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## **Wettability Survey in Bakken Shale Using Surfactant Formulation Imbibition**

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### **Abstract**

For ultra-tight 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. In our previous study for Bakken shale imbibition, a group of surfactant formulations were examined—balancing the temperature, pH, salinity, and divalent cation content of aqueous fluids to increase oil production from shale with ultra-low porosity and permeability in the Middle Member of the Bakken Formation in the Williston Basin of North Dakota. To advance this work, this paper determines the wettability of different parts of the Bakken Formation. One goal of this research is to identify if the wettability can be altered using 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 examine the viability of a field application.

Using modified Amott-Harvey tests, the wettability was determined for cores from three wells at different portions of the Bakken Formation. The tests were performed under reservoir conditions (90–120°C, 150–300 g/L formation water salinity) using 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 to 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 EOR values of 6.80% to 10.15% OOIP, incremental over brine imbibition. Ten surfactant imbibition tests provided EOR values of 15.65% to 25.40% OOIP. Thus, imbibition of surfactant formulations appears to have a substantial potential to improve oil recovery from the Bakken Formation. For comparison, recovery factors using the existing production methods are only on the order of a few percent OOIP. Positive results were generally observed with all four surfactants: 17A, 58N, S2, and C1. From our work to date, no definitive correlation is evident in surfactant effectiveness versus (1) temperature, (2) core porosity, (3) whether the core was from the Upper Shale or the Middle Member and (4) whether the core was preserved (sealed) or cleaned prior to 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 ultra-low 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. As part of our investigation of chemical imbibition (using surfactant or brine formulations) to stimulate oil recovery from shale, surfactant formulation optimization is a key step. Our objective is to identify surfactant formulations that promote imbibition while minimizing clay swelling and formation damage. Initial surfactant screening and optimization involved the balancing of pH, salinity, and divalent cation content of the injected aqueous fluid (Wang *et al.* 2011a,b). However, the effectiveness of a surfactant formulation can also depend on wettability alteration. In this paper, we investigated if 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 which are named

the Lower shale, Middle Member, and Upper shale. The Middle Bakken Member ranges from 40 to 70 ft in thickness with lithologies varying from argillaceous dolostones and siltstones to clean, quartz-rich arenites and oolitic limestone with shale (Phillips *et al.* 2007). The porosity was determined to be 2-3%, and effective average permeability was only 0.04 md, based on a correlation between porosity and permeability (Pitman *et al.* 2001). The temperature of the Middle Member ranges from 80 to 120°C (Pitman *et al.* 2001). Based on chemical analysis of formation waters and statistical data from 200 well samples in the pre-Mississippian rocks (of which, the Bakken is the top formation) in the Williston Basin (Iampen and Rostron 2000), and chemical analysis of Bakken formation water by the Environmental Analytical Research Laboratory at University of the North Dakota (Wang *et al.* 2011a), brine salinities range from 150,000 to 300,000 mg/L (15% to 30 wt %) total dissolved solids (TDS).

There have been several previous studies using 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%. Acting as a wettability modifier for waterflooding, Zhang and Austad thought that sulfate in the imbibing fluid modified wettability, especially at low water-wet conditions. Also, using 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. Their spontaneous imbibition tests were conducted at 40 to 130°C (Zhang and Austad 2005). Høgnsen *et al.* (2005) used sulfate surfactant as the wettability modifier on chalk samples at temperatures from 70°C to 130°C. Their research results indicated that oil recovery increased at strongly water-wet conditions when the concentration of sulfate was three times higher than seawater (i.e., the highest TDS was 179.87 g/L) at 130°C (Høgnsen *et al.* 2005). Adibhatla, Mohanty and Gupta *et al.* (Adibhatla, Sun and Mohanty 2005; Adibhatla and Mohanty 2006; Gupta and Mohanty 2007; Gupta and Mohanty 2008) conducted a series of studies using 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 and Mohanty screened surfactants for wettability alteration in an oil-wet fractured carbonate reservoir (Gupta, Mohan and Mohanty 2009). In that study, anionic and nonionic surfactants were screened for high temperature ( $\sim 90^\circ C$ ) and high salinity ( $\sim 8\%$ ) 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 using a mixture of surfactants (Gupta and Mohanty 2009).

Sharma and Mohanty (2011) recently found that surfactants can change the wettability of a carbonate rock from mixed-wet towards water-wet at high temperature ( $\sim 100^\circ C$ ) and 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 non-wetting 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), as well as brine ionic composition (Sharma and Mohanty 2011).

During our work, we tested 30 core samples from three Bakken wells in different parts of the Williston Basin in North Dakota using a modified Amott-Harvey method. The tests were performed under reservoir conditions (90-120°C, 150-300 g/L formation water salinity) using 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, using 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 a Amott-Harvey cell, while the residual oil saturation and connate water saturation were obtained by core flooding with 20-30 pore volumes 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 (90-120°C) and salinity (15-30% TDS). Four main cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) were present in our brine, with the mol% ratios of 87.7%, 3.4%, 7.8% and 1.1%, respectively. Thus, the monovalent cations were up to ten times more prevalent than the divalent cations. In order to verify our test methodology, we used four approaches to measure the Amott-Harvey index. Here, we called them MA, MB, MC and MD. Liquid imbibition and injection volumes were obtained by weight measurements.

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 residual oil saturation and connate water saturation were obtained by centrifuge. Core thickness varied from 2 mm to 5 mm, and the test temperature was 23°C.

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

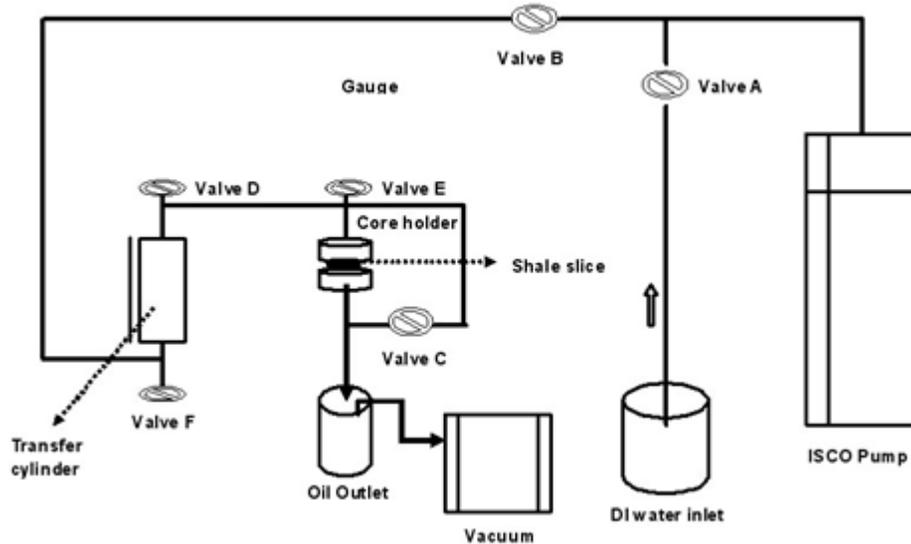


Fig. 1—Forced injection illustration for Method MB

For method MC, core plugs came from Well AV Wrigley (#17450) in northwest Burke County, and reservoir temperature varied from 90-120°C. Forced injection occurred using the coreflood setup shown in Fig. 2. Cores thickness varied from 13 mm 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 burette readings.

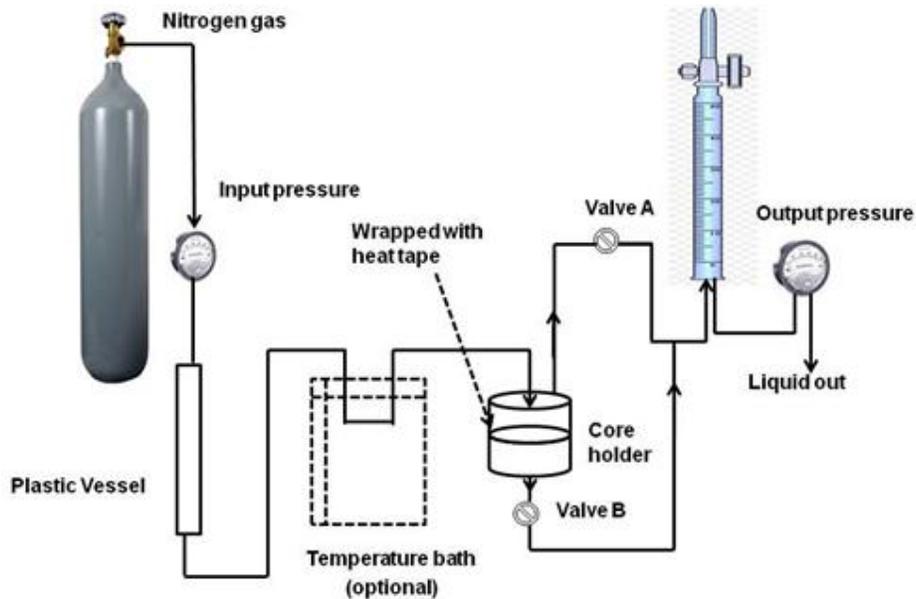


Fig. 2—Scheme for spontaneous imbibition and forced injection by Method MC

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

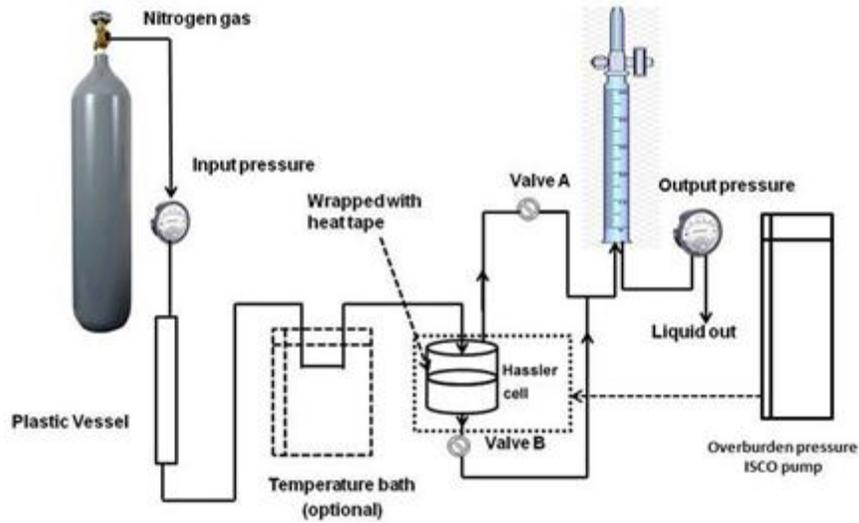


Fig. 3—Scheme for spontaneous imbibition and forced injection by Method MD with Hassler cell

Other test procedures included:

- Step 1: Filter the crude oil and brine waters through Whatman 4™ filter paper.
- Step 2: Measure oil viscosity using 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 them again with methanol to clean out brine, and then dry cores under at 105°C for 24 hours. For sealed core plugs, remove tin foil from cores carefully, and jump 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 5-10 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 mm 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).

Equations 1 to 5 were used to calculate the Amott-Harvey index. For Methods MA and MB, we used Eqs. 1 and 2 (Dake 1977 and Amott 1969); while for Methods MC and MD, we used Eqs. 3 and 4 (Glover 2001).

$$I_w = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{or}} \dots\dots\dots(1)$$

$$I_o = \frac{S_o - S_{or}}{1 - S_{wr} - S_{or}} \dots\dots\dots(2)$$

$$\delta_w = \frac{V_{Wimbibition}}{V_{Wimbibition} + V_{Winjection}} \dots\dots\dots(3)$$

$$\delta_o = \frac{V_{Oimbibition}}{V_{Oimbibition} + V_{Oinjection}} \dots\dots\dots(4)$$

$$AI = I_w - I_o \dots\dots\dots(5)$$

Where, AI =Amott-Harvey index,  $I_o$  = Harvey index,  $I_w$  = Amott index,  $S_o$ = oil saturation during oil imbibition,  $S_{or}$ = residual oil saturation after water imbibition,  $S_w$ = water saturation during water imbibition,  $S_{wr}$ = irreducible water saturation after oil imbibition,  $V_{Oimbibition}$ = oil volume spontaneously imbibed,  $V_{Oinjection}$  =oil volume increase by forced injection,

$V_{Wimbibition}$  = water volume spontaneously imbibed,  $V_{Winjection}$  = water volume increase by forced injection,  $\delta_o$  = ratio of spontaneous oil imbibition to total oil imbibition,  $\delta_w$  = ratio of spontaneous water imbibition to total water imbibition.

**Porous Media.** The tested rock plugs came from the Middle Member of Bakken Formation in Well #16433, Lars Rothie 32-29H; the Upper shale and Middle Member in Well # 17450, and Well #16771, 3328-H. Generally, the core samples tested were gritty shale and shale interbedded with siltstone, limestone and dolomite, and 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 around 7 microdarcys, while porosity averaged 4.4%. Permeability for the Upper shale was considerably less (by 2-3 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 API gravity was 43.2°API, and oil density 0.777 g/cm<sup>3</sup> at 23.2°C. Brine water salinity was characteristic of the Bakken Formation.

**Surfactants:** Aqueous surfactant formulations as imbibition candidates included: (1) 0.1% C1+30% TDS brine, (2) 0.1% S2 + 0.1-0.25% alkaline +30% TDS brine, (3) 0.05% 58N+ 0.1-0.2% alkaline + 30% TDS brine, and (4) 0.1% 17A +0.1-0.2% alkaline +15% TDS brine. They were compared at different temperatures. Compositions (Table 1) 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<sub>2</sub>, and MgCl<sub>2</sub>:** These salts were used to change salinity of the aqueous phase based on the work in Wang *et al.* 2011b.

**NaBO<sub>2</sub>·4H<sub>2</sub>O:** This alkaline chemical was used to change pH of the aqueous phase. It buffered our solutions at pH values from 8.4 to 9. Without the alkaline buffer, pH values typically ranged from 5.6 to 6.8.

**Table 1 —Surfactant formulations**

Surfactant	Concentration, %	Alkaline additive, %	Salinity, % TDS	Type
17A	0.1	0.1 or 0.2	15	Amphoteric, Dimethyl Amine Oxide
58N	0.05	0.1 or 0.2	30	Nonionic, Alcohols Ethoxylated
S2	0.1	0.1 or 0.25	30	Anionic, Internal Olefin Sulfonate
C1	0.1	0	30	Anionic, Linear $\alpha$ -Olefin Sulfonate

Alkaline: NaBO<sub>2</sub>·4H<sub>2</sub>O

## Data Analysis

**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 10613 to 10649 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). Then, the residual oil saturation ( $S_{or}$ ) and the initial water saturation ( $S_{wi}$ ) were obtained by centrifuge (our Method MA)—using a HERMLE Labnet Z 206A (centrifuged 48 hours with 4600 rpm spinning rate). Cores thickness varied from 2 mm to 5 mm, and the test temperature was 23°C. Here, the Amott-Harvey index was calculated based on Eqs. 1 and 2.

Table 2 shows the wettability test results for Well #16433 with the surfactant formulation: 0.1% C1+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 C1 surfactant formulation. (pH was 5.85 for the C1 formulation, compared with 5.60 for brine water only.) The average residual oil saturation 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 3 shows.

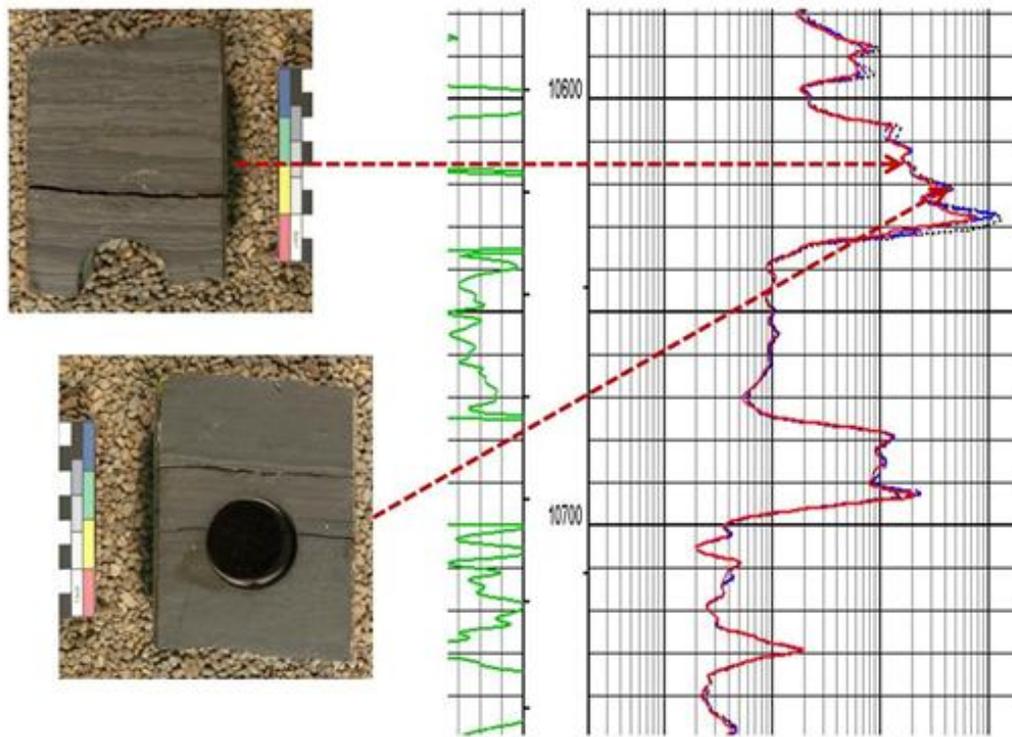
**Table 2—Well # 16433 at 23°C, D=25 mm, L=2-11 mm**

Sample	Aqueous liquid	$\delta_w$	$\delta_o$	$\delta_w - \delta_o$	Wettability	$S_{or}$	$S_{or}$ decrease, %	$Re$ %	EOR %
13C	Brine water	0.299	0.484	-0.184	Weakly oil wet	0.848	11.30	15.24	10.15
	C1 formulation	0.489	0.486	0.002	Neutral wet	0.735		25.39	
15B	Brine water	0.327	0.481	-0.150	Weakly oil wet	0.838	7.10	16.20	6.88
	C1 formulation	0.497	0.487	0.010	Neutral wet	0.767		23.08	

$Re$  is oil recovery by liquid imbibition or by centrifugation, and EOR is incremental oil recovery by surfactant vs. water. For Core Samples 13C and 15B, the wettability test was conducted by brine water first, with  $S_w=0$  at the start of the test. Then starting with  $S_w=2.54\%$  for Core 13C and with  $0.01\%$  for Core 15B, the test was repeated using the C1 formulation.

**Table 3—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. 4—Core samples location and well log curves for Well #16433**

**Wettability Tests for Well #16771 Cores.** For Well #16771, we selected cores from the Upper Bakken shale and Middle Member (Fig. 5). Lithology included black shale, and trace limestone in the Upper shale at depths of 10274 to 10310 ft, and shaly siltstone in the Middle Member at depths of 10311 to 10340 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  $S_{wi}$  were obtained by forced injection of 20-30 pore volumes (using Method MB, as illustrated in Fig. 1). Core thickness was 13 mm, and the test temperature ranged from 90 to 120°C. The Amott-Harvey index was calculated based on 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 4-7, core samples that are labeled with the same first three digit sequence (e.g., 1-10) 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 4 shows the wettability test results for Well #16771 for several surfactant formulations, with compositions of 0.05%

58N + 0.1-0.2% alkaline + 30% brine, 0.1% S2 + 0.1-0.25% alkaline + 30% brine and 0.1% 17A + 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 90-120°C and varied alkaline content. Wettability was altered from oil-wet to water-wet after imbibing 58N, 17A and S2 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 4, we note that brine imbibition worked very well for Core 1-46-2 before using Surfactant 17A. Even so, after Surfactant 17A imbibition, oil recovery still increased by 9.62 % OOIP, and the residual oil decreased by 7.70%.

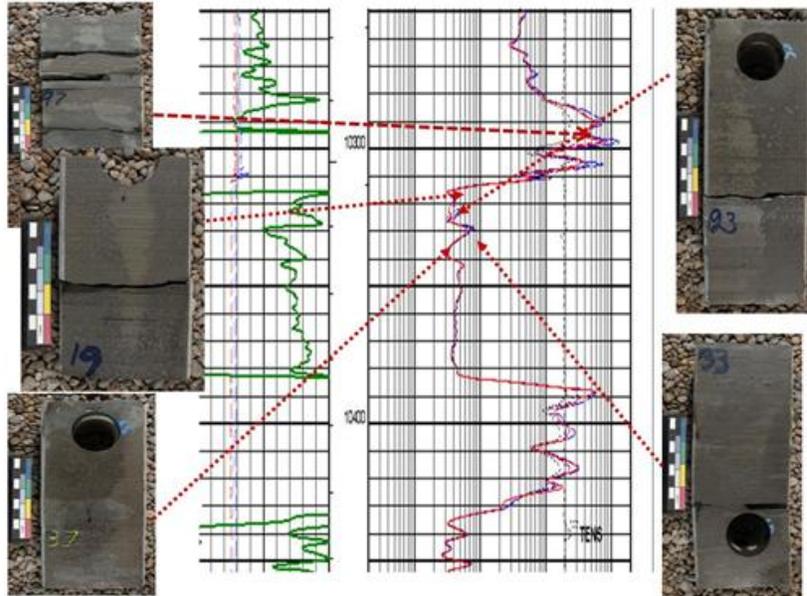


Fig. 5—Core sample location and well log curves for Well #16771

Table 4—Well #16771 at 90 to 120°C, D=38 mm, L=13 mm

Sample	Aqueous liquid	Tem. °C	pH(22°C)		$\delta_w$	$\delta_o$	$\delta_w - \delta_o$	Wettability	$S_{or}$	$S_{or}$ decrease, %	$R_e$ %	EOR %
			Alkaline content %	Value								
1-10-1	Brine water	90	0.00	5.60	0.100	0.500	-0.400	Oil wet	0.803	15.70	19.69	15.76
1-10-1	58N formulation		0.10	8.71	0.180	0.000	0.180	Water wet	0.646		35.45	
1-10-2	Brine water		0.10	8.48	0.050	0.525	-0.475	Oil wet	0.911		8.82	
1-32-2	58N formulation	90	0.10	8.71	0.987	0.949	0.038	Weak water wet	0.884	16.10	11.56	16.13
1-32-3	58N formulation		0.20	9.00	0.500	0.000	0.500	Water wet	0.723		27.69	
1-36-1	Brine water	90	0.00	5.60	0.451	0.868	-0.417	Oil wet	0.672	51.10	32.74	16.58
1-36-1	S2 formulation		0.10	8.61	0.857	0.456	0.420	Water wet	0.161		49.32	
1-36-3	S2 formulation		0.25	9.03	1.000	0.000	1.000	Water wet	0.142		53.00	
1-46-2	Brine water 17A formulation	110	0.00	5.60	0.260	0.770	-0.511	Oil wet	0.220	7.70	77.98	9.62
			0.10	8.44	0.833	0.750	0.083	Weak water wet	0.143		87.56	
1-50-3	Brine water	120	0.00	5.60	0.162	0.531	-0.369	Oil wet	0.629	47.80	37.09	24.24
1-50-1	S2 formulation		0.25	9.03	0.762	0.310	0.542	Water wet	0.266		62.60	

In Core Samples 1-10-1, 1-36-1 and 1-46-2, the wettability test was conducted with brine water first, with  $S_{w_i}=0$  at the start of the test. Then, starting with  $S_{w_i}=0.01\%$ ,  $S_{w_i}=11.42\%$  and  $16.40\%$  respectively, the test was repeated using the 58N, S2, and 17A formulations, respectively.

**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	Middle Member	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

**Wettability Tests for Well #17450 Cores.** Well #17450 cores were selected from the Upper shale (depths of 7338 ft and 7341 ft) and the Middle Member (depths of 7431 ft and 7349 ft), as Fig. 6 shows. The lithology was moderately hard, fissile, carbonaceous black shale with traces of disseminated pyrite both in the Upper shale and the Middle Member (<http://www.dmr.nf.gov/oilgas/FeeServices/wfiles/16/W17450.pdf>). 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  $S_{wi}$  were obtained by forced injection of 20-30 pore volumes 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 20-30 pore volumes using a Hassler cell as illustrated in Fig. 3. Cores thickness varied from 13 mm 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 using Method MD. The Amott-Harvey index was calculated based on Eqs. 3 and 4. When using Method MC, 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.

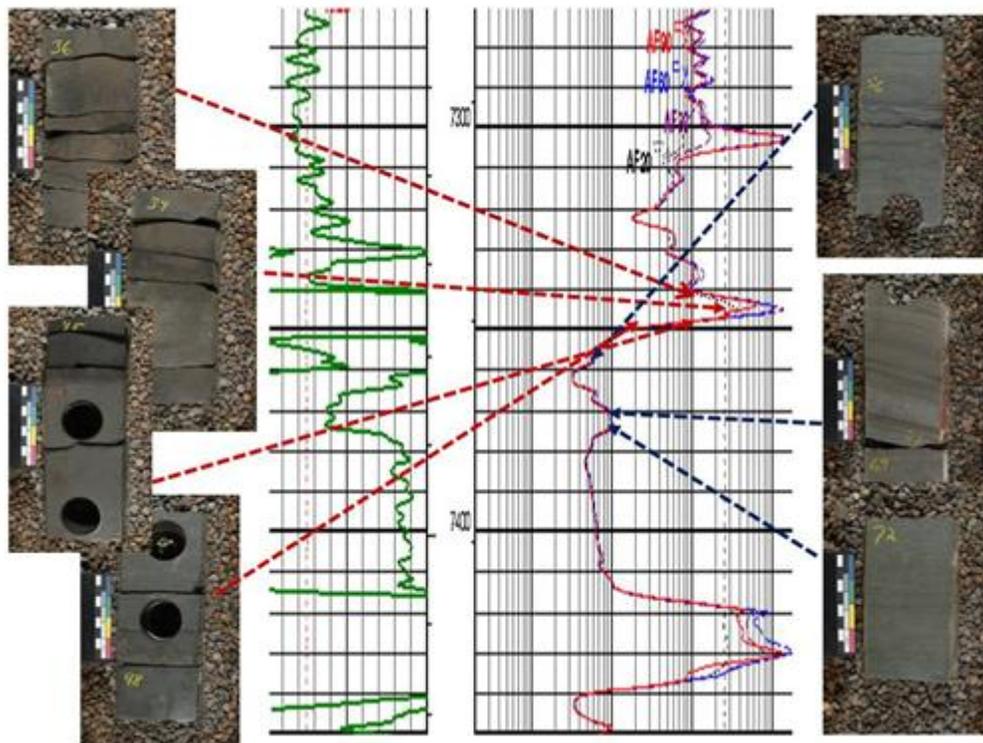
**Fig. 6—Core sample location and well log curves for Well #17450**

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<sup>3</sup>/min) for pressures up to 10,000 psi (690 bars 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 by-pass valve that is used during evacuation and saturation of the core slice. Valves D, E, F are three-way valves that control fluid input/outflow for the transfer cylinder. The core holder accommodates cylindrical core slices that are 25-26 mm in diameter and 0-10 mm in thickness, at pressures up to 3,000 psi (207 bars or 20.7 MPa).

Table 6 shows the wettability test results for Well #17450 with the surfactant formulations: (1) 0.05% 58N + 0.1-0.2% alkaline + 30% brine, (2) 0.1% S2 + 0.1-0.25 alkaline + 30% brine, and (3) 0.1% 17A + 0.1-0.2 alkaline + 15% brine. (Core properties are shown in Table 7.) Three findings were noted from Table 6. First, some cores from the Upper shale (1-42, 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, 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 to those for the cleaned cores (Table 6).

**Table 6 (a)—Well #17450 cores at 60 to 120°C, D=38 mm, L=4-52 mm, MC**

Sample	Aqueous liquid	Tem. °C	pH pH(22°C)		$I_w$	$I_o$	$AI$	Wettability	$S_{or}$	$S_{or}$ decrease, %	$Re$ %	$EOR$ %
			Alkaline content %	Value								
1-42-1	Brine water	60	0.00	5.60	0.498	0.498	0.000	Neutral wet	0.410	8.80	32.16	8.08
1-42-2	C1 formulation		0.00	5.85	0.501	0.465	0.036	Weak water wet	0.322		40.04	
1-45-1	Brine water	90	0.00	5.60	0.247	0.454	-0.207	Oil wet	0.756	18.70	24.39	21.64
1-45-2	17A formulation		0.10	8.44	0.500	0.500	0.000	Neutral wet	0.569		46.03	
1-51A sealed	Brine water 17A formulation	110	0.00	5.60	0.269	0.519	-0.250	Oil wet	0.293	6.80	70.69	6.80
			0.10	8.44	1.000	0.518	0.482	Water wet	0.225		77.48	
1-56-1	Brine water	110	0.00	5.60	0.500	0.500	0.000	Neutral wet	0.765	18.80	23.52	20.85
1-56-2	S2 formulation		0.25	9.03	0.278	0.002	0.276	Water wet	0.577		42.37	
1-70-1	Brine water	120	0.00	5.60	1.000	1.000	0.000	Neutral wet	0.788	15.50	21.18	15.65
1-70-2	S2 formulation		0.25	9.03	0.538	0.392	0.146	Water wet	0.633		36.73	

Here, for Core Sample 1-51A, the wettability test was conducted with brine water first, with  $S_w=0$  at the start of the test. Then starting with  $S_w=0.01\%$ , the test was repeated using the 17A formulation.

**Table 6(b)—Well #17450 cores at 90 to 120°C, D=38 mm, L=41-52 mm, MD**

Sample	Aqueous liquid	Tem. °C	pH pH(22°C)		$\delta_w$	$\delta_o$	$\delta_w - \delta_o$	Wettability	$S_{or}$	$S_{or}$ decrease, %	$Re$ %	$EOR$ %
			Alkaline content %	Value								
1-48A sealed	Brine water 17A formulation	90	0.00	5.60	0.601	0.959	-0.358	Oil wet	0.697	17.8	30.30	18.2
			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 sealed	Brine water 58N formulation	120	0.00	5.60	1.000	1.000	0.000	Neutral wet	0.352	25.40	64.83	25.40
			0.10	8.70	0.508	0.000	0.508	Water wet	0.098		90.23	

Note: sealed means that the core plug was sealed with wax and tin foil until tested. Cores were not cleaned by toluene and methanol, so presumably they had their original wettability.

**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

## Discussion

**Experimental Method.** As mentioned above, four approaches were employed to measure the Amott-Harvey index in this paper. Due to 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 that we tested, about one-third of the results were not usable due to apparatus failure or errors in data collection. Each of our four methods had positive and negative aspects. For Method MA, core plugs were weighed before and after spontaneous imbibition and before and after forced fluid injection. The advantage is that weight measurements can be very accurate (i.e., to 0.0001 grams 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, since we did not have a way to maintain temperature at 90-120°C during centrifugation, we could only use the method for studies at room temperature. Also, our centrifuge was not large enough to accommodate 3.8-cm-diameter cores.

For Method MB (Well #16771), 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 90-120°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 measurement are made. Also, 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 experience a weight loss, even though water has displaced less-dense oil.

Methods MC and MD were used for core plugs from Well #17450. For these methods, imbibition and injection volumes were determined by readings on burettes. Although readings are fairly accurate, they do have larger error bars than weight measurements. Also, if oil or water adheres to the core surface or an interior part of the flow line, it may not be displaced to the burette for measurement.

Experimental results are shown in Tables 2 and 3 for Method MA, in Tables 4 and 5 for Method MB, in Tables 6(a) and 7 for Method MC, and in Tables 6(b) and 7 for Method MD. For all methods, exposure to a surfactant formulation was found to shift the wetting state toward water-wet. Also, for all but one case (i.e., Core 1-46 in Table 4), exposure to a surfactant formulation resulted in more oil recovery by imbibition than exposure to brine alone. Specifically, the EOR (i.e., incremental recoveries for surfactant imbibition over brine imbibition) was 6.88% to 10.15% in Table 2, 9.62% to 24.24% in Table 4, 6.8% to 21.64% in Table 6(a), and 18.2% to 25.4% in Table 6(b).

**Initial Core Wettability.** For this study, we tested 30 core samples from three Bakken wells in different part of the Williston Basin in North Dakota using a modified Amott-Harvey method. Among the tested cores, results from 1/3 of samples could not be used due to apparatus failure or data reading errors. However, 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).

**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 from 0.629 to 0.911 (Tables 2, 4, and 6). However, four cases (Cores 1-46-2, 1-42-1, 1-51A, and 1-69A) 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 this exception. Even though brine apparently imbibed in some cases, in other cases, brine sometimes did not imbibe at all (e.g., Case 1-36A in Table 6).

**Effect of Alkaline Solutions.** In Table 4, 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 6(a), for Cores 1-42-1 and 1-42-2, a C1 surfactant formulation without added alkaline improved oil recovery by 8.08% 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 should reduce surfactant retention and enhance imbibition. The above mentioned results may bring this concept into question when applied to shale. On the other hand, we have two sets of experiments in Table 4 (Cores 1-32-2 vs. 1-32-3; and Cores 1-36-1 vs. 1-36-3) where addition of 0.2-0.25% 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 (1) consistently altered the wetting state of Bakken cores toward water-wet and (2) 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. Recovery factors using existing production methods are only a few percent OOIP. Three of the surfactant imbibition tests (Cores 13C, 15B, 1-42-2; and 1-51A) provided EOR values of 6.8% to 10.15% OOIP, incremental over brine imbibition. Ten surfactant imbibition tests (Cores 1-10-1, 1-32-3, 1-36-1, 1-36-3, 1-50-1, 1-45-2, 1-56-2, 1-70-2, 1-48A, and 1-69A) provided EOR values of 15.65% to 25.4% OOIP.

The four surfactants examined in this work (17A, 58N, S2, and C1) 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 using 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 1-10-1, 1-42-2, and 1-45-2 provided EOR values of 15.76% OOIP, 8.08% OOIP, and 21.64% OOIP, respectively (Table 4). As mentioned earlier, four cases were noted where 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 (Cores 1-51A, 1-48A, and 1-69A) ranged from 6.8% to 25.4% OOIP (Table 6). This is effectively the same range found in cleaned cores.

**Effect of Temperature and Porosity.** Experiments were performed at 23°C, 60°C, 90°C, 110°C, 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 3, 5, and 7). Surfactant effectiveness did not appear to correlate with porosity. For Surfactant 17A formulation, note that Core 1-48A from the Middle Member in Well #17450 (1.6% porosity) experienced 18.2% OOIP incremental oil (from surfactant imbibition compared with brine imbibition), while Core 1-45-2 from the Upper shale (6.0% porosity) experienced 21.64% OOIP EOR.

## Conclusions

1. Bakken shale cores were generally oil-wet or intermediate-wet (before introduction to the surfactant formulation).
2. The four surfactant formulations that we tested consistently altered the wetting state of Bakken cores toward water-wet.
3. The surfactants used consistently imbibed to displace significantly more oil than brine alone. Four of the surfactant imbibition tests provided EOR values of 6.80% to 10.15% OOIP, incremental recovery over brine imbibition. Ten surfactant imbibition tests provided EOR values of 15.65% to 25.40% OOIP. Thus, imbibition of surfactant formulations appears to have a substantial potential to improve oil recovery from the Bakken Formation. For comparison, recovery factors using the existing production methods may be only on the order of a few % OOIP.

4. Positive results were generally observed with all four surfactants: 17A, 58N, S2, and C1.
5. From our work to date, no definitive correlation is evident in surfactant effectiveness versus (1) temperature, (2) core porosity, (3) whether the core was from the Upper Shale or the Middle Member and (4) whether the core was preserved (sealed) or cleaned prior to use.

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### Nomenclature

$OOIP$  = original oil in place,  $\text{cm}^3$

$AI$  = Amott-Harvey index

$EOR$  = enhanced oil recovery vs. brine water imbibition alone

$I_o$  = Harvey index

$I_w$  = Amott index

$Re$  = oil recovery by spontaneous imbibition

$S_o$  = oil saturation during spontaneous oil imbibition

$S_{or}$  = residual oil saturation after water injection (forced)

$S_w$  = water saturation during spontaneous water imbibition

$S_{wr}$  = irreducible water saturation after oil injection (forced)

$V_{oimbibition}$  = oil volume spontaneously imbibed

$V_{oinjection}$  = oil volume displacement by forced oil injection

$V_{wimbibition}$  = water volume spontaneously imbibed

$V_{winjection}$  = water volume displacement by forced water injection

$\delta_o$  = ratio of spontaneous oil imbibition to total oil imbibition

$\delta_w$  = ratio of spontaneous water imbibition to total water imbibition

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### SI Metric Conversion Factors

cp × 1.0*	E-03	= Pa·s
ft × 3.048*	E-01	= m
in. × 2.54*	E+00	= cm
md × 9.869 233	E-04	= μm <sup>2</sup>
g/L × 0.1	E+00	= wt %
mg/L × 0.001	E+00	= wt %

\*Conversion is exact