Abstract
This paper investigates an idea for chemical imbibition using surfactant formulations to stimulate oil recovery from oil shale. One goal of this research is to identify a formulation that promotes imbibition while minimizing clay swelling and formation damage. Experiments directed toward this goal involved balancing the temperature, pH, salinity, and divalent cation content of aqueous fluids to enhance oil recovery from the shale with ultra-low porosity and permeability in the middle member of the Bakken formation in the Williston Basin of North Dakota. 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 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 where brine and surfactant (0.05−0.2 wt % concentration) imbibition yielded recovery values of 1.55 to 76% OOIP at high salinity (150−300 g/L: 15−30 wt %) and temperatures ranging from 23°C−120°C. Six key observations were noted: (1) an ethoxylate nonionic surfactant, an internal olefin sulfonate anionic surfactant, and an amine oxide cationic surfactant were more stable than the other surfactants for temperatures from 105−120°C. They were effective in imbibing and displacing oil at high temperature. (2) Adding alkali to surfactant formulations increased oil recovery from Bakken shale. However, sodium carbonate reacted with divalent cations and precipitated when added to our highly saline brines. To counter this effect, sodium metaborate was added to surfactant solutions to reduce or prevent precipitation. (3) An ethoxylate nonionic surfactant and an internal olefin sulfonate anionic surfactant were more tolerant of high salinity than other surfactants and display higher oil recoveries at high temperature. For Bakken cores, surfactants did not imbibe effectively using distilled or low salinity water. (4) Varying the hardness of the surfactant formulation had a major effect on imbibition and oil displacement. (5) In some cases, clay flaking from the shale was observed when contacting brine (without surfactant) or contacting amine oxide cationic surfactant with higher alkane numbers in brine. However, for the later situation, it could be improved by changing pH of surfactant solution. (6) For a given surfactant, oil recovery can be maximized by identifying the optimal surfactant concentration, brine salinity, sodium metaborate concentration, and divalent cation content.

Introduction
Shale is an important source of oil and gas 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 formula optimization is a key step. The primary target is to identify a surfactant formulation that promotes imbibition while minimizing clay swelling and formation damage. Surfactant screening and optimization will involve balancing the pH, salinity, and divalent cation content of the injected aqueous fluid.

As a 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. Lithologies vary from argillaceous dolostones and siltstones to clean, quartz-rich arenites and oolitic limestones 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 (Janet et al, 2001). Based on chemical analysis of formation waters and statistical data from 200 well samples in the Pre-Mississippian formation (of which, the Bakken is the top formation) in the Williston Basin (Iampen and Rostron, 2000), the brine salinities ranged from 150,000 to 300,000 mg/L (15 wt% to 30 wt%) of total dissolved solids (TDS).

Examination of the literature reveals a number of studies using surfactant imbibition to improve the reservoir oil recovery from sandstone, carbonate, and chalk reservoirs, with rock permeability ranging from 1 to 15 md and porosity up to 29.1%. Chen et al. (2008) studied imbibition of two anionic surfactants and one nonionic surfactant (dodecyl benzene sulfonate, carboxylate, and OP-10) in a low permeability fractured sandstone reservoir. At room temperature, their study showed that imbibition declined with increased concentration of the surface active agent. Surfactants with high concentration (0.2 wt%) gave a lowest imbibition in sandstone cores (Chen et al, 2008). Acting as a wettability modifier for waterflooding, Zhang and Austad suggested that using cationic surfactants of the type \(^{+}[^{3}N(CH_{3})_{3}]^{-}\) improved oil recovery from chalk significantly, especially when the rock wettability was close to a neutral wetting condition. Their spontaneous imbibition tests were conducted at 70°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 completely water-wet conditions when the concentration of sulfate was increased three times relative to seawater (highest TDS was 179.87 g/L) at 130°C (Høgnsen et al., 2005). Adibhatla, Mohanty and Gupta et al conducted a series of studies using anionic and nonionic surfactants to change the oil-wet carbonate wettability (Adibhatla, Sun and Mohanty, 2005; Adibhatla and Mohanty, 2006; Gupta and Mohanty, 2007; Gupta and Mohanty, 2008). Their researches 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. \(\text{Na}_2\text{CO}_3\) was added to reduce surfactant adsorption. Subsequently, Gupta and Mohanty screened surfactant 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 (˜90°C) and high salinity (˜8 wt%) 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).

Wang et al. (2010) studied flow behavior and imbibition using brine in shale rock. They indicated that aqueous imbibition could increase oil recovery from shales. Also, Shuler (2010) suggested that specialized surfactant formulations may recover oil from Bakken shale. No other literature has described utilizing surfactant imbibition to enhance oil recovery in shale reservoirs.

During our preliminary work, we chose seventeen surfactants to screen a possibility of oil recovery increases in Bakken shale. These surfactants included anionic, nonionic and cationic surfactants. A number of these surfactants exhibited stability for 15 days at 105°C (220°F), and 7–10 days at 110–120°C with 15–30 wt % TDS. Certain samples were selected for further studies on the effects of temperature, \(\text{pH}\), salinity, divalent cation content, and surfactant concentration effect on oil recovery. More extensive studies of surfactant phase behavior, wettability alteration, and imbibition are underway and will be reported separately in the future.

Methodology

Previous research and the mineralogical analysis on core samples from well #15722 of Bakken (https://www.dwr/nd.gov/oil/gas/) indicated that formation damage from aqueous contact is a concern for shale formations. Consequently, it is important to understand clay chemistry so that a surfactant formulation can be developed to enhance imbibition while causing minimum formation damage.

Surfactant formulations were studied by examining different factors that affect spontaneous imbibition. First, brines with different water compositions were examined as imbibing fluids. Later, surfactant solutions were used. A fixed imbibing period was employed before a new imbibing fluid was introduced. Using oil from the Bakken formation in the Williston Basin, significant differences in recoveries were observed and calculated during the period of application of the surfactant.

Porous Media.

The tested rock plugs came from the middle member of Bakken formation, Well #16433, Lars Rothie 32-29H. Generally, the core samples tested were from the middle member of a depth of 10613–10649 ft and were gritty shale and limestone, and
poor to no porosity (Fig. 1). Table 1 shows the characteristics of the core materials used in the experiments. Core plugs were 25 mm in diameter and 1 to 5 mm in thickness. Average geological parameters and fluid saturations of core samples are listed in Table 2.

In order to provide reliable experimental results, our results in the following studies were obtained using average values for cores of varying depth.

![Table 1 — Core plug descriptions](image)

<table>
<thead>
<tr>
<th>Sample resource</th>
<th>Depth, ft</th>
<th>Color</th>
<th>Lithology, depositional environments, and other attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>middle member of Bakken</td>
<td>10613-10649</td>
<td>Light to dark grey, light brown to tan</td>
<td>Very fine crystalline, argillaceous, thin laminations, gritty, limey shale.</td>
</tr>
</tbody>
</table>

![Table 2 — Summary of geological parameters and fluid saturations](image)

<table>
<thead>
<tr>
<th>Sample Depth</th>
<th>Dean-Stark Fluid Saturation</th>
<th>Clean Dry Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil % Pore Volume</td>
<td>Water % Pore Volume</td>
</tr>
<tr>
<td>10613 ~ 10649</td>
<td>26.81</td>
<td>32.04</td>
</tr>
</tbody>
</table>

**Test Fluids.**

Cores were saturated with crude oil from the Bakken formation in the Williston basin of North Dakota: Well H. Davidson 2-11H. The API gravity was 43.2°API, and oil density 0.777 g/cm$^3$ at 23.2°C. Brine water was selected because its salinity is characteristic of the Bakken Formation.

**Surfactants:** 17 surfactant samples were selected as imbibition candidates and compared at different temperatures listed in Table 3.

**Brines:** Waters with 0 wt% (distilled water), 7.5 wt%, 15 wt%, and 30 wt% TDS were used as imbibing fluids.

**NaCl, KCl, CaCl$_2$, and MgCl$_2$:** These salts were used to change salinity of the aqueous phase based on the chemical analysis in Table 4.

**Na$_2$CO$_3$ & NaBO$_2$•4H$_2$O:** These alkaline chemicals were used to change pH of the aqueous phase.

**Core Preparation**

1. Cut and polish the rock slabs into 1 to 5 mm thin slices. Clean surfaces of slices with toluene, and dry slices at 105°C for 24 hours. Weigh dry weights of slices, taken as $W_0$.
2. Measure length (thickness) and diameters at 5-10 locations for each core. All measurements deviated less than ±0.01 mm from the average value.
3. Vacuum sample rocks for 2 to 3 hours, and then saturate the core slices with the oil sufficiently until no gas bubbles are seen exiting the core. Remove the oil from the surface of the slices. Weigh the slices after saturation, taking this weight as $W_{oil}$.

**Surfactant Optimization Procedures**

1. Based on the chemical (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$) concentrations of the formation water (Table 4), prepare the brines with 0 – 30 wt% TDS brine and surfactant solutions. Filter the waters.
2. Test water, oil, and surfactant viscosity with a Brookfield viscometer at various temperatures. Calculate the liquid density (weight/volume) with experimental equations (Zhiyong Kang, 1999).
3. Put surfactant samples into laboratory oven at a specific temperature for 15 days to observe changes in the samples with increasing temperature. Particularly test at high temperatures above 100°C. Surfactant samples were sealed in glass bottles with temperature tolerance caps.
4. Select surfactant samples that are stable at high temperature with a specific salinity, then immerse the slice into the aqueous solutions, and imbibe brine or surfactant solution into the core samples with one surface of slice closed for 24 to 48 hrs, depending on thickness of core plugs.
6. Set up different temperatures in the oven. Repeat Steps 4 to 5 to estimate the oil produced (Eq. 1).
(7) Change solution salinity; then repeat Steps 4 to 5.
(8) Change pH of surfactant samples with 0.1−0.25 wt% of alkaline chemicals. Repeat Steps 4 to 5 to estimate the oil produced (Eq. 1).
(9) Change divalent cation content in the brine and surfactant solution. Repeat Steps 4 to 5 to estimate the oil produced with Eq. 1.
(10) Change surfactant concentrations. Repeat Steps 4 to 5 to estimate the oil produced according to Eq. 1.

\[
\%OOIP = 100 \times \left( W_o - W_{oil} \right) / \left[ \left( \rho_{w(x)} / \rho_o - 1 \right) \times OOIP \right]
\]  

(1)

Here, water density is assumed equal to surfactant solution density under the same salinity and temperature. The liquid densities change with temperatures and salinities.

**Data Analysis and Discussion**

**Initial Aqueous Solution Screening.**

Laboratory tests were performed at the room temperature (23.2°C) with a salinity of 30 wt% brine. Imbition tests involved 17 surfactants. Most surfactants were found to increase the oil recovery from 3.47 to 60.67% compared with oil recovery by brine water alone (3.23%). Among the brine water and surfactant samples, some core flakes were produced in brine without surfactant during imbibition, as shown in Fig. 2. The amount of oil recovered with brine was small compared to the amount from surfactant imbibition. An anionic alkyl benzene sulfonate surfactant of medium \( M_W \) (molecular weight) was not soluble between 15 − 30 wt% salinity, and therefore dropped from further testing.

**Temperature Stability Study At High Salinity.**

Surfactants samples were studied for high temperature stability from 105°C to 120°C with brine containing 5% cationic divalent ions. 20 ml of each surfactant solution with 15−30 wt% TDS were sealed into vials with temperature-tolerant caps. These vials were put into a laboratory oven of a fixed temperature. All surfactants in Table 3 remained in aqueous solutions for 15 days to confirm stability of the surfactants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Supplier</th>
<th>Type</th>
<th>15 wt%</th>
<th>30 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>105°C</td>
<td>110°C</td>
</tr>
<tr>
<td>A-6</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>C-1</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>C-2</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>14 days</td>
</tr>
<tr>
<td>C-8</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>S2</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>S3B</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>cloudy</td>
</tr>
<tr>
<td>S12</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>9 days</td>
</tr>
<tr>
<td>S14</td>
<td>Tiorco</td>
<td>Anionic</td>
<td>O</td>
<td>10 days</td>
</tr>
<tr>
<td>17A</td>
<td>Champion</td>
<td>Cationic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>17B</td>
<td>Champion</td>
<td>Cationic</td>
<td>O</td>
<td>10 days</td>
</tr>
<tr>
<td>58N</td>
<td>Champion</td>
<td>Nonionic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>12J</td>
<td>Champion</td>
<td>Cationic</td>
<td>O</td>
<td>10 days</td>
</tr>
<tr>
<td>O332</td>
<td>Shell Chemicals</td>
<td>Anionic</td>
<td>cloudy</td>
<td>cloudy</td>
</tr>
<tr>
<td>A771</td>
<td>Shell Chemicals</td>
<td>Anionic</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>SS-7593</td>
<td>Oil Chem</td>
<td>Nonionic</td>
<td>O</td>
<td>10 days</td>
</tr>
<tr>
<td>1688</td>
<td>Oil Chem</td>
<td>Nonionic</td>
<td>O</td>
<td>12 days</td>
</tr>
<tr>
<td>N969</td>
<td>Oil Chem</td>
<td>Unknown</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

"O" is stable for more than 15 Days; "x day(s)" = days stable prior to precipitation; "N" is not soluble to brine waters with 15−30 wt % salinity.

In Table 3, five surfactant structures were studied for temperature stability: anonic surfactants with sulfonate or sulfate groups, cationic surfactants with dimethyl amine oxide groups, and nonionic surfactants with ethylene glycol butyl ether or...
ethoxyate groups. Concentrations of these surfactant solutions were diluted to 0.1 wt%. Several observations were noted:

A. For solution salinity of 30 wt%:

(1) Ethoxylate surfactant, internal olefin sulfonate anionic surfactants, and amine oxide cationic surfactants were more stable than other surfactants at a temperature of 105°C. In Figs. 3 and 4, Surfactants 17A, 17B, 58N, S2 were clear liquids before and after 15 days. (2) One linear alpha olefin sulfonate (C-2) and one ethylene glycol butyl ether (SS-1688) was slightly cloudy after 15 days at 105°C. These surfactants were supposed to work as co-surfactants. (3) Other surfactants (C-1, SS-7593) were cloudy in 30 wt % TDS brine at 105°C and experienced phase transitions (Fig. 4) at high temperature—making them unusable by themselves. However, after 0.3 wt% alcohol was added, the surfactant formulations became clear, as shown in Figs. 5 and 6. (4) Sulfonates with carboxylate heads were unacceptable at high temperature at salinity of 30 wt%. C-8 (low M_w) clouded heavily (Fig.4), S-12 (medium MW) and S-14 (Alcohol ethoxy sulfate) precipitated and not stable at 15 days, as did higher olefin sulfonate O332. (5) Ethoxylate alcohol surfactant-58N showed good stability at 110°C for 15 days (Fig. 7). (6) For cationic surfactants, 17A, 17B, and 12J, an ultrathin layer with a brown color developed on the top of the solution at 110°C and 120°C after aging. It is possible reason to make clay flaking as molecules of 17A reacted with divalent ions in salt water. However, at a different pH in 17A solution, this brown color disappeared (Fig. 8).

B. For solution salinity of 15 wt%:

Most surfactants in Table-3 showed good temperature stability at 105°C with 15 wt% TDS. Surfactant ethoxylate alcohol-58N, Alcohol alkoxy sulfate-771 and N969 showed good stability at 120°C for 15 days with 15 wt% TDS under Bakken conditions. When comparing surfactant stability for two salinities, more surfactants were stable at lower salinities (15 wt%) than at the higher salinities (30 wt%).

Three surfactants [cationic (17A), nonionic (58N) and anionic (S2)] were selected for imbibition studies, discussed next:

Spontaneous Imbibition

Reservoir conditions in the Bakken indicated a temperature range of 80 to 120°C (Janet et al, 2001). Three surfactant samples were selected to determine oil recovery of 60°C to 110°C. These tested samples were anionic, nonionic, and cationic surfactants with 0.1% wt concentration. Our core plugs (Well #16433) were typically 25-26 mm in diameter and 2-3 mm in thickness. Core plugs selected from 15A to 49A with 12 sections. The dimensions of each core were measured very accurately to 0.01mm with a Carrera precision digital caliper. The average porosity of the core slices was 0.06, and average permeability to Bakken oil was 4.84×10⁻³ md at 23°C. Assume the initial water saturations were zero.

Using the one-face-closed imbibition method, Fig. 9 demonstrates that surfactant solutions can improve oil recovery from the shaly parts of middle member from 6.5% to 76% with initial water saturation (S_wi) was zero, salinity 30 wt%, and temperature ranged from 60°C to 120°C.

Before imbibition tests at high temperature, experiments were conducted at 23–60°C with brine water alone and the three selected surfactants. Interestingly, in most circumstances, surfactant formulations recovered more oil than brine alone. The exceptions occurred in the cores without clay flaking. For example, at a solution salinity of 15 wt% and 23°C, an oil recovery up to 15.19% was noted for brine water alone. This is more than the amount using surfactant 17A (3.30%). However, this outcome only represents 1.2% of the total core slices tested.

Fig. 9 shows that imbibition and oil recovery increased with increased temperature at 30 wt% TDS. Guessing imbibition is promoted by greater ion exchange at higher temperatures. These experimental results are consistent with previous work reported by Gupta (2009) for carbonate. Since our core slices had one surface closed, oil recovery may have been less than with all faces open during the imbibition. Future research will examine this issue. Previous studies indicated higher concentrations of cationic surfactant effectively promoted imbibition (Zhang and Austad, 2005). In our experiments, 0.1% wt concentration of surfactant was always used. This might explain the lower oil recoveries for 17A were less than for the other two types of surfactants. Future studies will focus on the the effects of surfactant concentration on imbibition. On the other hand, for Surfactant 17A, we noted core variations produced different results. As mentioned above, the brown color after high temperature aging indicated a reaction when surfactant and ions exchanged/adsorbed on Bakken clays. It is also possible that there was less oil to recover compared to the other two surfactants or clay flaking occurred in the particular core slice.

Also Fig. 9 shows that the anionic surfactant, S2, produced more oil as the temperature increased to 120°C. From one viewpoint, anionic surfactant is more likely to promote partitioning of the surfactant between oil and water, favoring driving the oil phase away from rock.

Fig. 10 shows the imbibition and oil recovery change vs. temperature at 15 wt% TDS. Oil recovery trends did not always
increase with temperature. We speculate that mineral dissolution might vary with temperature. Consequently, when the surfactants are applied to an oil field in the future, temperature optimization should be considered, particularly with respect to clay reactions, wettability changes, and ion exchange.

**Salinity of aqueous solution.**

According to chemical analysis of Bakken formation water (Well H. Davidson 2-11H), chlorine ions are the major ionic component of Bakken formation water, account for 61.50% of total dissolved salts. The other univalent ions sodium and potassium, account for 30.32% of the total salts. The divalent cations calcium and magnesium ions, account for 4.79% of the total salts (Table 4).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Detection limit, mg/L</th>
<th>Result in sample, mg/L</th>
<th>Methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>300,000</td>
<td></td>
<td>Cond. meter</td>
</tr>
<tr>
<td>Inorganic carbon</td>
<td>0.2</td>
<td>16.5</td>
<td>TOC analyzer</td>
</tr>
<tr>
<td>Cl</td>
<td>0.05</td>
<td>184,500</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Na</td>
<td>0.02</td>
<td>85,322</td>
<td>FAAS</td>
</tr>
<tr>
<td>K</td>
<td>0.05</td>
<td>5,643</td>
<td>FAAS</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.2</td>
<td>13,177</td>
<td>FAAS</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.01</td>
<td>1,175</td>
<td>FAAS</td>
</tr>
</tbody>
</table>

Based on the relative properties indicated in Table 4, brine waters with four salinities were prepared with the following TDS values: 0%, wt, 7.5 wt%, 15 wt%, and 30 wt%. The inorganic carbon was neglected.

Fig. 11 shows the relationship between TDS of surfactant solutions and oil recovery at 90°C. Experiments used salinities ranging from 0 wt% to 30 wt%. Core plugs were labeled 31B and 49A (Bakken Well #16433). The results demonstrate three facts: (1) At high temperature, no imbibition or oil recovery occurred using distilled water or surfactant solutions in distilled water. This phenomenon might be due to clay swelling during imbibition. Brine water alone with 7.4 wt% TDS also caused rock damage. Rock flakes were observed after brine contact (see Fig. 2). According to clay analysis (X-ray diffraction) of core samples from Well AnSBRO Loucks 44-30 (Bakken formation in North Dakota), the major mineral was illite—47 meq/100g of total minerals (https://www.dmr.nd.gov/oilgas/FeeServices/wfiles/15/W15722.pdf). Theoretically, illite could be swelled by fresh water. (2) For the cationic surfactant 17A, the optimum salinity for maximum oil recovery is 15 wt%. For the other two surfactants (anionic and nonionic), 30 wt% TDS promoted more oil production from the core plugs.

For salinity optimization, surfactant-brine and surfactant-oil-brine phase behaviors are also very important factors affecting oil recovery. Phase behavior will be studied in our future work.

**pH Changes.**

Alkali was added to change the brine pH in our study, using a Cole Parmer model 510 pH meter to monitor the solution pH before imbibition. Generally, alkali reduces adsorption of surfactants on to rocks. Two alkalis were studied: (1) With Na<sub>2</sub>CO<sub>3</sub>, a precipitate formed at 0.1 wt% Na<sub>2</sub>CO<sub>3</sub> (Fig. 12) due to the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup>. This alkali is not suitable with high salinity and hard brines. (2) With NaBO<sub>2</sub>.4H<sub>2</sub>O, no precipitation was observed at 0.1 wt% NaBO<sub>2</sub>.4H<sub>2</sub>O mixed with brine (Fig. 11). In experiments with hard brine, this alkali can be added to the surfactant solutions to increase pH in future testing.

Table 5 shows results of changing pH with 0.1—0.25 wt% NaBO<sub>2</sub>.4H<sub>2</sub>O at 90°C and 30 wt% salinity, no precipitation was observed. Core plugs, with thickness 1—5mm were labeled 31B, 46A, and 49A (Well #16433). Anionic surfactant S2, was more stable at higher alkali concentrations than the other two surfactant types. Based on Table 5, as the additive content increased from 0% to 0.1%, oil recoveries increased for all three surfactants. However, when the alkali content was increased to 0.25%, oil recovery only increased for the anionic surfactant. Table 6 shows, for a given surfactant, as the temperature and alkali content was increased from 23°C to 90°C, and 0.1% to 0.25%, respectively, the pH of target aqueous solutions founded to decreased.
Table 5 —pH values vs. oil recovery
(90°C, 0.1% surfactant concentration, 30 wt% of TDS, and 5% divalent content)

<table>
<thead>
<tr>
<th>Alkali content, %</th>
<th>Sample</th>
<th>pH</th>
<th>Oil recovery, %</th>
<th>pH</th>
<th>Oil recovery, %</th>
<th>pH</th>
<th>Oil recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17A</td>
<td>7.51</td>
<td>9.19</td>
<td>8.75</td>
<td>10.33</td>
<td>8.83</td>
<td>5.88</td>
</tr>
<tr>
<td>0.1</td>
<td>58N</td>
<td>5.91</td>
<td>15.42</td>
<td>8.71</td>
<td>18.29</td>
<td>8.81</td>
<td>10.61</td>
</tr>
<tr>
<td>0.25</td>
<td>S2</td>
<td>7.24</td>
<td>12.87</td>
<td>8.67</td>
<td>13.08</td>
<td>8.77</td>
<td>13.61</td>
</tr>
<tr>
<td>brine</td>
<td></td>
<td>6.45</td>
<td>1.54</td>
<td>8.71</td>
<td>17.83</td>
<td>8.73</td>
<td>13.53</td>
</tr>
</tbody>
</table>

Table 6 —pH values vs. temperature

<table>
<thead>
<tr>
<th>Alkali content, %</th>
<th>Sample</th>
<th>pH, 23.2°C</th>
<th>pH, 90°C</th>
<th>pH, 23.2°C</th>
<th>pH, 90°C</th>
<th>pH, 23.2°C</th>
<th>pH, 90°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17A</td>
<td>7.42</td>
<td>7.51</td>
<td>8.88</td>
<td>8.75</td>
<td>9.19</td>
<td>8.83</td>
</tr>
<tr>
<td>0.1</td>
<td>58N</td>
<td>5.34</td>
<td>5.91</td>
<td>8.94</td>
<td>8.71</td>
<td>9.32</td>
<td>8.81</td>
</tr>
<tr>
<td>0.25</td>
<td>S2</td>
<td>7.84</td>
<td>7.24</td>
<td>8.76</td>
<td>8.67</td>
<td>9.11</td>
<td>8.77</td>
</tr>
<tr>
<td>brine</td>
<td></td>
<td>6.25</td>
<td>6.45</td>
<td>8.93</td>
<td>8.71</td>
<td>9.42</td>
<td>8.73</td>
</tr>
</tbody>
</table>

In Table 6, we noticed that for NaBO$_2$.4H$_2$O, the pH change was small as the alkaline content increased (i.e., pH only increased 0.1 units for surfactant 58N when the alkali content increased from 0.1% to 0.25%). The pK$_a$ (dissociation constant) for this alkali is about 9.24 (Goldberg 2002, http://en.wikipedia.org/wiki/Borate#cite_note-2). Because the buffer capacity for sodium metaborate is greatest near the pK$_a$, the pH trends toward the pK$_a$ during dissolution—thus explaining observed pH behavior at room temperature in Table 6. Values for pK$_a$ are known to be sensitive to temperature (http://wiki.answers.com/Q/What_is_pka_value_for_sodium_bicarbonate#ixzz1O3owAFzA). Table 6 suggests that the pK$_a$ may be closer to 8.8 at 90°C. For sodium carbonate (at room temperature), the pK$_a$ is 10.35. Thus, pH values when using sodium bicarbonate to be greater than those for sodium metaborate.

**Divalent Cation Content.**

Fig. 13 shows the results of varying the content of divalent cations in imbibing aqueous liquids. (Salinity was fixed at 30 wt% and the temperature at 90°C). Core plugs (42B and 49A from Well #16433) were 1~3 mm thick. The lower curve in Fig. 13 shows that variations in divalent cation content had little effect on oil recovery when imbibing brine only. However, the three surfactant formulations experienced a maximum in oil recovery when the divalent cation content was 5 wt%. Increasing or decreasing the divalent cations content (hardness of solution) from 5% to 10% and 0% significantly reduced imbibition and oil displacement (Fig. 13). The CEC (cation exchange capacity) values in three cores (Well AnSBRO Loucks 44-30) were 4.1, 7.1, and 10.6 meq/100 g. These CEC values are considered low, suggesting the content of reactive clays is low (see https://www.dmr.nd.gov/oilgas/FeeServices/wfiles/15/W15722.pdf).

**Surfactant Concentration.**

Fig. 14 shows the effect of varying the surfactant concentration in imbibing aqueous liquids. (Salinity was held constant at 30 wt% and temperature at 90°C). Core plugs (41 and 49A from Well #16433) were 3–5 mm in thick. For the anionic surfactant S2, a maximum oil recovery was noted at 0.1% surfactant. For the nonionic surfactant, 58N, as concentration increased from 0.05 to 0.1%, oil recovery increased, and only a few additional increase at 0.2%. For the cationic surfactant 17A, as concentration increased, oil recovery decreased. At the highest surfactant concentration (0.2%), the core sample flaked (as shown in Fig. 15).

**Optimal Surfactant Formulation.**
Table 7 summarizes results of many experimental tests for Surfactants 17A, 58N, and S2 at 90°C. For cationic surfactant 17A, the optimal formulation contained 0.1 wt% surfactant, 0.1% alkali (NaBO₂.4H₂O), and 15 wt% salinity—achieving 10.12% oil recovery at 90°C. For nonionic Surfactant 58N, the optimal formulation contained 0.05 wt% surfactant, 0.1% alkali (NaBO₂.4H₂O), and 30 wt% salinity—achieving 19.12% oil recovery at 90°C. For the anionic surfactant S2, the optimal formulation contained 0.2 wt% surfactant, 0.25% alkali (NaBO₂.4H₂O), and 30 wt% salinity—achieving 14.05% oil recovery at 90°C. Table 7 shows that addition of alkali improved oil recovery for all three surfactants.

Additional testing is underway to find the optimal surfactant formulation to alter the wettability of Bakken shale, and further enhanced oil recovery for aqueous imbibition with all faces open using large size core samples, and a larger variety of lithologies.

### Table 7 —Surfactant formulation

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration, %</th>
<th>Alkaline additive, %</th>
<th>Salinity, wt%</th>
<th>Oil Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>17A, cationic</td>
<td>0.1</td>
<td>0</td>
<td>15</td>
<td>8.30</td>
</tr>
<tr>
<td>58N, nonionic</td>
<td>0.1</td>
<td>0.1</td>
<td>15</td>
<td>10.12</td>
</tr>
<tr>
<td>S2, anionic</td>
<td>0.1</td>
<td>0</td>
<td>30</td>
<td>12.87</td>
</tr>
<tr>
<td>0.2</td>
<td>0.25</td>
<td>30</td>
<td>14.05</td>
<td></td>
</tr>
</tbody>
</table>

Alkaline: NaBO₂.4H₂O

### Conclusions

Laboratory studies were conducted to find surfactant formulations best suited to imbibe into and enhanced oil recovery from Bakken shale. Even though our Bakken core samples had significant lithological variations compared to our previous study on Pierre shale (Wang, 2010), aqueous fluid exhibited definitive imbibition. Additional experiments are planned to test more core samples and further explore the role of these findings in taking our results from the lab to the field.

Although more extensive investigations are needed, the following preliminary results can be highlighted:

1. An ethoxylate nonionic surfactant, internal olefin sulfonate anionic surfactants, and an amine oxide cationic surfactant were more stable than the other surfactants for temperatures at 105−120°C. They were effective in imbibing and displacing oil at high temperatures.

2. Sodium carbonate (added to increase alkalinity) precipitated with divalent cations in the saline brines (15-30 wt %). Sodium metaborate may help increase alkalinity without precipitation in the brine.

3. An ethoxylate nonionic surfactant and an internal olefin sulfonate anionic surfactant were more tolerant of high salinity than other surfactants and displayed higher oil recoveries at high temperature. For Bakken cores, surfactants did not imbibe effectively using distilled or low salinity water.

4. For a given surfactant, there is an optimum hardness level. Excess or insufficient divalent cation content significantly reduces imbibition and oil displacement.

5. Clay flaking of shale was observed when contacting (a) brine without surfactant or (b) an amine oxide cationic surfactant in brine. However, for Case (b), changing the pH of the surfactant solution may reduce flaking.

6. For a given surfactant, oil recovery can be maximized by identifying an optimal surfactant concentration, brine salinity, sodium metaborate concentration, and divalent cation content.

### Acknowledgement

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Mohanty for good suggestion on surfactant options. We also thank the Environmental Analytical Research laboratory of University of North Dakota for the Bakken formation water analysis.

Nomenclature

- \( M_w \) = molecular weight
- \( OOIP \) = original oil in place, \( \text{cm}^3 \)
- \( \text{p}K_a \) = the symbol for the acid dissociation constant on a logarithmic scale
- \( S_wi \) = initial water saturation
- \( W_o \) = dry weight of the shale rock, g
- \( W_{Oi} \) = weight after oil saturation, g
- \( W_a \) = weight after aqueous imbibtion, g
- \( \rho_o \) = oil density, \( \text{g/cm}^3 \)
- \( \rho_{(s)} \) = brine or surfactant density, \( \text{g/cm}^3 \)

References


**SI Metric Conversion Factors**

\[
\begin{align*}
\text{cp} \times 1.0^{*} & = \text{E-03} = \text{Pa} \cdot \text{s} \\
\text{ft} \times 3.048^{*} & = \text{E-01} = \text{m} \\
\text{in.} \times 2.54^{*} & = \text{E+00} = \text{cm} \\
\text{md} \times 9.869233 & = \text{E-04} = \mu \text{m}^2 \\
\text{g/L} \times 0.1 & = \text{E+00} = \text{wt %} \\
\text{mg/L} \times 0.001 & = \text{E+00} = \text{wt %}
\end{align*}
\]

*Conversion is exact

**Fig. 1 — Partial core slabs of Well #16433**
Fig. 2 — Clay flake at brine water, 23°C

Fig. 3 — Temperature stability of surfactant samples before and after 105°C aging with 30 wt% TDS -1

Fig. 4 — Temperature stability of surfactant samples before and after 105°C aging with 30 wt% TDS -2

Fig. 5 — C-1 alone at 23°C

Fig. 6 — C-1 after 30% alcohol added for 15 days at 105°C
Fig.7 — 58N with 30 wt% at 110°C for 15 days

Fig.8 — 17A before and after 0.1% alkaline added at 110°C after 7 days

Fig.9 — Temperature vs. oil recovery (30 wt% TDS, 0.1 % surfactant concentration and 5% divalent cation content)

Fig.10 — Temperature vs. oil recovery (15 wt% TDS, 0.1 % surfactant concentration and 5% divalent cation content)
Fig. 11—Solution salinity vs. oil recovery (90°C, 0.1% surfactant concentration, and 5% divalent content)

Fig. 12 — 0.1% alkali added to surfactant samples
Fig. 13 — Effect of divalent content on oil recovery (90°C, 0.1% surfactant concentration, and 30 wt% TDS)

Fig. 14 — Effect of surfactant concentration on oil recovery

Fig. 15 — 0.2% concentration of 17A