Wettability Survey in Bakken Shale With Surfactant-Formulation Imbibition

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Summary

For ultratight shale reservoirs, wettability strongly affects fluid flow behavior. However, wettability can be modified by numerous complex interactions and the ambient environment, such as pH, temperature, or surfactant access. This paper is a third-phase study of the use of surfactant imbibition to increase oil recovery from Bakken shale. The surfactant formulations that we used in this paper are the initial results that are based on our previous study, in which a group of surfactant formulations was examined—balancing the temperature, pH, salinity, and divalent-cation content of aqueous fluids to increase oil production from shale with ultralow porosity and permeability in the Middle Member of the Bakken formation in the Williston basin of North Dakota. In our previous study, through the use of spontaneous imbibition, brines and surfactant solutions with different water compositions were examined. With oil from the Bakken formation, significant differences in recoveries were observed, depending on compositions and conditions. Cases were observed in which brine and surfactant (0.05 to 0.2 wt% concentration) imbibition yielded recovery values of 1.55 to 76% original oil in place (OOIP) at high salinity (150 to 300 g/L; 15 to 30 wt%) and temperatures ranging from 23 to 120°C.

To advance this work, this paper determines the wettability of different parts of the Bakken formation. One goal of this research is to identify whether the wettability can be altered by means of surfactant formulations. The ultimate objective of this research is to determine the potential of surfactant formulations to imbibe into and displace oil from shale and to examine the viability of a field application.

In this paper, through the use of modified Amott-Harvey tests, the wettability was determined for cores and slices from three wells at different portions of the Bakken formation. The tests were performed under reservoir conditions (90 to 120°C, 150- to 300-g/L formation-water salinity), with the use of Bakken crude oil. Both cleaned cores (cleaned by toluene/methanol) and untreated cores (sealed, native state) were investigated. Bakken shale cores were generally oil-wet or intermediate-wet (before introduction of the surfactant formulation). The four surfactant formulations that we tested consistently altered the wetting state of Bakken cores toward water-wet. These surfactants consistently imbibed to displace significantly more oil than brine alone. Four of the surfactant imbibition tests provided enhanced-oil-recovery [(EOR) vs. brine water imbibition alone] values of 6.8 to 10.2% OOIP, incremental over brine imbibition. Ten surfactant imbibition tests provided EOR values of 15.6 to 25.4% OOIP. Thus, imbibition of surfactant formulations appears to have a substantial potential to improve oil recovery from the Bakken formation. Positive results were generally observed with all four surfactants: amphoteric dimethyl amine oxide, nonionic ethoxylated alcohol, anionic internal olefin sulfonate, and anionic linear α-olefin sulfonate. From our work to date, no definitive correlation is evident in surfactant effectiveness vs. temperature, core porosity, core source (i.e., Upper Shale or the Middle Member), or core preservation (sealed) or cleaning before use.

Introduction

Shale rock is an important source of oil and gas in a number of sedimentary basins in North America. Most shale reservoirs have a low porosity and ultralow permeability with natural fractures. Shale formations have long been considered important source rocks, capable of producing oil at economic rates when completed by hydraulically fractured horizontal wells. Surfactant-formulation optimization is a key step in our investigation of chemical imbibition (with the use of surfactant or brine formulations) to stimulate oil recovery from shale. Initial surfactant screening and optimization involved the balancing of pH, salinity, and divalent-cation content of the injected aqueous fluid that promote imbibition while minimizing clay swelling and formation damage (Wang et al. 2011a, b). However, the effectiveness of a surfactant formulation can also depend on wettability alteration. In this paper, we investigated whether our initial optimized surfactant formulations can modify Bakken shale wetness.

As a relatively thin, clastic unit, the Bakken formation in North Dakota consists of three informal units that are named the Lower Shale, Middle Member, and Upper Shale. The Middle Bakken Member ranges from 40 to 70 ft in thickness, with lithologic content varying from argillaceous dolostones and siltstones to clean, quartz-rich arenites and oolitic limestone with shale (Phillips et al. 2007). Measured core porosities in the Middle Member range from 1 to 16% and average approximately 5% by plot vs. permeability. A few high-pressure mercury-injection measurements indicate that in-situ porosities are on the order of approximately 3%. Measured permeability ranges from 0 to 20 md in the Middle Member and typically is low, averaging 0.04 md by plot of porosity vs. permeability. As burial depth increases, permeability in sandstones in the Middle Member has been shown to decrease from a range of approximately 0.06 to 0.01 md, where the adjacent shales are immature, to a range of approximately $\leq$ 0.01 to 0.01 md, where these shales are mature. The temperature of the Middle Member ranges from 80 to 120°C (Pitman et al. 2001). On the basis of the chemical analysis of Bakken formation water by the Environmental Analytical Research Laboratory at the University of the North Dakota, the brine salinities range from 150,000 to 300,000 mg/L (15 to 30 wt%) total dissolved solids (TDS) in the Williston basin (Wang et al. 2011a). Also, the statistical data from 200 well samples in the pre-Mississippian rocks (of which the Bakken is the top formation; Iampen and Rostron 2000) proved this range.

Generally, wettability strongly affects fluid flow behavior. In a water-wet status, water can be imbibed into bypassed zones by capillary forces. Alternatively, if the porous media are oil-wet, capillary force prevents water from entering the bypassed zones (Sharma and Mohanty 2011). For most shale reservoirs, waterflooding has limitations because of relatively higher clay content, even though waterflooding is favorable for neutral-wet status. The mechanism of wettability alteration involves surfactant added related with capillary pressure. As wettability is altered, the capillary pressure changes from negative to positive, and countercurrent imbibition mobilizes more oil. Furthermore, the relative permeabilities and residual saturations are changed to provide a higher oil recovery from the core. Several previous studies were performed with the use of surfactant imbibition to alter wettability in carbonate and chalk reservoirs, with rock permeability ranging from 1 to 15 md and porosity up to 29.1%. Zhang and Austad

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(2005) thought that sulfate, acting as a wettability modifier for waterflooding in the imbibing fluid, modified wettability, especially under water-wet conditions. The use of cationic surfactants of the type $[R^{-}N(CH_3)_3]^+$ significantly improved oil recovery from chalk, especially when the rock wettability was close to a neutral wetting condition. The spontaneous-imbibition tests were conducted at 40 to 130°C (Zhang and Austad 2005). Høgnesen et al. (2005) used sulfate surfactant as the wettability modifier on chalk samples at temperatures from 70 to 130°C. Their research results indicated that oil recovery increased at strongly water-wet conditions when the concentration of sulfate was 3 times higher than it is in seawater (i.e., the highest TDS was 179.9 g/L) at 130°C (Høgnesen et al. 2005). Adibhatla et al. (2005), Adibhatla and Mohanty (2006), and Gupta and Mohanty (2007, 2008) conducted a series of studies that used anionic and nonionic surfactants to change the oil-wet wettability of carbonates. Their research involved coupling imbibition of aqueous surfactant solutions with gravity drainage. Both anionic and nonionic surfactants showed good potential for increasing oil recovery in a fractured limestone carbonate reservoir at 90°C. Na_2CO_3 was added to reduce surfactant adsorption. Subsequently, Gupta et al. (2009) screened surfactants for wettability alteration in an oil-wet fractured carbonate reservoir. In that study, anionic and nonionic surfactants were screened for high-temperature (90°C) and high-salinity (8%) systems containing significant concentrations of magnesium and calcium ions. Alkali was added to keep the brine pH above neutral and reduce adsorption on carbonate surfaces. In their study, the optimal salinity was tuned by either changing surfactant concentration or by use of a mixture of surfactants (Gupta et al. 2009).

Sharma and Mohanty (2011) found that surfactants can change the wettability of a carbonate rock from mixed-wet toward water-wet at high temperature (100°C) and with high-salinity (20%) brine. Our previous work (Wang et al. 2011a, b), along with that of Shuler et al. (2011), found surfactant compositions that can imbibe into shale under various conditions. However, there is a need to study whether surfactant imbibition changes wettability in shale reservoirs.

Research has demonstrated that wettability for a given rock/brine/oil system is affected by contact angle and capillary changes between the wetting and nonwetting phases (Hirasaki 1991; Sharma and Mohanty 2011). Wettability can be affected by rock boundary conditions (Xie and Morrow 2001), components and solvent quality of the crude oil (Buckley et al. 1998), and brine ionic composition (Sharma and Mohanty 2011).

Wettability test methods are divided into two categories: One is quantitative measurement, such as contact-angle measurement, Amott-Harvey, and US Bureau of Mines (USBM) methods; the other is the qualitative analysis method, such as nuclear magnetic resonance (NMR) and relative permeability determination. To date, for shale reservoirs, there are few literature reports of wettability tests except for the NMR method used by Elijah et al. (2011).

For Bakken shale, it is challenging to test wettability through the use of existing methods because of the complex reservoir conditions with high reservoir temperature (up to 120°C) and ultrahigh salinity (up to 30% TDS). If we use a regular Amott-Harvey cell to test wettability with liquid imbibition and secondary drainage, precipitation occurs easily; precipitation accumulates on the top of the core surface because of high temperatures and high salinity, so the liquid cannot get though the porous rock. A modified Amott-Harvey method was introduced (Methods MC and MD in the following text) in this paper. This modified method is used not only for Bakken shale but also can be applied to other shale rocks with similar reservoir conditions. Compared with the regular quantitative wettability test method, such as contact-angle measurement and conventional Amott-Harvey methods, this modified method is more suitable for complex reservoir conditions with high temperature and high salinity. On the other hand, compared with USBM methods, this method is sensitive to all kinds of wetness and not only for neutral-wet states.

During the course of our work, we tested 30 core and sample slices from three Bakken wells in different parts of the Williston basin in North Dakota, with the use of a modified Amott-Harvey method. The tests were performed under reservoir conditions (90 to 120°C, 150- to 300-g/L formation-water salinity) with the use of Bakken crude oil. Both cleaned cores (cleaned by toluene/methanol) and untreated cores (sealed, native state) were investigated.

Methodology

Wettability was studied by a modified Amott-Harvey method, with the use of cores from different depths in the three Bakken wells. Certain aqueous surfactant formulations were tested for their capability to alter wettability of shale rocks. For a given core, spontaneous aqueous imbibition was assessed in an Amott-Harvey cell, whereas the residual-oil saturation (ROS) and connate-water saturation were obtained by coreflooding with 20 to 30 pore volumes (PV) of fluid. Our oil was from the Bakken formation in southeast Williams County. The crude-oil viscosity was 2.0 cp at room temperature. Cores from one well were tested at room temperature. For cores from the other two wells, wettability tests were conducted at reservoir temperature (90 to 120°C) and salinity (15 to 30% TDS). Four main cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) were present in our brine, with mol% ratios of 87.7, 3.4, 7.8, and 1.1%, respectively. Thus, the monovalent cations were up to 10 times more prevalent than the divalent cations. To verify our test methodology and obtain reliable results not only by single measurement, we used four approaches to measure the Amott-Harvey index (AI). We call them Methods MA, MB, MC, and MD. Liquid-imbibition and -injection volumes were obtained by weight measurements.

For method MA, core plugs were weighted before and after spontaneous imbibition and before and after forced fluid injection. The advantage is that weight measurements can be accurate (i.e., to 0.0001 g in our case). For Method MA, a centrifuge was used to drive cores to residual saturations. This is a relatively easy and reliable method. However, because we did not have a way to maintain temperature at 90 to 120°C during centrifugation, we could use the method only for studies at room temperature. In addition, our centrifuge was not large enough to accommodate 3.8-cm-diameter cores.

For Method MA, we selected the cores from the Middle Member of Bakken from Well Lars Rothie 32-29H (#16433) in eastern McKenzie County. For this well, the ROS and connate-water saturation were obtained by centrifuge. Core thickness varied from 2 to 5 mm, and the test temperature was 23°C.

For Method MB, core plugs were weighed before and after spontaneous imbibition and before and after forced fluid injection (just as for Method MA). During injection, the coreflooding apparatus shown in **Fig. 1** was used. This apparatus allowed flooding to occur at 90 to 120°C. However, errors can be introduced because of cooling and/or evaporation during the time that the core is removed from the core holder and the weight measurements are made. In addition, if any part of the rock (e.g., small grains or core pieces) becomes separated from the main core, the core can incorrectly appear to have a weight loss, even though water has displaced less-dense oil.

For Method MB, core plugs were from Well EN Ruland 3328-H (#16771) in western Mountrail County. Reservoir temperature varied from 90 to 120°C. Forced injection occurred with the use of the coreflood setup shown in Fig. 1. Core thickness varied from 13 to 15 mm. Liquid-imbibition and -injection volumes were obtained by weight measurements.

For Method MC, core plugs came from Well AV Wrigley (#17450) in northwest Burke County, and reservoir temperature varied from 90 to 120°C. Forced injection occurred with the use of the coreflood setup shown in **Fig. 2.** Core thicknesses varied from 13 to 50 mm. Core samples were wrapped with a silicone Rescue tape to seal the cylinder surface. Liquid-imbibition and -injection volumes were obtained by means of burette readings.

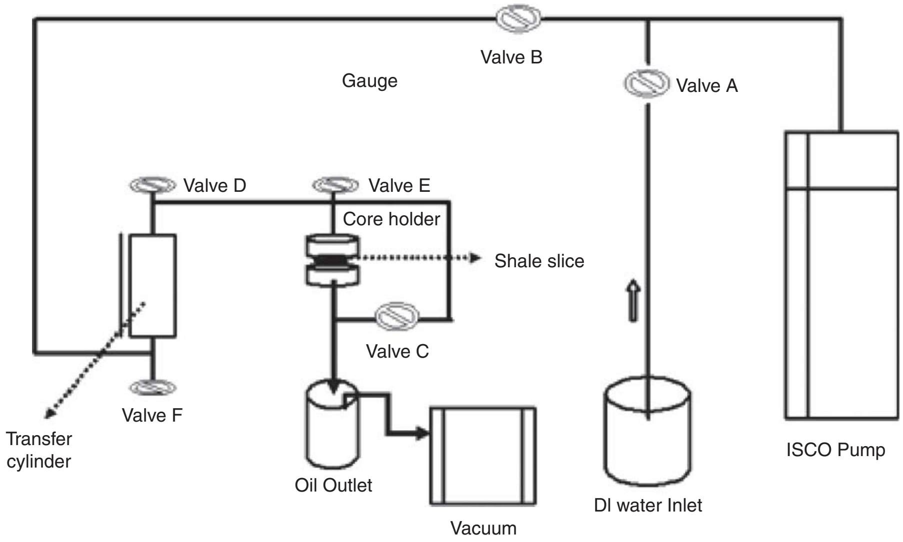

Fig. 1—Forced-injection illustration for Method MB.

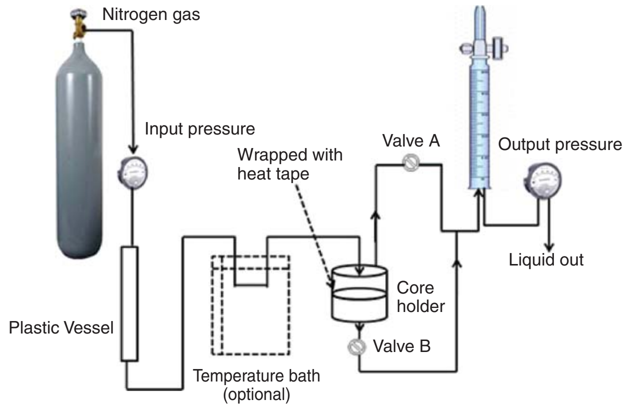

Fig. 2—Scheme for spontaneous imbibition and forced injection by Method MC.

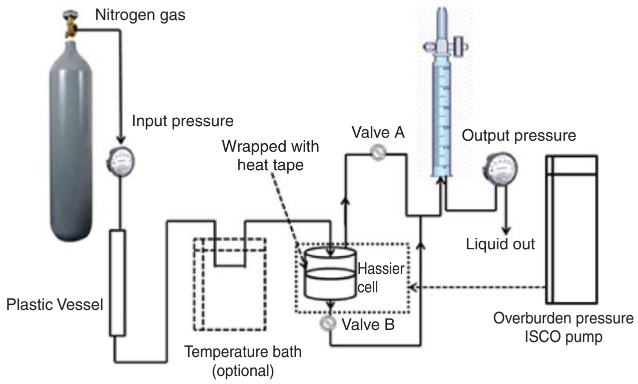

Fig. 3—Scheme for spontaneous imbibition and forced injection by Method MD with Hassler cell.

For Method MD, core plugs also came from Well #17450. A Hassler core holder was used during both imbibition and injection, as shown in **Fig. 3.** The reservoir temperature varied from 90 to 120°C. Overburden pressure was applied to the confined core. Core thickness varied from 40 to 50 mm. Liquid-imbibition and -injection volumes were obtained by means of burette readings.

Methods MC and MD were used for core plugs from Well #17450. For these methods, imbibition and injection volumes were determined by means of readings on burettes. Because of the 0.05-cm^3 calibration in the burettes, the accuracy of these methods is relative. Because of the 0.05-cm^3 calibration in the burettes, these methods are fairly accurate. In addition, if oil or water adheres to the core surface or an interior part of the flowline, it may not be displaced to the burette for measurement.

An overview of the similarities and differences of Methods MA through MD can be seen in **Table 1.**

Other test procedures included the following.

Step 1: Filter the crude oil and brine waters through Whatman 4 filter paper.

Step 2: Measure oil viscosity with the use of a Brookfield viscometer with UL-adapter at various temperatures.

Step 3: For regular core plugs (slices), wash with toluene to clean chemicals from the rock, wash again with methanol to clean out brine, and then dry cores under at 105°C for 24 hours. For

TABLE 1—OVERVIEW OF METHODS MA THROUGH MD

Method	MA	MB	MC	MD
Cores source	Well #16433	Well #16771	Well #17450	Well #17450
Test temperature	23°C	90–120°C	90–120°C	90–120°C
Core thickness (mm)	2–5	13	4–52	41–52
Method				
Water/oil saturation	Beaker imbibition, weight measurement	Beaker imbibition, weight measurement	Core-holder imbibition, burette reading	Hassler-cell imbibition, burette reading
Residual/connate saturation	Centrifuge spinning, weight measurement	Isco Pump injection, weight measurement	Core-holder injection, burette reading	Hassler-cell injection, burette reading
Calculation equations	1 and 2	1 and 2	3 and 4	3 and 4

TABLE 2—SURFACTANT FORMULATIONS

Surfactant	Concentration (%)	Commercial Name	Alkaline Additive (%)	Salinity (% TDS)	Manufacturer
Amphoteric dimethyl amine oxide	0.1	YYC3-17A	0.1 or 0.2	15	CorsisTech
Nonionic ethoxylated alcohol	0.05	YYC1-58N	0.1 or 0.2	30	CorsisTech
Anionic internal olefin sulfonate	0.1	Petrostep S2	0.1 or 0.25	30	Tiorco
Anionic linear α-olefin sulfonate	0.1	Petrostep C1	0	30	Tiorco

Alkaline: $NaBO_2{\cdot}4H_2O$.

sealed core plugs, remove aluminum foil from cores carefully, and go to Step 4.

Step 4: Measure core plug (slices) diameter and thickness with Carrera precision calipers. We routinely measured the length (thickness) and diameters at 5 to 10 spots on each core. All measurements were within ±0.01 mm of the average value, demonstrating consistency of the surfaces.

Step 5: Vacuum the shale material for 1 hour for core thin slices or 2 to 3 hours for thicker cores (13 to 50 mm) to remove any gas from the lines and core.

Step 6: Soak the cores in crude oil for 24 hours to saturate them.

Unless specified differently, the water salinity was 30% (300 000 mg/L).

Eqs. 1 through 5 were used to calculate the AI. For Methods MA and MB, we used Eqs. 1 and 2 (Amott 1959; Dake 1977), whereas for Methods MC and MD, we used Eqs. 3 and 4 (Glover 2001).

$$Iw = \frac{Sw - Swr}{1 - Swr - Sor} \quad \ldots\ldots (1)$$

$$Io = \frac{So - Sor}{1 - Swr - Sor} \quad \ldots\ldots (2)$$

$$\delta w = \frac{V_{w\text{imbibition}}}{V_{w\text{imbibition}} + V_{w\text{injection}}} \quad \ldots\ldots (3)$$

$$\delta_o = \frac{V_{o\text{imbibition}}}{V_{o\text{imbibition}} + V_{o\text{injection}}} \quad \ldots\ldots (4)$$

$$AI = I_w - I_o \quad \ldots\ldots (5)$$

where AI = Amott-Harvey index, I_o = Harvey index, I_w = Amott index, S_o = oil saturation during oil imbibition, S_{or} = ROS after water imbibition, S_w = water saturation during water imbibition, S_{wr} = irreducible water saturation after oil imbibition, $V_{o\text{imbibition}}$ = oil volume spontaneously imbibed, $V_{o\text{injection}}$ = oil volume increase by forced injection, $V_{w\text{imbibition}}$ = water volume spontaneously imbibed, $V_{w\text{injection}}$ = water volume increase by forced injection, δ_o = ratio of spontaneous oil imbibition to total oil imbibition, and δ_w = ratio of spontaneous water imbibition to total water imbibition.

Porous Media. The tested rock plugs came from the Middle Member of the Bakken formation in Well #16433, Lars Rothie 32-29H; the Upper Shale and Middle Member in Well #17450, AV Wrigley 163-94-0607H-1; and Well #16771, EN-Ruland-156-94-3328H-1. Generally, the core samples tested were gritty shale and shale interbedded with siltstone, limestone, and dolomite, with poor-to-zero porosity. Core plugs were 25 mm in diameter and 2 to 50 mm in thickness. For the Middle Member, permeability to Bakken oil for our core samples was typically approximately 7 md; porosity averaged 4.4%. Permeability for the Upper Shale was considerably less (by two to three orders of magnitude) than for the Middle Member, although our porosity values were comparable.

Test Fluids. Cores were saturated with Bakken crude oil from Well B.L. Davidson 2-11H. The gravity was 43.2°API, and oil density was 0.777 g/cm^3 at 23.2°C. Brine-water salinity was characteristic of the Bakken Formation.

Surfactants. Aqueous surfactant formulations as imbibition candidates included (1) 0.1% linear α-olefin sulfonate +30% TDS brine, (2) 0.1% internal olefin sulfonate + 0.1 to 0.25% alkaline +30% TDS brine, (3) 0.05% ethoxylated alcohol + 0.1 to 0.2% alkaline + 30% TDS brine, and (4) 0.1% dimethyl amine oxide +0.1 to 0.2% alkaline +15% TDS brine. They were compared at different temperatures. Compositions **(Table 2)** were based on our earlier surfactant-formulation optimization studies (Wang et al. 2011b).

Brines. Waters with 15 to 30% TDS were used as imbibing fluids.

NaCl, KCl, $CaCl_2$, and $MgCl_2$. These salts were used to change salinity of the aqueous phase, on the basis of work by Wang et al. (2011b).

$NaBO_2{\cdot}4H_2O$. This alkaline chemical was used to change pH of the aqueous phase. It was used to buffer our solutions at pH values from 8.4 to 9. Without the alkaline buffer, pH values typically ranged from 5.6 to 6.8.

Results

Wettability Tests for Well #16433 Cores. We selected the cores from the Middle Member of Bakken from Well 32-29H (#16433), shown in **Fig. 4.** Most core slices tested from this well were gritty and limey shale from depths of 10,613 to 10,649 ft (http://www.dmr.nf.gov/oilgas/FeeServices/wfiles/16/W16433.pdf). For this well, the water saturation (S_w) and oil saturation (S_o) were first obtained by spontaneous imbibition (after 24 hours). The ROS (S_{or}) and the initial water saturation (S_{wi}) were then obtained by centrifuge (Method MA) with the use of a HERMLE Labnet Z 206A (centrifuged for 48 hours at 4,600 rev/min). Core thicknesses varied from 2 to 5 mm, and the test temperature was 23°C. The AI was calculated from Eqs. 1 and 2.

Table 3 shows the wettability test results for Well #16433 with the surfactant formulation: 0.1% linear α-olefin sulfonate +30% TDS brine. Cores from two depths in the Middle Member of this well indicated weak oil-wettability characteristics at 23°C. Wettability altered from weakly oil-wet to neutral-wet after imbibing the linear α-olefin sulfonate surfactant formulation. (pH was 5.85 for the linear α-olefin sulfonate formulation compared with 5.60 for brine water only.) The average ROS decreased 9.2%, and incremental oil recovery by surfactant was 8.52%. The well-logging curves and core photos are shown in Fig. 4. The rock porosity was obtained experimentally (Wang et al. 2011a), as **Table 4** shows. Porosity of the shale cores was determined by weight differences before and after saturation with the oil. Weight measurements were made with the use of a Mettler Toledo Model XP504 analytical balance that read weights to 0.0001 g.

Wettability Tests for Well #16771 Cores. For Well #16771, we selected cores from the Upper Shale and Middle Member **(Fig. 5).** Lithologic content included black shale and trace limestone in the Upper Shale at depths of 10,274 to 10,310 ft and shaly siltstone in the Middle Member at depths of 10,311 to 10,340 ft (http://www.dmr.nf.gov/oilgas/FeeServices/wfiles/16/W16771.pdf). S_w and S_o were obtained by imbibition with liquid (top of core surface open for 48 hours), and S_{or} or S_{wi} was obtained by forced

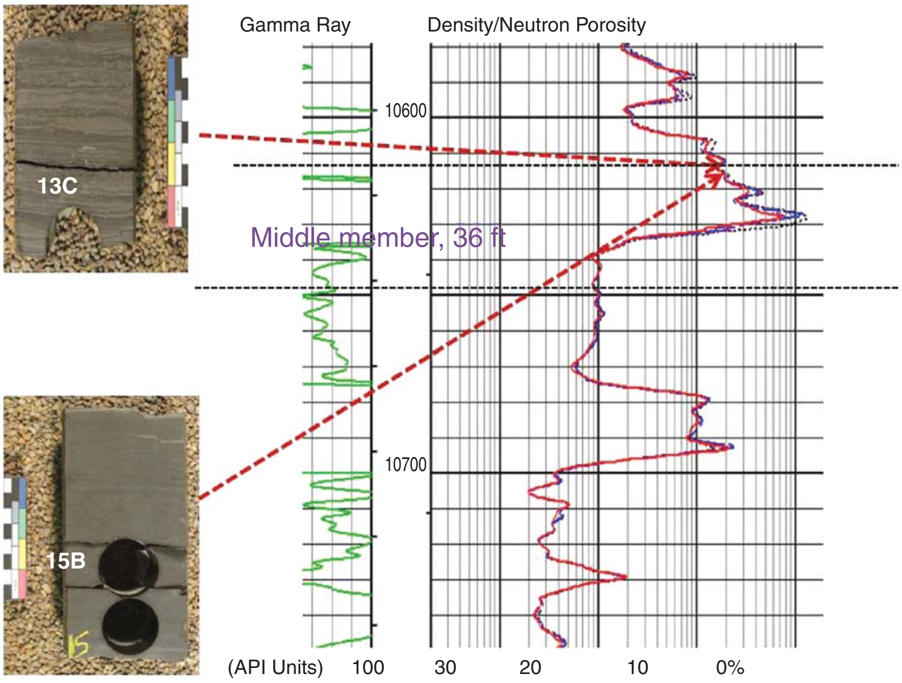

Fig. 4—Core sample location and well log curves for Well #16433, Lars Rothie 32-29H. Whole cores are 6 in. in diameter. (See Tables 3 and 4 for test results.) Note: The original well log cures (without arrows of direction) are referred to at the website of North Dakota Industry Commission, https://www.dmr.nd.gov/oilgas/feeservices/getscoutticket.asp. Also, see Figs. 5 and 6.

TABLE 3—WELL #16433 AT 23°C, $D = 25$ mm, $L = 2$ TO 5 mm

Sample	Aqueous Liquid	I_w	I_o	*AI*	Wettability	S_{or}	S_{or} Decrease (%)	*Re* (%)	EOR (%)
13C	Brine water	0.299	0.484	−0.184	Weakly oil-wet,	0.848	11.3	15.2	10.2
	linear α-olefin sulfonate	0.489	0.486	0.002	neutral-wet	0.735		25.4	
15B	Brine water	0.327	0.481	−0.150	Weakly oil-wet,	0.838	7.1	16.2	6.9
	linear α-olefin sulfonate	0.497	0.487	0.010	neutral-wet	0.767		23.1	

Note: *Re* is oil recovery by liquid imbibition or by centrifugation, and EOR is incremental oil recovery by surfactant vs. water. For Cores 13C and 15B, the wettability test was conducted by brine water first, with $S_w = 0$ at the start of the test. Starting with $S_w = 2.54\%$ for Core 13C and with 0.01% for Core 15B, the test was then repeated by means of the anionic linear α-olefin sulfonate formulation.

injection of 20 to 30 PV (with the use of Method MB, as illustrated in Fig. 1). Core thickness was 13 mm, and the test temperature ranged from 90 to 120°C. The AI was calculated on the basis of Eqs. 1 and 2. Core samples were tightly wrapped with a temperature-tolerant tape before placement in the core holder (to prevent leakage from the radial surface during flooding). In **Tables 5 through 7,** core samples that are labeled with the same first three-digit sequence (e.g., 1 through 10) were cut from the same core in same depth range. Samples were of similar lithology. Core dimensions and porosities are listed in Table 5.

Table 6 shows the wettability test results for Well #16771 for several surfactant formulations, with compositions of 0.05% ethoxylated alcohol + 0.1 to 0.2% alkaline + 30% brine, 0.1% internal olefin sulfonate + 0.1 to 0.25% alkaline + 30% brine, and 0.1% dimethyl amine oxide + 0.1% alkaline + 30% brine. Cores from three depths in the Upper Shale and the Middle Member of this well were tested for wettability at 90 to 120°C and varied alkaline content. Wettability was altered from oil-wet to water-wet after imbibing ethoxylated alcohol, dimethyl amine oxide, and internal olefin sulfonate surfactant formulations (with alkaline). Consistent with ideas expressed by Hamouda and Karoussi (2008), the wettability inclined to stronger water-wetness after exposure to the alkaline surfactant formulations. In Table 6, we note that brine imbibition worked well for Core 1-46-2 before the use of surfactant dimethyl amine oxide. Even so, after surfactant dimethyl amine oxide imbibition, oil recovery still increased by 9.6% OOIP, and the residual oil decreased by 7.7%.

Wettability Tests for Well #17450 Cores. Well #17450 cores were selected from the Upper Shale (depths of 7,336 and 7,348 ft)

TABLE 4—DIMENSIONS AND POROSITIES OF CORES FROM WELL #16433

Core	Location	Length (mm)	Diameter (mm)	Porosity (volume fraction)
13C	Middle Member	1.80	24.79	0.094
15B	Middle Member	4.61	24.92	0.045

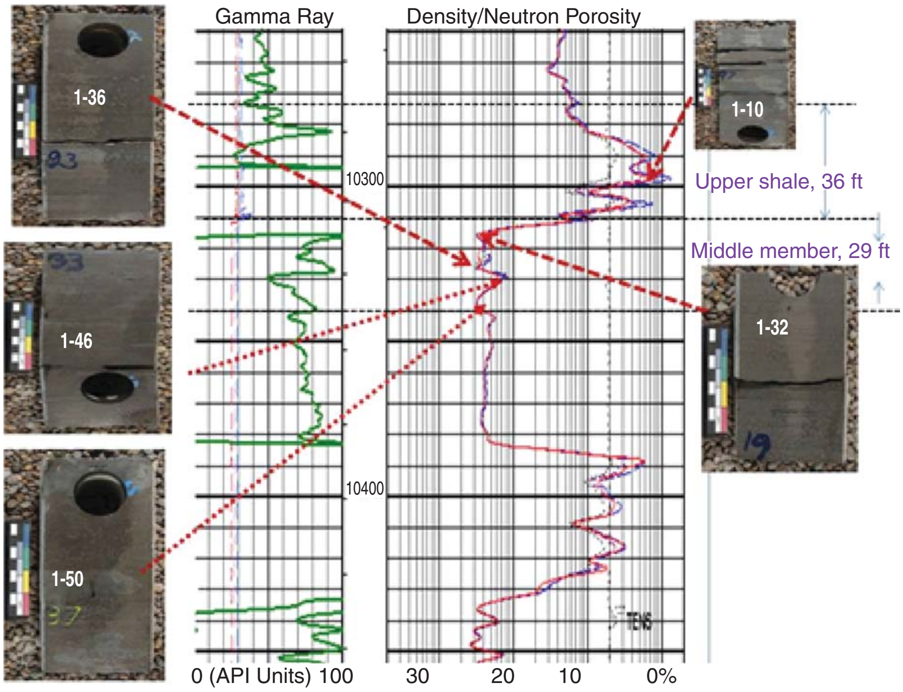

Fig. 5—Core sample location and well log curves for Well #16771, EN-Ruland-156-94-3328H-1. Cores are 6 in. in diameter. (See Tables 5 and 6 for test results.)

and the Middle Member (depths of 7,349 and 7,374 ft), as **Fig. 6** shows. The lithologic content was moderately hard, fissile, carbonaceous black shale with traces of disseminated pyrite in both the Upper Shale and the Middle Member (http://www.dmr.nf.gov/oilgas/FeeServices/wfiles/16/W17450.pdf). In Fig. 6, core sample photo of 1-51A was not presented in the database. Two methods were applied to cores from this well: (1) MC, where S_w and S_o were obtained by spontaneous imbibition for 48 hours and S_{or} or S_{wi} was obtained by forced injection of 20 to 30 PV, as illustrated in Fig. 2; and (2) MD, where S_w and S_o were obtained by imbibition (with all rock surfaces open) for 48 hours and S_{or} and S_{wi} were obtained by forced injection of 20 to 30 PV with the use of a Hassler cell, as illustrated in Fig. 3. Core thicknesses varied from 13 to 50 mm (mostly using sealed, preserved cores), and the test temperature ranged from 90 to 120°C. Overburden pressure was applied to the cores when Method MD was used. The AI was calculated on the basis of Eqs. 3 and 4. When method MC was used, core samples were tightly wrapped with temperature-tolerant tape (silicone Rescue) before they were put into the core holder. Core dimensions and porosities are shown in Table 7.

Fig. 2 illustrates the injection system. In this method, an Isco Model DX-100 syringe pump was used. The pump (which has a built-in pressure transducer) provides a wide range of flow rates (from 0.001 to 60 cm^3/min) for pressures up to 10,000 psi (690 bar or 70 MPa). Valves A and B are two-way valves to control flow of distilled water to/from the pump. Valve C is a two-way bypass valve that is used during evacuation and saturation of the core slice. Valves D, E, and F are three-way valves that control fluid input/outflow for the transfer cylinder. The core holder accommodates cylindrical core slices that are 25 to 26 mm in diameter and 0 to 10 mm in thickness, at pressures up to 3,000 psi (207 bar or 20.7 MPa).

Table 8 shows the wettability test results for Well #17450 with the surfactant formulations: (1) 0.05% ethoxylated alcohol + 0.1 to 0.2% alkaline + 30% brine, (2) 0.1% internal olefin sulfonate + 0.1 to 0.25 alkaline + 30% brine, (3) 0.1% dimethyl amine oxide + 0.1 to 0.2 alkaline + 15% brine, and (4) 0.1% linear α-olefin sulfonate. Core properties are shown in Table 7. Three findings were noted from Table 6. First, some cores from the Upper Shale (1-42 and 1-45) of this well indicated neutral-wetting at 60 to 90°C. Core 1-36 (from the top of the Upper Shale) was oil-wet, as was Core 1-45. Second, cores from the Middle Member of the same well exhibited neutral-, mixed-, or oil-wetting characteristics (Cores 1-48A, 1-51, 1-56, 1-69A, and 1-70). Third, the sealed core plugs (1-48A, 1-51A, and 1-69A) were not cleaned with toluene or methanol before testing (i.e., to keep original wetting condition). Incremental oil recovery attributed to surfactant imbibition for these cores was comparable with that for the cleaned cores **(Table 9).**

TABLE 5—DIMENSIONS AND POROSITIES OF CORES FROM WELL #16771

Core	Location	Length (mm)	Diameter (mm)	Porosity (volume fraction)
1-10-1	Upper Shale	12.36	38.14	0.034
1-10-2	Upper Shale	13.13	38.64	0.034
1-32-2	Middle Member	13.90	38.08	0.066
1-32-3	Middle Member	13.71	38.12	0.064
1-36-1	Middle Member	14.08	38.09	0.066
1-36-3	Middle Member	13.71	30.48	0.075
1-46-2	Middle Member	13.87	38.05	0.073
1-46-3	Middle Member	13.76	38.08	0.069
1-50-2	Middle Member	13.87	38.05	0.069
1-50-3	Middle Member	13.76	38.08	0.069

TABLE 6—WELL #16771 AT 90 TO 120°C, D=38 mm, L=13 mm

			pH (22°C)									
Sample	Aqueous Liquid	Temperature °C	Alkaline Content (%)	Value	I_w	I_o	AI	Wettability	S_{or}	S_{or} Decrease (%)	Re (%)	EOR (%)
1-10-1	Brine water	90	0.00	5.60	0.100	0.500	−0.400	Oil-wet	0.803	15.7	19.7	15.8
1-10-1	Ethoxylated alcohol		0.10	8.71	0.180	0.000	0.180	Water-wet	0.646		35.5	
1-10-2	Brine water		0.10	8.48	0.050	0.525	−0.475	Oil-wet	0.911		8.8	
1-32-2	Ethoxylated alcohol	90	0.10	8.71	0.987	0.949	0.038	Weak water-wet	0.884	16.1	11.6	16.1
1-32-3	Ethoxylated alcohol		0.20	9.00	0.500	0.000	0.500	Water-wet	0.723		27.7	
1-36-1	Brine water	90	0.00	5.60	0.451	0.868	−0.417	Oil-wet	0.672	51.1	32.7	16.6
1-36-1	Internal olefin sulfonate		0.10	8.61	0.857	0.456	0.420	Water-wet	0.161	53.0	49.3	20.9
1-36-3	Internal olefin sulfonate		0.25	9.03	1.000	0.000	1.000	Water-wet	0.142		54.7	
1-46-2	Brine water	110	0.00	5.60	0.260	0.770	−0.511	Oil-wet	0.220	7.7	78.0	9.6
	Dimethyl amine oxide		0.10	8.44	0.833	0.750	0.083	Weak water-wet	0.143		87.6	
1-50-3	Brine water	120	0.00	5.60	0.162	0.531	−0.369	Oil-wet	0.629	47.8	37.1	24.2
1-50-1	Internal olefin sulfonate		0.25	9.03	0.762	0.310	0.542	Water-wet	0.266		62.6	

Note: In Core Samples 1-10-1, 1-36-1, and 1-46-2, the wettability test was conducted with brine water first, with $S_w = 0$ at the start of the test. Starting with $S_w = 0$, $S_w = 11.4\%$, and 16.4%, the test was then repeated with the use of the ethoxylated alcohol, $S_w =$ internal olefin sulfonate, and dimethyl amine oxide formulations, respectively. EOR is incremental oil recovery by surfactant vs. water.

Discussion

Experimental Methods. Four approaches were used in this paper to measure the AI. Because of challenges in measuring wettability under our conditions, the four methods were examined with a goal of identifying a best method or at least in hopes of finding a consistent direction in the results. Of the many cores or slices that we tested, approximately one-third of the results were not usable because of apparatus failure or errors in data collection. Each of our four methods had positive and negative aspects.

Initial Core Wettability. For this study, core samples were tested with the use of three Bakken wells from different parts of the Williston basin in North Dakota, by means of a modified Amott-Harvey method. The majority of results demonstrated that Bakken shale cores were generally oil-wet or intermediate-wet (before introduction to the surfactant formulation). This result was consistent with an NMR study by Elijah et al. (2011). In that study, three shales from the Eagle Ford, Barnett, and Floyd strata showed oil-wetness or mixed-wetness when the shales imbibed brine or oil (dodecane). The Eagle Ford formation was generally lower in silica content and was carbonate rich. The Floyd shale had significant clay content, and the average total-organic-carbon value was 4.0% in the Barnett shale. Like other shales, the Bakken formation is also composed mainly of quartz, carbonate, clay, and pyrite. The major clay in the Bakken formation is illite: 47 mEq/100 g of total minerals (https://www.dmr.nd.gov/oilgas/FeeServices/wfiles/15/W15722.pdf).

Oil Saturation After Brine Imbibition. A significant variation occurred in the oil saturations achieved after brine imbibition. For 11 cases, the oil saturation after brine imbibition was in the range of 0.629 to 0.911. However, four cases achieved oil saturations between 0.220 and 0.410 during brine imbibition. We are planning additional tests on similar properties in other cases to verify

TABLE 7—DIMENSIONS AND POROSITIES OF CORES FROM WELL #17450

Core	Location	Length (mm)	Diameter (mm)	Porosity (volume fraction)
1-36A	Upper Shale	41.34	38.68	0.037
1-42-1	Upper Shale	5.78	24.85	0.036
1-42-2	Upper Shale	5.60	25.04	0.036
1-45-1	Upper Shale	4.15	38.29	0.061
1-45-2	Upper Shale	13.57	38.02	0.060
1-48A	Middle Member	51.14	38.00	0.016
1-51A	Middle Member	51.33	38.25	0.029
1-56-1	Middle Member	14.68	38.00	0.063
1-56-2	Middle Member	14.01	38.02	0.074
1-69A	Middle Member	52.11	38.70	0.016
1-72-1	Middle Member	10.11	38.03	0.064
1-72-2	Middle Member	10.17	38.02	0.051
1-72-3	Middle Member	10.25	38.00	0.030

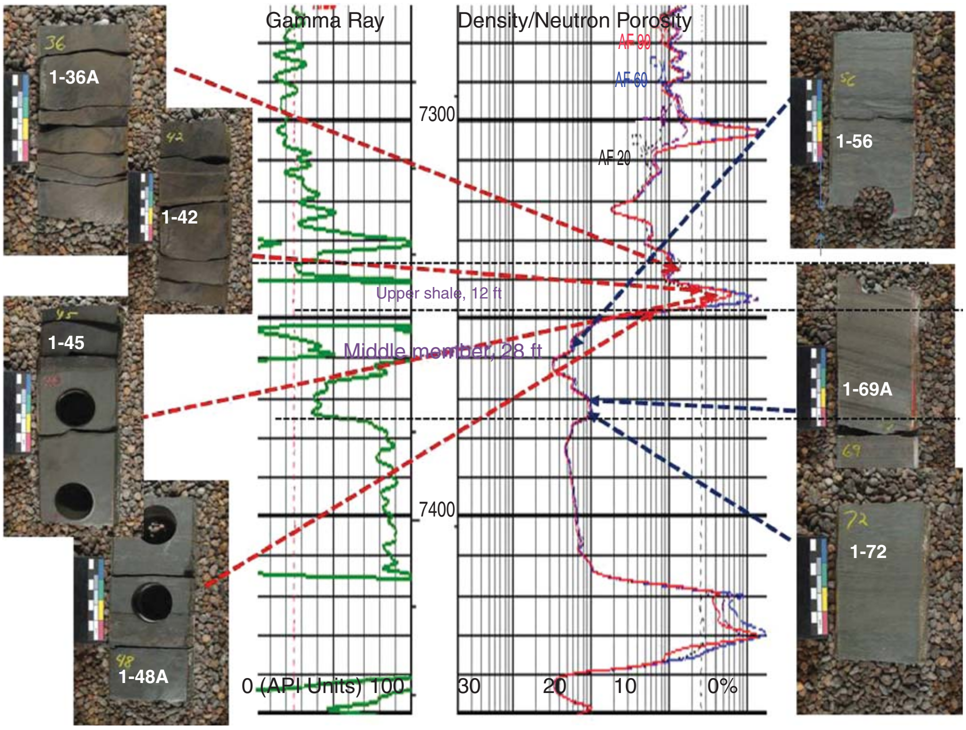

Fig. 6—Core sample location and well log curves for Well #17450, AV Wrigley 163-94-0607H-1. Cores are 6 in. in diameter. (See Tables 7, 8, and 9 for test results.)

this exception. Even though brine apparently imbibed in some cases, in other cases, brine sometimes did not imbibe (e.g., Sample 1-36A in Table 9).

Effect of Alkaline Solutions. In Table 6, Cores 1-10-1 and 1-10-2 tested whether simple addition of 0.1% sodium metaborate to the brine could enhance imbibition (i.e., no surfactant). Interestingly, for these cases, oil recovery was noticeably less with the alkaline present. Also, note in Table 8, for Samples 1-42-1 and 1-42-2, a linear α -olefin-sulfonate-surfactant formulation without added alkaline improved oil recovery by 8.1% OOIP over brine imbibition. For most of our other tests, alkaline was typically added to our surfactant formulations because the literature suggested that its presence would reduce surfactant retention and enhance imbibition. The afore-mentioned results may bring this concept into question when applied to shale. On the other hand, we have two sets of experiments in Table 6 in which addition of 0.2 to 0.25% alkaline provided noticeably higher recoveries than for 0.1% alkaline. More experiments are needed to establish the positive and negative contributions of alkaline material.

Effect of Surfactant Formulation. The most important findings of this study are that the surfactant formulations consistently altered the wetting state of Bakken cores toward water-wet and

TABLE 8—WELL #17450 CORES AT 60 TO 120°C, D = 38 mm, L = 4 TO 52 mm, MC

			pH (22°C)									
Sample	Aqueous Liquid	Temperature (°C)	Alkaline Content (%)	Value	δ_w	δ_o	$\delta_w - \delta_o$	Wettability	S_{or}	S_{or} Decrease (%)	Re (%)	EOR (%)
1-42-1	Brine water	60	0.00	5.60	0.498	0.498	0.000	Neutral-wet weak	0.410	8.8	32.2	8.1
1-42-2	Linear α-olefin sulfonate		0.00	5.85	0.501	0.465	0.036	Water-wet	0.322		40.0	
1-45-1	Brine water	90	0.00	5.60	0.247	0.454	−0.207	Oil-wet	0.756	18.7	24.4	21.6
1-45-2	Dimethyl amine oxide		0.10	8.44	0.500	0.500	0.000	Neutral-wet	0.569		46.0	
1-51A	Brine water	110	0.00	5.60	0.269	0.519	−0.250	Oil-wet	0.293	6.8	70.7	6.8
Sealed	Dimethyl amine oxide		0.10	8.44	1.000	0.518	0.482	Water-wet	0.225		77.5	
1-56-1	Brine water	110	0.00	5.60	0.500	0.500	0.000	Neutral-wet	0.765	18.8	23.5	20.9
1-56-2	Internal olefin sulfonate		0.25	9.03	0.278	0.002	0.276	Water-wet	0.577		42.4	
1-70-1	Brine water	120	0.00	5.60	1.000	1.000	0.000	Neutral-wet	0.788	15.5	21.2	15.7
1-70-2	Internal olefin sulfonate		0.25	9.03	0.538	0.392	0.146	Water-wet	0.633		36.7	

Note: For Core Sample 1-51A, the wettability test was conducted with brine water first, with $S_w = 0$ at the start of the test. Starting with $S_w = 0$, the test was then repeated with the use of the dimethyl amine oxide formulation. EOR is incremental oil recovery by surfactant vs. water.

TABLE 9—WELL #17450 CORES AT 90 TO 120°C, D = 38 mm, L = 41 TO 52 mm, MD

			pH (22°C)									
Sample	Aqueous Liquid	Temperature (°C)	Alkaline Content (%)	Value	δ_w	δ_o	$\delta_w - \delta_o$	Wettability	S_{or}	S_{or} Decrease (%)	Re (%)	EOR (%)
1-48A	Brine water	90	0.00	5.60	0.601	0.959	−0.358	Oil-wet	0.697	17.8	30.30	18.2
Sealed	Dimethyl amine oxide		0.10	8.44	0.470	0.360	0.110	Weak water-wet	0.519		48.10	
1-36A	Brine water	120	0.00	5.60	0.000	0.810	−0.810	Oil-wet	0.803	N/A	0.00	N/A
1-69A	Brine water	120	0.00	5.60	1.000	1.000	0.000	Neutral-wet	0.352	25.40	64.83	25.40
Sealed*	Ethoxylated alcohol		0.10	8.70	0.508	0.000	0.508	Water-wet	0.098		90.23	

*The core plug was sealed with wax and aluminum foil until tested.Cores were not cleaned by toluene and methanol, so presumably they had their original wettability. EOR is incremental oil recovery by surfactant vs. water.

consistently imbibed to displace significantly more oil than brine alone. Thus, imbibition of surfactant formulations appears to have a substantial potential to improve oil recovery from the Bakken Formation. Uncertainly exists about recovery factors from the Bakken formation during primary-recovery operations (LeFever and Helms 2010), but values of 3 to 10% OOIP have been suggested. Three of the surfactant-imbibition tests provided EOR values of 6.8 to 10.2% OOIP, incremental over brine imbibition. Ten surfactant-imbibition tests provided EOR values of 15.7 to 25.4% OOIP.

The four surfactants examined in this work (amphoteric dimethyl amine oxide, nonionic ethoxylated alcohol, anionic internal olefin sulfonate, and anionic linear α-olefin sulfonate) were selected because they showed the best performances during our preliminary studies (Wang et al. 2011a, b). However, it is not obvious that any one of these surfactants performed definitively better than the others during these experiments. On the whole, all show potential for providing positive recovery values.

Upper Shale Vs. Middle Member. Most of the surfactant tests were performed with the use of cores from the Middle Member of the Bakken. However, cores from the Upper Shale showed responses to surfactant imbibition that were consistent with those observed in the Middle Member. In particular, Upper Shale cores provided EOR values of 15.8, 8.1, and 21.6% OOIP, respectively. As mentioned earlier, four cases were noted in which brine imbibition provided exceptionally low oil saturations. We presume that lithology played a role in this exceptional behavior. However, further work will be needed to sort out the effect.

Preserved (Sealed) Vs. Cleaned Cores. Incremental recoveries from the preserved (sealed) cores ranged from 6.8 to 25.4% OOIP. This is effectively the same range found in cleaned cores.

Effects of Temperature and Porosity. Experiments were performed at 23, 60, 90, 110, and 120°C. No definitive effect of temperature is apparent at this time. Porosity values for our cores ranged from 1.6 to 9.4% (Tables 4, 5, and 7). Surfactant effectiveness did not appear to correlate with porosity. For surfactant dimethyl amine oxide formulation, note that Core 1-48A from the Middle Member in Well #17450 (1.6% porosity) had 18.2% OOIP incremental oil (from surfactant imbibition compared with brine imbibition), whereas Core 1-45-2 from the Upper Shale (6.0% porosity) had 21.6% OOIP EOR.

Methods Recommended. On the basis of the preceding discussion, we recommend Method C or D (if a Hassler cell is available) to assess wettability for cores from a high-temperature and high-salinity shale reservoir.

Oilfield Application Processes. Recovery values of 3 to 10% OOIP have been suggested for the Bakken formation during primary-recovery operations (LeFever and Helms 2010). Part of the uncertainty about exact recovery figures from the Bakken arises because oil production from this formation is in a relatively early stage. In addition, because the Bakken formation covers a broad area, there are substantial variations in reservoir character (degree of fracturing, pressure, oil saturation, permeability, and temperature) from location to location. Nevertheless, our results suggest that imbibition of surfactant formulations has a substantial potential to improve oil recovery from some parts of the Bakken formation.

Ideas for field implementation of our findings are at a relatively early stage. In one type of application, the surfactant/water formulation could be injected through a horizontal injection well at the bottom of the reservoir; similarly, a horizontal production well at the top of the reservoir could be used to collect oil and other fluids. Injection and production rates should be adjusted to maximize the oil cut in the producer. The optimum timing, volumes, and rates associated with this process depend on fracture intensity, local permeability, spacing between the wells, and the inherent imbibition rates for the rock. Our future simulation efforts will examine these parameters to identify viable conditions for a field application.

Alternatively, our process could be adapted through the use of the huf 'n' puff method in individual wells. Fractures are assumed to be perpendicular to the horizontal wells. As with the flooding application mentioned in the preceding, optimum timing, volumes, and rates associated with this process depend on fracture intensity and the inherent imbibition rates for the rock, as well as the formation pressure. Identification of viable conditions for a field application for this type of process will also be part of our future analysis.

Conclusions

- Bakken shale cores were generally oil-wet or intermediate-wet (before introduction to the surfactant formulation).
- The four surfactant formulations that we tested consistently altered the wetting state of Bakken cores toward water-wet.
- The surfactants used consistently imbibed to displace significantly more oil than did brine alone. Four of the surfactant-imbibition tests provided EOR values of 6.8 to 10.2% OOIP, incremental recovery over brine imbibition. Ten surfactant-imbibition tests provided EOR values of 15.7 to 25.4% OOIP. Thus, imbibition of surfactant formulations appears to have a substantial potential to improve oil recovery from the Bakken formation. For comparison, recovery factors with the use of the existing production methods may be on the order of a few %OOIP.
- Positive results were generally observed with all four surfactants: dimethyl amine oxide, ethoxylated alcohol, internal α-olefin sulfonate, and anionic linear α-olefin sulfonate.
- From our work to date, no definitive correlation is evident in surfactant effectiveness vs. temperature, core porosity, core source (i.e., Upper Shale or the Middle Member), and core preservation (sealed) or cleaning before use.

Nomenclature

AI = Amott-Harvey index
I_o = Harvey index
I_w = Amott index
S_o = oil saturation during spontaneous oil imbibition
S_{or} = ROS after water injection (forced)
S_w = water saturation during spontaneous water imbibition
S_{wr} = irreducible water saturation after oil injection (forced)
$V_{o\text{imbibition}}$ = oil volume spontaneously imbibed
$V_{o\text{injection}}$ = oil volume displacement by forced oil injection
$V_{w\text{imbibition}}$ = water volume spontaneously imbibed
$V_{w\text{injection}}$ = water volume displacement by forced water injection
δ_o = ratio of spontaneous oil imbibition to total oil imbibition
δ_w = ratio of spontaneous water imbibition to total water imbibition

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SI Metric Conversion Factors

cp × 10^{-3}* = Pa·s
ft 3.048 × 10^{-1}* = m
in. 9.869 233 × 2.54* = cm
md × 10^{-4} = μm^2
g/L × 0.1 = wt%
mg/L × 0.0001 = wt%

*Conversion factor is exact.

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