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Final Report

Enhanced Oil Recovery from the Bakken Shale using Surfactant Imbibition Coupled with Gravity Drainage

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Abstract

With its low permeability and oil-wet character, using existing methods, oil recovery factors of the naturally fractured Bakken formation have only been a few percent of original oil in place. This project investigates whether a new surfactant imbibition concept can significantly improve oil recovery from the Bakken shale. This concept involves formulating special surfactant solutions that will alter the wettability of the formation, without causing formation damage. This alteration should promote imbibition of a dilute aqueous surfactant solution and increase oil displacement from the shale. The concept also relies on exploitation of gravity for collection and recovery of the oil in the system from natural and hydraulic fractures associated with horizontal wells.

In this project, we first tested the degree of imbibition for available waters in different portions of the Bakken shale, to establish their true wetting state. We also investigated whether imbibition can be induced using only pH or salinity variations. We then tested a number of surfactants to identify formulations that will promote maximum imbibition into and oil displacement from Bakken shale cores. Based on those laboratory results, we will produce a numerical model that incorporates the relevant physics of surfactant imbibition and oil displacement for the Bakken shale. This model will then be used to assess the potential of this surfactant imbibition process for existing completions within the Bakken shale and assess whether alternative well completion/fracture configurations might provide higher oil recoveries.

In the Bakken shale formation located in the middle of the Williston Basin, an increase of 1% in recovery could lead to an increase of 2 - 4 billion barrels or more of domestic oil production. We will team with one or more small producers during this project to field test our developments.

By the end of Decemebr 2013, we have accomplished all subtasks include laboratory research and numerical simulation prediction. Based on the research results, we found: (1) Imbibition rate increases as the temperature increases in the range tested. (2) Cationic surfactants with less carbon number heads exhibited a lower imbibition rate and low capability for enhanced oil recovery. On the other hand, cationic surfactants with large carbon numbers have a fast imbibition rate and strong effect on oil production at higher temperature, and also at room temperature. (3) Nonionic surfactants also exhibit a favorable imbibition rate and oil recovery at high temperature. (4) Oil was not imbibed out at room temperature with brine water and fresh water. Although oil was recovered from rocks at high temperature, the very low imbibition rate indicates these were not favorable aqueous liquids for increasing Bakken oil recovery. (5) Effective permeability was increased by surfactant formulation compared to fresh water or brine water alone. Imbibition rate was increased due to a higher permeability. (6) Optimal salinities can be estimated from curves showing the relationship between microemulsion phases and corresponding oil/water volumes proportions for most selected surfactants at 2% concentrations at lower temperatures. However, at higher temperatures, it was difficult to evaluate this effect in some solutions due to the limited volumes recovered. (7) Without mixing alkaline in anionic surfactant solutions, interfacial tensions (IFT) were reduced to 10^{-2} orders of magnitude at high temperature. Under the same conditions, nonionic surfactants, amphoteric surfactants, and cationic surfactants, IFT was reduced to10^{-1} order of magnitude. Concentrations of 0.1% were used in IFT measurements. (8) The optimal salinities obtained by IFT curves are consistent with phenomena observed in the phase behavior studies at reservoir temperatures near 90 ℃. (9) With optimal salinity, inverse Bond number N_B^{-1} which dominates the IFT reduction mechanism, could be decreased below a value of 1 in cores from the Middle member of Bakken. (10) Laboratory results suggest that wettability change is the key mechanism if the surfactants show favorable behavior for oil recovery when

there is no obvious middle phase exhibited in the same temperature range. (11) Compared with the current production methods, the enhanced oil recovery of more than 10% could be achieved in a few years using the surfactant imbibition process for Bakken Well #17450, based on numerical simulation prediction. (12)Injection rate and production sequence apparently affect oil recovery. A reasonable injection rate and production sequence should be considered completely when designing a field trial.

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Table of Contents

List of Tables

List of Figures

Acknowledgements

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Chapter 1. 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. However, with its low permeability and oil-wet character, using existing methods, the oil recovery factors of the naturally fractured Bakken formation have only been a few percent of original oil in place. As part of our investigation of chemical imbibition (using surfactant or brine formulations) to stimulate oil recovery from shale, this report focuses on surfactant formulation optimization and wettability tests on different parts of the Bakken formation. 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.

Project objective

The objective of this research project is to determine whether surfactant solutions can alter the wettability of the Bakken shale formation (in North Dakota's Williston Basin), so that oil recovery can be enhanced by a mechanism involving imbibition. The project has two primary goals:

(1) Test the degree of imbibition in different wells of the Bakken shale using formation water to establish the true wetting state. We investigate whether significant imbibition can be induced using only pH or salinity variation in available waters.

(2) Investigate the ability of certain surfactant solutions to alter wettability of the Bakken shale. Such alteration seeks to promote imbibition of dilute aqueous surfactant solutions and increase oil displacement from the shale.

State of work

Tasks performed in this project include:

Task 1: Project Management Plan (PMP)
Task 2: Technology Status Assessment
Task 3: Technology Transfer
Task 4: Aqueous Solution Imbibition Evaluation
  Subtask 4a: Surfactant formulation optimization
  Subtask 4b: Wettability experiments
  Subtask 4c: Imbibition experiments
  Subtask 4d: Phase behavior study
  Subtask 4e: Interfacial tension tests
Task 5: Numerical Simulation and Modeling of Imbibition
  Subtask 5a: Ideal model building
  Subtask 5b: Field-scale numerical simulation prediction
Task 6: Routine Reports and Other Activities

Work Progress and Deliverables Summary

By the end of December of 2013, the tasks listed above have all been completed and previously reported. For Task 3—Technology transfer, in additional to constructing a public website for the project, we also participated in four SPE and three RPSEA technical conferences. In these conferences, we published and presented four SPE papers on Bakken oil recovery research: SPE 138521, 145510, 153853 and 167142. Two of them were also published in the journal of *SPE Reservoir Evaluation and Engineering*. The deliverable summary is shown in Table 1. Details of Task 4 to 5 are discussed in this report.

Table 1 — Deliverable summary

Deliverable	Complete Date
Project Management Plan	4/18/2011, 1 month after the project kickoff date (3/18/2011)
Technology Status Assessment Report	4/18/2011, 1 month after the project kickoff date
Technology Transfer Plan	4/18/2011, 1 month after the project kickoff date
Website Construction	9/2011, and to be maintained for duration of 36 month project
Annual Report #1	3/18/2012, interim report for Task 4
Annual Report #2	3/18/2013, interim report for Task 4 & 5
Draft Final Report	12/31/2013, 3 months prior to project completion date
Presentation #1 & 2	SPE: 11/2/2011 in Denver, 4/16/2012 in Tulsa, 11/7/2013 in Calgary RPSEA: 4/10/2012 in Midland, 11/29/2012 in Houston, 10/17/2013 in Long Beach
Article publication # 1	SPE 138521, March 2011, *SPERE&E*
Article publication # 2	SPE 153853, December 2012, *SPERE&E*
Final Report	12/23/2013

Report content

Chapter 2 discusses group formulations that promote 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 shale with ultra-low porosity and permeability in the Middle Member of the Bakken Formation in the Williston Basin of North Dakota. Chapter 3 discusses 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. Chapter 4 discusses the phase behavior between brine water, surfactant solutions, and Bakken oil. IFT (Interfacial Tension) changes with optimal salinity of selected surfactant solutions also discussed in this chapter. Chapter 5 discusses the results of extensive imbibition testing using water only and surfactant formulations in an imbibition glass cell. The surfactant imbibition effect using the optimal salinities was investigated. In the Chapter 6 of this report, we discuss an ideal numerical model to scale the laboratory results. Based on the ideal model simulation, we think the numerical simulation performance basically support our laboratory results on oil recovery by surfactant imbibition. Lastly, in Chapter 7, a field-scale numerical simulation prediction to estimate oil production in reservoir-scale matrix blocks is discussed. Fracture dimensions in an actual well were considered. A history match of oil production and water cut was included in the surfactant imbibition prediction work.

Our research results, along with detail documentation can be found on our web site at https://www.und.edu/instruct/dwang/Research.

Chapter 2. Surfactant Formulation Preliminary Optimization

This chapter investigates an idea for chemical imbibition using surfactant formulations to stimulate oil recovery from oil shale. One goal of this research task 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.

2.1 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 at a depth of 10613−10649 ft and consisted of gritty shale and limestone, with poor to almost no porosity (Fig. 1). Table 2 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 3.

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

Table 2 — Core plug descriptions

Sample resource	Depth, ft	Color	Lithology, depositional environment, and other attributes
Middle Member of Bakken	10613-10649	Light to dark grey, light brown to tan	Very fine crystalline, argillaceous, thinly laminated, gritty, limey shale.

Table 3 — Summary of geological parameters and fluid saturations

Sample Depth	Dean-Stark Fluid Saturation		Clean Dry Sample	
	Oil % Pore Volume	Water % Pore Volume	Gas Permeability, md	Porosity, fraction
10613 ~ 10649	26.81	32.04	4.68E-2	0.059

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 0.82 g/cm^3 at 23.2 ℃. 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% TDS (distilled water), 7.5% TDS, 15% TDS, and 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 based on the chemical analysis in Table 4.

Na_2CO_3 & $NaBO_2 \cdot 4H_2O$: These alkaline chemicals were used to change pH of the aqueous phase.

2.2 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. Measure 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}.

2.3 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 %TDS brine and surfactant solutions. Filter the waters.

(2) Test water, oil, and surfactant viscosity with a Brookfield viscometer at various temperatures.

(3) Measure water and oil density with a density meter, DA-300 at various temperatures from 23 to 90 °C. Extrapolate the data based the temperature trend lines at temperatures higher than 90 °C. Here, we assumed water density is assumed equal to surfactant solution density under the same salinity and temperature. The liquid densities change with temperatures and salinities.

(4) Place surfactant samples into laboratory oven at a specific temperature for 15 days to observe changes in the samples of increasing temperature. Particularly test at high temperatures above 100 °C. Surfactant samples were sealed in glass bottles with temperature tolerance caps.

(5) 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 hours, depending on thickness of core plugs.

(6) Weigh slices after imbibition, taken as Wa . Estimate oil recovery using Eq. 1.

(7) Set up different temperatures in the oven. Repeat Steps 5 to 6 to estimate the oil produced (Eq. 1).

(8) Change solution salinity; then repeat Steps 5 to 6.

(9) Change pH of surfactant samples with 0.1−0.25 wt% of alkaline chemicals. Repeat Steps 5 to 6 to estimate the oil produced (Eq. 1).

(10) Change divalent cation content in the brine and surfactant solution. Repeat Steps 5 to 6 to estimate the oil produced with Eq. 1.

(11) Change surfactant concentrations. Repeat Steps 5 to 6 to estimate the oil produced according to Eq. 1.

$$\%OOIP = 100 \times (W_a - W_{oil}) / [(\rho_{w(s)} / \rho_o - 1) \times OOIP] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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

2.4 Data Analysis and Discussion

2.4.1 Initial Aqueous Solution Screening

Laboratory tests were performed at the room temperature (23.2 °C) with a salinity of 30% TDS brine.

Imbibition tests involved 17 surfactants. Most surfactants were found to increase the oil recovery, from 3.47 to 60.67%, compared to 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% TDS salinity, and therefore dropped from further testing.

2.4.2 Temperature Stability Study at High Salinity

Surfactants samples were studied for high temperature stability from 105 ℃ to 120 ℃ with brine containing 5% cationic divalent ions. 20～50 ml of each surfactant solution with 15−30 % TDS were sealed into vials with temperature-tolerant caps. These vials were put into a laboratory oven at a fixed temperature. All surfactants in Table 4 remained in aqueous solutions for 15 days to confirm stability of the surfactants.

In Table 4, five surfactant structures were studied for temperature stability: anionic surfactants with sulfonate or sulfate groups, amphoteric surfactants with dimethyl amine oxide groups, and nonionic surfactants with ethylene glycol butyl ether or ethoxylate groups. Concentrations of these surfactant solutions were diluted to 0.1 wt%. Several observations were noted:

A. For solution salinity of 30% TDS:

(1) Ethoxylate surfactant, internal olefin sulfonate anionic surfactants, and amine oxide amphoteric surfactants were more stable than other surfactants at a temperature of 105 ℃. In Figs. 3 and Fig.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 ℃. 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 ℃ 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% TDS. C-8 (low M_W) clouded heavily (Fig.4), S-12 (medium MW) and S-14 (Alcohol ethoxy sulfate) precipitated and were not stable at 15 days, as did olefin sulfonate O332. (5) Ethoxylate alcohol surfactant-58N showed good stability at 110 ℃ for 15 days (Fig. 7). (6) For amphoteric surfactants, 17A, 17B, and 12J, an ultrathin layer with a brown color developed on the top of the solution at 110 ℃ and 120 ℃ after aging. Some clay flaking occurred 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). Fig. 9(a), 9(b) show surfactants S2, 58B and 17A before and after 50 days ageing at 110 ℃, showing good stability at high temperature.

B. For solution salinity of 15% TDS:

Most surfactants in Table 3 showed good temperature stability at 105 ℃ with 15 %TDS. Surfactant ethoxylate alcohol-58N, Alcohol alkoxy sulfate-771, and N969 showed good stability at 120 ℃ for 15 days with 15 %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 [amphoteric (17A), nonionic (58N) and anionic (S2)] were selected for imbibition studies, as discussed next:

Table 4 — Surfactant stability at high temperature

Sample	Supplier	Type	15% TDS			30% TDS		
			105°C	110°C	120°C	105°C	110°C	120°C
A-6	Tiorco	Anionic	N	N	N	N	N	N
C-1	Tiorco	Anionic	**O**	**O**	7 days	Phase transition	11 days (added alcohol)	5 day
C-2	Tiorco	Anionic	**O**	14 days	10 days	Slightly cloudy	11 days	9 days
C-8	Tiorco	Anionic	**O**	**O**	7 days	cloudy	cloudy	cloudy
S2	Tiorco	Anionic	**O**	**O**	**O**	**O**	**O**	10 days
S3B	Tiorco	Anionic	**O**	cloudy	cloudy	**O**	cloudy	cloudy
S12	Tiorco	Anionic	**O**	9 days	7 days	**O**	7 days	5 day
S14	Tiorco	Anionic	**O**	10 days	5 days	**O**	7 days	2 days
17A	Champion	Amphoteric	**O**	**O**	12 days	**O**	**O**	10 day
17B	Champion	Amphoteric	**O**	**O**	10 days	**O**	7 days	5 day
58N	Champion	Nonionic	**O**	**O**	**O**	**O**	**O**	14 days
12J	Champion	Amphoteric	**O**	10 days	9 days	7 days	6 days	5 day
O332	Shell Chemicals	Anionic	cloudy	cloudy	cloudy	cloudy	cloudy	cloudy
A771	Shell Chemicals	Anionic	**O**	**O**	**O**	10 days	6 days	5 day
SS-7593	Oil Chem	Nonionic	**O**	10 days	5 days	Phase transition	6 days (added alcohol)	7 day
1688	Oil Chem	Nonionic	**O**	12 days	9 days	Slightly cloudy	10 days	7 day
N969	Oil Chem	Unknown	**O**	**O**	**O**	**O**	10 days	2 days

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

2.4.3 Spontaneous Imbibition

Reservoir conditions in the Bakken indicate a temperature range of 80 to 120˚C (Pitman *et al*, 2001). Three surfactant samples were selected to determine oil recovery at 60 ℃ to 110 ℃. The tested samples were anionic, nonionic, and amphoteric 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 include 15A to 49A, with 12 sliced 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^{-4} md at 23 ℃. Initial water saturations were assumed to be zero.

Using the one-face-closed imbibition method, Fig. 10 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}) of zero, salinity 30% TDS, and temperatures from 60 ℃ to 120 ℃.

Before imbibition tests at high temperature, experiments were conducted at 23−60 ℃ 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% TDS and 23 ℃, 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. 10 shows that imbibition and oil recovery increased as temperature increased at 30 %TDS. Imbibition may have been promoted by greater ion exchange at higher temperatures. These experimental results are consistent with previous work reported by Gupta, *et al* (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 amphoteric surfactant effectively promoted imbibition (Zhang and Austad, 2005). In our experiments, 0.1% wt concentration of surfactant was always used. This might explain why lower oil recoveries for 17A were less than for the other two types of surfactants. Later work focus on 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 whereby 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 was unique to the particular core slice.

Also Fig. 10 shows that the anionic surfactant, S2, produced more oil as the temperature increased to 120℃. From one viewpoint, anionic surfactant is more likely to promote partitioning of the surfactant between oil and water, favoring the driving of the oil phase away from rock.

Fig. 11 shows the imbibition and oil recovery change vs. temperature at 15 %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.

2.4.4 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, accounting for 61.50% of total dissolved salts. The other univalent ions sodium and potassium account for 30.32% of total salts. The divalent cations calcium and magnesium ion account for 4.79% of total salts (Table 5).

Table 5 — Chemical analysis of Bakken formation water

Analyte	Detection limit, mg/L	Result in sample, mg/L	Methodology
Salinity		300,000	Cond. meter
Inorganic carbon	0.2	16.5	TOC analyzer
Cl^-	0.05	184,500	Ion chromatography
Na^-	0.02	85,322	FAAS
K^-	0.05	5,643	FAAS
Ca^{2+}	0.2	13,177	FAAS
Mg^{2+}	0.01	1,175	FAAS

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

Fig. 12 shows the relationship between TDS of surfactant solutions and oil recovery at 90℃. Experiments used salinities ranging from 0% to 30% TDS. Core plugs were labeled 31B and 49A (Bakken Well #16433). The results indicate: (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. 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 is 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 amphoteric surfactant 17A, the optimum salinity for maximum oil recovery is 15% TDS. For the other two surfactants (anionic and nonionic), 30 %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 was be studied in the next phase of work.

2.4.5 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 onto rocks. Two alkalis were studied: (1) With Na_2CO_3, a precipitate formed at 0.1 wt% Na_2CO_3 (Fig. 13) due to the presence of Ca^{2+} and Mg^{2+}. This alkali is not suitable with high salinity and hard brines. (2) With $NaBO_2.4H_2O$, no precipitation was observed at 0.1 wt% $NaBO_2.4H_2O$ 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 6 shows results of changing pH with 0.1 to 0.25 wt% $NaBO_2.4H_2O$ at 90 ℃ and 30 wt% salinity. No precipitation was observed. Core plugs with thickness 1 to 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 7 shows, for a given surfactant, as the temperature and alkali content was increased from 23 ℃ to 90 ℃, and 0.1% to 0.25%, respectively, the pH of target aqueous solutions was found to decrease.

Table 6 —pH values vs. oil recovery
(90°C, 0.1% surfactant concentration, 30% TDS, and 5% divalent content)

Alkali content, wt% / Sample	0		0.1		0.25	
	pH	Oil recovery,%	pH	Oil recovery,%	pH	Oil recovery,%
17A	7.51	9.19	8.75	10.33	8.83	5.88
58N	5.91	15.42	8.71	18.29	8.81	10.61
S2	7.24	12.87	8.67	13.08	8.77	13.61

Table 7 —pH values vs. temperature

Alkali content, wt% / Sample	0		0.1		0.25	
	pH, 23.2°C	pH, 90°C	pH, 23.2°C	pH, 90°C	pH, 23.2°C	pH, 90°C
17A	7.42	7.51	8.88	8.75	9.19	8.83
58N	5.34	5.91	8.94	8.71	9.32	8.81
S2	7.84	7.24	8.76	8.67	9.11	8.77

In Table 7, we noticed that for $NaBO_2.4H_2O$, 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 ℃. 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.

2.4.6 Divalent Cation Content

Fig. 14 shows the results of varying the content of divalent cations in imbibing aqueous liquids. (Salinity was fixed at 30% TDS and temperature at 90 ℃). Core plugs 42B and 49A from Well #16433 were 1~

3mm 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 cation content (hardness of solution) above the optional 5% significantly reduced imbibition and oil displacement (Fig. 14). 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).

2.4.7 Surfactant Concentration

Fig. 15 shows the effect of varying the surfactant concentration in imbibing aqueous liquids. (Salinity was held constant at 30% TDS and temperature at 90 ℃. Core plugs 41 and 49A from Well #16433 were 3−5 mm in thick. For the anionic surfactant 17A, a maximum oil recovery was noted at 0.1% surfactant. At the highest surfactant concentration (0.2%), the core sample flaked (as shown in Fig. 16). For the anionic surfactant S2, as concentration increased from 0.05 to 0.1%, oil recovery increased with no additional increase beyond 0.2%. For the amphoteric surfactant 58N, as concentration increased, oil recovery decreased.

2.4.8 Optimal Surfactant Formulation

Table 8 summarizes results of many experimental tests for Surfactants 17A, 58N, and S2 at 90 ℃. For amphoteric surfactant 17A, the optimal formulation contained 0.1 wt% surfactant, 0.1% alkali ($NaBO_2.4H_2O$), and 15 % TDS salinity--achieving 10.12% oil recovery at 90 ℃. For nonionic surfactant 58N, the optimal formulation contained 0.05 wt% surfactant, 0.1% alkali ($NaBO_2.4H_2O$), and 30% TDS salinity--achieving 19.12% oil recovery at 90 ℃. For the anionic surfactant S2, the optimal formulation contained 0.2 wt% surfactant, 0.25% alkali ($NaBO_2.4H_2O$), and 30 % TDS salinity--achieving 14.05% oil recovery at 90 ℃. Table 7 shows that addition of alkali improved oil recovery for all three surfactants.

We also studied co-surfactant solutions thermal stability under 90 ℃ and 110 ℃ conditions. These co-surfactants including Linear Alpha Olefin Sulfonate + Ethanol (30%), Higher Olefin Sulfonate + Ethylene glycol butyl ether (50%), Internal Olefin Sulfonate + Ethylene glycol butyl ether, and Med Mw Alkyl Sulfonate-carboxylate + Ethylene glycol butyl ether(50%). The experimental results show that two co-surfactant formulations : Linear Alpha Olefin Sulfonate + Ethanol (30%), and Internal Olefin Sulfonate + Ethylene glycol butyl ether had good thermal stability when the salinity was 30 % TDS at 0.1% concentration after aging 50 days (Fig. 17).

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

Table 8 —Surfactant formulations optimization

Surfactant	Concentration,%	Alkaline additive,%	Salinity, % TDS	Oil Recovery,%
17A, amphoteric	0.1	0	15	8.30
	0.1	0.1	15	10.12
58N, nonionic	0.1	0	30	15.42
	0.05	0.1	30	19.12
S2, anionic	0.1	0	30	12.87
	0.2	0.25	30	14.05
C1+Ethanol	0.1	0	30	11.13
1688+S3B	0.1	0	30	6.82

Alkaline: **$NaBO_2.4H_2O$, 90 ℃**

2.5 Summary

Laboratory studies were conducted to find surfactant formulations best suited to imbibe into and enhance 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 (surfactant solutions) exhibited definitive imbibition. Additional experiments are planned to test more core samples and further explore the role of these findings before taking our results from the lab to the field.

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

(1) Ethoxylate nonionic surfactant, internal olefin sulfonate anionic surfactants, and amine oxide amphoteric surfactant were more stable than the other surfactants at temperatures of 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 % TDS). Sodium metaborate may help increase alkalinity without precipitation in the brine.

(3) 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, and (b) an amine oxide amphoteric 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.

(7) Proper co-surfactant formulations show potential for increased oil recovery.

Chapter 3. Wettability Experiments

This chapter examines if the wettability can be altered using surfactant formulations. Using the modified Amott-Harvey test, the wettability was determined for cores from three wells from different portions of the Bakken Formation. The tests were performed under reservoir conditions (90-120 ℃, 150–300 g/L formation water salinity) with Bakken crude oil. 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 10.16% 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 may be only on the order of a few percent OOIP.

3.1 Methodology

Wettability was studied by a modified Amott-Harvey method, using cores from different depths in 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, 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, North Dakota. 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 ℃) and salinity (15-30% 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, 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, labeled MA, MB, MC and MD. Liquid imbibition and injection volumes were obtained by weight measurements.

For method MA, we selected ores from the Middle Member of Bakken from Well Lars Rothie 32-29H (#16433) in eastern Mckenzie County. Residual oil saturation and connate water saturation were obtained by centrifuge. Core slice thickness varied from 2 mm to 5 mm, and the test temperature was 23 ℃.

For method MB, core plugs were from Well EN Ruland 3328H-1 (#16771) in western Mountrail County. Reservoir temperature varied from 90-120 ℃. Forced injection occurred using the coreflood setup shown in Fig. 18. Core slice thickness varied from 13 mm to 15 mm. Liquid imbibition and injection volumes were obtained by weight measurements.

For method MC, core plugs were from Well AV Wrigley 0607H-1 (#17450) in northwest Burke County. Reservoir temperature varied from 90-120 ℃. Forced injection occurred using the coreflood setup shown in Fig. 19. Cores slice 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.

For method MD, core plugs were also from Well #17450. A Hassler core holder was employed during both imbibition and injection, as shown in Fig. 20. The reservoir temperature varied from 90-120 ℃. Overburden pressure was applied to the confined core. Cores samples thickness varied from 40 mm to 50 mm. Liquid imbibition and injection volumes were obtained by burette readings.

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 rocks, wash them again with methanol to clean out brine, and then dry cores under at 105 ℃ 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 locations for each core. All measurements were within ±0.01 mm of the average value—ensuring the consistency of 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 to saturate them for 24 hours.

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

Equations 2 to 6 were used to calculate the Amott-Harvey index. For Methods MA and MB, we used Eqs. 2 and 3 (Dake, 1977 and Amott, 1969); while for Methods MC and MD, we used Eqs. 4 and 5 (Glover, 2001).

$$I_w = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{or}} \quad \text{(2)}$$

$$I_o = \frac{S_o - S_{or}}{1 - S_{wr} - S_{or}} \quad \text{(3)}$$

$$\delta_w = \frac{Vw_{imbibition}}{Vw_{imbibition} + Vw_{injection}} \quad \text{(4)}$$

$$\delta o = \frac{Vo_{imbibition}}{Vo_{imbibition} + Vo_{injection}} \quad \text{(5)}$$

$$AI = I_w - I_o \quad \text{(6)}$$

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, $Vo_{imbibition}$= oil volume spontaneously imbibed, $Vo_{injection}$=oil volume increase by forced injection, $Vw_{imbibition}$= water volume spontaneously imbibed, $Vw_{injection}$=water volume increase by forced injection, δ_o = ratio of spontaneous oil imbibition to total oil imbibition, δ_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, and the Upper shale and Middle Member in Well # 17450, AV Wrigley 0607-H1 and Well #16771, EN Reland 3328H-1. Generally, the core samples tested were gritty shale and shaly layers in siltstone, limestone, and dolomite, with poor to almost no porosity. Core plugs were 25 mm in diameter and 1 to 50 mm in thickness. For the Middle Member, permeability to Bakken oil for core samples was typically about 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 porosity values were comparable.

Test Fluids. Cores were saturated with Bakken crude oil from Well #16434 H. Davidson 2-11H. The API gravity was 43.2 °API, and oil density 0.777 g/cm^3 at 23.2 ℃. Brine water was selected because its salinity is 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, $CaCl_2$, and $MgCl_2$: These salts were used to change salinity of the aqueous phase based on the work in Wang *et al*. 2011b).

$NaBO_2$•$4H_2O$: 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, solution pH values typically ranged from 5.6 to 6.8.

Table 9—Surfactant formulations for wettability tests

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 α-Olefin Sulfonate

Alkaline: **$NaBO_2.4H_2O$**

3.2 Data Analysis

3.2.1 Wettability Test for Well #16433 Cores

We selected cores from the Middle Member of Bakken from Well 32-29H (#16433) shown in Fig. 21. 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 slices thickness varied from 2 mm to 5 mm, and the test temperature was 23 ℃. The Amott-Harvey index was calculated based on Eqs. 2, 3 and 6.

Table 10 shows 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 ℃. 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. 21. The rock porosity was obtained experimentally (Wang *et al*. 2011a) as Table 11 shows.

Table 10—Wettability of Well #16433 at 23°C, D=25 mm, L (Thickness) =2-4 mm

Sample	Aqueous liquid	I_w	I_o	AI	Wettability	S_{or}	S_{or} decrease, %	*Re* %	*EOR* %
13C	Brine water C1 formulation	0.299 0.489	0.484 0.486	-0.184 0.002	Weakly oil wet Neutral wet	0.848 0.735	11.30	15.24 25.39	10.16
15B	Brine water C1 formulation	0.327 0.497	0.481 0.487	-0.150 0.010	Weakly oil wet Neutral wet	0.838 0.767	7.10	16.20 23.08	6.88

***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 with 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 11—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

Length: Thickness

3.2.2 Wettability Test for Well #16771 Cores

For Well #16771, we selected cores from both the Upper Bakken shale and Middle Member (Fig. 22). Lithology included black shale, with of 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. 19). Core thickness was 13 mm, and the test temperature ranged from 90 to 120 ℃. The Amott-Harvey index was calculated based on Eqs. 2, 3 and 6. 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 13 and Table 15, core samples 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 12.

Table 12 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 ℃ and variable 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 tended toward stronger water-wetness after exposure to the alkaline surfactant formulations. In Table 13, 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%.

Table 12—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

Length: Thickness

Table 13— Wettability of Well #16771 at 90 to 120°C, D=38 mm, L (Length: Thickness) =13 mm

Sample	Aqueous liquid	Tem. °C	pH(22°C)		I_w	I_o	AI	Wettability	S_{or}	S_{or} decrease %	*Re* %	*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		32.74	
1-36-1	S2 formulation		0.10	8.61	0.857	0.456	0.420	Water wet	0.161	51.10	49.32	16.58
1-36-3	S2 formulation		0.25	9.03	1.000	0.000	1.000	Water wet	0.142	53.00	54.67	20.93
1-46-2	Brine water	110	0.00	5.60	0.260	0.770	-0.511	Oil wet	0.220	7.70	77.98	9.62
	17A formulation		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=0 at the start of the test. Then, starting with S_w=0.01%, S_w=11.42% and 16.40% respectively, the test was repeated using the 58N,S2, and 17A formulations, respectively.

3.2.3 Wettability Test 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. 19 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. 20; 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. Core thickness varied from 13 mm to 50 mm (mostly using sealed, preserved cores), and the test temperature ranged from 90 to 120 ℃. Overburden pressure was applied to the cores when using Method MD. The Amott-Harvey index was calculated based on Eqs. 4 and 5. 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 14.

Fig. 18 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 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 15 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 15.) 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 ℃. 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 15).

Table 14—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

Length: Thickness

Table 15 (a)—Wettability of Well #17450 at 60 to 120°C, D=38 mm, L(Length: Thickness)=4-52 mm, MC

Sample	Aqueous liquid	Tem. °C	pH(22°C)		δ_w	δ_o	$\delta_w - \delta_o$	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	Brine water	110	0.00	5.60	0.269	0.519	-0.250	Oil wet	0.293	6.80	70.69	6.80
sealed	17A formulation		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 15(b)—Wettability of Well #17450 cores at 90 to120°C, D=38 mm, L(Length: Thickness)=41-52 mm, MD

Sample	Aqueous liquid	Tem. °C	pH(22°C)		δ_w	δ_o	$\delta_w - \delta_o$	Wettability	S_{or}	S_{or} decrease, %	*Re* %	*EOR* %
			Alkaline content %	Value								
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	17A formulation		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	58N formulation		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.

3.3 Discussion

3.3.1 Experimental Method

As mentioned above, four approaches were employed to measure the Amott-Harvey index in this study. Because of the challenges in measuring wettability under our conditions, four methods were examined to identify the best method, or at least, find a consistent direction in the results. Of the many cores that we tested, about one-third of the results were not useable 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 the 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 ℃ 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 (used for core plugs from 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. 17 was used. This apparatus allowed flooding to occur at 90-120 ℃. However, errors can be introduced because of cooling and/or evaporation during the time that the core was removed from the core holder and the weight measurement was 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. Imbibition and injection volumes were determined by readings on burets. Although readings are fairly accurate, they can 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 10 and 11 for Method MA, in Tables 12 and 13 for Method MB, in Tables 14(a) and 15 for Method MC, and in Tables 14(b) and 15 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 12), exposure to a surfactant formulation resulted in more oil recovery by imbibition than exposure to brine alone. Specifically, the EOR (i.e., incremental for surfactant imbibition over brine imbibition) was 6.88% to 10.16% in Table 10, 16.58% to 24.24% in Table 13 (excluding Core 1-46), 6.8% to 21.64% in Table 15(a), and 18.2% to 25.4% in Table 16(b).

3.3.2 Initial Core Wettability

In this phase of work, we tested 30 core samples from three wells from different portions of the Bakken Formation in North Dakota using a modified Amott-Harvey method. Among the tested cores, 1/3 of sample results were not be useable due to apparatus failure that resulted in data reading errors. However, our results demonstrated that the 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 their study, three shales from Eagle Ford, Barnett, and Floyd Formation showed oil-wetness or mix-wetness when the shales imbibed brine or oil (dodecane).

3.3.3 Oil Saturation after Brine Imbibition

A significant variation occurred in oil saturations achieved after brine imbibition. For 12 cases, the oil saturation after brine imbibition ranged from 0.629 to 0.911 (Tables 10, 13, and 15). However, in four cases (Cores 1-46-2, 1-42-1, 1-51A, and 1-69A) oil saturations of 0.220 and 0.410 were reached during brine imbibition. We will conduct more imbibition tests in cores with similar properties to verify this exception to our results. Even though we note that brine was imbibed in some cases, brine sometimes did not imbibe at all (e.g., Case 1-36A in Table 15).

3.3.4 Effect of Alkaline

In Table 13, Cores 1-10-1 and 1-10-2 were tested for 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 15(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 12 (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. Of course, we recognize that many more experiments are needed to establish the positive and negative contributions of the alkaline material.

3.3.5 Effect of Surfactant Formulation

The most important findings from work thus far is that the surfactant formulations (1) consistently altered the wetting state of Bakken cores toward water-wet and (2) consistently (i.e., in all cases but one) imbibed to displace significantly more oil than brine alone. Thus, imbibition of surfactant formulations appears to have substantial potential to improve oil recovery from the Bakken Formation. (Recall that recovery factors using the existing production methods may be only on the order of a few percent OOIP.) Five of the surfactant imbibition tests (Cores 13C, 15B, 1-10-2, 1-42-2, and 1-51A) provided EOR values of 6.8% to 10.16% OOIP, incremental over brine imbibition. Nine surfactant imbibition tests (Cores 1-32-3, Cores 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 one of these surfactants performed definitively better than the others during our experiments. On the whole, all show potential for providing positive recovery values.

3.3.6 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 response to surfactant imbibition that was consistent with that in the Middle Member. In particular, Upper Shale Core 1-42-2 provided 8.08% OOIP EOR, while Upper Shale Core 1-45-2 provided 21.64% OOIP EOR (Table 12). 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.

3.3.7 Preserved (Sealed) vs. Cleaned Cores

Incremental recoveries from preserved (sealed) cores (Cores 1-51A, 1-48A, and 1-69A) ranged from 6.8% to 25.4% OOIP (Table 15). This is effectively the same range as in cleaned cores.

3.3.8 Effect of Temperature and Porosity

We performed experiments at 23 ℃, 60 ℃, 90 ℃, 110 ℃, and 120 ℃. No definitive effect of temperature is apparent at this time. Porosity values for our cores ranged from 1.6% to 9.4% (Tables 11, 12, and 15). Surfactant effectiveness did not appear to correlate with porosity. For the Surfactant 17A formulation, note that Core 1-48A (1.6% porosity) experienced 18.2% OOIP incremental oil (from surfactant imbibition compared with brine imbibition), while Core 1-45-2 (6.0% porosity) experienced 21.64% OOIP EOR.

3.4 Summary

(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) These four surfactants consistently imbibed to displace significantly more oil than brine alone. Four of the surfactant imbibition tests provided EOR values of 6.8% to 10.16% OOIP, incremental over brine imbibition. Ten surfactant imbibition tests provided EOR values of 15.65% to 25.4% OOIP. Thus, imbibition of certain surfactant formulations appears to have 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. 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.

Chapter 4. Phase Behavior and Interfacial Tension Study

In general, increasing salinity of an aqueous phase (brine) decreases the solubility of an ionic surfactant. The surfactant is driven out of brine as electrolyte concentration increases. Thus, brine salinity has a significant effect on phase behavior (Green and Willhite, 1998). For an ideal system, multiphase behavior is divided into three classes (called Windsor type). Furthermore, if the third phase forms within a certain range of surfactant concentration, an optimal salinity exists. Here, the third phase is called the Microemulsion phase.

4.1 Methodology

Phase behavior

At lower temperatures of 23 ℃ to 60 ℃, glass tubes were used to test phase behavior. The tubes are autoclaving tubes which have a protective coating to prevent or reduce the hazards of breakage and shattered glass, and any leakage of toxic or corrosive chemicals. Aqueous solutions (surfactant with brine and crude oil from Bakken) were mixed in a ratio of 50% of oil, 0.05%-0.2% of surfactant (v/v), and the remainder was brine in different tubes of 20 mL total capacity with sealed caps. In one test case, surfactant solution concentrations ranged from 0.05% to 0.2%. The tubes were placed in the laboratory oven for 42 days. In the second case, concentrations were 2.0% and the test period 21 days.

For higher temperatures of 90 ℃ to 120 ℃, an encased-pipette (2 mL) was immersed in 20 mL tubes. The silicon oil reduces heat loss when samples are taken out of the oven for photographing. The encased-pipette test was modified after a method developed at Rice University (Puerto, et al, 2012).

In both methods, samples were left to equilibrate at the test temperature after mixing. Typically, they were briefly removed during equilibration and shaken by hand a few times. This procedure was continued until phase volumes remain unchanged. Photographs were taken at different time intervals. All tubes or pipettes were marked by fine graduations to clearly indicate changing levels of water and oil over time.

IFT Measurement

IFT measurements between oil and surfactant were conducted at temperatures of 30, 60, 90 °C by means of a M6500 Spinning drop Tensiometer (Grace Instrument Company, TX). All surfactants were studied with and without an alkaline present.

Porous Media. The tested rock plugs came from the Middle Member of Bakken Formation in Well # 17450, AV Wrigley 163-94-0607H-1 at depth of 7347 to 7401 ft. Generally, the core samples tested were gritty shale and shale interbedded with siltstone, limestone and dolomite, with poor to zero porosity. Core plugs were 38 mm in diameter and 38 to 50 mm in thickness. For the Middle Member, permeability to Bakken oil for our core samples was typically around 6 microdarcys, while porosity averaged 5%.

Test Fluids. Cores were saturated with Bakken crude oil from Well #16083, B.L. Davidson 2-11H, 155-96-1102-2. The API gravity was 43.2 °API, and oil density 0.82 g/cm^3 at 23.2 ℃. Brine water salinity was characteristic of the Bakken Formation.

Surfactants: Aqueous surfactant candidates included: (1) internal olefin sulfonate anionic surfactant, (2) ethoxylated alcohol nonionic surfactant, (3) ethoxylated tallow amine cationic surfactant, and (4) dimethyl amine oxide amphoteric surfactant. They were compared at different salinities for phase behavior and IFT measurement. Compositions were based on our earlier surfactant formulation optimization studies (Wang *et al*. 2011b). Details for each case are shown in Table 1 to Table 5.

Brines: Waters with 0% to 30% TDS were used during phase behavior and IFT studies.

NaCl, KCl, $CaCl_2$, and $MgCl_2$: These salts were used to change salinity of the aqueous phase based on the work of Wang *et al*. 2011b.

$NaBO_2$•$4H_2O$: This alkaline chemical was used to change pH of the aqueous phase. It buffered solutions to

pH values of 8.4 to 9.

4.2 Phase Behavior Study

In general, increasing salinity of an aqueous phase (brine) decreases the solubility of an ionic surfactant. The surfactant is driven out of brine as electrolyte concentration increases. Thus, brine salinity has a significant effect on phase behavior (Green and Willhite, 1998). For an ideal system, multiphase behavior is divided into three classes which are called Windsor types (Windsor, 1954). Furthermore, if the third phase forms within a certain range of surfactant concentration, an optimal salinity exists. Here, the third phase is called the microemulsion phase (Healy, *et al*, 1976).

A candidate surfactant for use in EOR can be affected by (1) crude oil effective alkane carbon number (EACN), (2) temperature, (3) salinity, and (4) surfactant carbon number. For Bakken oil, EACN typically varies from C6 (hexane) to C10 (Decane) based on analysis of reservoir fluid composition from Well #15845, Nelson Farms 1-24H ((http://www.dmr.nf.gov/oilgas/FeeServices/wfiles/16/W15845.pdf). In our study, test temperatures varied from 23 ℃ to 120 ℃ and salinity varied from 0 to 30% TDS. Here, Chemical compositions included ***NaCl, KCl, $CaCl_2$, and $MgCl_2$,*** based on analysis of Bakken formation water. Four main cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) are present in our brine, with mol % ratios of 87.7%, 3.4%, 7.8% and 1.1%, respectively.

Six surfactant formulations with different molecular structures were investigated for phase behavior at various water salinities using surfactant-brine liquids and crude oil from the Bakken Formation (Table 16). Preliminary optimal salinity of surfactant solutions was determined by the change in phase behavior. Optimal salinity was further examined in conjunction with testing of interfacial tension (IFT) changes between oil and water, and results included in the next section. In order to observe the microemulsion phase phenomena, 0.05～0.1% and 2% concentrations of surfactant were adopted.

Table 16 — Surfactant formulations for phase behavior study

Surfactant	Type	Molecular structure	Concentration	Added reagent	Manufacturer
C-1	Anionic	Linear alpha olefin sulfonate	0.1%	30% ethanol	Tiorco
S-2	Anionic	Internal olefin sulfonate	0.1%	0.1% $NaBO_2.4H_2O$	Tiorco
S-2	Anionic	Internal olefin sulfonate	2%		Tiorco
58N	Nonionic	Alcohols, ethoxylated	0.05%	0.1% $NaBO_2.4H_2O$	CorsisTech
58N	Nonionic	Alcohols, ethoxylated	2%		CorsisTech
N 2512	Nonionic	Alcohols, ethoxylated	0.1%		CorsisTech
N 2512	Nonionic	Alcohols, ethoxylated	2%		CorsisTech
17A	Amphoteric	Dimethyl amine oxide	0.1%	0.1% $NaBO_2.4H_2O$	CorsisTech
17A	Amphoteric	Dimethyl amine oxide	2%		CorsisTech
TA-15	Cationic	Ethoxylated tallow amines	0.2%		Tiorco

At the high temperature (80-120 ℃) and high salinity (15-30% TDS) conditions of Bakken reservoirs, the surfactant must remain chemically stable during the period of imbibition, which might last several years. Moreover, precipitation or other undesirable phase separations must be avoided when using these surfactants. Initial screening of surfactant behavior at high temperature and high salinity conditions was discussed in SPE 145510 (Wang, *et al* 2011). The following discussion focuses on salinity optimization based on phase behavior between surfactants, brine, and crude oil for the various surfactant formulations shown in Table 16.

In the following discussion, all surfactants are assumed to be in the microemulsion phase (Green and Willhite, 1998).

Based on laboratory experimental results, for most of the very dilute surfactants with concentrations of 0.05～0.2%, very thin layers of the microemulsion phase (～0.1 mL) appeared at lower temperatures (23 ℃ to 60 ℃). However, this amount is too small to determine an optimal salinity even after aging a long time (～42 days). Consequently, the following discussions only focus on the five surfactants with 2% solution concentration. A salinity range of 0% TDS to 30% TDS was tested and these five surfactants were soluble in this range.

4.2.1 Anionic internal olefin sulfonate surfactant

Surfactant S-2 (low molecular weight internal olefin sulfonate) with 2% concentration remained clear at 0～30% TDS salinity from very beginning of the test at 120 ℃, and beginning of aging. Observations of solubility indicated that S-2 was cloudy at 23 ℃ and 60 ℃ when the salinity was 30% TDS.

For an overall composition of 50% oil, 48% brine, and 2% surfactant, four 10-mL samples with different salinities were mixed and allowed to equilibrate at 23 ℃, and 0.2 mL samples to equilibrate at 120 ℃. A microemulsion phase formed after 2 hours aging for all four salinities, except for a cloudy volume at 30% TDS salinity. After 14 days, microemulsion phases stabilized in the two samples with salinities of 0% at 23 ℃. As Fig.1a shows, phase behavior changed to upper phase (15 % TDS) from middle phase (0% TDS). At a temperature of 120 ℃, phase behavior changed to middle phase (10.0 % TDS) from lower phase (7.5, 8.5% TDS), and then to upper phase (12.5~15 5TDS) after 9 days stabilization, as Fig. 25 shows.

Plots of V_o/V_s and V_w/V_s are shown in Fig. 24b corresponding to the appearance of phase behavior after equilibration at room temperature (23 ℃, Fig. 24a). Based on these data, the optimal salinity is 7.5% TDS for $V_o/V_s = V_w/V_s = 1$ at 23 ℃. However, when temperature was changed to 120 ℃, the optimal salinity could not be determined by V_o/V_s and V_w/V_s plots even though there small amounts of microemulsion phases formed as shown in Fig. 25. We assumed the optimal salinity was 10.0% TDS based on observations when the temperature was 120 ℃.

Here, V_o= oil volume in the microemulsion phase, V_w= water volume in the microemulsion phase, and V_s= surfactant volume assumed to be in microemulsion.

4.2.2 Ethoxylated alcohol nonionic surfactant

Two surfactants: 58N with lower carbon number and N-2512 with higher carbon number were studied. Mixtures of both surfactants were clear at all salinities (0～30%) from the very start of testing at 23～120 ℃ at concentrations of 2%. A large phase behavior change occurred in N- 2512 at 10 days aging when the temperature was 23 ℃, as Fig.3 illustrates. Based on observation, the optimal salinity cannot be confirmed at 23 ℃, but at the very least, we estimate the optimal salinity for this situation would be large (close to 30% TDS). When temperature is increased to 60 ℃, the optimal salinity is 26.5% TDS at V_o/V_s and $V_w/V_s = 4$, as Fig. 28a and 28b shows. The phase behavior stabilized after 16 days. In Fig. 27, we assume that the colored liquid in the lower part of the tubes (30% TDS) was not a transparent microemulsion phase. It might be a component that diffused from the oil phase into the water phase, and the color change represents a concentration gradient.

In the higher temperature range from 90 ℃ to 120 ℃, both surfactants show upper phase status even though a tiny microemulsion phase can be observed in N-2512, as shown in Fig. 29. This phenomenon indicates this kind of surfactant is more hydrophobic at high temperature when mixed with Bakken oil, especially for the low carbon number surfactant, 58N (Fig. 30). However, our previous studies (SPE 145510, and SPE 153853) proved this kind of surfactant also shows favorable oil recovery under the current salinity ranges. Perhaps, for each surfactant, the question is "How does it displace oil?”—possibly indicating that wettability change is the key mechanism— not IFT reduction where no emulsion phase forms at high temperature in detailed salinity scans. Additional IFT studies are needed.

4.2.3 Dimethyl Amine Oxide amphoteric surfactant

Fig. 31a and 31b show the appearance and phase volumes at 23 ℃ for this surfactant at 2% concentration. Optimal salinity at 23 ℃ was 8.43% TDS for V_o/V_s and V_w/V_s = 3.75. However, at high temperatures from 90 ℃ to 120 ℃, this surfactant shows lower phase status in all tests over a broad salinity range (0 ～ 30% TDS), including detailed scans (7.5～15 TDS%). This indicates Surfactant 17A is somewhat hydrophilic at high temperature when mixed with Bakken oil. It also suggests that wettability change is the key mechanism responsible for the favorable oil recovery over the same temperature range. Phase behavior of 17A at 90 ℃ is shown in Fig. 32a and Fig.32b.

4.2.4 Ethoxylated tallow amines cationic surfactant

Phase behavior of Surfactant TA-15 at high temperature 90 and 120 ℃ is shown in Fig. 33 and Fig. 34. Lower phase was observed after aging for days up to 90 ℃, and more upper phase after aging for days up to 120 ℃, if the very small volume of third phase (dark color in the middle part of the figures) is ignored. Laboratory results indicate this kind of surfactant exhibits a hydrophilic character at high temperature, and then the switches to hydrophobic character as temperature is increased, when mixed with Bakken oil.

4.3 Interfacial tension (IFT) Study

Surfactant treatment of a fractured reservoir is very different from traditional surfactant–alkaline or surfactant-alkaline-polymer (ASP) floods that need ultra-low IFT (10^{-2}～10^{-3}). For a surfactant-aided gravity drainage process in fractured reservoirs, the target oil recovery will be driven toward a residual saturation value. Even though the IFT values between surfactants and oil in this research are not expected in the ultra-low range (10^{-2}～10^{-3}), the reduction should still be low enough compared to IFT between brine water and oil for sufficiently rapid oil drainage into the fracture system under gravity. The efficiency of this process is determined by a combination of capillary, gravity, and viscous forces.

Based on the research of Adibhatla and Mohanty (2006), when the oil-wet cores with a negative capillary pressure are immersed in a surfactant solution, oil displacement will be determined by the inverse Bond number (Eq. 7). For water alone, the macroscopic inverse Bond number, N_B^{-1}, may be greater than 1. However, if IFT is lowered, N_B^{-1} may become less than 1, and the surfactant solution will diffuse into the core and change IFT and wettability. This aqueous invasion into the core drives the oil out. As wettability is altered, the capillary pressure changes from negative to positive, and counter-current imbibition mobilizes more oil. Furthermore, relative permeabilities and residual saturations will be changed to provide a higher oil recovery from the core.

$$N_B^{-1} = \frac{\sqrt{\frac{\phi}{k}}\,\sigma}{\Delta\rho g L} \quad \text{……………………………………………………………………………………} \quad (7)$$

Here, φ is the rock porosity, k is rock permeability, σ is interfacial tension between oil and water, $\Delta\rho$ is the density difference, g is the gravitational constant, and l is length of the core. The numerator of Eq.7 is capillary pressure.

Cases where IFT measurement and calculation were performed are listed in Table 17. Surfactant CDS17-31C was not investigated for phase behavior.

Table 17 — Surfactant formulations for IFT study

Surfactant	Type	Molecular structure	Concentration	Temperature	Added reagent	Manufacturer
S-2	Anionic	Internal olefin sulfonate	0.1%	30～90 ℃	0.25% $NaBO_2.4H_2O$	Tiorco
58N	Nonionic	Alcohols, ethoxylated	0.1%	30～90 ℃	0.1% $NaBO_2.4H_2O$	CorsisTech
N 2512	Nonionic	Alcohols, ethoxylated	0.1%	30～90 ℃	0.1% $NaBO_2.4H_2O$	Tiorco
CDS17-31C	Nonionic	Alcohols, ethoxylated	0.1%	30～90 ℃	0.1% $NaBO_2.4H_2O$	CorsisTech
17A	Amphoteric	Dimethyl amine oxide	0.1%	30～90 ℃	0.1% $NaBO_2.4H_2O$	CorsisTech
TA-15	Cationic	Ethoxylated tallow amines	0.1%	30～90 ℃	0.1% $NaBO_2.4H_2O$	CorsisTech

4.4 Results Analysis

The average IFT between oil and brine water is generally high: in the range of 9.0～29 mN/m for oil viscosities of 2.8 to 694 cP, as studied by (Green and Willhite, 1998; Buckley and Fan, 2007). In our study, optimal salinities were tested at salinities of 3.75 to 22.5 % TDS. At several salinities, the IFT between brines and Bakken oil was decreased to 10^{-1} mN/m.

Fig. 34 shows the IFT reduction vs. salinity of surfactants with and without alkaline at 90 ℃. Results for anionic surfactant S-2 indicate that IFT reductions to 10^{-2} mN/m are possible when salinity is about 11.25% TDS. For nonionic surfactant N2512, amphoteric surfactant 17A, and cationic surfactant TA-15, IFT reductions to 10^{-1} mN/m are possible at salinities of 4.38, 28.97, and 15% TDS, respectively. For nonionic surfactants, optimal salinity was relatively low compared to the other types of surfactants; the optimal salinity for the IFT of the amphoteric surfactant was very high. This is consistent with phenomena observed during the phase behavior studies. For surfactant 58N, the IFT measurement was very challenging due to oil drops attaching to the inside wall of the spinning tube even though the equipment is spinning at high speed. As indicated previously in the phase behavior study, this surfactant is more hydrophobic. It is possible that the wet status of the inlet end of tube was altered to oil wet from water wet, therefore the oil drops are hard to separate from the wall. It should be stressed, that the explanation is not contradictory to with the wettability modification of the shale rocks by this surfactant.

Compared to the previous phase behavior study previously, the optimal salinities obtained by IFT curves are basically consistent with the phenomena observed in the pipettes shown in Fig. 31 to Fig. 33 at high temperatures. As a consequence, the salinities when IFT reached its lowest value can be taken as the optimal salinities for the corresponding surfactants when the reservoir temperature is near 90 ℃.

Fig. 35 illustrates an example of IFT reduction at various temperatures. Based on Fig. 35, for nonionic surfactant N-2512, the lower the temperature, the larger the optimal salinity obtained with the least IFT reduction. Cationic surfactant TA-15 and amphoteric surfactant 17A show the same trend.

Table 18 shows estimated inverse Bond number N_B^{-1} for five surfactants based on optimal salinity from IFT curves. According to Table 18, most N_B^{-1} values are less than 1. By reducing the IFT, surfactant solutions will diffuse into the core and drive the oil out at optimal salinity.

Table 18 — Inverse Bond number N_B^{-1} estimation (90°C)

Surfactant	S-2	58N	N-2512	17A	TA-15
N_B^{-1}	**0.202**	*NM*	**0.474**	**1.164**	**0.221**
Core	1-65	1-77	1-79	1-78	1-80
$\Delta\rho$, g/cm^3	0.286	*NM*	0.236	0.393	0.314
σ, mN/m	0.056	*NM*	0.098	0.550	0.44
TDS, %	11.25	*NM*	4.38	28.92	15.00
φ, fraction	0.062	0.050	0.058	0.039	0.052
k, md	4.070	1.790	1.950	4.14	4.53
l, mm	39.81	38.50	38.00	38.41	38.69

Here, *k* is the permeability with respect to surfactant. For surfactant 58N that only involved brine water and 0.1% 58N, IFT measurement was very challenging at 90 ℃ using current equipment because the oil drops could not be separated from the tube wall of the Spinning Drop Tensiometer. *NM* is not measured.

4.5 Summary

(1) Optimal salinities can be estimated from the curves showing the relationship between the microemulsion phase and corresponding proportions of oil/water volumes for most selected surfactants at low temperatures. However, for high temperatures, a relationship was difficult to determine in some solutions due to the limited volumes recovered.

(2) IFT was reduced with anionic and nonionic surfactants by 10^{-2} order of magnitude at high temperature. IFT reductions for other type of surfactants were 10^{-1} order of magnitude.

(3) The optimal salinities obtained from IFT curves are consistent with phenomena observed in phase behavior study for reservoir temperature near 90 ℃.

(4) For the optimal salinity, the inverse Bond number NB^{-1}, which dominated the IFT reduction mechanism, could be decreased to below a value of 1 in cores from the Bakken Middle member in Well # 17450.

(5) For nonionic surfactant, the lower the temperature, the larger the optimal salinity obtained with the least IFT reduction. Cationic surfactant and amphoteric surfactant show the same trend.

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Chapter 5. Extensive Imbibition Experiments

This chapter discusses results of studies on the effect of aqueous imbibition over time using a glass imbibition cell. The imbibition rate of different aqueous liquids including fresh and brine water, as well initial optimized surfactant formulations, based on phase behavior and IFT studies, were investigated.

In this study, imbibition cells were immersed into a temperature bath with high temperature adjustment. Core plugs were saturated with Bakken oil and stored for 4 to 8 weeks in order to achieve to oil wet status, and then were put into Glass Imbibition Cells with precision graduations in 0.1 mL. The cells filled with a volume of surfactant solution first, and then were immersed into a temperature bath at 120 ℃ for 300 to 500 hours until no more oil was displaced out. The volume of oil expelled was used to calculate the oil rate and %OOIP of oil recovery. During the spontaneous imbibition process, cores with all faces opened, and cores with two faces (top face and bottom face) were tested. No confining pressure was added during the process of Imbibition. We assume there was no gas presented in the cores and oil because they were vacuumed prior to imbibition.

Core samples were from the Middle member of the Bakken in NDIC Well #17450. Reservoir temperatures of 23 ℃ to 120 ℃ were simulated. Two groups of surfactant formulations and two groups of core samples were studied in this section: (1) surfactants with preliminary optimization at 30% TDS (Wang, *et al*, 2011b), (2) surfactants at optimal salinity based on phase behavior and IFT study, (3) cores with all faces opened, and (4) cores with two faces (top face and bottom face) opened. Extensive imbibition tests were conducted at a reservoir temperature of 120 ℃. Core samples were from the Middle Member of Bakken Formation in Well # 17450, at depths of 7347 to 7401 ft. Core sample properties are provided in Table 19.

5.1 Imbibition rate and oil recovery

The tested aqueous solutions included:

Group 1:

(1) Fresh water
(2) Brine water with 30% TDS;
(3) 0.1% of surfactant formulation N2512 (nonionic) with 30% TDS;
(4) 0.05% of 58N (nonionic) with 30% TDS, 0.1% alkaline content;
(5) 0.2% of TA-15 (cationic) with 30% TDS.

Group 2:

(1) 0.1% of S-2 (nonionic) with 10% TDS; 0.25% alkaline content
(2) 0.1% of 58N (nonionic) with 7.5% TDS, 0.1% alkaline content
(3) 0.1% of N-2512 (nonionic) with 4.38～5.62% TDS, 0.1% alkaline content
(4) 0.1% of 17A (amphoteric) with 29% TDS; 0.1% alkaline content
(5) 0.1% of TA-15 (cationic) with 12.5～15% TDS, 0.1% alkaline content
(6) 2% of S-2 (nonionic) with 10% TDS; 0.25% alkaline content

For the fresh water and Brine water in Group 1, four reservoir temperatures ranging from 23 ℃ to 120 ℃ were simulated in cores from Well # 17450. Experimental results show that imbibition using fresh water or brine water resulted in very little imbibition at low temperatures. However, oil was extracted out at higher temperatures from the tested core. It was noted that some oil drops imbibed out (2 -3 hours) using fresh water, but imbibition times for fresh water or brine water took much longer to obtain a reading on the imbibition cell compared to the surfactants. The explanation for these phenomena is that using fresh water or brine water alone, the wettability cannot be altered, or not obviously with Bakken oil. Even though oil drops imbibed out at high temperature, the wetness of glass tube was changed into oil wet from water wet by these waters (especially fresh water).

Table 19— Core sample dimension and porosity

Surfactant	Alkaline %	Optimal salinity % TDS	Boundary condition	Core sample	Diameter mm	Thickness mm	Rock permeability md	Porosity fraction	Type	Molecular structure	Manufacturer
S2	0.25%	10	AFO	1-65	38.05	39.01	0.0600	0.062	Anionic	Internal olefin sulfonate	Tiorco
S2-2%	0.25%	10	AFO	1-71	38.04	39.33	0.0099	0.061	Anionic	Internal olefin sulfonate	Tiorco
S2	0.25%	10	TFO	1-95	38.02	38.57	0.0035	0.061	Anionic	Internal olefin sulfonate	Tiorco
S2	0.25%	30	AFO	1-87	37.94	39.51	0.0049	0.052	Anionic	Internal olefin sulfonate	Tiorco
58N	0.1%	7.5	AFO	1-77	38.04	38.05	0.0052	0.069	Nonionic	Alcohols, ethoxylated	CorsiTech
58N	0.1%	7.5	TFO	2-3	38.05	38.80	0.0062	0.055	Nonionic	Alcohols, ethoxylated	CorsiTech
58N	0.1%	30	TFO	1-94	38.08	39.40	0.0039	0.051	Nonionic	Alcohols, ethoxylated	CorsiTech
YYC5-44	0.1%	5.62	AFO	1-84	38.03	39.08	0.0034	0.059	Nonionic	Alcohols, ethoxylated	CorsiTech
YYC5-44	0.1%	30	AFO	1-85	38.03	39.43	0.0044	0.054	Nonionic	Alcohols, ethoxylated	CorsiTech
N2512		4.38	AFO	1-79	38.02	38.22	0.0034	0.062	Nonionic	Alcohols, ethoxylated	Tiorco
N2512	0.1%	4.38	AFO	1-82	38.04	38.89	0.0027	0.056	Nonionic	Alcohols, ethoxylated	Tiorco
17A		28.9	AFO	1-78	38.02	38.41	0.0033	0.042	Amphoteric	Dimethyl amine oxide	CorsiTech
17A	0.1%	28.9	AFO	1-81	38.04	38.66	0.0036	0.0057	Amphoteric	Dimethyl amine oxide	CorsiTech
17A		28.9	TFO	2-2	38.06	39.17	0.0015	0.049	Amphoteric	Dimethyl amine oxide	CorsiTech
TA-15		15	AFO	1-80	38.02	38.69	0.0042	0.054	Cationic	Ethoxylated tallow amines	Tiorco
TA-15	0.1%	12.5	AFO	1-83	38.03	39.26	0.0089	0.061	Cationic	Ethoxylated tallow amines	Tiorco
TA-15	0.1%	12.5	TFO	2-1	38.03	39.68	0.0270	0.057	Cationic	Ethoxylated tallow amines	Tiorco
TA-15	0.1%	30	AFO	1-88	38.04	38.85	0.0089	0.061	Cationic	Ethoxylated tallow amines	Tiorco

Here, AFO= All Faces Opened, and TFO= Two Faces Opened. Except surfactant in row 3, all other surfactants were 0.1% concentration.

For these surfactant formulations, experimental results show that imbibition using optimal salinities resulted in a higher imbibition rate and faster oil extraction times at high temperature compared to solutions without salinity optimization, as Table 5 shows. Based on Table 20, at optimal salinity, the average instantaneous imbibition rate was increased up to 45%. The imbibition time was 380 hours.

Table 20— Imbibition rate vs. time (optimal salinity), 120°C, 0.1% concentration

Core sample	Diameter mm	Thickness mm	Aqueous liquid	Instantaneous imbibition rate, ft/day	
1-47A	38.07	50.99	TA-15		0.028 at 30% TDS
1-80	38.03	38.69	TA-15	0.132 , at 15% TDS	
1-53A	38.17	51.46	N 2512		0.069 at 30% TDS
1-79	38.02	38.00	N2512	0.101 at 4.38 % TDS	
1-44A	38.07	51.10	58N		0.120 at 30% TDS
1-77	38.04	38.50	58N	0.158 at 7.5% TDS	

For surfactant formulations at optimal salinity, we found: (1) at 0.1% concentration, nonionic surfactants with an ethoxylated alcohol molecular structure exhibited a fast imbibition rate and strong effect on oil recovery at reservoir temperature (~120 ℃, N2512 and 58N), (2) at higher concentration (2%), an anionic surfactant, internal olefin sulfonate, shows a slow imbibition rate compared to the lower concentration (0.1%) surfactant with same molecular structure (Fig.36(a)), (3) higher oil recovery was seen with amphoteric surfactant 17A without alkaline. In contrast, when using cationic surfactant TA-15, higher oil recovery was seen with alkaline compared to 17A. Fig 37 shows the imbibition effect on oil recovery for times up to 450 hours(a) and the oil recovery for dimensionless time (b), and (4) strong oil recovery using optimal salinity up to 18% compared to the surfactant with formation water salinity (Fig. 38). In Fig. 38, cationic surfactant solutions, TA-15 and nonionic surfactant solutions, YYC5-44 was mixed at a similar salinity range with surfactant 58N (these two surfactants have similar molecular structures) and formation water salinity, respectively.

In Fig. 14b, dimensionless time t_D is defined by Eq. 8, as described by Fischer and Morrow (Fischer and Morrow, 2008):

$$t_D = t\sqrt{\frac{k}{\phi}}\,\frac{\sigma}{\sqrt{\mu_o \mu_w}}\,\frac{1}{L_c^{\,2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (8)$$

Where, t is the imbibition time; k is the rock permeability, φ is the rock porosity; σ is the surfactant/brine/oil interfacial tension; μ_w and μ_o are water and oil viscosities at 120 ℃ (reservoir temperature), respectively; and L_c (Fischer and Morrow, 2008) is the characteristic length which depends on the core sample size, shape and boundary conditions, as Eq. 9 describes. In Eq.9, d is the diameter of core sample, and l is the thickness of core sample. Here, we assume the core faces were opened with cylindrical boundary conditions.

$$L_c = \frac{ld}{2\sqrt{d^2 + 2l^2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (9)$$

5.2 Boundary conditions

The tested surfactant formulations included:

Group (3): cores with all faces opened, treated by toluene and methanol before being oil soaked

(1) 0.1% of S-2 (anionic) with 10% TDS; 0.25% alkaline content
(2) 0.1% of 58N (nonionic) with 7.5% TDS, 0.1% alkaline content
(3) 0.1% of TA-15 (cationic) with 15% TDS.

Group (4): cores with two faces opened, without treatment by chemicals before being oil soaked

(1) 0.1% of S-2 (anionic) with 10% TDS; 0.25% alkaline content
(2) 0.1% of 58N (nonionic) with 7.5% TDS, 0.1% alkaline content
(3) 0.1% of TA-15 (cationic) with 15% TDS.

Fig. 39 imbibition experiments show the effect of dimensionless time on oil recovery between cores with all faces open and only two faces open during the period of imbibition. Based on the experimental results, oil recovery was not affected by the exposed area or contact area of core sample, but was affected by the oil extraction rate. With less area contacted, the oil extracted out slowly.

5.3 Discussion

Major surfactant imbibition mechanism. In general, wettability modification and interfacial tension reduction are the major mechanisms for oil recovery improvement using surfactant imbibition. For most of the surfactants we tested, optimal salinity obtained by IFT reduction is consistent with phenomena observed in the phase behavior study. Also, with the optimal salinity, good potential was observed for increasing oil recovery using surfactant imbibition compared to the solutions using formation water only (30% TDS). These results demonstrate that IFT reduction can be taken as one mechanism for increasing oil recovery in the Bakken Formation. However, this conclusion is tempered by two experimental phenomena:

For ethoxylated alcohol nonionic surfactant 58N with a low carbon number, IFT measurement was very challenging due to oil drops attached to the inside wall of the spinning tube even though the equipment was spinning at high speed. As indicated previously in phase behavior study, this surfactant was more hydrophobic. It is possible that the inlet end of the glass tube was altered to oil wet from water wet, therefore, the oil drops were hard to separate from the wall. However, we cannot ignore that the wettability modification of the shale rocks by this surfactant (Wang, *et al*, 2012).

As a consequence, we suggest that wettability alteration is an important mechanism when using ethoxylated alcohol nonionic surfactant to improve oil recovery in the Bakken Formation.

Effect of Alkaline Solutions. In Fig.36, for nonionic surfactant N-2512, the optimal salinity value increased when alkaline was added to the surfactant solution. For amphoteric surfactant 17A, the result went the opposite way compared to N-2512. Even though the IFT reduction value was not affected much by the two optimal salinities, the oil recovered by extensive imbibition in these two cases presented a different trend (Fig. 37). Based on Fig. 37, surfactant 17A recovered less oil when alkaline was included at optimal salinity.

Issue of optimal salinity. A fast oil extraction rate and favorable oil recovery was obtained by ethoxylated alcohol nonionic surfactant N-2512 with a relative large carbon number, using optimal salinity 4.38～5.62% TDS. However, for a field application at very high formation salinity, such as the Bakken (～30 % TDS), this might presented a challenging problem as the displacing front advances and a mixing zone developed in the reservoir. As a result, the optimal salinity should be adjusted to adapt to reservoir conditions if this surfactant is applied to the field.

Number of open faces for the cores. Incremental recoveries from the two-face-open cores ranged from 20% to 60% OOIP. This is effectively the same range found in all faces opened cores. Oil recovery was not affected by the contact area of core sample, but was affected by the oil extraction rate.

5.4 Summary

(1) In most cases, optimal salinities obtained by phase behavior and IFT study aided surfactant imbibition into the Bakken Formation.

(2) For the four types of surfactants tested (anionic, cationic, nonionic, and amphoteric with specific molecular structures), all exhibited favorable imbibition rates and good effect on oil recovery at reservoir temperature.

(3) At optimal salinity, the incremental oil recovery (during imbibition into Bakken cores at 120 ℃) can be up to 18% OOIP higher than seen during comparable experiments using formulations with 15～30% TDS, and the average instantaneous imbibition rate increased up to 45%.

Chapter 6. Ideal Numerical Simulation Model Building

In this Chapter, an ideal numerical model to scale the laboratory results was built using UTCHEM developed by the University of Texas in Austin. Certain equations that describe different parameters including IFT, wettability alteration, surfactant concentration, and effect of rock fluid properties on amount and rate of oil recovery were utilized by our simulation model. In the ideal model, fractures were not considered, but will be factored into the actual well model in the next phase of work.

6.1 Mathematical model

According to the experimental observations, the following assumptions are made regarding the distribution of components among different phases:

- Hydrocarbons can exist in the aqueous phase and oil phase.
- Water can exist in the aqueous phase and oil phase.
- Surfactant can exist in the aqueous and/or oil phases, and it can absorb onto solid surfaces.
- Salt can exist in the aqueous phase and can be absorbed onto matrix surface.

Additionally, the capillary pressure, relative permeability, and residual saturations of phases are considered as a function of IFT and wettability, which are correlated to the surfactant and salt concentrations in the model. The conceptual model qualitatively captures the typical trends observed in previous studies of the effects of capillary number and wettability on relative permeabilities. The mass balance equations are spatially discrete with a finite volume method for all the components.

Based on UTCHEM, equations that describe the mechanisms of phase behavior, interfacial tension, capillary, and wettability are as follows:

(1) Phase behavior

For both Type II(-) and Type II(+) phase behavior, there are only two phases present.

$$\frac{C_{3l}}{C_{2l}} = E \bullet \left[\frac{C_{3l}}{C_{1l}}\right]^F \quad l=1,2 \qquad \text{……………………………………………………………….(9)}$$

Where, A and B are empirical parameters, C_{kl} is concentration of composition *k* in phase *l*. F is calculated by *F= —1/B.*

For Type III, assuming that the excess oleic and aqueous phases are pure, the microemulsion phase composition is defined by the coordinates of the invariant point, as Eq. 10 described.

$$\begin{cases} \dfrac{C_{3m}}{C_{2m}} = A\left(\dfrac{C_{3m}}{C_{1m}}\right)^B \\ C_{1m} + C_{2m} + C_{3m} = 1 \\ C_{2m} = \dfrac{C_{SE} - C_{SEL}}{C_{SEU} - C_{SEL}} \end{cases} \qquad \text{………………………………………………………….(10)}$$

Where, C_{SE} is salinity， C_{SEL} and C_{SEU} are the lower and upper limits of effective salinity.

Note: the concept of Type II and Type III was discussed in Chapter 2, Phase behavior study presented in the Annual report of March, 2013.

(2) IFT

The interfacial tensions between microemulsion and the excess phases (σ_{13}—microemulsion/water and σ_{23}—microemulsion/oil) are calculated as functions of solubilization.

$$\begin{cases} \log_{10}\sigma_{l3} = \log_{10}F_l + G_{l2} + \dfrac{G_{l1}}{1+G_{l3}\bullet R_{l3}}, & R_{l3} > 1 \\ \log_{10}\sigma_{l3} = \log_{10}F_l + (1-R_{l3})\bullet\log_{10}\sigma_{ow} + R_{l3}\bullet\left[G_{l2} + \dfrac{G_{l1}}{1+G_{l3}}\right], & R_{l3} < 1 \end{cases} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where, G_{l1}、G_{l2}、G_{l3}（l=1,2）are the input parameters. R_{l3} is the solubilization ratio:

$$R_{l3} = \frac{G_{l3}}{G_{33}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

The correlation factor introduced by Hirasaki, $F_l = \dfrac{1-e^{-\sqrt{Con_l}}}{e^{-\sqrt{2}}}$, l=1,2,

and $Con_l = \sum_{k=1}^{3}(C_{kl}-C_{k3})^2$ ……………………………………………………………… (13)

In the absence of surfactant or the surfactant concentration below CMC (Critical Micelle Concentration), the interfacial tension is combined with Hirasaki's correlation and Chun-Huh's equation $\sigma_{l3} = c/R_{l3}^2$ as:

$$\sigma_{l3} = \sigma_{ow}e^{-aR_{l3}} + \frac{cF_l}{R_{l3}^2}(1-e^{-aR_{l3}}) \text{ for } l = 1 \text{ or } 2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Where, c = 0.3, σ_{ow} = water-oil IFT

(2) Capillary pressure for oil-wet or mixed-wet rocks

The capillary pressure for an oil-wet or mixed-wet status is calculated using the modified van Genuchten function:

$$P_c = P_{neg} + \frac{1}{\partial}\left[\frac{1}{(\overline{S_w})^{1/m}} - 1\right]^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

Where, $\overline{S_w} = \dfrac{S_w - S_{wr}}{1-S_{wr}-S_{or}}$, P_{neg} is the maximum negative capillary pressure at which the water saturation reaches a maximum value on the main imbibition path, α, m and n are model fitting parameters. S_{wr} is connate water situation, and S_{or} is residual oil saturation.

6.2 Ideal simulation model description

As Fig. 39 illustrates, the ideal model is built with a 1-D homogeneous grid block 35×1×1 in x, y, and z directions based on an average core size of 38mm thickness and 38 mm diameter. For a single grid block, dx = 1.086 mm, and $dy = dz$ = 38mm. Based on the imbibition experimental conditions, assume only the top-face and the bottom-face are open, one well is located on the top—injector, and one well at the bottom end—producer (forcibly imbibition), or one on top as injector, and another on top end as producer (spontaneous imbibition) of the model domain. A fixed pressure condition is applied in the model.

Based on the properties of core samples from Middle Bakken, the porosity of the matrix (no fractures considered) is 0.05, and the average permeability is 0.001 md with original oil-wet wetting status. Oil viscosity is 2 cp at 25 ℃.

6.3 Oil recovery

Two cases were simulated in this model: imbibition by brine water only, and imbibition by surfactant solutions. Five main ions constitute the brine: 61.5% chloride ion, 4.39% calcium ion, 0.39% magnesium, 28.4% sodium, and 1.88% potassium. Simulations were performed at the same reservoir condition (pressure, temperature and imbibition rate) with brine water imbibition, and surfactant imbibition with 0.1% concentration and 0.1% alkaline added. Fig. 5 shows the oil recovery comparison between the two cases. Surfactant imbibition has good oil recovery potential compared to brine water alone. The increased oil recovery is about 20%. This result is consistent with our laboratory work described in previous reports.

6.4 Surfactant concentration

Five cases were simulated for effect of surfactant concentration on oil recovery at concentrations of 0.05% to 1%. Based on the simulation model, we found: (1) oil recovery increased as surfactant concentration increased, although there is not a large difference for small concentration differences. (2)A similar phenomenon (Fig.1 (a) was found with surfactant S-2) that the initial oil recovered increased slowly with within 0.21 to 0.72PV (pore volume) up to 0.4% or higher concentration difference, and then increased quickly above that. However, for field application, higher surfactant concentrations are not recommended due to economics. Simulation results are shown in Fig. 41.

6.5 Water salinity

Six cases were simulated for the effect of water salinity on oil recovery at salinities that ranged from 3.75% to 30% TDS (Fig.42). Based on the simulation model, we found: (1) there is an optimal salinity for maximum oil recovery in the simulated surfactant. By this surfactant, at an optimal salinity (22.5% TDS), the oil recovery achieved highest value, (2) the two ends of salinities (highest salinity- 30 % TDS and lowest salinity- 3.75%) shows poor oil extraction from rocks because no middle phase (microemulsion phase) forms and there is higher interfacial tension between water and oil. These results are consistent with the laboratory results on phase behavior and IFT study discussed in the Annual report of March 2013.

6.6 Injection rate

Four cases were simulated for the effect of surfactant injection rates on oil recovery, varying from 0.0052 to 0.1ft^3/PV. Based on the simulation model, we found the oil recovery increased as injection rate increased (Fig.43). However, for a fractured field case, a moderate injection rate was suggested, based on the actual reservoir case design where the actual water cut lifted up quickly in fractures before the aqueous liquid imbibed into the matrix.

6.7 Summary

IFT and wettability, correlated to the surfactant and salt concentrations in the ideal model, simulation were scaled I simulations to typical trends observed in laboratory studies related to the effects of oil recovery due to brine water and surfactant formulations, surfactant concentration, water salinity and injection rate, and effect of rock fluid properties on amount and rate of oil recovery. Further predictions based on actual well production data and fracture networks will be attempted in the next task.

Chapter 7. Field-Scale Numerical Simulation Prediction

For the field-scale numerical simulation, the well modelled represents an actual well site, and reservoir dimensions are based on real data. In the simulation, fractures are assumed to be of infinite permeability and higher conductivity and always filled with surfactant solution. The fracture length is assumed 30 ft. This would be an ideal case, but still useful to indicate the potential for scale-up of the laboratory results. The properties of the reservoir are those from the Bakken formation, with gravity drainage considered. Although fracture dimensions are described in the simulation model, fracture geometry distribution, geomechanical stress and other factors were beyond of this project. The current average spacing between wells in the target oil field (North Dakota) is relative large (800-1000 ft). There may be very good natural fracture connection between wells, but well to well injection in this Chapter is not modeled, although future well infilling patterns may necessitate changing the model. Another assumption in this model is: the fracture networks have two wings that are directed in opposite vertical directions from the horizontal well. Since our main objective in this project is to determine whether oil recovery can be improved by the aqueous imbibition process, other fracture patterns (horizontal way and network configuration) will not discussed here.

The simulation model was built based on STARS of CMG but not GEM as in other simulation studies. The reason is: the GEM module is a compositional simulator which can simulate all the mechanisms of a miscible gas injection process, i.e. vaporization and swelling of oil, condensation of gas, viscosity and interfacial tension reduction, and the formation of a miscible solvent bank through multiple contacts. Since our project objective is focus on surfactant imbibition coupled with gravity drainage, STARS should be the best choice to target our goal.

7.1 Well model

Well AV Wrigley 0607-H1 (#17450) is a Bakken Well located in northwest Burke County in the Williston in North Dakota. This well is a hydraulically fractured horizontal well that started production in October 2008 in a 1280 aces test. The reservoir temperature in the Middle member is about 95 ℃. By the end of June 2013, the cumulative oil production was 135,504 bbl. The basic properties used in the simulation model were based on an actual reservoir model of the matrix as Table 21 shows. The well location is shown in Fig. 44. Based on laboratory results, the wettability of reservoir was set to oil-wet with a pressure drop scheme until the end of June 2013. Beginning July 2013, we assumed use of a surfactant imbibition drive, and wettability was set to water-wet status in the model. The lowest interfacial tension was set to 10^{-2} order of magnitude, based on laboratory results. The other parameters described in the simulation model are succeeded by the ideal model described in section 6.1. Also, in this model, the gas phase was considered since the current displacement mechanism in Bakken involves a pressure decline associated with gas expansion.

Fig.45 (left) shows plan view of the well trajectory from the well survey of the drilling paths (mostly horizontal). Fig.45 (right) is the 2D simulation model based on the well trajectory. A 3D simulation model was built using $10\times38\times3$ = 1140 cell blocks. The grid dimension in the x direction and y direction is: dx =500ft, dy=500 ft, and dz is variable in the vertical direction from 87.7 to 349.2 ft. The thickness of net pay was set at 87ft, based on the drilling record of Well #17450. Considering actual fracture dimensions and fracturing stages, a Dual-porosity and Dual-permeability model was adopted for the history match, and imbibition effectiveness predicted using the STARS Module of CMG (Fig. 46). Refined grid blocks were used for the perforation segments shown in Fig.46. Fig.47 and Fig. 48 illustrate the perforation design and fracture distribution simulated in the model. The imbibition mechanism considers fluid flow imbibed into fractures, and fluid diffusion into the matrix due to gravity drainage. Oil is extracted through the fractures after a period soaking.

Table 21— Parameters used in the simulation model

Parameter	Reservoir (3-layers in vertical direction-Z)	
	Matrix	Fracture
Porosity, %	4.7, 4.7, 1.5	0.1, 0.1, 0.1
Permeability, md	0.031, 0.031, 0.0128	310, 310, 128
S_w, current water saturation, %	38.0, 38.0, 48.7	38.0, 38.0, 48.7
S_{wi}, connate water saturation, %	12.0	0.0
S_{or}, residual oil saturation, %	13.0	0.0
Average grid width, ft	500	50
Reservoir pressure, psi	2700	2700
Reservoir temperature, °C	95	95

7.2 History match

Simulation history matching starts October 1, 2008, and ends June 30, 2013. The history match focuses on water cut change and cumulative oil production for this time. Some observations are made from history match:

From the very beginning of production—October 1, 2008, the estimated OOIP (original oil in place in the simulation area) was 2.05×10^6 bbl. Based on this value, the actual **oil recovery** for the well #17450 was 6.61% OOIP, while the simulated oil recovery from the numerical model was 6.53%. The relative error was 1.21%. The actual average **water cut** for the well was 27.00%, while the value by simulation was 26.41%, and the relative error was 2.19%. These two relative errors compare favorably for simulation history matches.

Fig. 49 shows the history match of water cut and cumulative oil production for Well #17450. Based on the curves shown in Fig. 49, the water cut change and oil production between actual data and the simulation have indicates reasonable agreement.

7.3 Surfactant imbibition prediction

Based on this history match, the predicted effectiveness of the current production method is compared to brine water imbibition, and surfactant imbibition (Fig. 50). In Fig. 50, we assume using a huff-puff method for imbibition starting July 2013. The enhanced oil recovery by surfactant imbibition is predicted to be 8.58% OOIP (624, 750 bbl) over brine alone, and 10.43% (766,605 bbl) OOIP greater than the current production practices. The injection aqueous volume amount of 0.0283PV (Pore Volume) equates to 62,993 bbl over 6.5 years. Based on the trends of these curves, the oil production would not be increased but remain stable with the current production method (red color). Under brine imbibition (blue color), the oil production increases as the green curve shows. The surface pressure was set to 4000 to 8000 psi according to different cases. Assuming the aqueous liquid injection sequence is:

(1) Injection of aqueous liquid (brine water or surfactant solution with 0.1% concentration and an optimal salinity of 22.5% TDS if using amphoteric surfactant) for 20 days;

(2) Shut in well and soak the liquid along the wellbore for 10 days;

(3) Open the well and produce for 60 days.

7.4 Production sequence

Three pumping sequences were simulated based on the history match: MBSTW, MDSTW and MESTW. The process of each sequence and its effectiveness are shown in Table 22. Details of different huff-puff trials are shown in Table 22 and effectiveness are shown in Fig.51. Based on the simulation prediction, the most favorable effect on oil recovery could be obtained by sequence MESTW. Considering filed site conditions, a well that is frequently shut-in and re-opened may cause mechanical issues. As the result, an appropriate case design for a production sequence selection will be depend on the feasibility of actual well operation.

Table 22— Production sequence effect on oil recovery

Sequence	Injection period, days	Injection rate, BWPD	Imbibition (soak) time, days	Production period, days	Period oil recovery, %
MBSTW	15	242.28	45	60	11.94
MDSTW	20	242.28	10	60	18.36
MESTW	30	242.28	10	50	23.68

7.5 Injection rate

Three injection rates were simulated based on the production sequence MESTW. Assuming the injection rate ranges from 500 BPD to 1500 BWPD (barrel water per day), and the injection pressure ranges from 4000 to 8000 psi, the predicted oil recovery would be 13.43 to 27.27% within 15 months as Fig. 52 shows. The predicted oil recovery would be 1.38% per month compared to only 0.11% per month before the surfactant imbibition process. The predicted period oil recovery (include the period from Oct. 2008 to June 2013) over 15 month period would be 20.57, if the injection rate is 1500 BWPD (Table 23) under the fracture distribute assumption in the model.

Table 23— Injection rate effect on oil recovery

Injection volume, bbl	Injection rate, BWPD	Imbibition (soak) time, days	Total cycling period, month	Period oil recovery, %
77,000	500	10 per cycle	15	13.43
154,001	1500	10 per cycle	15	20.57
231,000	2000	10 per cycle	15	27.27

7.6 Summary

(1) Compared with current production methods, the enhanced oil recovery using the surfactant imbibition process could yield more than 10% OOIP in a few years for this Bakken Well.

(2) Injection rate and production sequence will apparently affect oil recovery. A reasonable injection rate and production sequence should be considered completely when designing field trial.

(3) The predicted oil recovery factor may be different for a pilot trial due to assumptions used in the simulation model. Future development field development of a field case design needs to consider fracture geometry distribution, and the loss of surfactant solutions used in the imbibition process during transition from fractures to matrix among other factors.

Chapter 8. Conclusions

Laboratory studies and numerical simulations were conducted to find surfactant formulations best suited to imbibe into and enhance oil recovery from the Bakken Formation. Even though our research shows a tremendous potential to increase oil recovery from Bakken, more extensive research is needed on how to accelerate fluid penetration contact area invading matrix, among other issues to be explored in the future. Moreover, an appropriate case design is a key factor for a field application in a future field test. Findings based on our research include:

1. Ethoxylate nonionic surfactant, internal olefin sulfonate anionic surfactants, and amine oxide amphoteric surfactant were more stable than the other surfactants at temperatures of 105−120°C. All were effective in imbibing and displacing oil at high temperatures.
2. Sodium carbonate (added to increase alkalinity) precipitated with divalent cations in brines (15-30 % TDS). Sodium metaborate may help increase alkalinity without precipitation in brines.
3. 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 amphoteric 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.
7. Proper co-surfactant formulations show potential for increased oil recovery.
8. Bakken shale cores were generally oil-wet or intermediate-wet (before introduction of the surfactant formulation).
9. The surfactant formulations that we tested consistently altered the wetting state of Bakken cores toward water-wet.
10. Surfactants we tested consistently imbibed to displace significantly more oil than brine alone displaced. Four of the surfactant imbibition tests provided EOR values of 6.8% to 25.4% OOIP, incremental over brine imbibition. For comparison, recovery using existing production methods is typically only a few % OOIP.
11. Positive imbibition results were generally observed with all surfactants: anionic, cationic, nonionic, and amphoteric with specific molecular structures. 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.
12. Optimal salinities can be estimated from the curves showing the relationship between the microemulsion phase and corresponding proportions of oil/water volumes for most of the selected surfactants at low temperatures. However, for high temperatures, this relationship was difficult to determine in some solutions due to the limited volumes recovered.
13. IFT was reduced with anionic and nonionic surfactants by 10^{-2} order of magnitude at high temperature. IFT reductions for other type of surfactants were 10^{-1} order of magnitude.
14. The optimal salinities obtained from IFT curves are consistent with phenomena observed in phase behavior study at reservoir temperature near 90 ℃.

15. For the optimal salinity, the inverse Bond number N_B^{-1}, which dominated the IFT reduction mechanism, could be decreased to below a value of 1 in cores from the Bakken Middle member in Well# 17450.
16. For nonionic surfactant, the lower the temperature is, the larger the optimal salinity obtained with the least IFT reduction. Cationic surfactant and amphoteric surfactant show the same trend.
17. In most cases, optimal salinities obtained by phase behavior and IFT study aided surfactant imbibition into the Bakken Formation.
18. For the four types of surfactants tested (anionic, cationic, nonionic, and amphoteric with specific molecular structures), all exhibited favorable imbibition rates and good effect on oil recovery at reservoir temperature.
19. At optimal salinity, the incremental oil recovery (during imbibition into Bakken cores at 120 ℃) can be up to 18% OOIP higher than observed in comparable experiments using formulations of 15～30% TDS, and the average instantaneous imbibition rate was increased by as much as 45%.
20. IFT and wettability, correlated to the surfactant and salt concentrations in the ideal model were simulated and scaled to typical trends observed in laboratory studies on the effects of oil recovery of brine water and surfactant formulations, surfactant concentrations, water salinity and injection rate, and effect of rock fluid properties on amount and rate of oil recovery.
21. Compared to current production methods, enhanced oil recovery using the surfactant imbibition process resulted in more than 10% OOIP in a Bakken Well #17450, based on numerical simulation prediction.
22. Injection rate and production sequence apparently affect oil recovery. A reasonable injection rate and production sequence should be considered completely when designing a field trial.

Nomenclature

CMC= Critical Micelle Concentration
EOR=enhanced oil recovery vs. brine water imbibition alone
IFT= Interfacial Tension
Mw = molecular weight
OOIP = original oil in place, cm^3
PV=pore volume
A = empirical parameter
B = empirical parameter
C_{kl} = concentration of composition *k* in phase *l*
C_{SE} = salinity
C_{SEL} = lower limit of effective salinity
C_{SEU} = upper limit of effective salinity
d = diameter of core sample
dx = grid size in *x*-direction
dy = grid size in *y*-direction
*d*z= grid size in *z*-direction
F_l= correlation factor
G_{l1} = input parameter
G_{l2} =input parameter
G_{l3} = input parameter
g= gravitational constant
k = rock permeability
l = thickness of core samples
L_c =characteristic length which depends on core sample size, shape and boundary conditions
m =model fitting parameter

n=model fitting parameter

P_c = capillary pressure

P_{neg} = maximum negative capillary pressure

R_{l3} = solubilization ratio

S_{wr} =connate water saturation

S_{or} = residual oil saturation

t = Imbibition time

t_D =dimensionless time

α= model fitting parameter

$\Delta\rho$= density difference between oil and water

φ = rock porosity

σ = surfactant/brine/oil interfacial tension

σ_{13}= microemulsion/water interfacial tension

σ_{23}= microemulsion/oil interfacial tension

σ_{ow}= water/oil interfacial tension

μ_w = water viscosity

μ_o = oil viscosity

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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^2
g/L × 0.1 E+00 = % TDS

mg/L × 0.0001 E+00 = % TDS

* Conversion is exact

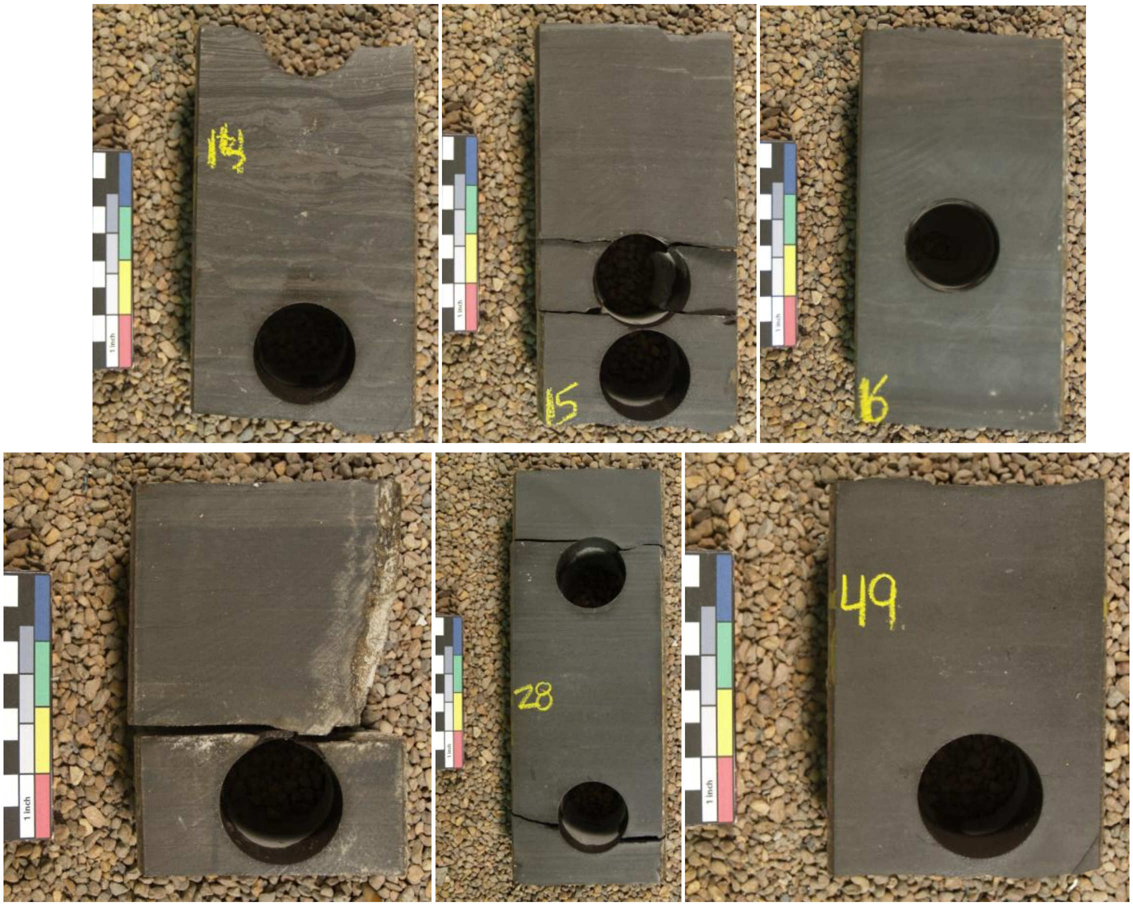


Fig.1 — Partial core slabs of Well #16433

Fig. 2 — Clay flaking with brine water at 23°C

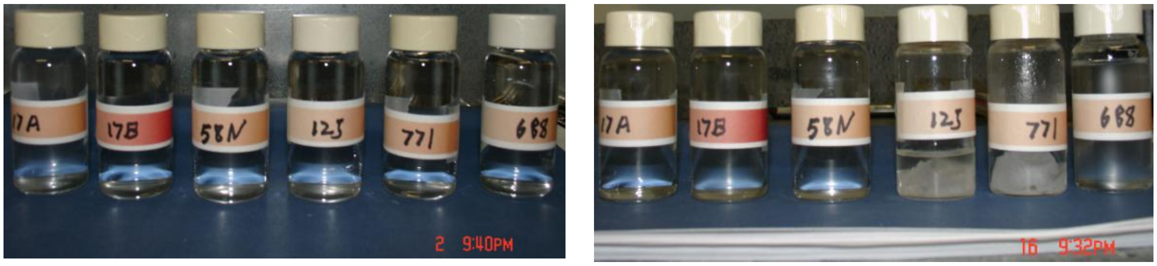


Fig. 3 — Temperature stability of surfactant samples before and after 105°C aging with 30 %TDS -1

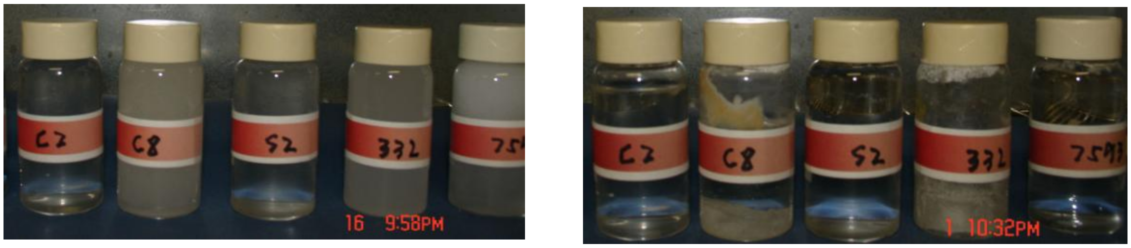


Fig. 4 — Temperature stability of surfactant samples before and after 105°C aging with 30 %TDS -2

Fig.5 — C-1 alone aging at 23°C

Fig. 6 — C-1 after 30% alcohol added aging for 15 days

Fig.7 — 58N with 30% TDS aging at 110°C for 15 days

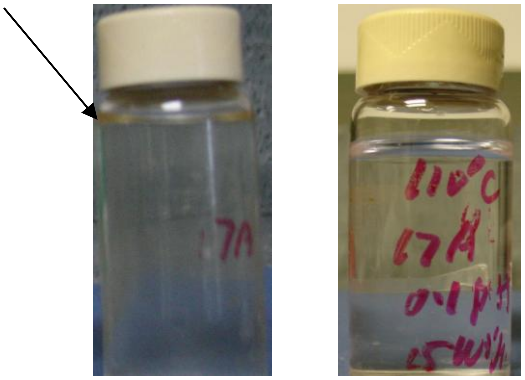


Fig.8 — 17A before and after 0.1% alkaline added aging at 110°C after 7 days

Fig.9 (a) and (b) — Aging at 110°C and 30 %TDS before and after 50 days

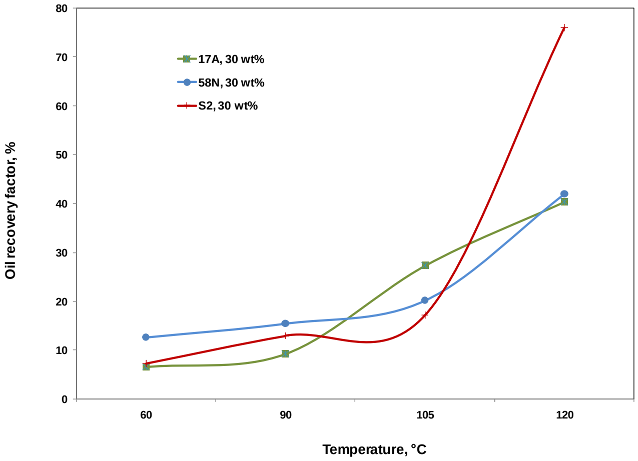


Fig.10 — Temperature vs. oil recovery
(30 %TDS, 0.1 % surfactant concentration and 5% divalent cation content)

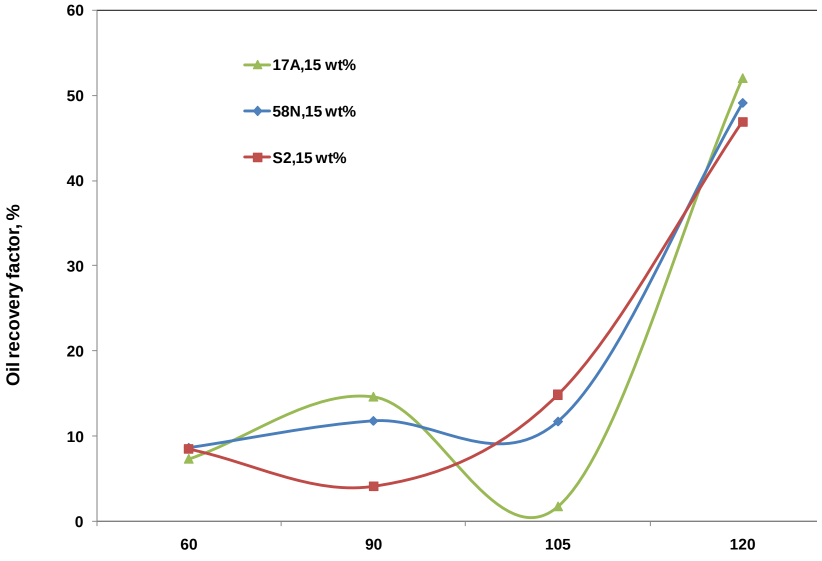


Fig.11 — Temperature vs. oil recovery
(15 %TDS, 0.1 % surfactant concentration and 5% divalent cation content)

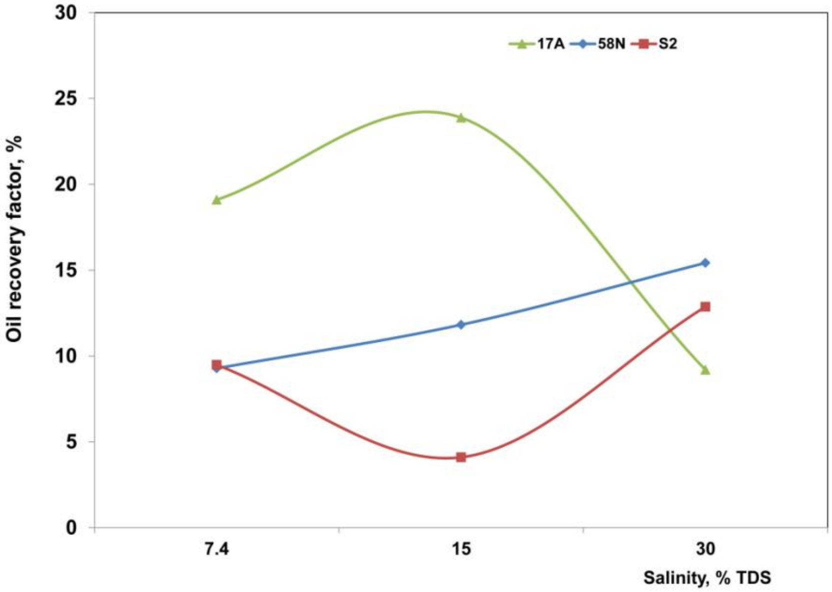


Fig. 12— Solution salinity vs. oil recovery (90°C, 0.1% surfactant concentration, and 5% divalent content)

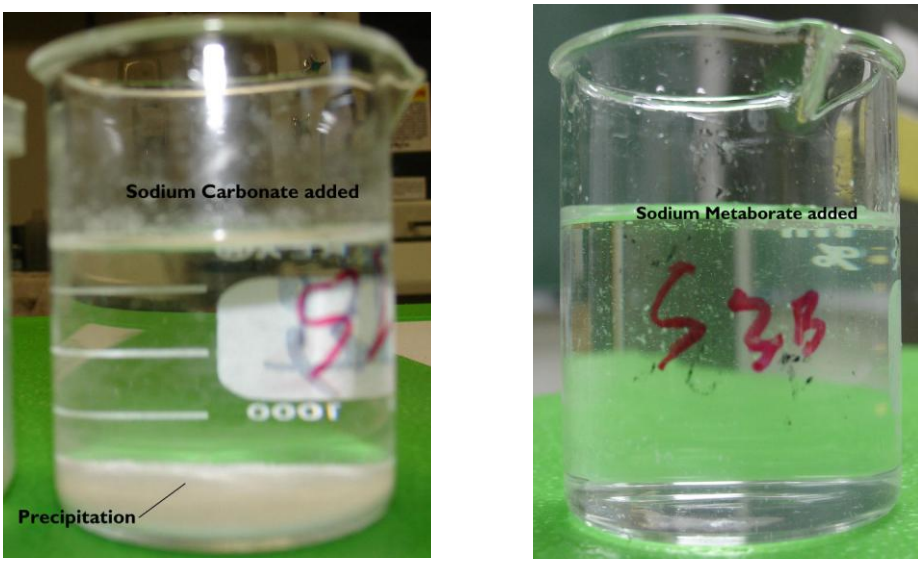


Fig.13 — 0.1% alkalis added to surfactant samples

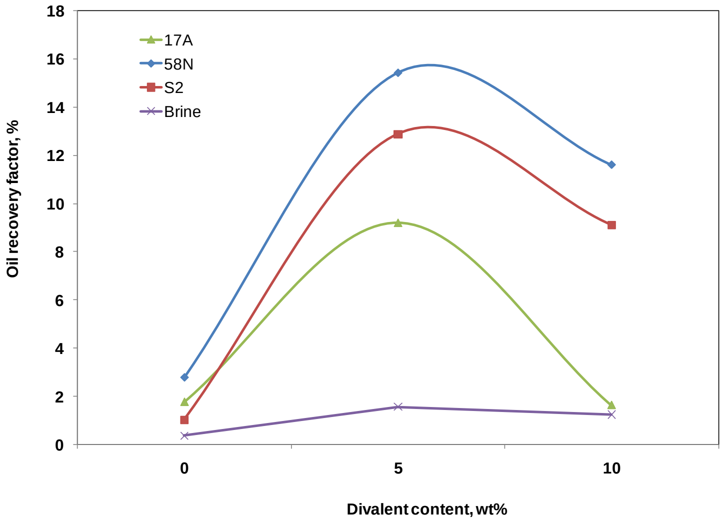
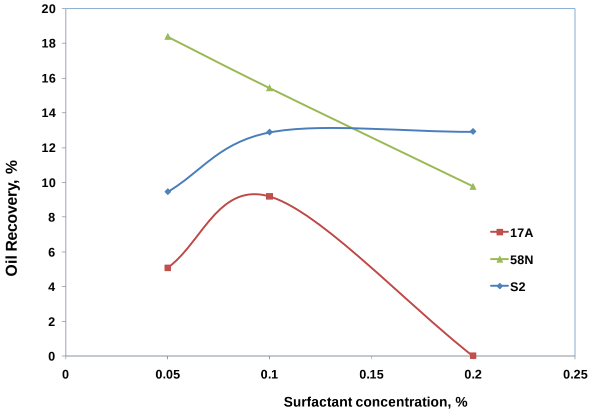


Fig.14 — Effect of divalent content on oil recovery (90°C, 0.1% surfactant concentration, and 30 %TDS)



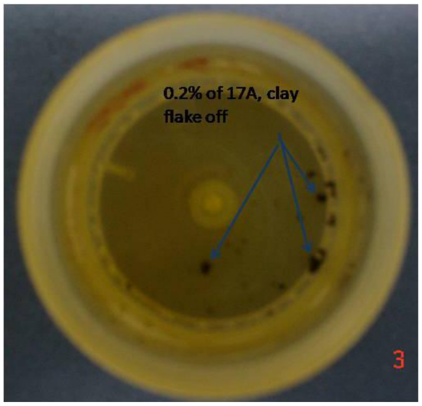


Fig.15 — Effect of surfactant concentration on oil recovery

Fig.16 — 0.2% concentration of 17A

Fig.17 — Co-surfactant aged before and after 50 days and 17 days (right) at 110°C

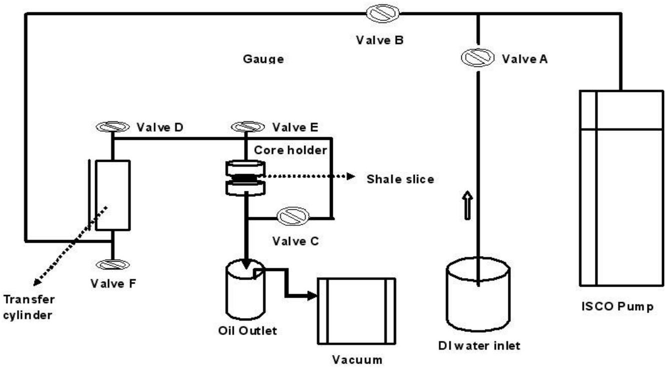


Fig. 18—Forced injection illustration for Method MB

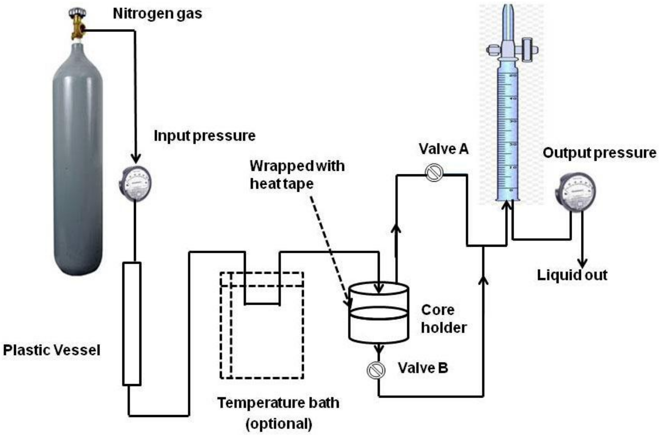


Fig. 19—Scheme for spontaneous imbibition and forced injection by Method MC

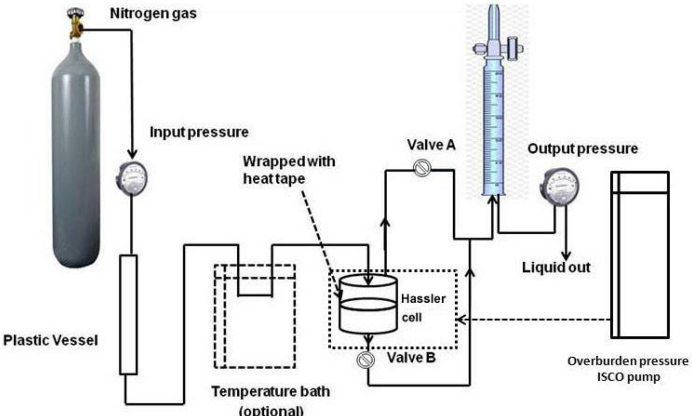


Fig. 20—Scheme for spontaneous imbibition and forced injection by Method MD with Hassler cell

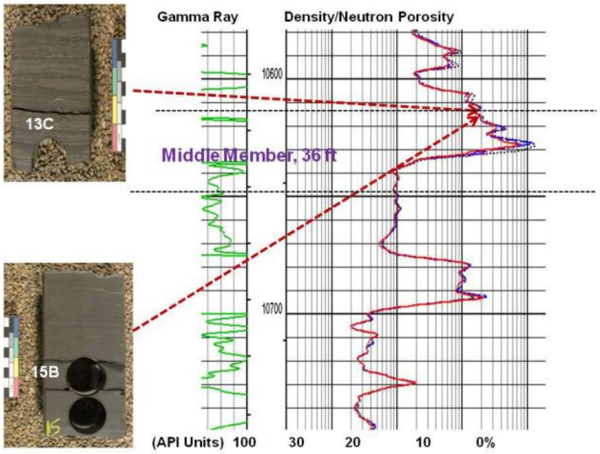


Fig. 21—Core sample location and well log curves for Well #16433

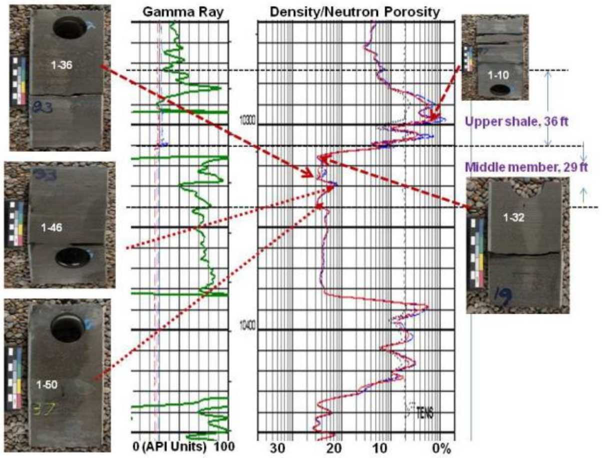


Fig. 22—Core sample location and well log curves for Well #16771

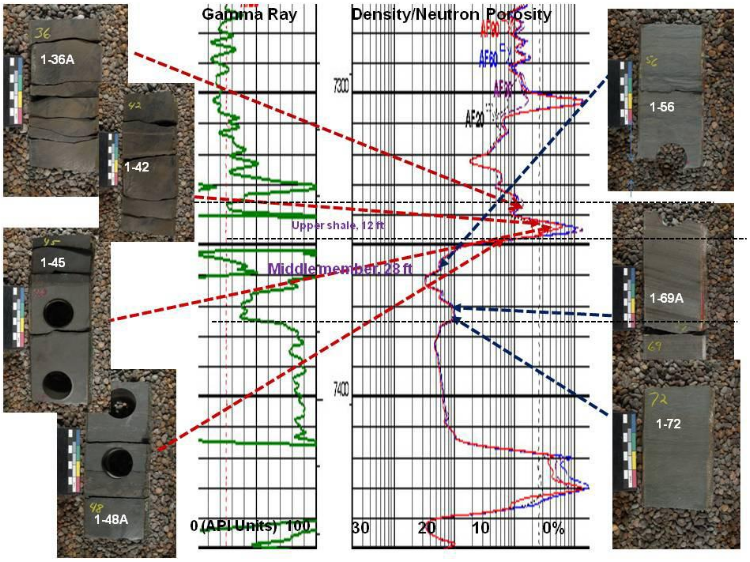


Fig. 23—Core sample location and well log curves for Well #17450

Fig.24a — Phase behavior of S-2 at 23°C

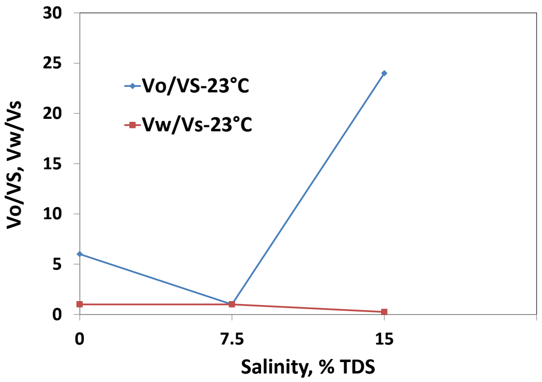


Fig.24b —V_o/V_s and V_w/V_s of S-2 at 23°C

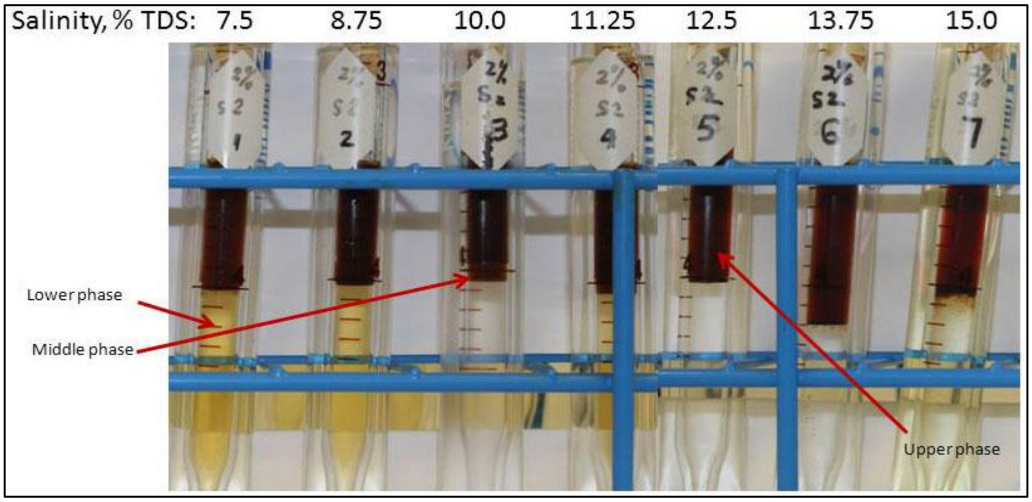
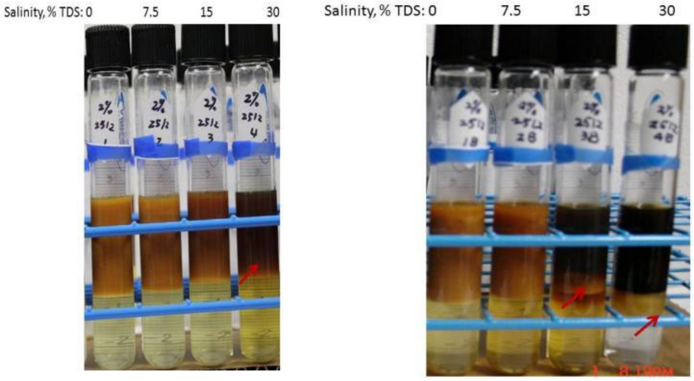


Fig.25 — Phase behavior of S-2 at 120°C



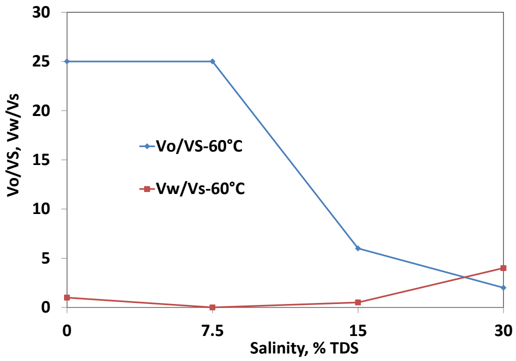
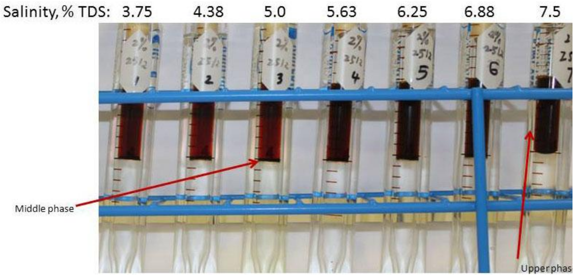


Fig.26a —Phase behavior of N-2512 at 23°C and 60°C

Fig.26b —V_o/V_s and V_w/V_s of N-2512 at 60°C



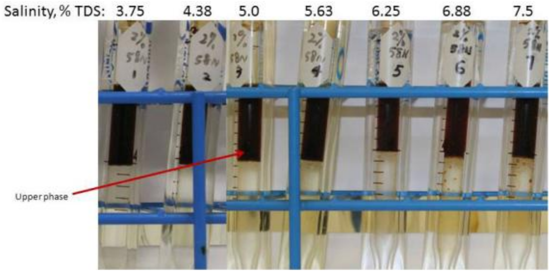
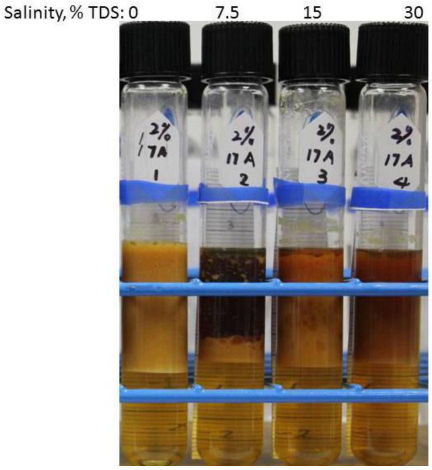


Fig.27 —Phase behavior of N-2512 at 120°C

Fig.28 —Phase behavior of 58N at 120°C



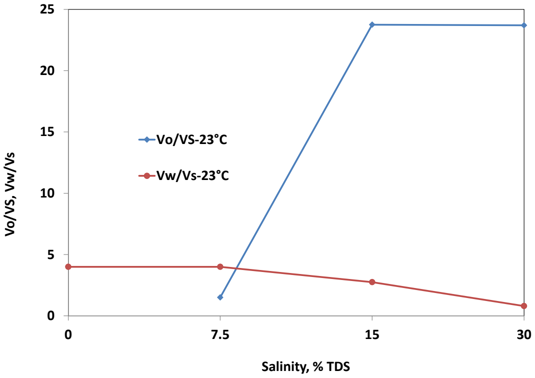


Fig.29a —Phase behavior of 17A at 23°C

Fig.29b —V_o/V_s and V_w/V_s of 17A (2%) at 23°C

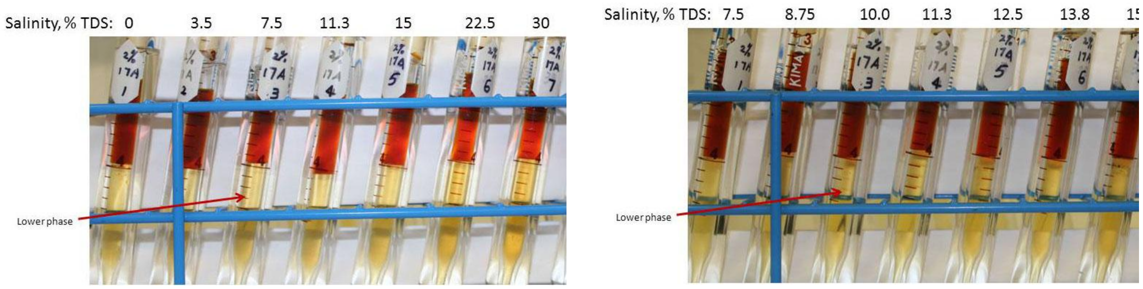


Fig.30a (left) and b (right) —Phase behavior of 17A at 90°C (0～30% TDS)

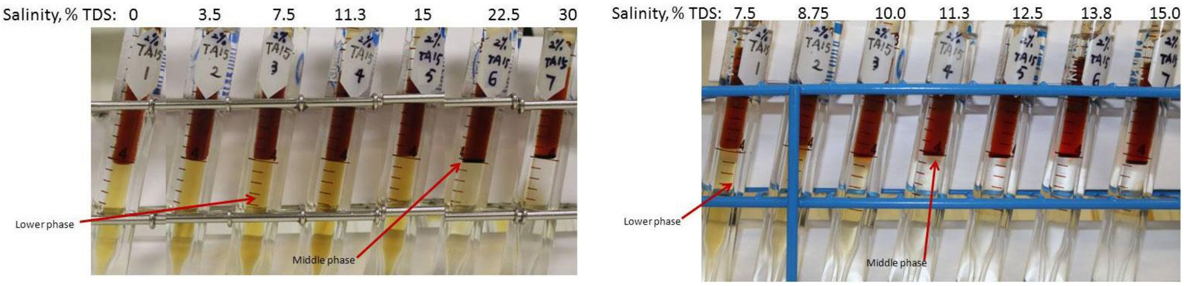


Fig.31 —Phase behavior of TA-15 at 90°C (0～30% TDS)

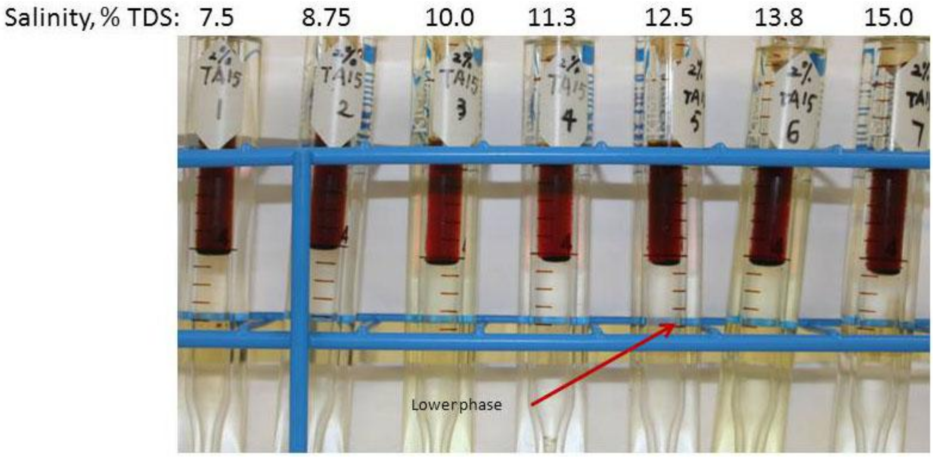


Fig.32 —Phase behavior of TA-15 at 120°C

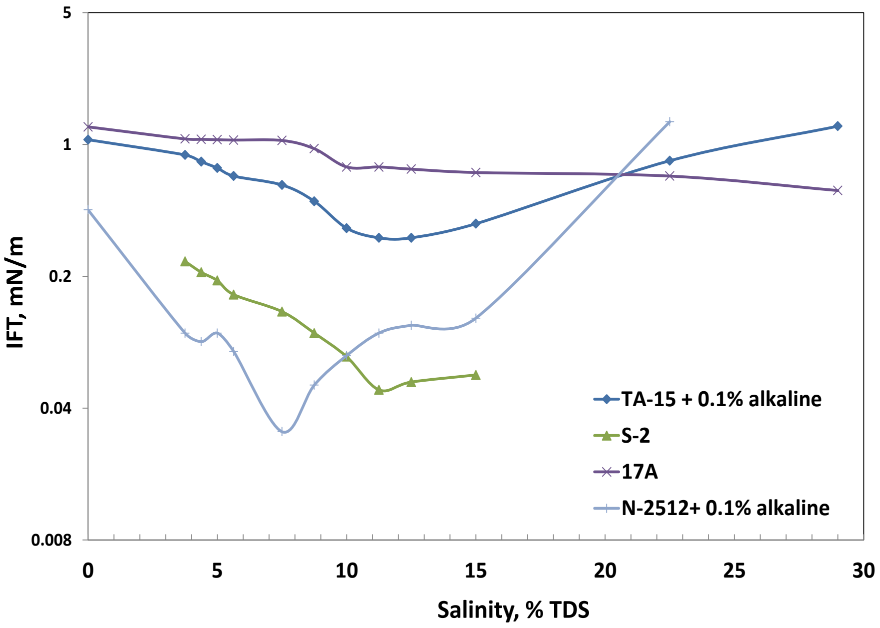


Fig.33 —IFT vs. salinity of surfactants at 90°C

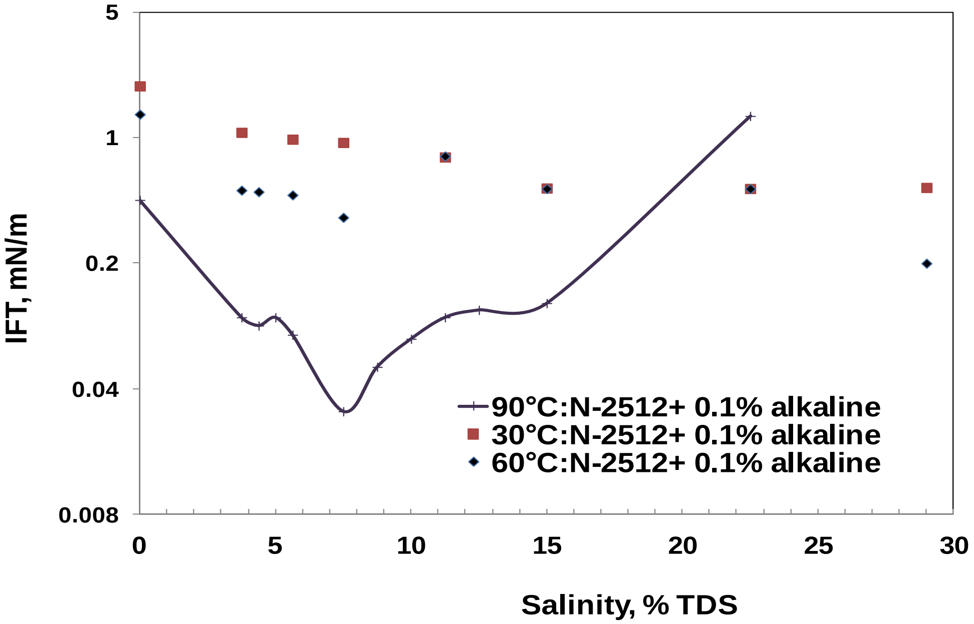


Fig. 34(a) — IFT reduction of N-2512 at three temperatures

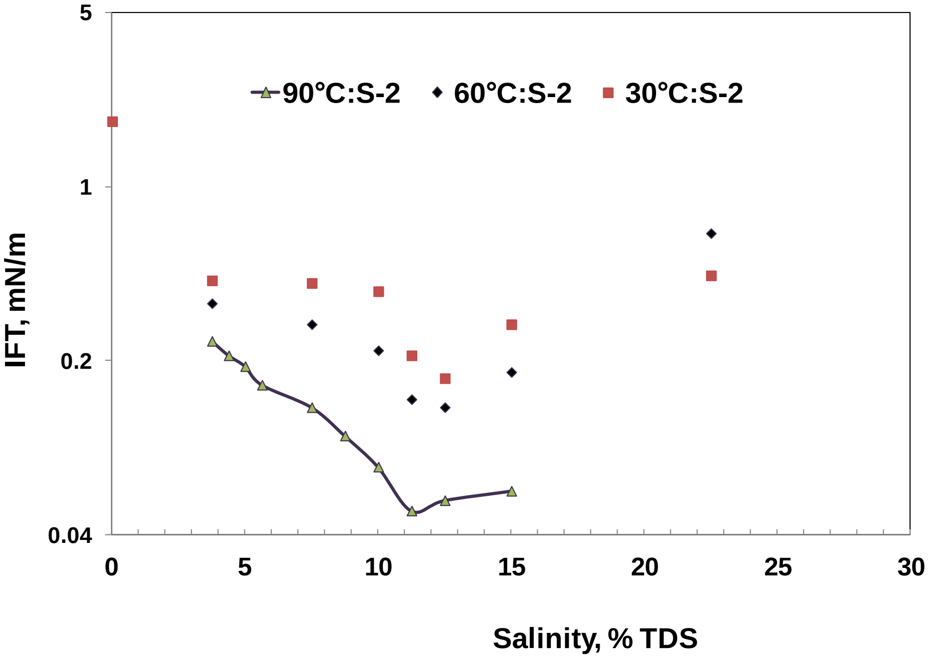


Fig. 34(b) — IFT reduction of S-2 at three temperatures

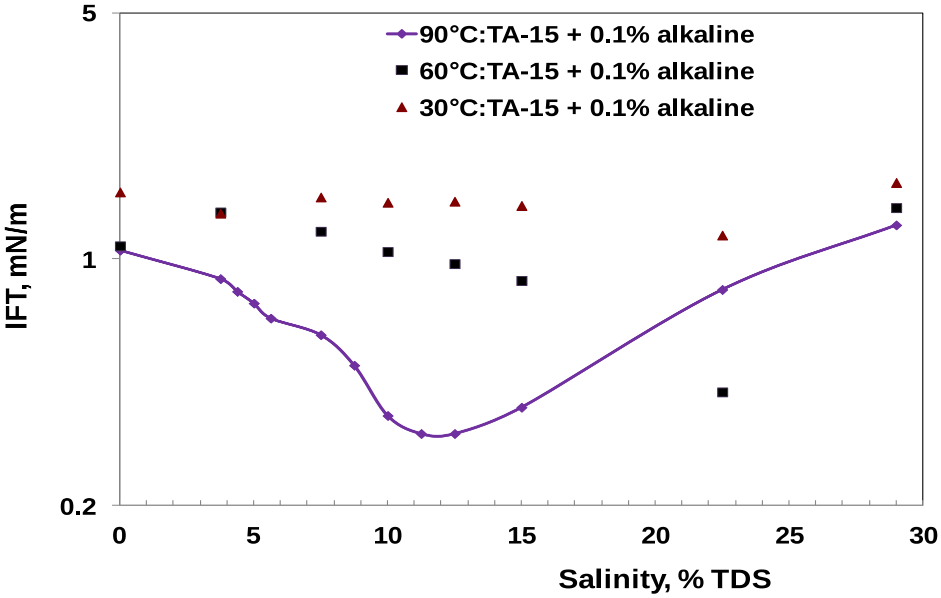


Fig. 34(C) — IFT reduction of TA-15 at three temperatures

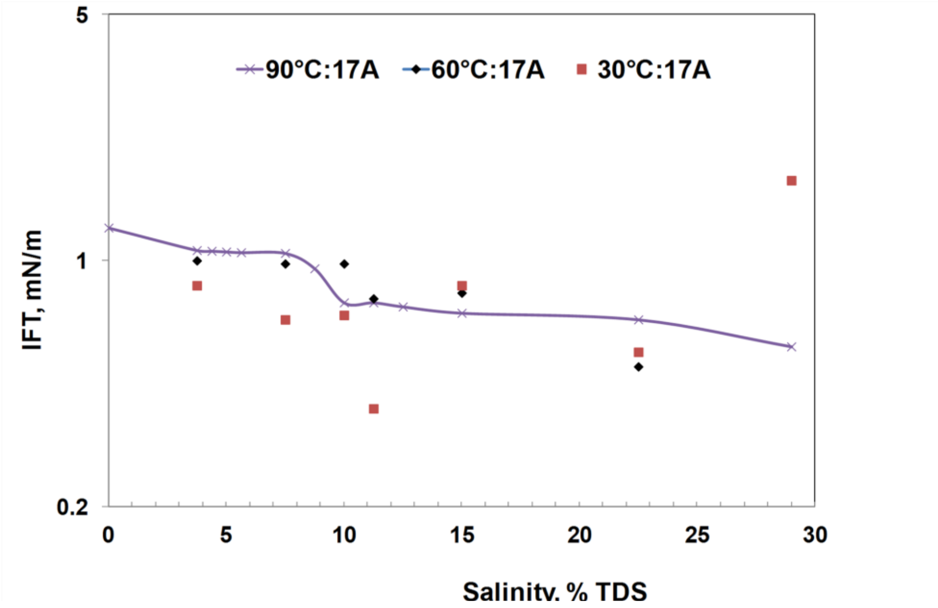


Fig. 34(d) — IFT reduction of 17A at three temperatures

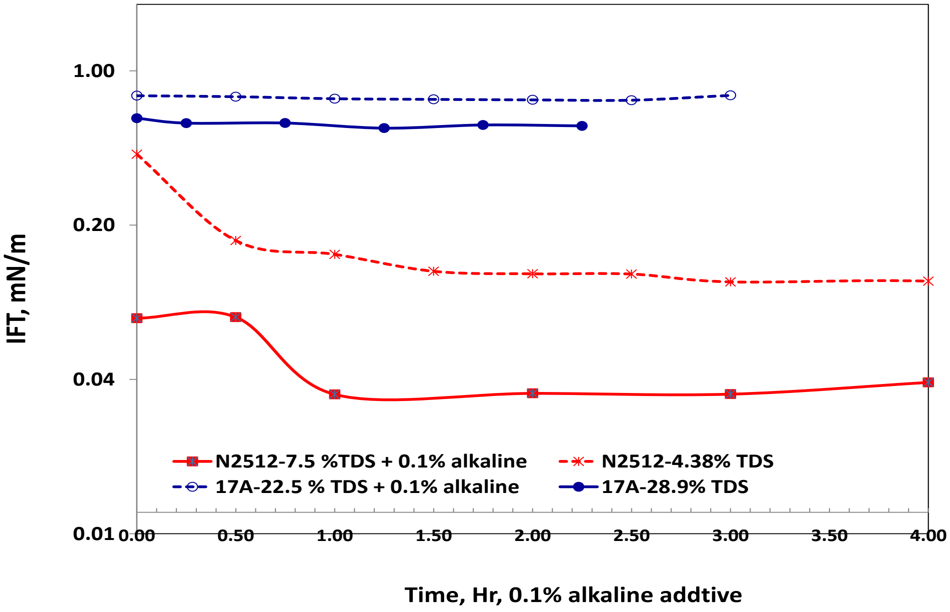


Fig.35 — Alkaline effect on IFT reduction at 90°C

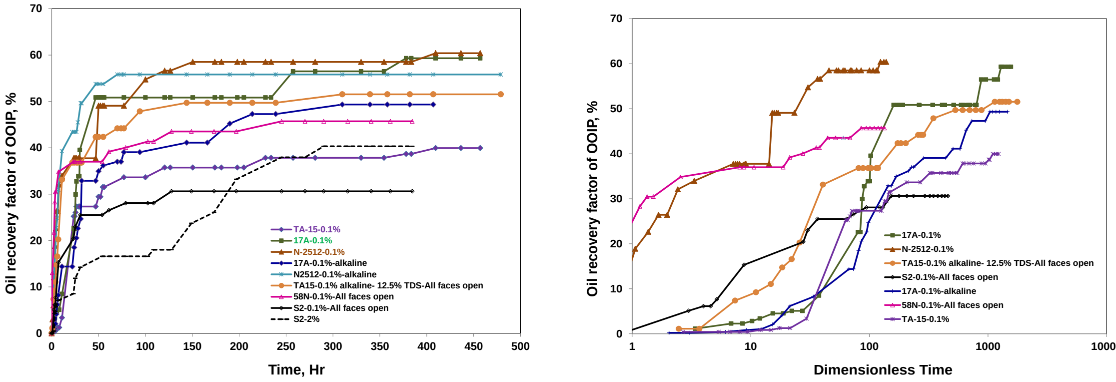


Fig.36 —Oil recovery at optimal salinity at 120°C vs. (a) time(left) and (b) dimensionless time(right)

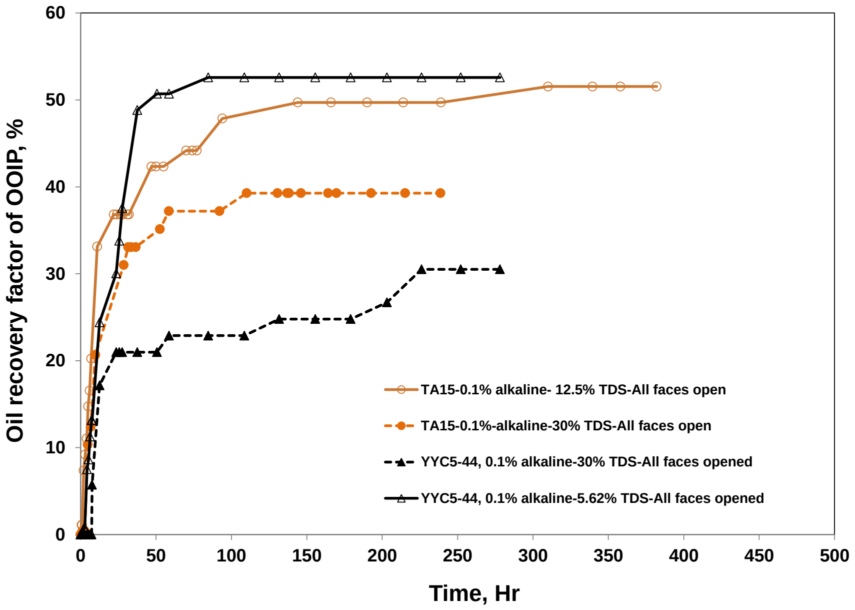


Fig.37 —Oil recovery comparison at optimal salinity and formation water salinity at 120°C

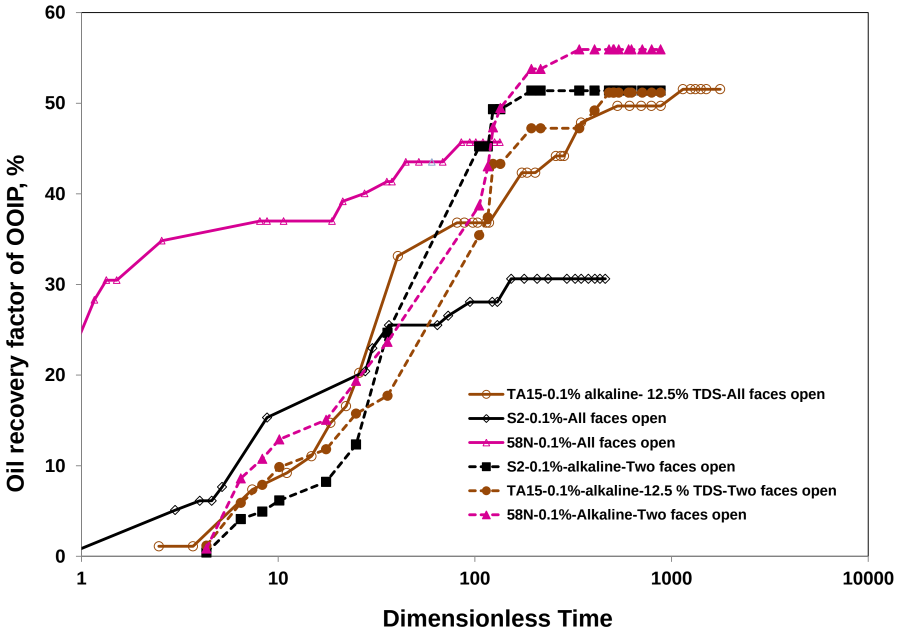


Fig.38 —Oil recovery comparison vs. boundary conditions at 120°C

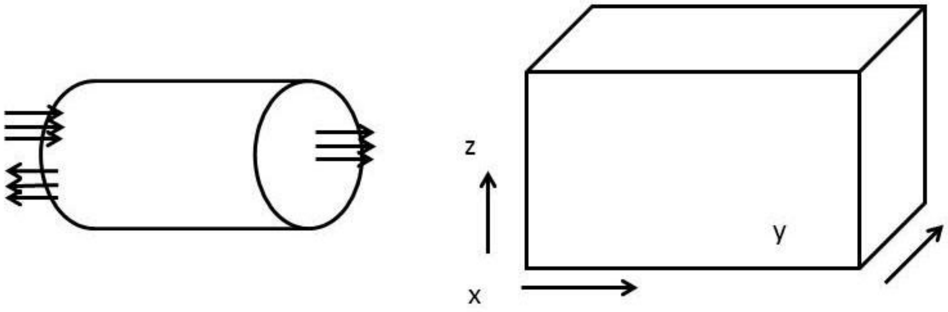


Fig.39 —Illustration of ideal simulation model

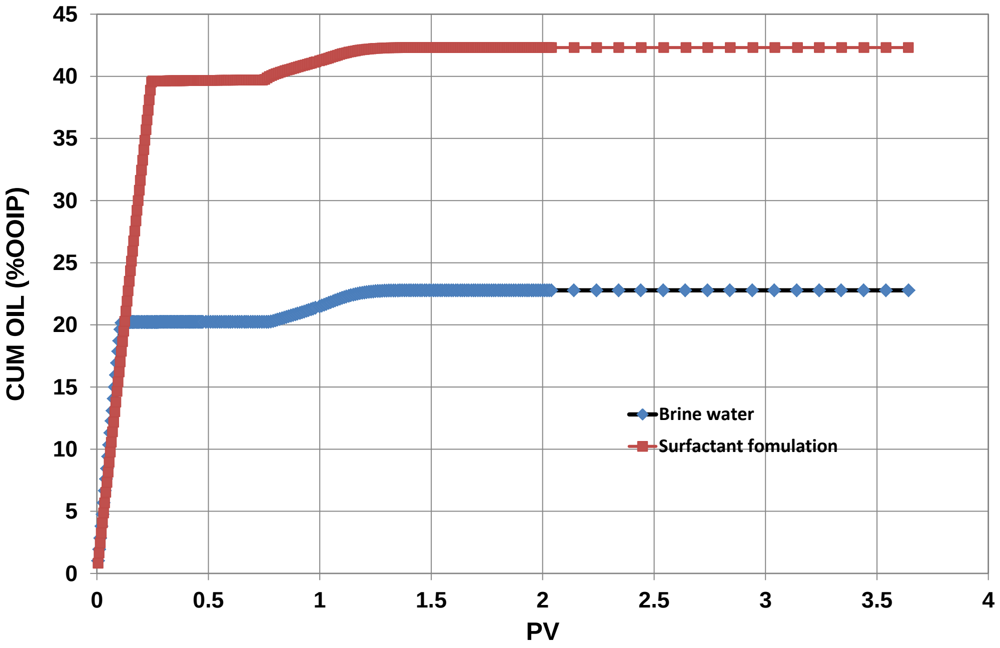


Fig.40 —Oil recovery comparison between surfactant formulation imbibition and brine alone

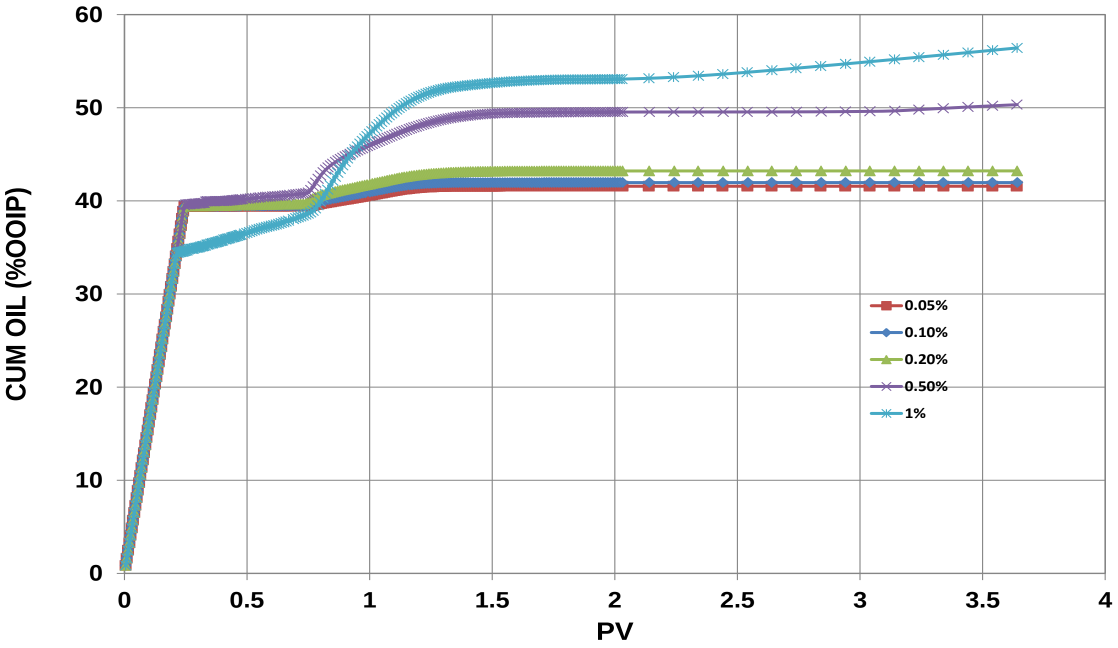


Fig.41 —Surfactant concentration vs. oil recovery

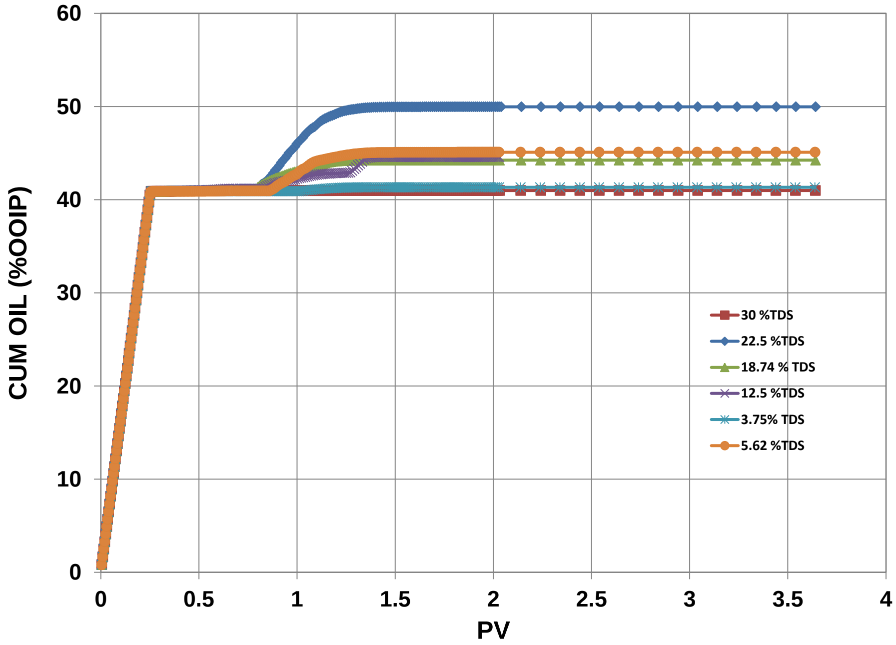


Fig.42 —Water salinity vs. oil recovery

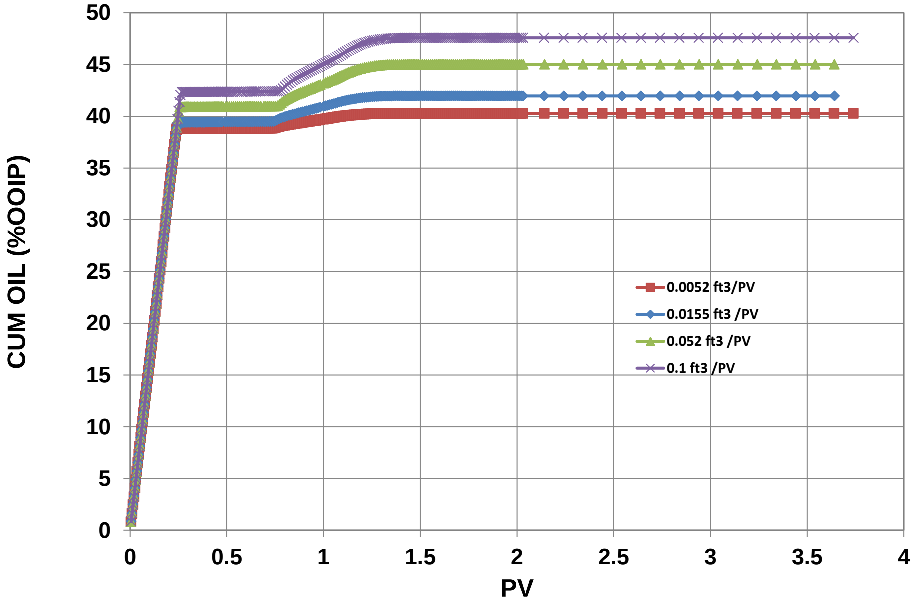


Fig.43 —Injection rate vs. oil recovery

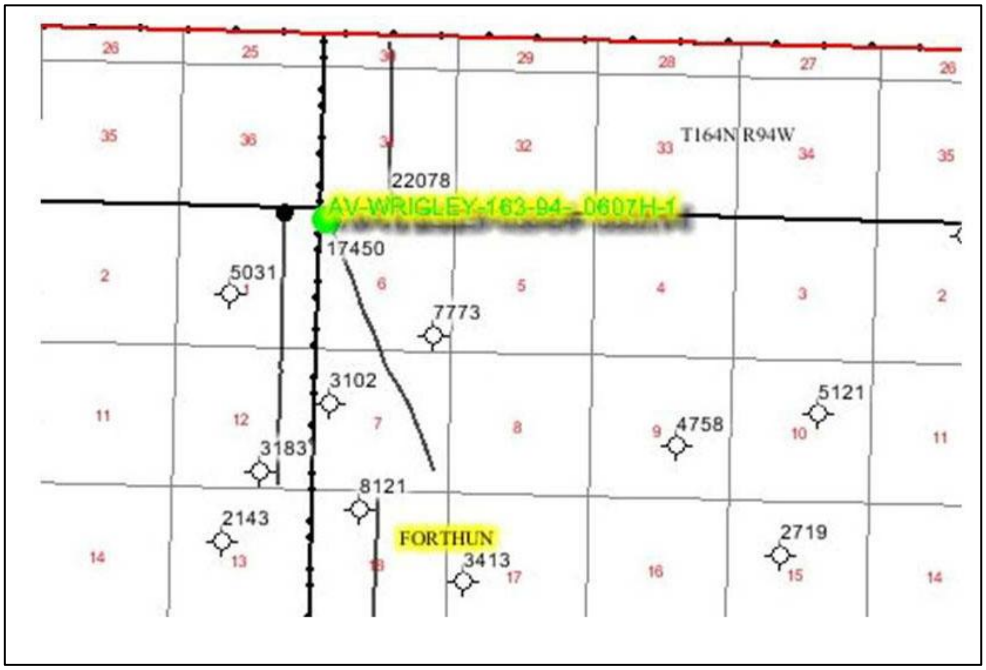


Fig.44 —Well location map of Well #17450

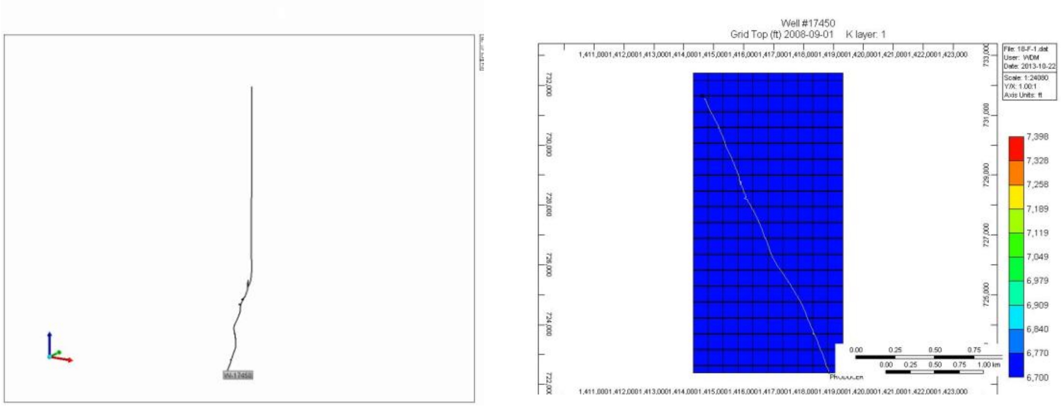


Fig.45 —Trajectory map of Well #17450 (left) and simulation model (right)

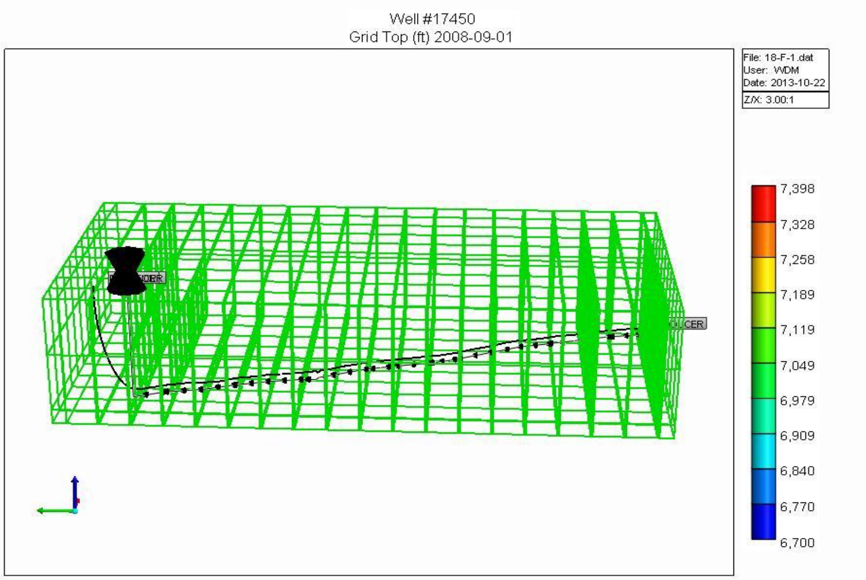
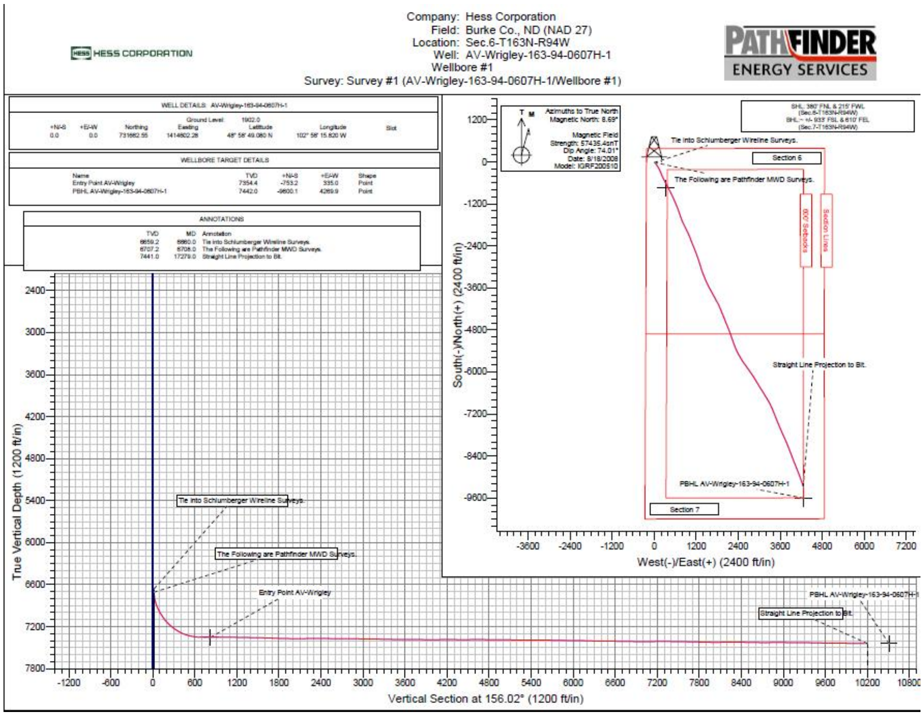


Fig.46 —3D simulation model of Well #17450 (scale is depth)


Company: Hess Corporation
Field: Burke Co., ND (NAD 27)
Location: Sec.6-T163N-R94W
Well: AV-Wrigley-163-94-0607H-1
Wellbore #1
Survey: Survey #1 (AV-Wrigley-163-94-0607H-1/Wellbore #1)

WELL DETAILS: AV-Wrigley-163-94-0607H-1

Ground Level: 1902.0

+N/-S	+E/-W	Northing	Easting	Latitude	Longitude	Slot
0.0	0.0	731682.55	1414802.28	48° 58' 49.080 N	102° 58' 15.820 W	

WELLBORE TARGET DETAILS

Name	TVD	+N/-S	+E/-W	Shape
Entry Point AV-Wrigley	7354.4	-753.2	335.0	Point
PBHL AV-Wrigley-163-94-0607H-1	7442.0	-9600.1	4269.9	Point

ANNOTATIONS

TVD	MD	Annotation
6659.2	6660.0	Tie into Schlumberger Wireline Surveys.
6707.2	6708.0	The Following are Pathfinder MWD Surveys.
7441.0	17279.0	Straight Line Projection to Bit.

Fig.47 —Drilling direction and perforation segment in Well #17450

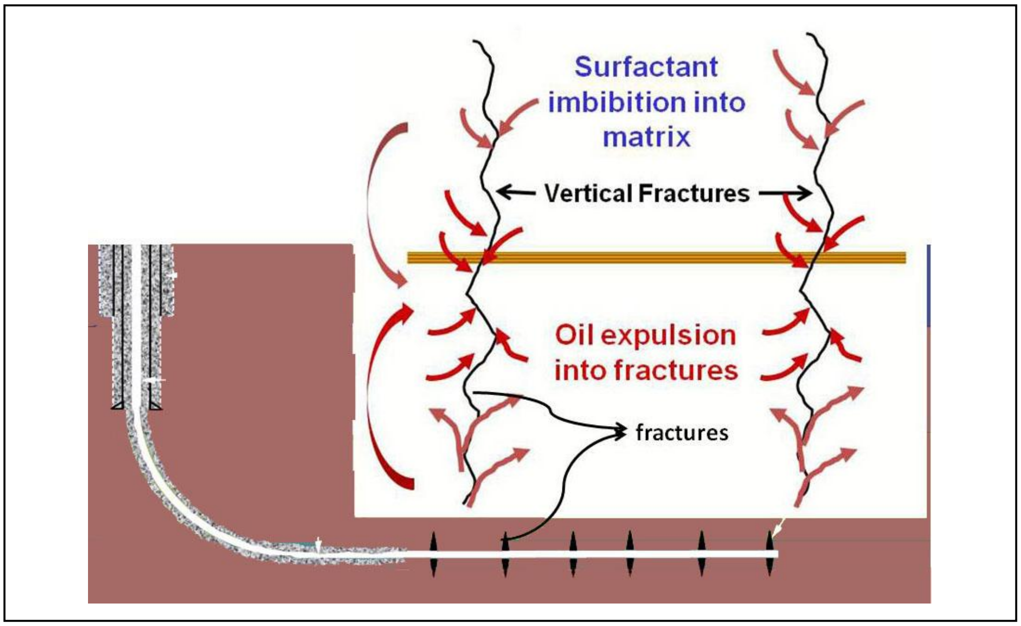


Fig.48 —Illustration of hydraulic fracture distribution in Well #17450 and imbibition mechanism

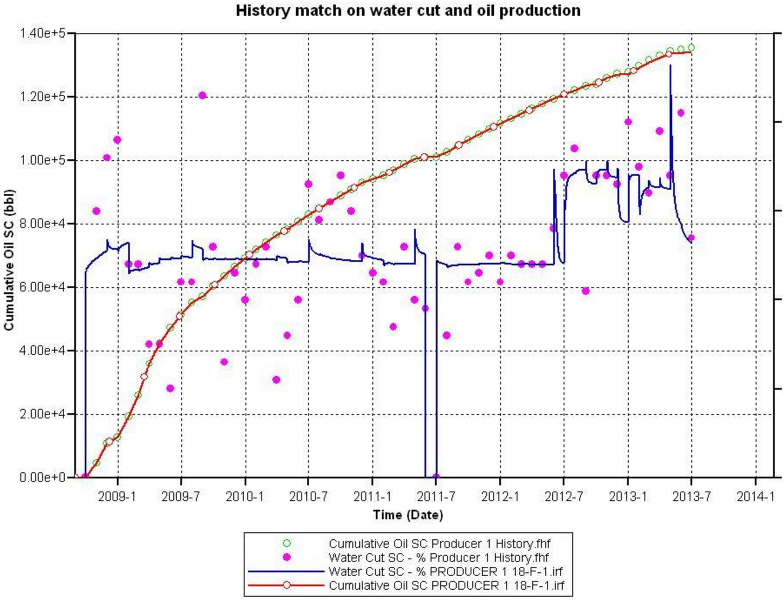


Fig.49 —History match of cumulative oil production and water cut in Well #17450

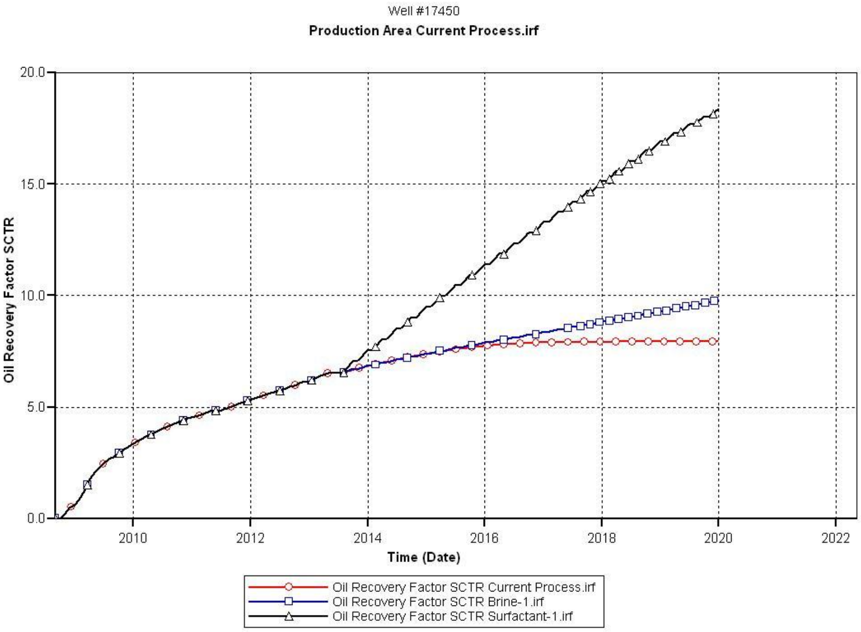


Fig.50 — Oil recovery effectiveness prediction for aqueous liquid imbibition in Well #17450

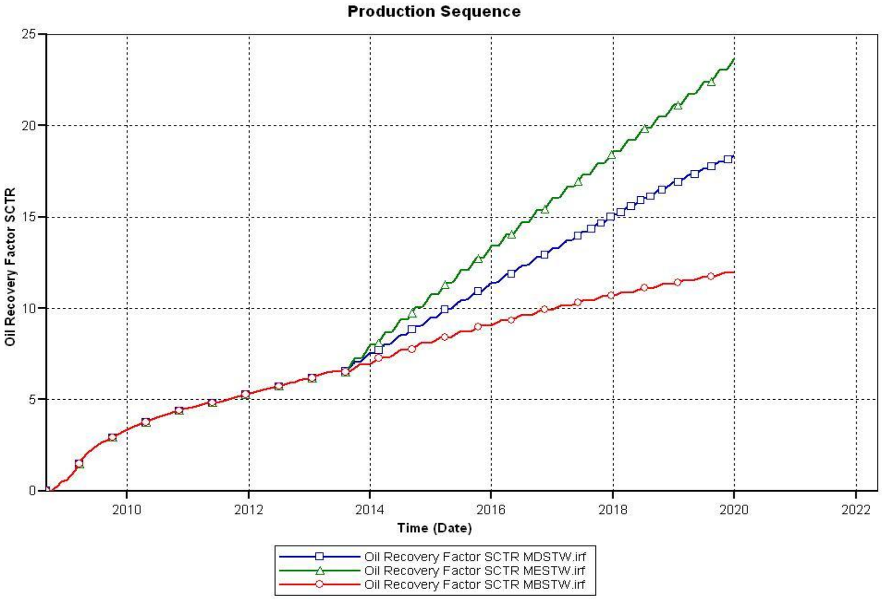


Fig.51 —Production sequence effect on oil recovery

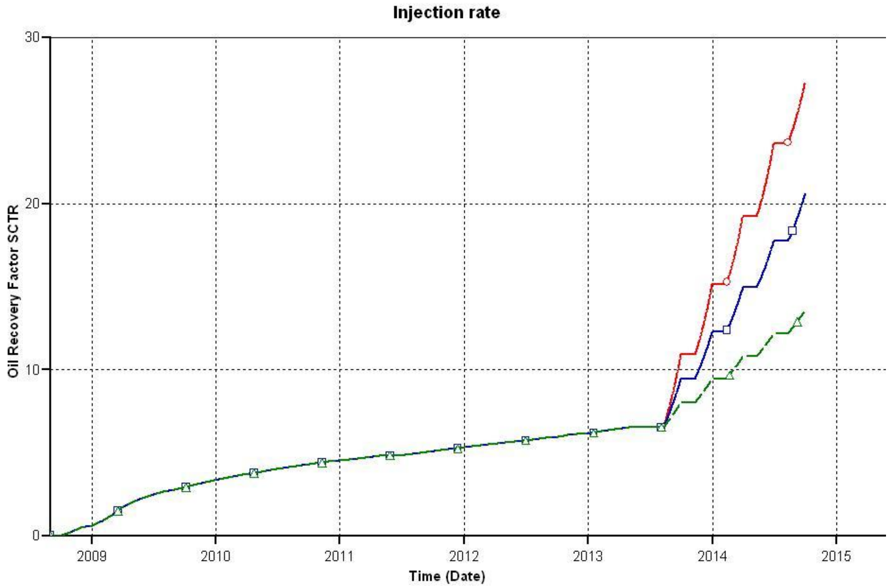


Fig.52 —Injection rate effect on oil recovery in Well #17450