Monitoring Chemical EOR Processes
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Abstract
A laboratory study on core plugs from a carbonate field confirmed the efficacy of an alkaline surfactant (AS) formulation at reservoir conditions. Continuous monitoring of remaining oil saturation (ROS) in short core plugs using spatially resolved nuclear magnetic resonance (NMR) can provide insights into the processes by which surfactants release post-water-flood remaining oil. In single short plugs, volumetric averages do not correctly quantify remaining oil due to capillary end effects (high remaining oil saturation post water flood observed at the outlet face of the plug), oil banks, and other flow heterogeneities. These effects are all quantifiable by NMR, allowing accurate monitoring of ROS. Here, consistent ROS values are obtained in the laboratory, in single-well pilots, and in single-well chemical-tracer (SWCT) tests. Laboratory core floods with nuclear magnetic resonance (NMR) monitoring at low magnetic fields therefore provide a valuable calibration of the NMR logs, in addition to the direct assessment of ROS. Corroboration across multiple length scales, spatial resolution, and correspondence with preferred logging measurements, all contribute to the value of NMR-monitored core-floods as a complement to field pilot studies.

Introduction
Monitoring the efficacy of enhanced oil recovery (EOR) processes is an important step in the screening of new chemical agents. This screening process begins at the laboratory scale (Stoll et al. 2011). It is important to understand both the liquid-liquid and liquid-rock interactions. A possible EOR agent is identified and then adjusted to provide the required fluid-phase behavior for a given set of reservoir conditions (temperature, salinity, crude composition, restore reservoir wettability). The role of surfactants is to reduce the interfacial tension (IFT) between oil and water; this is a critical requirement of the chosen formulation. The alkaline converts some of the oil into surfactant, further reducing the oil/water interfacial tension. Laboratory-scale core floods constitute the next stage of screening to explore liquid-rock interactions before reservoir pilots. Here, the alkaline alters the charge of the rock surface to reduce surfactant adsorption.

Nuclear magnetic resonance (NMR) is a powerful tool for assessing remaining oil saturation (ROS) during EOR both in the reservoir—via NMR logging—and in the laboratory with a low-field bench-top instrument. Quantitative EOR evaluation has been demonstrated on short plugs at the laboratory scale using spatially resolved low-field NMR. The spatial dimension is important at all EOR piloting length scales, but is critical when studying short plugs where bulk volumetrics may be dominated by capillary or geometry end effects and yield inaccurate ROS values. At the laboratory scale, it is usual to construct long composite cores (length > 30 cm [12 in.]) from plugs to reduce the significance of end effects and other flow heterogeneities on bulk assays of remaining oil (e.g., effluent gravimetrics). Commercial NMR systems are not suited to bulk measurements of such long samples, thereby requiring some form of mechanical scanning to explore the entire core. Such methodology prevents continuous monitoring of ROS during a core flood. In the laboratory, NMR offers the capability to spatially resolve the distribution of ROS within a short core plug (length = 5 cm [2 in.]). Previously, we demonstrated the quantitative measurements of ROS, consistent with well logs, in such short plugs by monitoring a central portion of the plug expected to be free from capillary or geometry end effects. Magnetic resonance imaging (MRI) of core plugs has been unsuccessful as a probe of ROS; implemented at high field, the solid/fluid magnetic susceptibility contrast prevents quantitative assay of in-situ liquid volumes, and limits the practical spatial resolution, preventing pore-scale imaging. The history of MRI in special core analysis (SCAL) is given by Mitchell et al. (2013b). Here, we use a low-field permanent magnet ($B_0 = 50$ mT [500 G]) to obtain a spatial distribution of oil saturation in a profile (single image axis). The signal-to-noise ratio
(SNR) achievable on such a system is comparatively poor to, say, a 1.5 T medical imaging scanner, and this limits the usable spatial resolution. Notwithstanding, it is possible to observe flow heterogeneities of interest occurring on the millimeter to centimeter length scales.

For this case study, core plugs were obtained from a microporous carbonate (limestone) layer within a North Oman field. An alkaline surfactant (AS) formulation was chosen for compatibility with the light crude and low-salinity brine. The core floods were monitored using rapid NMR measurements of spatially resolved $T_2$ relaxation time distributions, providing direct comparability to the data acquired in a standard NMR well log, albeit on a smaller length scale (Mitchell et al. 2012a; 2012b; 2013a). The combination of light oil in a weakly relaxing carbonate formation makes liquid-phase separation challenging in the NMR experiment. Consequently, NMR liquid-phase contrast was obtained by heavy water ($\text{D}_2\text{O}$) substitution in all aqueous liquid-phases. As the NMR signal is obtained only from $^1$H, heavy water is not observed. Brine and AS solution were flowed continuously through the core plug at a flow rate consistent with reservoir transport some distance from the well bore. NMR relaxation time profiles were acquired continuously throughout the flood. Even though the NMR measurement was sensitive only to the oil, the inclusion of a relaxation time measurement allowed the remaining oil volume to be quantified.

A corresponding single-well in-situ EOR pilot was performed in the reservoir by Edwards et al. (2011). Injectivity problems resulted in a small flood zone for which the vertical resolution of NMR logging was inadequate. NMR logging was carried out prior to injection, but logging after injection was abandoned. Wideband dielectric measurements, with their finer spatial resolution, then became the measurement of choice. Nevertheless, in the absence of injectivity problems, the combination of joint diffusion-relaxation NMR measurements, and wideband-dielectric measurements, remains a viable combination for the single-well in-situ EOR pilot, and the laboratory NMR response at various stages of the flood is of high value for full interpretation of the downhole data. ROS values were also obtained from single-well chemical-tracer (SWCT) tests conducted in the same formation. Two core floods were completed in the laboratory with differing volumes of AS injection. In the first flood, a large volume of AS was injected to mimic the observations of the wireline tools being sensitive only to saturation states near the well bore. In the second flood, a smaller quantity of AS was injected to emulate the EOR process farther away from the well bore. The availability of data over a range of length scales (laboratory to field) allows a comparison of these different methods for assessing EOR agents.

**Materials**

**Brine.** The same synthetic brine, formulated using $\text{D}_2\text{O}$ (Aldrich Chemicals), was used in both the formation and injection water. A variety of sodium and potassium salts were included and the final brine preparation had a total dissolved solids content of approximately 10 g dm$^{-3}$; the concentrations are given in Table 1. At the reservoir temperature of 69ºC, the brine had a density of $\rho_w = 1.061$ g cm$^{-3}$. The AS solution ($\text{D}_2\text{O}$) contained 0.3 wt% tridecylalcohol propoxy sulfate (Petrostep S-8A surfactant, supplied by client), 3 wt% diethylene glycol monobutyl ether (DGBE co-solvent, supplied by client), and 1.75 wt% sodium carbonate (alkali; Aldrich Chemicals). The AS density at reservoir temperature was $\rho_{\text{AS}} = 1.107$ g cm$^{-3}$.

**Crude Oil.** The dead crude oil was mixed with hexane at 35 wt% to emulate the viscosity of live crude oil downhole. No visible precipitation of asphaltenes occurred. At the reservoir temperature the crude had a density $\rho_o = 0.7413$ g cm$^{-3}$ (API gravity 49.6º). The viscosity of $\eta_o = 1.87$ mPa s was determined at ambient conditions (elevated temperature measurements were not practical due to the volatile content). The crude/AS IFT was measured from ambient to 48ºC [118ºF], where $\gamma_{\text{oil}} = 0.01$ mN m$^{-1}$, using a DataPhysics SVT20N spinning drop tensiometer; based on these results, an ultra-low interfacial tension (ULIFT) $\gamma_{\text{ulift}} \approx 0.003$ mN m$^{-1}$ was predicted at the reservoir temperature (Mitchell et al. 2012b).

**Carbonate Core Plugs.** The carbonate core plugs were well consolidated with a uniform texture. The pore structure was dominated by microporosity and visually free from macroscopic defects such as vugs. The core plugs were cleaned following a standard Soxhlet procedure. Gas porosity and Klinkenberg permeability measurements were made on the cleaned, dried plugs. The physical properties are summarized in Table 2. The plugs were vacuum saturated with the synthetic brine for 12 hours before being spun under oil in a centrifuge at 7500 rpm for 36 hours. The initial oil saturation was determined volumetrically as $S_o = 93$ s.u. (saturation units). High oil saturation was achieved due to the large density contrast between the oil and $\text{D}_2\text{O}$ brine. The plugs were aged for 4 weeks in oil at 69ºC and 275 kPa [40 psig] in an attempt to restore downhole wettability. This restoration process was at least partially successful as oil-wet capillary end effects were observed in the NMR monitored core floods.

**Experimental Method**

NMR transverse ($T_2$) relaxation times are the archetypal well logging acquisition protocol. The exponential time constant $T_2$ is encoded in the amplitude of spin echoes, generated by a train of radio frequency (rf) pulses; this experiment is the Carr-Purcell Meiboom-Gill pulse sequence (Carr and Purcell 1954; Meiboom and Gill 1958). The $T_2$ of a liquid confined in a porous material is sensitive to the local geometry (pore size) and chemistry (liquid-phase). If a single liquid saturates a core plug, the range of $T_2$ relaxation times observed can be used to infer a distribution of pore sizes. In the case of oil recovery monitoring, multiple liquid phases are present, and $T_2$ is used to separate the contributions from oil and brine in the NMR signal. Here,
signal is obtained only from the oil and will be weighted according to spin relaxation occurring at the solid/liquid interface. To determine the saturation, a $T_2$ distribution is generated following the method given by Wilson (1992). The integral area under the distribution is proportional to ROS; the scaling constant is obtained from a $T_2$ measurement of a known volume of bulk crude.

Spatially resolved $T_2$ profiles were acquired using the multi-echo imaging sequence of Majors et al. (1997). A schematic of this NMR pulse sequence is shown in Fig. 1. Spatial position is encoded by the application of a magnetic field read gradient according to Callaghan (1991). The observed spins precess at a frequency determined by their local magnetic field, so the measured spin echo contains frequency components associated with each spatial position in the sample; hence this imaging technique is referred to as “frequency encoding.” A Fourier transform of the spin echo shape provides a profile of the sample. As multiple profiles are acquired in an echo train, the signal obtained at each spatial position decays with $T_2$. Numeric inversion of the signal decays yields a $T_2$ distribution for each pixel in the profile. We refer to these data as $y$-$T_2$ maps, where $y$ is the Cartesian coordinate along which the profile is acquired; in this case, the long axis of the cylindrical core plugs. Details of the processing methods used to generate the $T_2$ profiles are given by Mitchell et al. (2013a). The alternative imaging method of phase encoding could be used; this offers improved SNR per scan and shorter echo spacing as described by Mitchell et al. (2013b). However, depending on the required SNR and number of pixels, a phase-encoded $T_2$ profile can be slower to acquire. We have used this method previously in a brine-only core flood by Mitchell et al. (2013a).

All the NMR experiments were conducted on a bench-top permanent magnet operating at $B_0 = 56$ mT [560 G], corresponding to a resonant frequency of $f_0 = 2.4$ MHz for $^1$H. The magnet was equipped with a 53 mm [2.1 in.] diameter solenoid rf resonator and single-axis ($y$) magnetic field gradient coils. Acquisitions of NMR $T_2$ profiles and bulk CPMG measurements were interleaved; data were acquired continuously throughout the flood. The bulk CPMG experiments were performed with the following parameters: $n = 1024$ and $2\tau = 0.3$ ms. Each CPMG decay was acquired in 5 minutes. $T_2$ profiles were acquired with the following parameters: $n = 128$, $2\tau = 1$ ms, $g = 27$ mT m$^{-1}$ [2.7 G cm$^{-1}$], 64 pixels, and a dwell time of $\Delta t = 0.01$ ms. The resultant field of view (FOV) in the profiles was $FOV = 8.6$ cm [3.6 in.] with a resolution of $\Delta y = 1.3$ mm [0.05 in.]. Each $T_2$ profile was acquired in 15 minutes. NMR data acquisitions were completed every 20 minutes during the core-flood.

Two complete floods were performed on plugs A and B; see Table 3 for details. The floods were nominally equivalent except in the volume of injected surfactant. Plug A was subjected to a large volume of AS, 8 PV (pore volumes), to emulate oil displacement near the well bore, as explored by the wireline tools in single-well pilots. The flood of plug A is therefore our comparator against results obtained in the reservoir. Plug B was subjected to a reduced AS flood of 2.2 PV to investigate the oil displacement efficacy that might be expected further from the well bore when the concentration of active surfactant has been reduced by adsorption on rock grains or portioning into the oil.

For the duration of the core-floods, the plugs were confined in an NMR-compatible core holder. Temperature and confining pressure were supplied by a perfluorinated oil. The confining pressure was raised by dual-cylinder piston pumps configured for continuous flow. The core floods were performed at the reservoir temperature of 69ºC [156 oF] and an isostatic confining pressure of 3 MPa [435 psi]. A single-cylinder piston pump was used to inject the flooding fluids at a constant volumetric rate of 0.084 cm$^3$ min$^{-1}$ [1 ft/day in the formation]. Each flood proceeded in the order: brine, AS, brine; the injection of the AS causes notable changes in the oil saturation: the bulk remaining oil is observed as the AS mobilizes and reduces oil saturation as brine injection continued. A capillary end effect (high remaining oil at end of water flood, $S_w(c)$) is observed as the AS mobilizes and transports trapped oil through the plug. Continued injection of AS resulted in further displacement of oil at the inlet region, attributed to the transport of a microemulsion. The final, bulk oil saturation after further brine flooding was $S_w = 15$ s.u.

**Results**

**Laboratory Core Floods.** The spatial variations in oil saturation along plugs A and B are shown in Fig. 2 as a function of flood progress (PV of injected fluid). First, we consider the oil recovery process in plug A. The recovery protocol, given in Table 3, included the injection of 8 PV AS. This flood is therefore an emulation of the recovery expected at the well during a local pilot (as observed by wireline logs). Approximately 62 s.u. oil is recovered during the initial brine flood and a long tail of reducing oil saturation is observed as brine injection continued. A capillary end effect (high remaining oil at end of water flood, $S_w(w)$) is observed at the outlet face of the plug due to the change in wettability and permeability between the rock and the core-holder distribution plate. The injection of the AS causes notable changes in the oil saturation: the bulk remaining oil saturation is reduced from $S_w(w) = 27$ s.u. (remaining oil at end of water flood) to $S_w(c) = 18$ s.u. (remaining oil at end of chemical flood), and the capillary end effect is removed. An oil bank (increase in local $S_w$) is observed as the AS mobilizes and transports trapped oil through the plug. Continued injection of AS resulted in further displacement of oil at the inlet region, attributed to the transport of a microemulsion. The final, bulk oil saturation after further brine flooding was $S_w = 15$ s.u.
An almost identical recovery process is observed in plug B with the exception that the reduced volume of injected AS (2.2 PV) did not elicit additional recovery at the inlet region of the plug. Notwithstanding, the other salient features were observed (oil bank formation, removal of capillary end effect), indicating that the AS can be expected to enhance oil recovery away from the injector well. The differential pressure across plug A during the initial brine injection stabilized around Δp = 70 kPa [10 psi] which decreased to Δp = 20 kPa [3 psi] during the AS injection, see Figure 3. No subsequent increase was observed, contrary to the poor injectivity found in the field by Edwards et al. (2011). Similar pressures were observed for the EOR process in plug B.

The influence of capillary end effects on the bulk oil saturation determined in such short plugs can be negated by considering recovery in a central region of the plug (Mitchell et al. 2012a; 2012b; 2013a). In Fig. 4, we divide the plug profiles into three regions of equal volume (inlet, middle, and outlet) and consider the oil recovery from each third separately. This detailed analysis is possible only with the inclusion of a spatial dimension in the NMR experiments. The middle third is indicative of recovery occurring independent of capillary end effects where the final oil saturation at the end of the flood is S_w = 17 s.u. This oil saturation is the same in the outlet third once the AS has removed the capillary end effect, but prior to AS injection the oil saturation in the inlet third is approximately 5 s.u. higher than in the middle and inlet thirds. On AS injection, the formation of an oil bank is observed, and its progress is visible through the inlet, middle, and outlet thirds. By the end of the flood, the oil saturation at the inlet third is lower than the middle/outlet thirds at S_w = 12 s.u. In a plug of infinite length (reservoir), such that end effects are negligible, ROS of S_w^(w) = 25 s.u. and S_w^(c) = 17 s.u. based on the middle third results obtained by NMR monitoring of a short plug. However, gravimetric effluent assays from the same short plug would suggest S_w^(w) = 27 s.u. and S_w^(c) = 15 s.u. at the end of the flood. Although these two sets of values are not different greatly, the bulk measurement contains no information on the distribution of oil or the significance of end effects on the measured ROS values.

Progress of the AS through the plugs is determined through a combination of careful NMR CPMG measurements and effluent analysis. Although the NMR measurement is not sensitive enough to detect the active surfactant component directly, the DGBE cosolvent is present in sufficient quantities to be observed as a short relaxation time component in a T2 distribution on AS injection. This short relaxation time is used to distinguish the oil and cosolvent, allowing a correctedbulk remaining oil saturation to be calculated; see Fig. 5. The cosolvent present in the rock is persistent at a saturation of 3 s.u. during the AS injection, consistent with the concentration of DGBE in the bulk AS formulation. We assume, therefore, that the cosolvent does not become trapped in the rock or associate with slow moving oil. The same level of analysis was not possible with the T2 profiles due to the low SNR and long echo times associated with these data.

The progress of the cosolvent through the rock is not intrinsically related to the progress of the active surfactant component in the AS. The recovery of the surfactant was determined by analysis of the effluent. The variation in surfactant concentration observed for plug A is shown in Fig. 6. There is a slight delay (equivalent to 1.5 to 2 PV injected fluid) between the start of the AS injection and significant surfactant recovery, suggesting the surfactant is held up in the rock, possibly due to partitioning into the oil or association with a microemulsion. The total surfactant recovery was equal to 78 % of the injected volume, although continued brine flooding may have recovered more. In plug B, where 2.4 PV of AS were injected, only 55 % of the surfactant was recovered, suggesting an initial portion of the surfactant is adsorbed or partitions into the oil.

This study shows the importance of a spatial resolution of the flood geometry in addition to the measurement of oil saturation. Liquid-phase-specific NMR provides the saturation; MRI methods provide the spatial resolution. The combination of saturation with spatial resolution is also important at larger length scales.

**Field Pilots.** The single-well in-situ EOR evaluation (Arora et al. 2010; Edwards et al. 2011; Ramamoorthy et al. 2011) followed a log-inject-log protocol, wherein a small volume (1 PV) of brine then AS was injected into the formation near the well-bore. Logging was performed by a combination of NMR, array dielectric dispersion, and electric image. The single-well in-situ EOR evaluation can be completed in 2 days, depending on well and reservoir conditions, thereby minimizing cost compared to SWCT with a typical duration of 4 weeks. An electric image of the flooded zone and visualization of the resultant oil bank accompanied saturation logs by wireline NMR and array dielectric dispersion. The electric image logs enable the determination of when the tool-sensitive volumes are completely in the flooded zone. Interpretation of ROS without knowledge of the flood geometry puts the results in doubt. The NMR log after AS injection was abandoned because antenna resolution was insufficient to scan the small flood volume according to Edwards et al. (2011). Ordinarily, NMR logs would be acquired after the flood.

A separate pilot was performed by Soek et al. (2011) with the same AS through perforated casing to explore a larger flood volume. Saturation measurements obtained were: (1) chemical tracers in the SWCT and (2) time-lapsed pulse neutron capture (PNC) logs. The SWCT relies on the injection of an ester solution. The ester partitions into the oil over time, such that chromatographic separation of the tracer occurs on recovery; the separation is related to the ROS. Therefore, ROS from SWCT relies on just one measurement: the shift between the chemical tracers. Cased-hole tools that provide PNC measurements can also measure the ratio of carbon to oxygen from gamma ray energy resulting from inelastic scattering of fast neutrons.
practice, the PNC measurements gave unrealistically high ROS values due to the flood parameters (uncertain flow geometry) being outside the recommended operating conditions. PNC remains valid for ROS measurements in usual modes of operation.

ROS measurements obtained using the various methodologies are compared in Table 4. Following the initial brine flood of 1 to 4 PV, the SWCT by Soek et al. (2011), single-well pilot by Edwards et al. (2011), and laboratory study reported here all gave consistent ROS values. After the chemical flood, excellent agreement is observed in the ROS values obtained across all length scales.

In general, it is important to have two independent saturation measurements to corroborate quantification, using entirely different physical principles. At the laboratory scale, these are NMR and effluent volumetrics, as reported here and in similar studies described previously (Mitchell et al. 2012; 2013a). Here, evaporation of volatiles was difficult to control and therefore not reported; effluent volumetrics will be determined in future with improved collection apparatus. For the single-well in-situ EOR evaluation (Arora et al. 2010; Edwards et al. 2011; Ramamoorthy et al. 2011), the corroborating techniques are NMR and dielectric dispersion.

Conclusions
Quantitative EOR evaluation has been demonstrated on short plugs at the laboratory scale using spatially resolved low-field NMR. The spatial dimension is important at all EOR piloting length scales, but is critical when studying short plugs where bulk volumetrics may be dominated by capillary or geometry end effects and yield inaccurate ROS values. Nevertheless, bulk assays of effluent retain value as a corroboration of the accuracy of the NMR saturation measurements. The speed of the NMR profile acquisitions enables a near-continuous monitoring of the oil saturation, rather than discrete measurements of effluent aliquots. Furthermore, under optimal conditions, the NMR experiment can monitor the progress of the AS co-solvent, from which the surfactant distribution may be inferred, although it is important to realize that the progress of the AS active components is not intrinsically linked to the cosolvent distribution. Effluent analysis showed that a portion of the surfactant was adsorbed or partitioned into the oil on initial injection. This study shows the importance of a spatial resolution of the flood geometry in addition to the measurement of oil saturation. Liquid-phase-specific NMR provides the saturation; MRI methods provide the spatial resolution. The combination of saturation with spatial resolution is also important at larger length scales. Overall, spatially resolved NMR monitoring adds significant value to core flood studies, especially in short plugs.

In the present study, ROS after chemical flood determined in the middle third of a short core-plug was consistent with that observed during single-well pilots in the actual reservoir. The single-well in situ EOR evaluation using wireline NMR and dielectric dispersion measurements by Edwards et al. (2011) and also SWCT tests by Soek et al. (2011), were in agreement with the laboratory study. Redundancy in these observations adds confidence to the laboratory scale ROS measurements through corroboration over a wide range of length scales. Laboratory core floods with NMR monitoring at low magnetic fields provide an additional direct assessment of ROS to complement field pilots, as well as performing the conventional role of wireline log calibration.

References


Glossary

- $B_0$: Magnetic field strength
- $f_0$: Resonance frequency
- $g$: Magnetic field gradient strength
- $n$: Number of echoes
- $\Delta p$: Pressure drop
- $S_o$: Oil saturation (initial)
- $S_{or}$: Remaining oil saturation
- $T_2$: Transverse relaxation time
- $\Delta t$: Dwell time
- $y$: Vertical position
- $\Delta y$: Vertical resolution
- $\gamma$: Interfacial tension
- $\eta$: Viscosity
- $\rho$: Density
- $\tau$: Half-echo time

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration / mg dm$^{-3}$</th>
<th>Concentration / mmol dm$^{-3}$</th>
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<tr>
<td>Na$^+$</td>
<td>3970</td>
<td>172.69</td>
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<tr>
<td>K$^+$</td>
<td>64</td>
<td>1.64</td>
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<tr>
<td>Cl$^-$</td>
<td>4731</td>
<td>133.44</td>
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<tr>
<td>SO$_4^{2-}$</td>
<td>1830</td>
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<td>HCO$_3^-$</td>
<td>170</td>
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<table>
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<tr>
<th>Plug</th>
<th>Well depth / m</th>
<th>Bulk volume / cm$^3$</th>
<th>Grain density / g cm$^3$</th>
<th>Grain volume / cm$^3$</th>
<th>Pore volume / cm$^3$</th>
<th>Porosity / p.u.</th>
<th>Permeability / mD</th>
<th>Initial $S_o$ / s.u.</th>
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<tr>
<td>A</td>
<td>xxx9.3</td>
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<td>2.703</td>
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<td>29.1</td>
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TABLE 3—CORE FLOOD PROTOCOLS SHOWING AQUEOUS-PHASE INJECTION VOLUMES

<table>
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<tr>
<th>Plug</th>
<th>Liquid</th>
<th>Cumulative volume pumped / PV</th>
<th>Duration / hours</th>
<th>Cumulative volume pumped / cm³</th>
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<tr>
<td>A</td>
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<td>15.5</td>
<td>46.90</td>
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<tr>
<td></td>
<td>AS</td>
<td>23.5</td>
<td>24.25</td>
<td>358.6</td>
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<tr>
<td></td>
<td>Brine</td>
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<td>6.21</td>
<td>389.9</td>
</tr>
<tr>
<td>B</td>
<td>Brine</td>
<td>13.6</td>
<td>40.73</td>
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<td></td>
<td>AS</td>
<td>15.8</td>
<td>6.73</td>
<td>239.2</td>
</tr>
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<td></td>
<td>Brine</td>
<td>22.9</td>
<td>21.37</td>
<td>346.9</td>
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TABLE 4—COMPARISON OF ROS MEASURED AT LENGTH-SCALES PROBED IN CORE FLOODS AND TWO TYPES OF SINGLE-WELL PILOT

<table>
<thead>
<tr>
<th>Mode</th>
<th>Context</th>
<th>Imaging method</th>
<th>Length-scales probed</th>
<th>Saturation magnitude</th>
<th>S_o(w) (x PV) / s.u.</th>
<th>S_o(w) (∞) / s.u.</th>
<th>S_o(c) / s.u.</th>
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<tr>
<td>Core flood</td>
<td>Laboratory</td>
<td>NMR profiles</td>
<td>~ cm</td>
<td>NMR</td>
<td>36 (1 PV)</td>
<td>25</td>
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<td>NMR</td>
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<tr>
<td>Open hole</td>
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<td>Electric image</td>
<td>~ dm</td>
<td>Dielectric dispersion</td>
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<tr>
<td>Single well</td>
<td></td>
<td>n/a</td>
<td>~ m</td>
<td>SWCT</td>
<td>35 (~1 PV)</td>
<td>n/a</td>
<td>19</td>
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<td>chemical tracer</td>
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</tbody>
</table>

1Shown are saturations after brine flood S_o(w) (nominal 1 PV flood volume), and also S_o(w)(∞) at the end of the brine flood. Data are taken from Fig. 5 (right) and Fig. 6. Except for a determination of initial saturation, measurement effluent volumes are unreliable in this case because of evaporation of volatiles. Residual oil after chemical flood S_o(c) is not available from wireline NMR because flood volumes were too low according to Edwards et al. (2011).

Fig. 1—NMR pulse sequence schematic for the multi-echo imaging sequence of Majors et al. (1997). The thin and thick vertical lines represent 90° and 180° rf pulses, respectively. A series of n spin echoes are generated; each echo is separated in time by 2τ. The shape of each spin echo is recorded in the presence of a magnetic field gradient pulse of amplitude g and duration τr. Each spin echo is Fourier transformed to provide a profile of the sample; the amplitude of the nᵗʰ profile is determined by the relaxation time T₂. Accordingly, a distribution of T₂ relaxation times (and hence a quantitative signal amplitude) is calculated for every pixel in the profile.
Fig. 2—Spatially resolved oil saturations in plugs A and B during the brine and AS flood. The vertical axes on the main plots show position in the plug. The inlet face of the plug is located at \( y = 0 \) cm and the outlet at \( y = 5 \) cm. Fluid flow occurred from bottom to top. The horizontal axes on all plots show the volume of injected liquid in pore volumes (PV), equivalent to time. AS injection occurred between the vertical dashed lines; brine was injected otherwise. The variation in bulk oil saturation is shown projected beneath each plot; note that the saturation scale has been reduced to highlight the additional desaturation that follows the AS injection. For both plugs, an initial piston-like displacement of oil is observed followed by a gradual recovery during the brine flood; elevated oil saturation is observed at the outlet: this is a capillary end effect. On AS injection, increased mobility of the oil leads to the transport of an oil bank (increased local \( S_o \)) through the plug, but the total \( S_o \) remains constant. The AS removes the capillary end effect on reaching the outlet face of the plug. In plug A, the continued injection of surfactant results in additional oil recovery at the inlet.

Fig. 3—Differential pressure drop recorded between the inlet and outlet faces of plug A. AS injection occurred between the vertical dashed lines; brine was injected otherwise. The pressure stability was reduced due to the effect of oil, brine, and emulsion transport through the back-pressure regulator. However, notable features in the pressure trace are seen to coincide with the displacement processes observed in the NMR data. An initial drop in pressure occurs (14.7 to 11.2 psi) during the brine flood, followed by a gradual reduction to 10.1 psi. A rapid reduction in differential pressure occurs on AS injection—with instabilities associated with transport of the oil bank and removal of the capillary end effect—reaching a plateau at 3.8 psi. A slight drop in pressure to a final value of 3.2 psi is observed on return to brine injection.
Fig. 4—Localized oil saturations determined for plug A. (a) Selection of profiles acquired during the flood (liquid flowed left to right). All profiles are normalized relative to the initial oil saturation to remove consistent image artefacts. The flood progressed from top to bottom with profiles shown at flood volumes of PV = 0 (blue crosses), 1 (blue open circles), 3 (blue solid circles), 10 (blue open squares), 17 (red open circles), 22 (red solid circles), and 25 (solid blue squares). The colors refer to brine injection (blue) and AS injection (red). In the first of the AS flood profiles, the oil bank (increased $S_o$) is visible. The profiles are divided into three spatial regions (inlet, middle, outlet). (b) The variation in oil saturation for each spatial region as a function of volume of liquid injected (time). AS injection occurred between the vertical (blue) dashed lines. $S_o^{(w)}$ in the outlet third is higher than for the rest of the plug due to the capillary end effect. The middle and the outlet thirds equilibrate after AS injection. During the initial brine flood, the inlet and middle thirds are equivalent, although the oil saturation in the inlet third decreases during and after the AS injection, attributed to the formation of a microemulsion. The middle third is considered equivalent to a bulk saturation measurement in a long core plug where end effects are unimportant.

Fig. 5—An increase in the amplitude of the shortest $T_2$ relaxation time component observed during AS injection in the bulk CPMG data was attributed to the presence of the DGBE cosolvent. The variations in $S_o$ and relative saturation of DGBE are shown as a function of liquid volume pumped. AS solution was injected between the vertical (blue) dashed lines. The oil $S_o$ is corrected here to account for the presence of the cosolvent. The cosolvent saturation does not exceed 3 s.u., equivalent to the 3 wt% present in the bulk AS. The constant saturation value implies the cosolvent is distributed evenly through the rock and does not accumulate during continued injection of AS.
Fig. 6—Concentration of surfactant in the aqueous phase of the effluent recovered from the flood of plug A (blue circles, right axis). There is a delay of approximately 2 PV between AS injection (vertical dashed lines) and significant surfactant recovery, suggesting some hold-up in the rock. The cosolvent saturation (red line) is repeated from Fig. 5, as is ROS (black line) for comparison. The initial surfactant recovery coincides with enhanced oil recovery (reduction in $S_o$), suggesting the surfactant is transported with the oil. The total recovered surfactant volume was equal to 78% of the injected volume. Surfactant may be lost by partitioning into the oil, adsorption on pore surfaces, or associated with a microemulsion.