation, S_{wi}, was established by continuous injection of highly viscous mineral oil, Marcol 152. During this process, the pressure drop across the cores never exceeded 20 bars. The initial water in the cores will be referred to as connate water. The drainage process was carried further by continuous flooding for 5 PV in the opposite direction, in order to obtain homogeneous water distribution in the cores. Finally, the mineral oil from the cores was replaced with crude oil A1 (properties are given in Table 3).

Cores B1 and B3 were aged for 3 weeks at 90 °C. After ageing, fresh crude oil was injected in both directions. Cores B2 and B4 were used in their natural state and were not subject to ageing.

Two floods were performed on each core. The first flood was a continuous injection of low salinity brine to remaining oil saturation, while the second flood was a combined low salinity and surfactant flood (LS-S). Remaining oil saturation after waterflooding was considered to be obtained when water cut values were high and stable over time. Following this, the LS-S flood was then initiated and run by continuous injection until high and stable water cuts were obtained. Properties of the injection fluids are presented in Table 4.

In the low salinity water injection step we chose an injection fluid containing only monovalent ions (Na^{+}) to obtain a maximal change in the concentration of divalent ions (Ca^{2+} and Mg^{2+}) between the low salinity brine and sea water. In the LS-S step, a sulfonate surfactant was added to the low salinity brine. It is well known that the properties of sulfonate surfactant solutions (e.g., solubility, interfacial tension, retention) are greatly improved in the absence of divalent cations, which is another motivation for choosing a simple sodium chloride solution as the low salinity brine solution (see e.g., Alagic and Skauge, 2010).

Identical flooding conditions, i.e. ambient temperature, gravity stable displacement, and 0.1 ml/min nominal flooding rate were carried out in all floods. Further, a backpressure of 5 bars was applied to avoid formation of gas by light ends in the crude oil. The pressure

Table 3
Properties of crude oil (filtered oil).

Crude oil ID	ρ 20 °C (g/cm^3)	μ 20 °C (mPa·s)	AN (mg KOH/g oil)	BN (mg KOH/g oil)
A1	0.8784	13.80	2.84 ± 0.01	0.95 ± 0.10