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Aqueous Imbibition With Enhanced Contact Area Approaches To Extract Oil From The Bakken Formation

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AQUEOUS IMBIBITION WITH ENHANCED CONTACT AREA APPROACHES TO EXTRACT OIL FROM THE BAKKEN FORMATION

by

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A Dissertation

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of the

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In partial fulfillment of the requirements

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Doctor of Philosophy

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2020

Name: Jin Zhang

Degree: Doctor of Philosophy

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Department	Geology & Geological Engineering
Degree	Doctor of Philosophy

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DEDICATION

This work is dedicated to my husband, Yong Hou; my daughter, Daisy;

and to my parents and parents-in-law

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ABSTRACT

The techniques of horizontal wells and hydraulic fracturing enable oil production from low-permeable shale, sandstone and carbonate rock formations. However, the extremely low permeability and porosity properties lead a sharp declination of oil production and a low oil recovery factor (typically, 5-15% of original oil in place) as reservoir pressures dropping. Surfactant EOR (enhanced oil recovery) has been considered as one of the best options for geological challenging formations. In our previous studies, we developed a method using surfactant formulation spontaneous imbibition to stimulate the oil recovery from tight formations through wettability alteration and the interfacial tension (IFT) reduction. However, the slow oil extraction rate and the limited penetrating area into the rock matrix in laboratory experiments may prove impractical for real-time extraction. To address this problem for the carbonate-rich formations, such as Bakken, Eagle Ford and Niobrara, this research attempted to investigate whether an approach – using a forced surfactant imbibition process coupled with enhanced contact area stimulation (acidizing, for instance) could speed up the oil extraction rate and also force the surfactant formulation deep into the carbonate–rich matrix through acidification, thereby improving oil recoveries.

In the first stage of this study, experiments were performed to evaluate the oil extraction by forced surfactant imbibition process (core flooding process) from three paired core plugs of the Middle Bakken. The effects of initial water saturation, surfactant concentration, and brine salinity were also investigated during the flooding process. In the second stage, a series of experiments were conducted to evaluate the feasibility of studied chemical formulations (CF) to the target rock formation by forced imbibition process. Although the methods of core flooding and acidizing have been used for conventional rock type oil production stimulation for decades, no literatures reported yet using above comprehensive studies for oil recovery improvement onto tight Bakken Formation prior to this thesis research.

Based on the laboratory studies, we conclude: (1) Forced surfactant imbibition EOR for tight rocks with low permeability (10^{-3} md) has good potential for oil recovery enhancement at various conditions in this study. (2) The ultimate oil recovery is dominated by permeability, heterogeneity or lithology differences. (3) Fractures apparently played an important role in oil recovery, especially in flooding process. (4) Positive oil extraction rate was observed compared to the spontaneous imbibition. (5) The aqueous imbibition process coupled with acidizing treatment was capable to recover oil in Bakken cores from 27.4% to 81.1%. (6) The contact area enhancement method – acidification was determined by the rock homogeneity (permeability distribution and mineral composition distribution). (7) The chemical formulation penetrated in and interacted with carbonate minerals in rock matrix resulted in the asperities on the fracture surface and adjacent matrix led petrophysical properties (porosity and permeability) improvements, thereby extracting more oil. The laboratory study result may serve as a possible approach for a field application to improve the hydrocarbon recovery using aqueous forcible imbibition process from well to well besides of huff-n-puff method.

1. INTRODUCTION

1.1 Background

Tight oil is embedded in low-permeable shales, sandstone and carbonate formations. Technology barrier and high cost made them were long ignored by operators who were seeking easier plays and faster return on investments. The application of horizontal well drilling techniques and hydraulic fracturing completion techniques have enabled increased oil production from these reservoirs since early 2000s. In recent years, the tight oil exploration has constituted a significant portion of domestic crude oil production in the United States (Fig. 1).

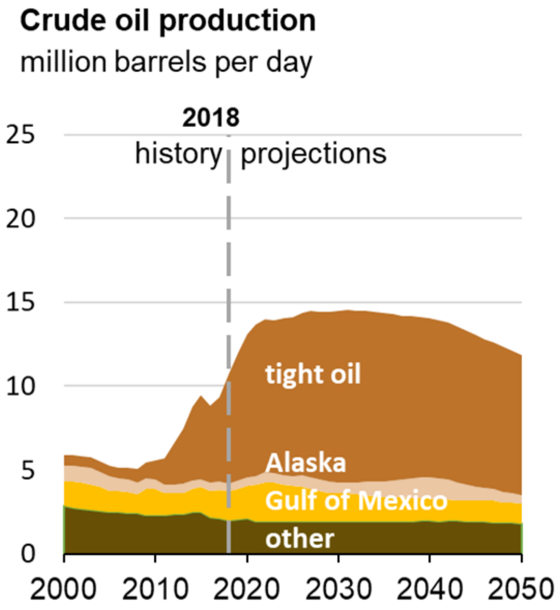


Fig. 1 Tight Oil and Crude Oil Production Rate in the United States (as of 2018)

Source: U.S. Energy Information Administration, *Annual Energy Outlook 2019*
https://www.eia.gov/todayinenergy/images/2019.03.28/chart2.svg

According to U.S. Energy Information Administration (EIA) estimate, from 2005 to 2018, the tight oil production (Fig. 2) increased from 0.41 to 6.5 million barrels per day (EIA 2019b), the equivalent of 8.0% to 59% of total domestic crude oil production (EIA 2019c). Furthermore, oil production from shale and tight formations greatly reduce the United States' reliance on petroleum imports. U.S. net imports of petroleum products (Fig. 3) from other countries declined from 60% in 2005 to 11% in 2018 (EIA 2019a). With more shale plays discovered and exploited in the United States and in other countries, hydraulic fracturing has taken a very important role for decades. However, apparent oil production declining trends using current hydraulic fracturing technologies have been observed in Bakken Formation after more than 10 years exploration in the Williston Basin. Therefore, using EOR (Enhanced Oil Recovery) method to stimulate oil production from tight rocks have been attractive to the operators more and more in recent years.

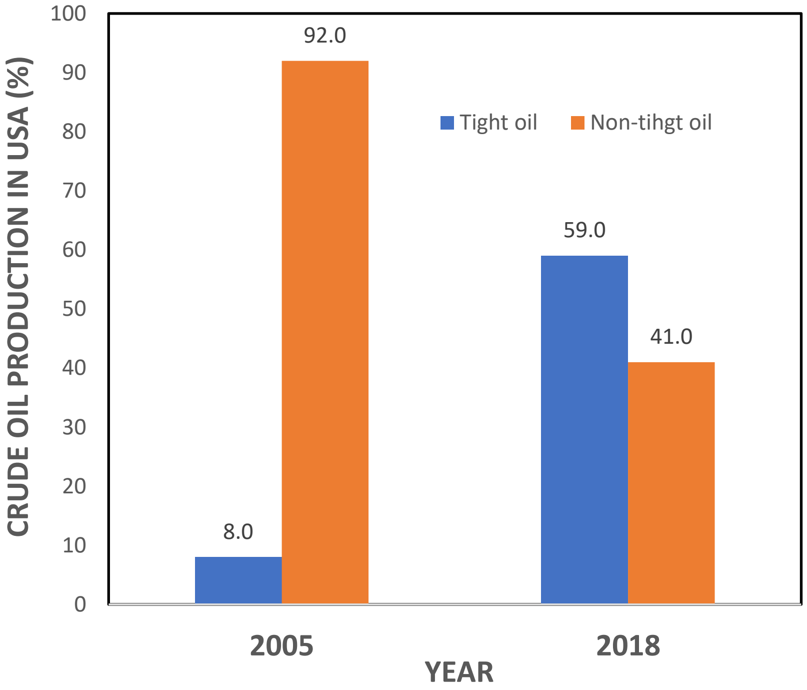


Fig. 2 Tight Oil and Non-tight oil Production in USA (as of Jan. 2019)

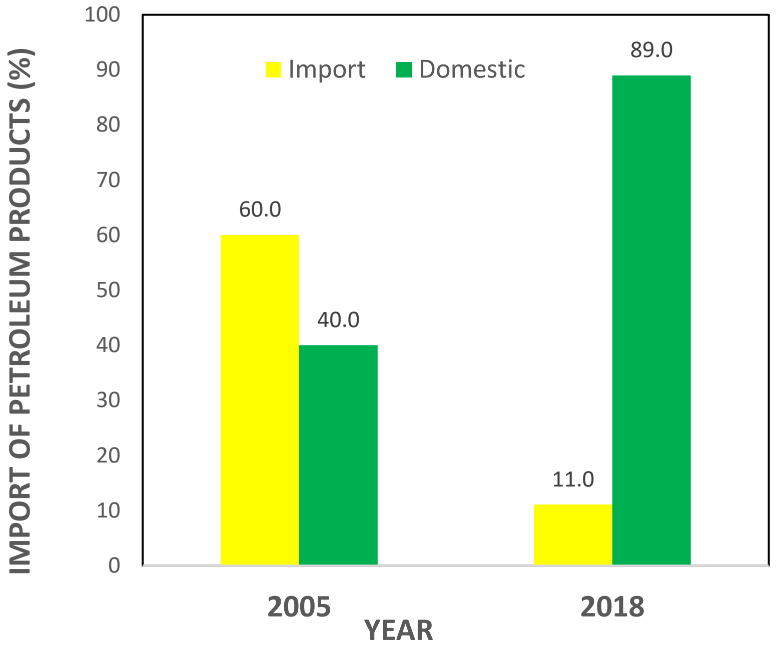


Fig. 3 Import of Petroleum Products in USA (as of Jan. 2019)

1.2 Statement of Problem

The successes of oil production from shale (tight oil/gas) bring America to a leading role in shale technology development in the world. Nevertheless, the extremely low permeability characterization in these reservoirs led to a rapid decline in oil production as reservoir pressure drops (Fig. 4). With current technologies, the oil recovery factor is still low, only 5-15% of original oil in place (OOIP). Clark (2009) demonstrated the results from three methods and concluded that the most likely value for oil recovery factor in the Bakken shale is approximately 7%. North Dakota Council (2012) predicted that only 1-2% of the reserve can be recovered. Sheng and Chen (2014a) showed that oil recovery factor in a fractured shale just can be improved by gas and water injection from 6.5% to 15.1% and 11.9%, respectively. The state of North Dakota is the second largest oil-producing State in the USA nowadays due mainly to Bakken production plays. In 2013, USGS assessed technically recoverable unconventional resource for the Bakken Formation was

3.65 billion barrels of oil, but the estimated OOIP for the Bakken Formation was 123 billion BBL (Gherabati et al. 2019), or 200-400 billion BBL (Pitman, Price, and LeFever 2001). The recoverable oil from Bakken is not more than 3% of OOIP, quite lower compared with 30-50% and up to 80% oil recovery factor which commonly seen in conventional formations (Stosur et al. 2003; Stosur 2003; Kokal and Al-Kaabi 2010), leaving vast target for EOR technologies.

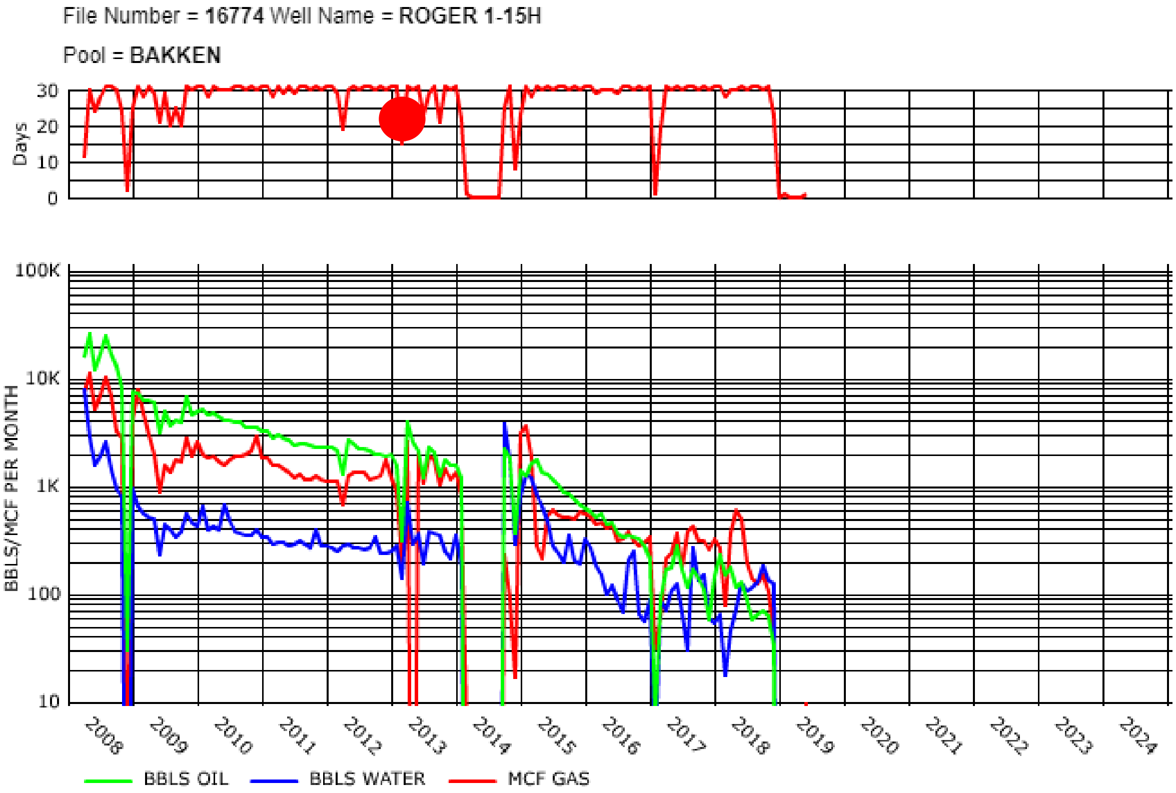


Fig. 4 Production Curves of Well #16774
Source: Department of Mineral Resource, ND
https://www.dmr.nd.gov/oilgas/feeservices/getscoutticket.asp

However, the conventional IOR (improved oil recovery) methods (e.g. water flooding) as well as some EOR techniques (e.g. polymer flooding) are relative inefficient or not applicable. A few ideas and their mechanisms have been proposed and studied in laboratories and piloted in fields. Such ideas include gas injection and surfactant injection or their combinations, especially in huff-n-puff mode (Sheng 2017; L. Wang et al. 2017). Surfactant EOR (enhanced oil recovery) has been considered as one of the best options for geological challenging formations. In previous study, our research group has developed a surfactant formulation spontaneous imbibition method to stimulate the oil recovery from tight formations since 2009. Based on the laboratory experimental results, we observed that using the optimized surfactant formulations, the wettability between tight oil and rocks was altered from oil-wet to intermediate-wet or water-wet status, the interfacial tension (IFT) between oil and formation water was reduced to a low range of 10^{-1} to 10^{-2} mN/m from 6 to 10 mN/m. The oil recovery from the tight formation reached to 20% incremental over brine imbibition alone (Wang et al. 2011a; 2011b; 2012a; Zhang et al. 2013). Other researchers also studied the surfactant spontaneous imbibition in shale (Makhanov, Dehghanpour, and Kuru 2012; Morsy, Gomaa, and Sheng 2014; Shuler et al. 2011; F. Zhang et al. 2018), proposed surfactant injection in huff-n-puff mode for EOR applications (Shuler et al. 2016; Zeng, S. Miller, and Mohanty 2018; F. Zhang et al. 2018). All the results showed the positive potentials for oil recovery improvement using surfactant stimulation. However, most of the studies used thin slices and small plugs for laboratory research because the spontaneous imbibition process is very slow and the penetrating area is limited. Sheng (2017) indicated that if the matrix is large, the oil extraction rate by spontaneous imbibition will be uneconomically slow, because the imbibition rate is inversely proportional to a square characteristic length.

The slow oil extraction rate and the limited penetrating area into the rock matrix in laboratory experiments may prove impractical for real-time extraction. In order to overcome the above barriers, this study attempted to investigate a new approach using forced surfactant imbibition process coupled with enhanced contact area stimulation (acidizing, for example), to speed up the imbibition rate and force the surfactant solution deep into carbonate-rich matrix, thereby improving the oil recovery. Currently, only a few papers have investigated the forced imbibition potential in tight rocks alone. These papers include a study of refract treatment in the Middle Bakken (Vincent 2011), and a simulation model study of EOR potential of surfactant flooding in Bakken (Dawson et al. 2015). Although the methods of core flooding and acidizing have been used for conventional rock type oil production stimulation for decades, no literatures reported yet using above comprehensive studies for the goal of penetration and contact area improvement in the tight Bakken Formation prior to this thesis research.

1.3 Objectives and Scope of Work

The ultimate objective of this thesis was to solve one of the key issues that identified by our previous research – to investigate the feasibility of an approach of forced surfactant imbibition coupled with acidizing treatment to enhance the rate of penetration of surfactant formulations into the rock and enhance contact area in the carbonate-rich tight rock matrix, thereby improving oil recoveries.

Considering the Bakken Formation geological lithologies, the research scope of work was focused on the following aspects:

- Determine oil extraction rate, ultimate oil recovery at reservoir conditions using forced imbibition process (surfactant flooding) with semi-preserved cores from the Middle Bakken.
- Study of the effect of initial water saturation, surfactant concentration, and brine salinity on forced imbibition process by paired cores.
- Compare the potential of oil recovery rate and ultimate oil recovery by spontaneous imbibition process and forced imbibition process.
- Investigate the acidic reaction of carbonate rich rocks.

- Examine a chemical formulation (surfactant formulation and a weak organic acid) effect on rock microstructures and pore structures using aging test measures.
- Examine the effect of chemical formulation on porosity, permeability and oil recovery using flooding process with Bakken cores.
- Evaluate the potential of this approach for the field application.

2. LITERATURE REVIEW

2.1 Geological Settings of the Bakken Formation

The Bakken Formation is located 3 km below the surface in the Williston basin, underlying parts of Montana, North Dakota in the United States and Saskatchewan, Manitoba in Canada (Fig. 5), which is relatively thin. The total formation ranges in thickness from a maximum of 140 ft. near the center of the basin to subsurface and “0” on the eastern, southern and southwestern flanks (Meissner 1978).

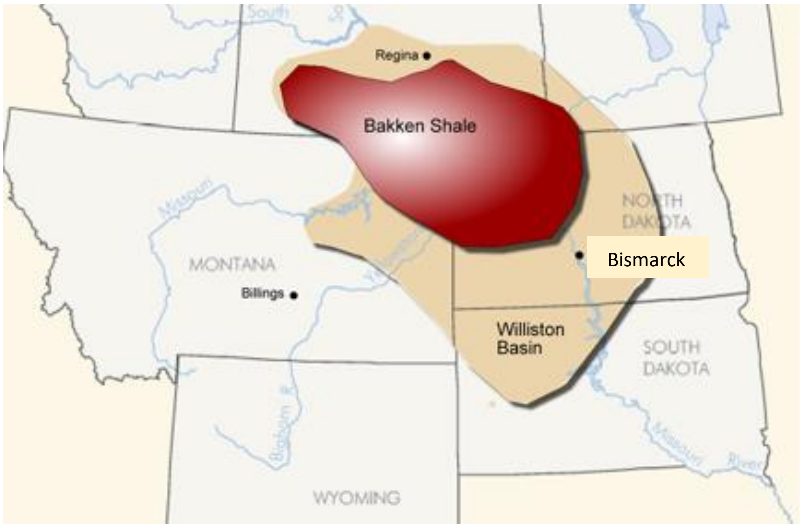


Fig. 5 Map of the Bakken Formation and Williston Basin
Modified from: https://coldfusion3.com/wp-content/uploads/2012/12/BakkenMap.gif

2.1.1 Depositional Environment

The Bakken Formation was deposited during a cycle of transgression and regression which began in latest Devonian-earliest Mississippian time (Gerhard and Ander 1982; Meissner 1978; Pitman, Price, and LeFever 2001) contains three members: an Upper Shale Member , a Middle

Siltstone Member, and a Lower Shale Member. The lower and upper members of the Bakken Formation were deposited in an offshore, deep water marine environment below wave base during periods of sea-level rise (LeFever et al. 1991; Webster 1984), and the middle member was deposited in a shallow offshore marine environment following a rapid sea-level drop and deposition of the lower shale (Smith and Bustin 1995). Deposition of the three distinctive Bakken members reflects significant changes in water depth within the Williston Basin as a result of the fluctuation of sea level.

2.1.2 Lithostratigraphy and Geochemical Properties

The Bakken Formation unconformably overlies the Upper Devonian Three Forks Formation and underlies the Lower Mississippian Lodgepole Formation (Fig. 6). It has been informally divided into lower, middle and upper members. The lower shale member and the upper shale members have apparently identical lithology resulting from similar deposition in a deep anoxic marine setting, which consist predominantly of quartz, feldspar, clay and organic matter. The lower member has an average thickness of 3m with a maximum thickness of 20m (Smith and Bustin 1995). Schmoker and Hester (1983) calculated 11.5% as the total organic carbon (TOC) content for the lower member, while Smith and Bustin (1995) estimated the lower Bakken member contains an average TOC of 8%.

The lithology of the middle member of the Bakken Formation varies from a light-to medium-gray, interbedded sequence of siltstones and sandstones with lesser amount of shale to dolomitic fine-grained siltstone and sandstone to silty dolomite (Meissner 1978; Pitman, Price, and LeFever 2001). The middle Bakken member has an average thickness of 13 m and a maximum of 30 m in thickness. The TOC average content in middle Bakken member is less than 0.1% (Smith and Bustin 1995).

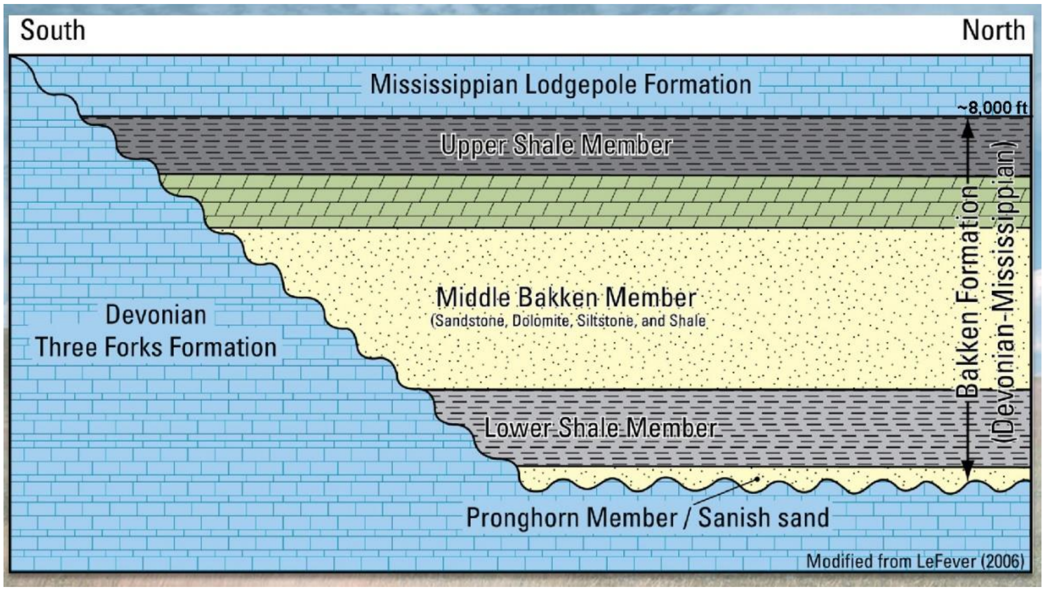


Fig. 6 Cross Section of the Bakken and Adjacent Frmations
Source: USGS (2013)

The upper member of the Bakken Formation is lithologically similar to the lower member, which is a dark-gray to brown-black to black, fissile, calcareous, organic-rich shale (Webster 1984). It has an average thickness of 2 m with a maximum of 7 m (Smith and Bustin 1995). The upper member differs from the lower member in that it lacks crystallized limestone and greenish-gray shale beds (Pitman, Price, and LeFever 2001) and has a higher TOC content of 12.1% (Schmoker and Hester 1983).

2.1.3 Reservoir Properties

Despite the thinness (0-46 m) and insignificant volume compared to the total sedimentary basin, the Bakken Formation is not only a widespread prolific source rock for oil when thermally matures, but also a producible fractured-type oil reservoir. Schmoker and Hester (1983) concluded that the average organic-carbon content of the lower and upper members of the Bakken Formation is near 12%, and 132 billion BBL of 43^{o} (API gravity) oil have been expelled from the mature region of the Bakken Formation in the United States portion at the time estimated (1983). The middle member is the principal oil reservoir.

2.1.4 Porosity and Permeability

Meissner (1978) indicated the porosity and permeability of the Bakken Formation were very low to nonexistent. Only the middle Bakken siltstone and sandstone have measurable reservoir properties. Murray (1968) measured the core material from the middle Bakken with porosities averaging 5.5% and permeability was ranged from 0.1 to 57 millidarcies. In the study by Pitman et al. (2001), the measured core porosities in the middle member ranged from 1 to16 percent but in general were low, averaging about 5%, and the measured permeability ranged from 0 to 20 millidarcies, averaging 0.04 millidarcies. It's believed that the reservoir rocks with lower permeability (0-0.01 millidarcies) are associated with the matrix permeability, while reservoir rocks with higher permeability (>0.01 millidarcies) commonly contain natural fractures with high residual oil concentrations. Core study in the Pitman et al. (2001) report also showed the highest permeability in the middle member is associated with naturally occurring fractures. At depths greater than 2,500 to 3,000 m, permeable fractures focus hydrocarbon fluids and locally serve as oil reservoirs.

2.1.5 Reservoir Pressure and Natural Fractures

Previous studies indicate the Bakken Formation is an overpressured fractured-type reservoir (Meissner 1978; Murray 1968; Pitman, et al. 2001). The abnormally high pressure resulted from the rapid hydrocarbon generation and confined by the tight strata. The fluid pressure gradients were as high as 0.73 psi/foot in Bakken in 1978 (Meissner 1978). Based on statistics from the drilled wells in North Dakota Industrial Commission (NDIC), the current reservoir pressure is 3000 psi compared 7,000 psi back to the very beginning of Bakken exploration. The natural fractures in the Bakken Formation occurred on a macroscopic and microscopic scale and especially abundant in the lower and middle members. Carlisle et al. (1992) stated that the fracture types are lithology dependent and there are three dominant fracture types present in the Bakken Formation: regional, tectonic and contractional or expulsion. The regional and tectonic fractures usually are present mostly in silty unit when they are present in the shale. Widths of these fractures usually exceed 30 μm with a horizontal direction. Expulsion fractures are common in the shale units with higher organic content suggesting the fractures were sourced by oil generation when pressure released. The widths of these fractures average are 10 to 20 μm. Therefore, the permeability of fractures is much higher than that of the one in matrix. Oil production occurs through the extensive fracture system.

2.1.6 Formation Water

Iampen and Rostron (2000) experimentally investigated the hydrogeochemistry of pre-Mississippian brine, Williston Basin (in which, the Bakken is the on top formation). In their studies, 200 formation water samples have been collected from producing wells in the Williston Basin. Chemical analysis reveals the brine concentration varies spatially ranged from 100,000 to 380,000 mg/L with an average 300,000 mg/L. Wang et al. (2011b) analyzed the water sample from the middle member of the Bakken Formation, well H. Davidson 2-11H (#16083) at a depth 10613-10649 ft. (3234.8- 3245.8 m), showed an average salinity of approximately 300,000 mg/L and a Na-Ca- Cl type water.

2.1.7 Formation Temperature

The Middle Bakken Member is the principal oil reservoir, roughly 3 km below the surface in the deepest center of Williston Basin. Pitman et al. (2001) concluded that the temperature of the middle member ranged from 80 to 120˚C based on organic acid experimental studies and a burial model.

2.2 EOR Study for Shale and Other Tight Formations

The existing technique to produce oil in tight reservoir has been utilized through hydraulic fracturing method coupled with horizontal well drilling placement. Due to the lithology of extremely low permeability and poor porosity, the oil recovery has been in relatively low range, typically, about in the range of 5-15% of OOIP (Clark 2009; North Dakota Council 2012; Sheng and Chen 2014a). Therefore, studies on enhanced oil recovery from tight reservoirs have brought more and more interests to researchers. However, some widely used EOR methods in conventional resources, such as water flooding or polymer flooding will not be feasible for tight reservoirs because of the reservoir characterizations. (Kokal and Al-Kaabi 2010; Sheng 2017). A few ideas have been proposed and studied in laboratories and simulation modellings. Such ideas include gas injection, water injection, and surfactant injection, especially in huff-n-puff mode (Sheng 2017).

2.2.1 Gas Injection

Although in most of the studies, gas injection can increase the oil recovery in laboratory scale (Tovar et al. 2014; Wan, Yu, and Sheng 2015; Yu, Li, and Sheng 2017), gas injection (CO_2, for example) may have limited potential if gas breaks through natural fractures or offset wells. In addition, the CO_2 injection has two disadvantages: facility corrosion and lack of availability (storage) in large field application. There were several CO_2 pilot tests in the USA 48 low states have been implemented. Currently, the pilot results that using CO_2 injection in Huff-n-Puff mode, the early breakthrough and poor sweep efficiency are the problems have been observed (Sorensen and Hamling 2016; Todd and Evans 2016).

2.2.2 Water Injection

Water injection has been successful in conventional reservoirs, especially water-wet formations. However, for tight reservoirs, many research indicate, water injection may results in clay swelling, permeability reduction, and mechanical strength weakness, especially in clay-bearing rocks (Behnsen and Faulkner 2011; Cheng et al. 2015; Duan and Yang 2014; Sheng and Chen 2014b).

2.3 Surfactant EOR

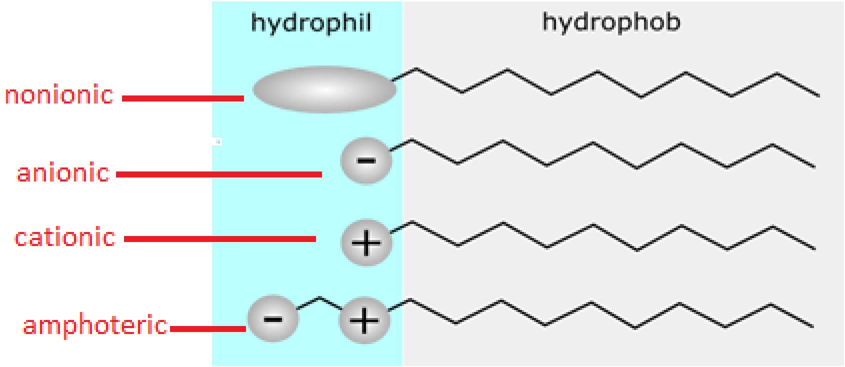


Fig. 7 Schematic of Surfactant Molecule

Surfactants, known as surface-active agents, are organic compounds in which molecule structures contain both hydrophilic groups (water-soluble heads) and hydrophobic groups (oil-soluble tails). Fig. 7 is a simplified sketch of the molecule. The particular structures make surfactants play an important role in cleaning, wetting, dispersing, emulsifying, and foaming agents, etc. Especially, the amphiphilic structures result in the adsorption of a surfactant at surface of rock particles, lowering the surface/interfacial tension (IFT) between liquids and solids (Green and Willhite 1998), altering wettability from oil-wet to water-wet (Gupta and Mohanty 2011; Standnes and Austad 2000; Dongmei Wang et al. 2012a) as well as functioning in dispersing, sludge prevention, penetration (Coulter and Jennings 1997). Therefore, surfactants are often used as additives in the practical application in the oil and gas industry include chemical flooding (e.g. Alkali/surfactant, Alkali/surfactant/polymer flooding in conventional reservoirs), fracturing fluids, and acidizing treatment for their multiple functions. However, there have been few field tests where surfactants were added for the direct EOR purpose (Sheng 2017). In recent years, surfactant is considered as one of the best options to improve oil recovery from geologically challenging reservoirs. There are a number of experimental studies (Adibhatla and Mohanty 2006; Austad and Milter 1997; Shuler et al. 2011; Zeng et al. 2018; F. Zhang et al. 2018) and numerical simulations (Dawson et al. 2015; Detwiler and Wang 2018; Lotfollahi et al. 2017; Wang et al. 2015) using surfactants EOR on shale and tight formations.

2.3.1 Surfactant Spontaneous Imbibition for Conventional Reservoirs

Spontaneous imbibition is the process by which a wetting fluid is imbibed into a porous media (e.g. rock) by capillary force. Although the mechanism of surfactant EOR is not completely understood. A number of studies indicate the surfactant aqueous solution can alter the wettability of the rocks and enhance water imbibition. Gupta and Mohanty (2011); Seethepalli, et al. (2004); Standnes and Austad (2000); Wang et al. (2012) experimentally studied wettability alteration using different type of surfactants reacting with different rocks (e.g. low permeable chalk, shale, and fractured carbonate). In most cases, surfactants can alter the wetting state of rock which is initially oil-wet toward water-wet and consistently imbibe into rock matrix. This make it possible for surfactant aqueous solution to displace more oil from matrix to fractures by the process of spontaneous imbibition and thus improve the oil recovery.

Many of the previous studies were conducted using surfactant imbibition to stimulate the oil recovery in chalk and carbonate reservoirs. Austad and Milter research team (1996a; 1996b; 1997b; 1998) conducted a series of experiments on spontaneous imbibition of water into low permeable chalk (2-3 mD) at different wettability using surfactants. They found in a water-wet and mixed-wet system, the mechanism of spontaneous imbibition was countercurrent flow governed by capillary force and/or gravity force in terms of wetting states and interfacial tension (IFT). In an oil-wet system, without surfactant in the water, the rate of imbibition is very small and only 13% of oil was recovered within 90 days. However, in the presence of a cation surfactant (1.0 wt. % dodecyl trimethyl ammonium bromide $C_{12}TAB$), the nearly oil-wet core turned toward water-wet during the imbibition process, and 65% oil recovery was obtained within 90 days.

Spinler et al. (2000) studied oil recovery using low concentration of surfactant (0.05-0.5%) in chalk. In their study, Oil recovery can be improved with low concentrations of surfactant for both spontaneous and forced imbibition process. In addition, surfactant adsorption can be reduced to very low levels if the surfactant concentration is low below the CMC (Critical Micelle Concentration).

In the study by Chen et al. (2000), they used 3500 ppm nonionic ethoxy alcohol (EA), and an anionic ethoxy sulfate (ES) to stimulate the imbibition. Wettability measurement for core-plug pairs showed that native-state rock shifts from oil-wet to a less oil-wet wettability when exposed to surfactant. The oil recovery from cores from Yates field in West Texas increased as much as 40% compared to pure brine imbibition. Computerized Tomography (CT) scans indicated radial penetration for dilute surfactants was much more rapid than for brine imbibition. A numerical model based on the process was developed, and a good agreement between the simulated and experiment results was obtained.

In the study of Standnes et al. (2002), the oil recovery from oil-wet fractured carbonate reservoir cores have been compared using aqueous solution of a nonionic surfactant ethoxylated alcohol (EA) and a cationic surfactant (C12TAB) by spontaneous imbibition. They demonstrated that C12TAB was more efficiency than the EA. C12TAB recovered 40-45% OOIP over 10% in short cores, as well as 65% OOIP over 5% in long cores. The contact angle measurement confirmed that the wettability alteration using EA is smaller than that of C12TAB.

Hirasaki and Zhang (2004) experimentally studied enhancing oil recovery by the spontaneous imbibition from oil-wet carbonate rocks using anionic surfactants and sodium carbonate solution. Phase behavior, IFT and oil recovery had been evaluated in various condition. In the presence of surfactants (0.025-0.05% of ethoxylated and propoxylated sulfate) and sodium carbonate in the brine, IFT reduction and/or wettability alteration from oil-wet to intermediate-wet and water-wet were observed. Oil recovery of 14-44% OOIP was obtained within 132-381 days.

Chen and Mohanty (2013) performed imbibition experiment to improve oil recovery at high temperature (100°C and above), high salinity (11.8%) and high hardness (Ca^{2+}, Mg^{2+} 4025 ppm) conditions. Three cationic surfactants and two anionic surfactants (sulfonate salts) were investigated for their performance of wettability alteration and oil recover. They stated, cationic surfactants altered the wettability of oil-wet calcite plates toward preferentially water –wet state and recovered 50-65% of OOIP at 100°C from dolomite cores by spontaneous imbibition. Anionic surfactants could alter the wettability of oil-wet calcite plates to strongly water–wet state only when brine salinity and divalent–ion concentration was reduced. With the added sequestration agent (e.g. ethylene diamine tetraacetic acid, EDTA), anionic surfactant solution could recover oil up to 45% of OOIP.

2.3.2 Spontaneous Imbibition for Tight Formations

The above studies have mainly focused on the conventional reservoirs. However, the shale and tight formations are even more challenging because they are most likely oil-wet or mixed-wet (Lan et al. 2015; Odusina et al. 2011; Wang et al. 2012b) and ultra-low permeability (millidarcy to nanodarcy). Limited literatures have focused on shale and tight formations.

Wang's research group first proposed a new approach to stimulate oil recovery from ultra-low permeable formations using diluted surfactant imbibition in 2009 (Wang et al. 2011a; 2011b;

2012a; 2014; 2016). A series experiments of wettability alteration, flow rate, and oil recovery factor with Bakken Cores had been conducted in the lab. Their findings include Bakken cores are generally oil-wet or mix-wet before introduction to the surfactant formulation. Three types of surfactants: Cationic, anionic, and non-ionic surfactants had been identified to alter the wettability and improve the oil recovery at reservoir conditions. The incremental oil recovery of surfactant imbibition is up to 6.8-25.4% over brine only. For a given surfactant, oil recovery can be maximized by identifying an optimal surfactant concentration, brine salinity, sodium metaborate concentration, and divalent cation content.

Shuler et al. (2011) experimentally demonstrated the specialized surfactant formulations in an aqueous phase (e.g. hydraulic fracturing fluids) to recover oil from two small Middle Bakken c (1.5” diameter by 0.5” thickness) and Texas Crème outcrop samples. More than 15 chemical formulations which were predominantly combinations of non-ionic and/or anionic surfactants had been screened for spontaneous imbibition process. The promising laboratory results showed that the customized surfactant formulations could improve oil recovery from the Bakken reservoir cores. The best surfactant formulations were compatible with common fracture fluid system and no emulsion tendency with Bakken oil.

In the study by Nguyen et al. (2014), various surfactants (non-ionic, cationic, anionic, and amphoteric) were studied for spontaneous imbibition into Bakken reservoir cores and Eagle Ford outcrop cores and provided mechanism. Also, IFT were tested to correlate with spontaneous imbibition. Their main findings include high oil recovery (48-55% OOIP) was obtained during spontaneous imbibition in Bakken and Eagle Ford shale cores with diluted anionic and nonionic surfactants (0.1-0.2%). The main oil displacement mechanism is driven by both buoyancy and countercurrent capillary imbibition. No correlation between IFT and oil recovery suggests wettability alteration is the dominant mechanism of oil recovery.

2.3.3 Forced Imbibition (Surfactant Flooding) for Tight Formations

Although those surfactant spontaneous imbibition studies got positive results in improving oil recovery, they only used thin slices or small cores in the lab. However, in practice the matrix is huge, spontaneous imbibition process will be significantly slow. A number of scaling studies for spontaneous imbibition indicate, the imbibition rate is inversely proportional to a squared characteristic length (Li and Horne 2006; Mattax and Kyte 1962; Ma, et al. 1997; Zhang, et al. 1996; Wang, et al. 2015). This will make it uneconomic when the method is applied to the fields.

In order to solve the problem, some forced imbibition ideas have been proposed to speed up the imbibition process, such as re-fracturing process, surfactant flooding. Vincent (2011) presented a detailed review of refract treatment in the Middle Bakken. With suitable proppant, fracturing fluid, and optimal design, fractures, fracture conductivity and contact area will be increased. Thus, large increase in oil production could be obtained.

Dawson et al. (2015) experimentally programmed the EOR potential of surfactant flooding in the Middle Bakken. They stated that the novel surfactant system exhibited the potential to enable the economic surfactant flooding in the Bakken. By altering the wettability of rock from oil-wet to water wet, the oil recovery can be improved up to ~30-40% in Bakken cores, and imbibition rates in excess of 10 cm/day was observed in ~1 μD core. In their simulation model, the Klinkenberg permeability of study area matrix was 1 to 20 μD at 3,000 psi NCS; the amount of fractures, fracture length, well spacing and chemical system (non-ionic surfactant solution) were carefully designed based on the lab test and history-matching experiments. The model predicted that after 12.5 years of primary production, the well to well surfactant flooding will bring a 100%

increase in the recovery in the following 12.5 years. Also, the model shows that the surfactant injection could have not only technical (EOR) potential in the target area of the Bakken, but also economic potential by reinjecting produced water back into the formation to enhance oil recovery.

2.3.4 Combinations of EOR Methods for Tight Formations

Sheng (2017) summarized EOR research results from the laboratory studies and reviewed the practice and applications in the fields. Either gas injection, water injection or surfactant injection, no matter they have been applied in huff-n-puff mode or flooding process, the EOR potential is limited. Thus, combinations of EOR methods and other stimulating techniques have been proposed and studied in the laboratory. Such as the combination of gas injection and surfactant imbibition, the synergistic effect of surfactant EOR and acidizing stimulation.

Zhang et al. (2018) demonstrated the potential of combination both CO2 Huff-n-Puff and Surfactant-Assisted Spontaneous Imbibition techniques in optimizing oil recovery in unconventional reservoirs. 49% of OOIP was recovered by CO2 Huff-n-Puff and an additional 8.6% oil recovery through spontaneous imbibition experiment was obtained on the Eagle Ford core plug. However, in the study by (Zeng, et al. 2019), CO2 Huff-n-Puff was efficient in improving oil recovery from outcrop shale plugs. The additional surfactant chemical blend seemed to impede the oil recovery. They suggested it might result from the heterogeneity in the sample.

About half of the hydrocarbon reserves are in carbonate reservoirs (Roehl and Choquette 1985). Therefore, acidizing is commonly used in conventional carbonate reservoirs to stimulate oil recovery by mineral dissolving. Recently, a few studies focused on the feasibility of surfactant EOR coupled with acid stimulation on carbonate-rich shale and tight formations. Miller et al. (2018); Mohanty et al. (2017) experimentally demonstrated the synergistic effect of surfactant EOR and acidizing treatment. In their studies, a chemical blend contains diluted surfactant and organic acid (weak acid) could generate more porosity and permeability in matrix, and extract 30-42% of oil from the imbibition test. However, in the flow cell test, the fracture conductivity was slightly reduced by the chemical blend treatment due to proppant movement.

2.4 Acid Stimulation

Acid stimulation treatment on oil and gas wells can date back to 1895. Herman Frasch, a chemist of Standard Oil was issued the first patent on acidizing in 1896. Frasch proposed an acidizing process to increase flow of oil well from carbonate formation and made great success in Lima, Ohio wells. However, for various reasons, acidizing treatment was not sustained and used infrequently in the following three decades. It has been a less preferred alternation to propped fracturing (non-acid fluid) since 1930s, and it didn't resume until the late 1970s. With the development of various models for acid reaction in carbonate formation and well understandings of the mechanism, the carbonate acidizing has been considered as a common stimulation technique in carbonate reservoir again. Because there are about 70 % of the worldwide hydrocarbon reserves are stored in carbonate formations (Kalfayan 2007).

Technically, productivity can be greatly improved by a properly designed acid stimulation treatment. Acidizing treatment falls into two categories: acid matrix acidizing on damaged formation is a treatment by injecting acid at low rate to allow the fluids to permeate to rocks creating small channels, often called "wormholes"; While acid fracturing is performed by injecting acid at a high enough pressure to break down the formation hydraulically, creating large conductive fractures in the reservoir (Bert et al., 1979; Muecke, 1982)

Many models have been developed to describe the acidizing process and predict the distribution, size, and length of the wormholes and fractures in acid treatment. Nierode and Williams (1971) developed a model to predict the length of wormholes, but the number of wormholes and their sizes were not addressed. Hung et al., (1989) used a mathematical model to describe the growth of wormholes during acidizing treatment. This model described relationships between injection rate, diffusion rate, fluid-loss rate and the formation of wormhole.

A relatively strong HCl (typically 15 wt%) is the most common acid system used in treating carbonates. However, the corrosion is of utmost concern. A weaker and less corrosive acid has been considered as a substitution in deep, hot wells. Van Domelen and Jennings (1995) present an application using blends of organic acids (acetic and formic) instead of HCl in a high-temperature (175 °C) and high pressure (1400 psi) Arun limestone formation in Indonesia. The blend solution (13% acetic – 9% formic) used in the acid treatment had an equivalent effectiveness as 15% HCl but less corrosive rates. Chang et al. (2008) suggested an approach of using mixture of HCl and organic acids (15 wt% HCl + 10 wt% Acetic /9 wt% formic) in carbonate reservoirs for a further penetration in matrix.

Coulter and Jennings (1997) provided a contemporary approach to matrix acidizing. As an additive, surfactant is common to all acidizing treatment due to its function of dispersing, sludge prevention, penetration, interfacial tension reduction.

Acid treatment has been widely used in conventional carbonate formation with relatively high permeability. For unconventional formation, it is hard to form wormholes due to the ultra-low permeability. More recent, Wu and Sharma (2017) studied the effect of dilute acid fracturing (3 wt% HCl in 3 wt% KCl) on Bakken shale. Acid fracturing can etch the fracture surface and form channels, macropores, cavities, and thus lead to surface asperities and improve the conductivity. However, acid fracturing can soften the fracture surface and reduce the fracture conductivity.

Most recently, a chemical blend of an organic solvent (1.0 -10.0 wt%), a surfactant (0.1-1.0 wt%), and an oxidizing agent (0.1-1.0 wt%, which produces a weak acid) was developed to stimulate the shale formation rich in calcite (Mohanty et al., 2017; Miller et al., 2018). The synergistic effect of the blend was observed included: improve the permeability of rock matrix by 25-100% and extract up to 30-42% of oil from the contact shale surface, alter the rock face to a water-wet status and improve the water imbibition. However, the fracture conductivity was decreased due to the proppants' movement during the treatment.

3. METHODOLOGIES

The experiments conducted in this study include two parts: Surfactant flooding and surfactant flooding coupled with acidizing treatment. The first part involved the forced surfactant imbibition process, the effects on the process, and the comparison to surfactant spontaneous imbibition process. The second part involved the acidizing stimulation, and the combination of acidizing and surfactant flooding. Because the experiment material and procedures for the two parts are different and thus are discussed separately.

3.1 Forced Surfactant Imbibition (Surfactant Flooding)

In this part, three pairs of reservoir core plugs were loaded in the Hassler Cell system for forced surfactant imbibition test through various process at reservoir conditions. Forced imbibition rate, relative permeability, oil recovery, effect of initial water saturation, surfactant concentration, and surfactant solution salinity on the process were examined.

3.1.1 Surfactant Flooding System

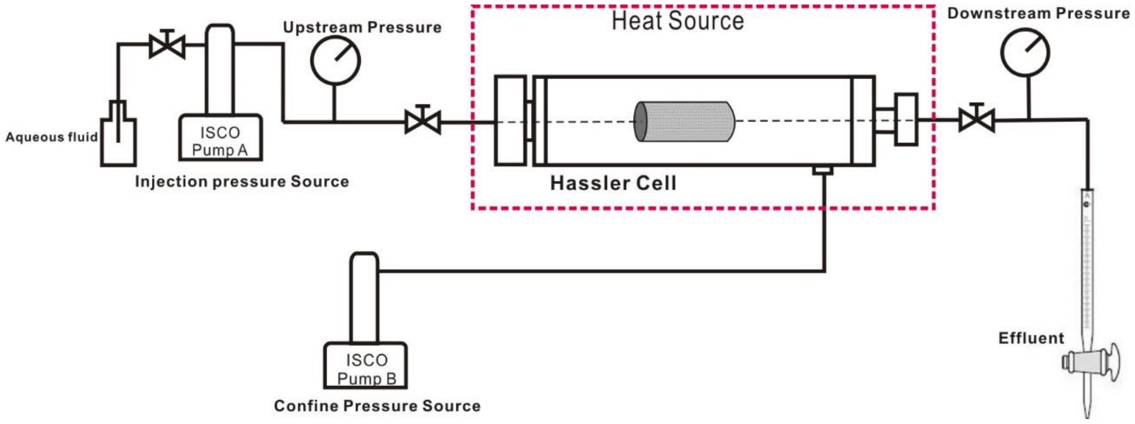


Fig. 8 Schematic of Core Flooding System

A surfactant flooding system was developed in our lab for the forced imbibition process. Fig. 8 illustrated the schematic of this system.

3.1.2 Materials

Porous Media

Core plugs: Three pairs of core plugs came from the Middle Member of the Bakken Formation in Well #18226 Williston Basin, Williams County, North Dakota (Fig. 9). The porosity of the cores ranged 4.6% - 8.2% based on NMR measurement. The permeability to water was 0.55 µd and 0.98 µd to oil, which measured by above flooding system. All the cores contained visible fractures indicated by red arrows shown in Fig. 10. Core descriptions were listed in Table 1. All the cores were cleaned by Dean-Stark with toluene and methanol, dried and vacuumed before core flooding.

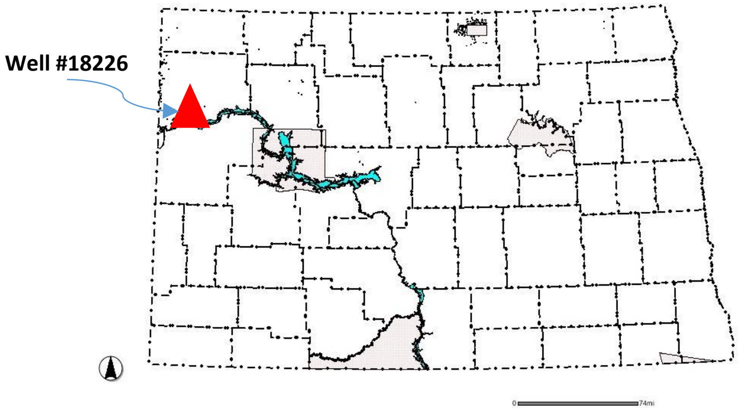


Fig. 9 Map of Well #18226 in North Dakota

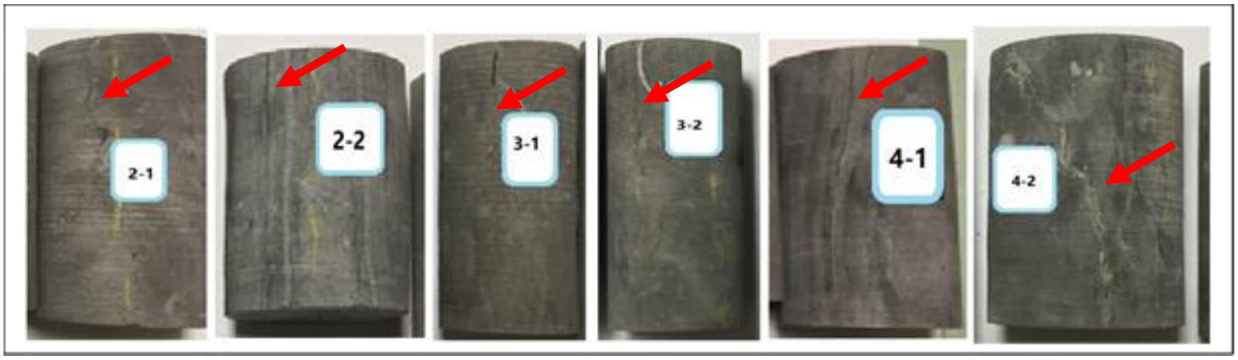


Fig. 10 Core Samples Before Flooding

Table 1 Description of Paired Cores for Surfactant Flooding

Sample #	Depth (ft.)	Diameter (mm)	Thickness (mm)	porosity	Permeability, md		Lithology
					water	oil	
2-1	10644.5	36.6	69.50	0.063	0.0003	0.0012	**Siltstone**, cream to off white, trace light gray, very fine grained, well sorted, calcareous to slightly dolomitic cement, moderately cemented.
2-2	10624.2	36.7	46.31	0.070	0.0010	0.0015	
3-1	10641.5	25.6	64.82	0.090	0.0003	0.0005	
3-2	10636.3	25.7	67.63	0.075	0.0006	0.0007	
4-1	10630.4	36.7	76.12	0.046	1.5920	17.9000	
4-2	10639.5	36.6	61.51	0.082	0.6570	1.0200	

Test Fluids

- ***Crude Oil.*** Oil was collected from Well Syverson 1-12 #1 of Bakken Formation in Williams County of North Dakota. The density and viscosity were 0.83 g/cm^3 and 4.2 cp at room temperature, respectively.
- ***Brine.*** The synthetic brine used in core flooding was characteristic of the reservoir brine in the Bakken Formation, consisting of 11.2 wt% $NaCl$, 1.7 wt% KCl, 4.9 wt% $CaCl_2$, and 0.43 wt% $MgCl_2$. The total salinity of the brine was 205064 mg/L (18.2 wt%). All salts were purchased from Acros Organics (A.C.S grade).
- ***Surfactants***. A selected anionic surfactant alcohol ethoxy-sulfate (AES) was used as testing surfactant, which provided by Shell Chemical.
- ***Alkali $NaBO_2 \bullet 4H_2O$:*** This alkaline chemical was used to buffer the pH of the aqueous phase to 8 to 9.
- ***Surfactant Formulation***: 0.1 - 0.15 wt% AES in 10 - 18.2 wt% brine.

3.1.3 Surfactant Flooding Procedures

Each core plug was loaded into the Hassler cell as shown in Fig. 8, starting with water saturation or oil saturation to obtain various initial saturation. Table 2 showed the different cases for flooding tests. Testing fluids such as brine, oil and surfactant formulation were injected at a flow rate of 0.1-0.3 ml/H, and the produced fluids were collected to determine the permeability, the oil recovery factor, core flooding rate, and water cut by equation 1&2. Paired cores were used to compare the effect of initial water saturation, surfactant concentration, and salinity.

Table 2 Cases for Core Flooding Test

Core sample	Cases	Surfactant		Salinity %	S_{wi}, %
		Concentration	Type		
2-1	Oil Saturation → SF	0.15 %	AES	18.2	0
2-2	Water saturation → Oil Saturation → SF	0.15 %	AES	18.2	33
3-1	Water saturation → Oil Saturation → SF	0.10 %	AES	10	45
3-2	Water saturation → Oil Saturation → WF	-	-	10	43
4-1	Oil Saturation → SF	0.10 %	AES	18.2	0
4-2	Water saturation → Oil Saturation → SF	0.10 %	AES	18.2	49

- WF: Brine water flooding
- SF: Surfactant flooding (Alkaline added to balance pH)
- $S_{wi} = 0$: cores were saturated by oil before testing
- $S_{wi} \neq 0$: cores were saturated by brine water before testing
- The pH was tested before surfactant injection and after displacement of effluent water.

$$\eta = \frac{V_{op}}{V_o} \times 100 \qquad \text{......} \quad 1$$

$$f_w = \frac{C_{uw}}{C_{uo} + C_{uw}} \times 100 \qquad \text{......} \quad 2$$

Where,
C_{uo} = cumulative oil production, *ml*;
C_{uw} = cumulative water production, *ml*;
f_w = *water cut, %*
V_o = oil volume saturated in the core, *ml*;
V_{op} = produced oil volume, *ml*;
V_w = produced water volume, *ml*;
η = oil recovery factor, %

3.2 Forced Surfactant Imbibition (Surfactant Flooding) Coupled with Acidizing

In this part, at first, the interaction of carbonate-rich rock and acidic solution and aging test were performed for formulation screening and evaluation; and then, core flooding experiment were conducted for evaluation of this combination approach.

3.2.1 Materials

Porous media: rock samples came from the Middle Member of the Bakken Formation in Well #18226 and Well #23285 in North Dakota (Fig. 11).

- Rock powder (for acid solubility test): pulverized and sifted by ASTM #200 sieve (74 µm)
- Rock Sections (for aging test): cut and polished to prepare the surface for SEM image
- Rock plugs (for flooding test): cleaned by Dean-stark with toluene and methanol, dried for 24 hours at 103 °C and vacuumed for 2 hours before test.

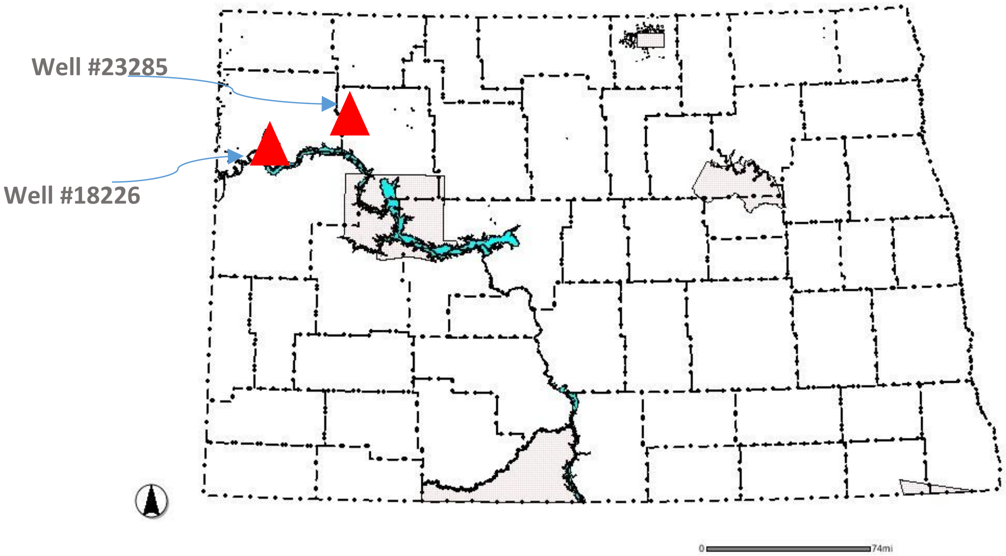
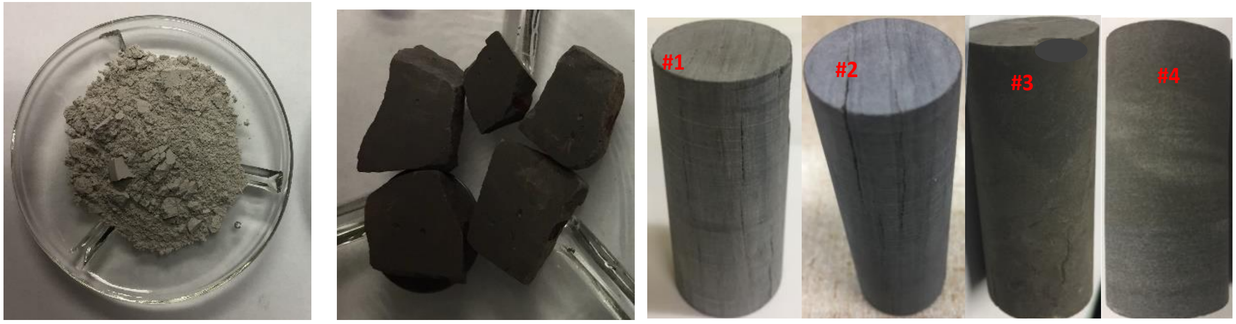


Fig. 11 Map of Well #18226 &Well #23285 in North Dakota



(a) (b) (c)

Fig. 12 Rack Samples from the Middle Bakken
(a) Powdered rock (b) Rock segments (c) Core plugs

Fluid

- ***Crude Oil.*** Oil was collected from Well Syverson 1-12 #1 of Bakken Formation in Williams County of North Dakota. The density and viscosity were 0.83 g/cm^3 and 4.2 cp at room temperature, respectively.
- ***Brine.*** Two synthetic brines were used in the study.

  The low salinity brine: 4 wt% $NaCl$. pH value of the brine typically ranged from 6.65 to 6.88 at room temperature.

  The high salinity brine: characterized the Bakken reservoir brine, consisting of 11.2 wt% $NaCl$, 1.69 wt% KCl, 4.91 wt% $CaCl_2$, and 0.43 wt% $MgCl_2$. The total salinity of the brine was 205,064 mg/L (18.2 wt%). All salts were purchased from Acros Organics (A.C.S grade). The pH value of the brine typically ranged from 6.16 to 6.85 at room temperature.
- ***Surfactant***. A selected anionic surfactant alcohol ethoxy-sulfate (AES) was used as testing surfactant, which provided by Shell Chemical.
- ***Acid***: An organic weak acid (OA), acetic acid was sourced from Acros Organics (A.C.S grade).
- ***Chemical Formulations***: 0.5-1.0 wt% OA and/or 0.1 wt% AES in brine of 4% or 18.24 wt%

3.2.2 Experimental Procedures

The procedures in this experiment involved rock characterization, carbonate-rich rock interaction with acidic solution, aging test and core flooding, the apparatus and method for the tests are different and thus are discussed respectively.

3.2.2.1 Rock Characterization

The reservoir rock was crushed and pulverized into a particle size less than 200 mesh. Then the powdered rock was used for total organic content (TOC) measurement using Weatherford SRA Source Rock Analyzer. Mineralogy was analyzed on Rigaku Smartlab X-ray Diffractometer (XRD) operated at 40 KV and 40 mA using Cu Kα radiation at a scan rate of 4^{o}/min from 3^{o} -90^{o}.

3.2.2.2 Acid Reaction and Rock Dissolving Test

This test was performed to study the interaction between the rock powders and acidic treatment solution. The procedure for acid reaction and solubility test is described in the flow chart (Fig. 13):

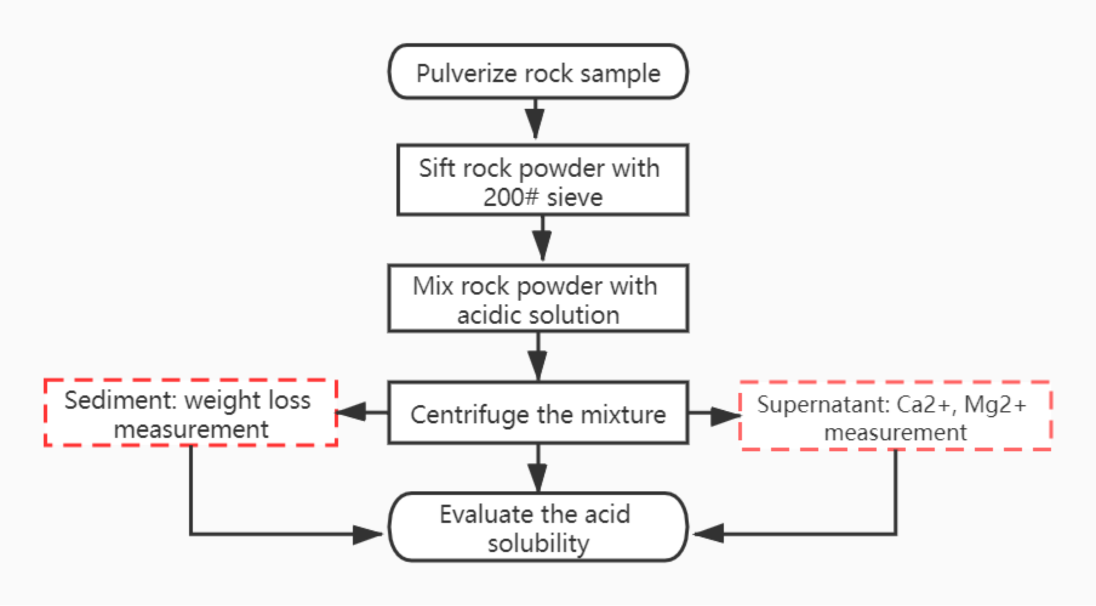


Fig. 13 Flowchart of Rock Dissolving Test

Rock samples were pulverized and sifted by ASTM #200 sieve (74 μm). The acidic solutions were prepared using varied concentration of OA and AES in 4% NaCl: 1) 0.5% OA, (2) 1.0% OA, (3) 2.0% OA, (4) 0.5% OA and 0.1% AES, (5) 1.0% OA and 0.1% AES, (6) 2.0% OA and 0.1% AES, (7) 4% brine only (used as blank/control). About 0.5 grams pulverized rock sample (accurate to 0.0001 g) was weighed and poured into 100 mL conical flask, then 50ml acidic solution was pipetted into the same conical flask. This was then sealed and placed into Barnstead MaxQ 4000 Orbital Incubator Shaker at 50 ℃ and 250 rpm for 24 hours. Then the mixture was removed, and then centrifuged at 5000 rpm for 1 hour. For those mixtures without AES (case 1-3), an additional centrifuging at 10000 rpm for 10 min. for separating the liquid phase from the solid phase. Next, the supernatant was taken out to measure the dissolved mineral (Ca^{2+}, Mg^{2+}) by iCAP Q inductively coupled plasma mass spectrometry (ICP-MS). The concentration differences between the blank (4 wt% NaCl) and the samples were used to evaluate the dissolution ability of the acidic solution. Meanwhile, the sediments during centrifugation were carefully removed from the vial, then filtered and rinsed with 100 ml DI water on a pre-weighed 0.45 μm filter paper, this was then dried at 103±2 ^{o}C for 24 hours to measure the total weight loss.

3.2.2.3 Aging Test

Aging test was performed to study the effect of acidizing treatments onto the rock surface and into the microstructures. The procedure of aging test is described in the flow chart (Fig. 14).

Samples were taken from semi-preserved cores and crush into small segments. These segments were ground into planed surfaces and polished with successively finer abrasives to obtain smooth surface. Then these polished segments were used for pre-treatment and post-treatment measurements: topography images and microstructures were captured by Scanning Electron Microscope (FEI Quanta 650 FEG SEM), rock surface composition was mapped by Energy-Dispersive X-ray Spectroscopy (EDS), interaction between rock segments and chemical formulation was determined by ICP-MS.

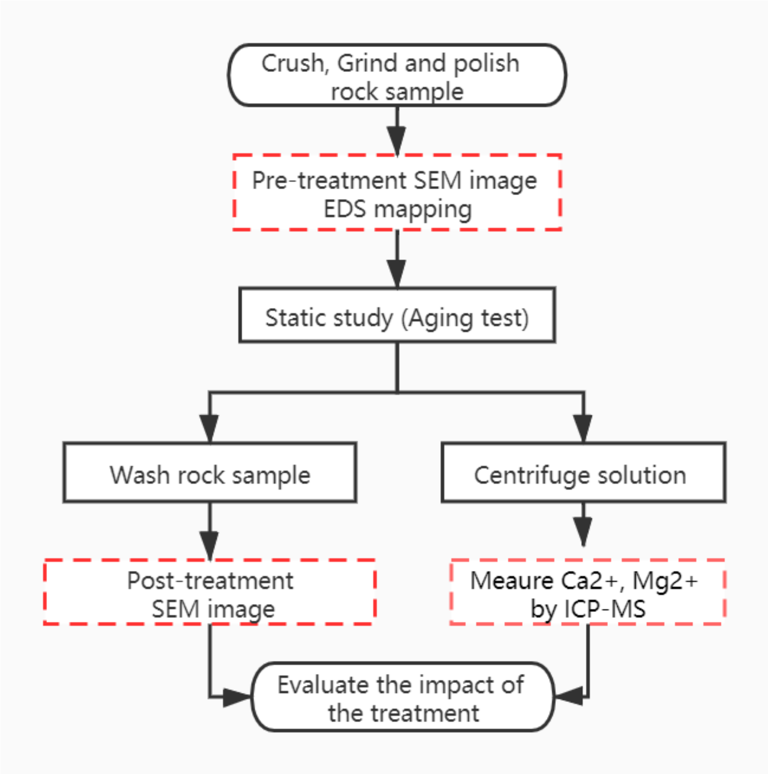


Fig. 14 Flow Chart of Aging Test

The aging tests were conducted in specific volume (15 ml) of solutions with desired salinity (18.24 wt%), organic acid (0.5-1.0 wt%) and AES surfactant (0.1 wt%). Varied solutions were pipetted into pressure vessels that can withstand vapor pressure of 150 psi, and weighed amount of rock segments (0.72-2.22 g) were placed into the pressure vessels at 115 °C for 5 days. Next, cool them down for 24 hours. Rock samples were taken out, and then the solutions were centrifuged at 5000 rpm for 30 min. An additional centrifuging of 10000 rpm for 10 min if needed. The third step, the supernatant was extracted to evaluate the changes of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} using ICP-MS. The rock segments were washed with isopropanol in ultrasonic cleaner, dried at 103±2 ^{o}C for 24 hours, and vacuumed for 2 hours. The rock samples were then used for the post-treatment test.

3.2.3.4 Flooding with Acidizing Treatment

Flooding with Acidizing Treatment was conducted to study the interaction of rock plug with designed chemical formulation by flooding test, and the effects on porosity, permeability, and oil recovery. Porosity and pore distribution pre and post-treatment were determined using Oxford Instrument GeoSpec 2 Nuclear Magnetic Resonance (NMR). Permeability and oil recovery were measured by flooding tests. Fig. 15 illustrated the schematic of flooding system:

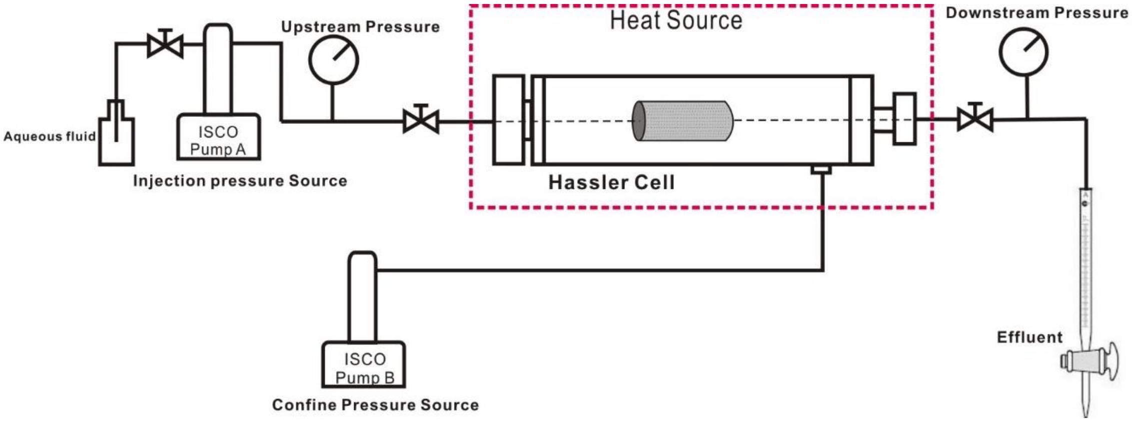


Fig. 15 Schematic of Flooding System

1” in diameter and 2” in thickness core plug was loaded into Hassler coreholder, and a confine pressure of 2500 psi was applied. The confine pressure was very close to the actual formation pressure. The flow chart for the flow cell experiment is shown in Fig. 16. Step 1) the core plug was pre-flushed at ambient temperature by injecting brine (4% NaCl or brine 18.2%) at 0.025-0.505 mL/Hr. The initial permeability to brine was measured during this process. And then the saturated core plug was taken out to measure the porosity and pore distribution using NMR. Step 2) the core plug was placed back into Hassler coreholder, then crude oil was injected to saturate the core plug. Step 3) Switch to flooding test at 115°C by injecting chemical formulation at 0.01-0.505 mL/Hr. The flooding effluent was collected at 4 PV, 8 PV and 13 PV. Step 4) the core plug was post-flushed with brine (4% NaCl or brine 18.2%), and then the core plug was taken out to measure the porosity and pore distribution using NMR one more time. Step 5) the core plug was washed by Dean-stark with toluene and methanol, dried for 24 hours at 103 ℃ and vacuumed for 2 hours. The core plug was then placed back into Hassler coreholder to measure the post-treatment permeability to brine as in step 1).

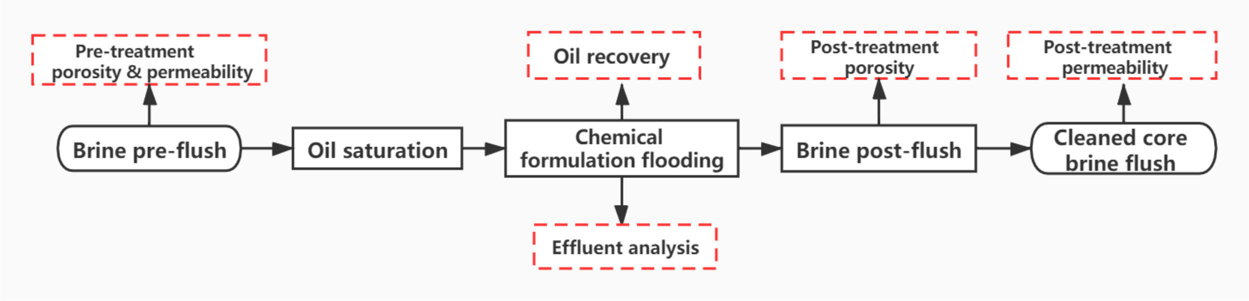


Fig. 16 Flow Chart of CF Flooding Process with Acidizing Treatment

4. RESULTS AND DISCUSSION

The results and discussion in this study have been divided in two parts. The forced surfactant imbibition is discussed in the first part, and the surfactant flooding coupled with acidizing treatment will be discussed in the second part.

4.1 Forced Surfactant Imbibition (Surfactant Flooding)

The results in this part consist of five sections. The first section demonstrates the oil recovery by surfactant flooding vs. by Brine flooding; The effect of initial water saturation, salinity and surfactant concentration on the process is described in the second, third and fourth section, respectively. Finally, the oil recover rate is discussed in the fifth section

4.1.1 Oil Recovery by Surfactant flooding vs. Brine water alone Flooding

The surfactant flooding tests were conducted in six cases at different surfactant concentration, salinity, and initial water saturation (Table 3). It was observed that for the higher water permeability cores (Cores 2-2, 4-1, and 4-2), the peak oil produced was quick, within 0.23-0.75 pore volume injection (PV, e.g.). However, with a relative low water permeability cores (Cores 2-1, 3-1, and 3-2), the peak oil recovered was relative slow, within 1.1 to 2.2 PV. The oil recovered by surfactant flooding ranged from 29.4% to 57.9% of OOIP, while by brine flooding alone was 17.0% as depicted by the star marks in purple line of the Fig. 17, the incremental oil recovery by surfactant flooding was ranged from 12.4 to 40.9%. These results are relative more favorable than the incremental oil recovery produced by the spontaneous imbibition process we had been pursued from our laboratory (Wang et al. 2012a). Our observation shows surfactant flooding by driving process for tight rocks has good potential for oil recovery enhancement at various conditions. In the Bakken shale formation in the Williston Basin, an increase of 1% in recovery could lead to an increase of 2 - 4 billion barrels of domestic oil production.

Table 3 Oil Recovery by Surfactant Flooding at Various Condition

Core sample	Cases	Surfactant Concentration	Salinity %	$S_{wi,}$ %	Oil Recovery %
2-1	Oil Saturation → SF	0.15 %	18.2	0	51.7%
2-2	Water saturation → Oil Saturation → SF	0.15 %	18.2	33	51.4%
3-1	Water saturation → Oil Saturation → SF	0.10 %	10	45	29.4%
3-2	Water saturation → Oil Saturation → WF	-	10	43	17.0%
4-1	Oil Saturation → SF	0.10 %	18.2	0	50.7%
4-2	Water saturation → Oil Saturation → SF	0.10 %	18.2	49	57.9%

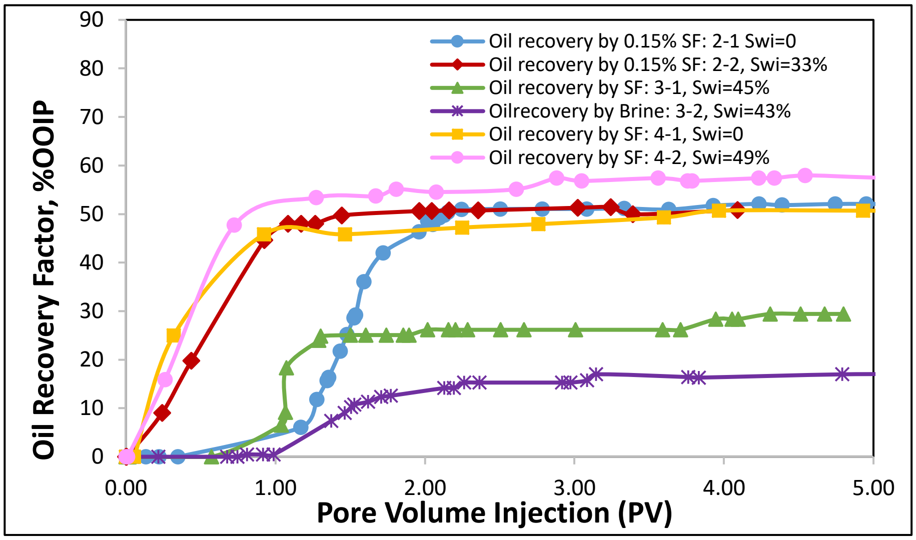


Fig. 17 Oil Recovery Factor by Forced Surfactant Imbibition Process

4.1.2 Effect of Initial Water Saturation

The objective of the flooding tests with paired Cores 2-1 and 2-2 was to investigate the surfactant EOR potential for different initial water saturations before surfactant flooding. For Core

2-1, the core flooding procedure involved oil saturation after core cleaning, followed by surfactant flooding. So, the initial water saturation in this core was zero ($S_{wi} = 0$). For Core 2-2, the procedures included brine saturation, oil saturation, and then surfactant flooding. Therefore, a certain initial water existed in the Core 2-2 before surfactant stimulation. The S_{wi} in the Core 2-2 was 33%. Prior to EOR process, Cores 2-1 and 2-2 contained multiple visible fractures before the tests (Fig. 18). Both of core 2-1 and Core 2-2 were flooded with surfactant concentration at 0.15%. The results demonstrate that these surfactant formulations have good potential for oil recovery improvement when fractures provide adequate connection in the pore spaces.

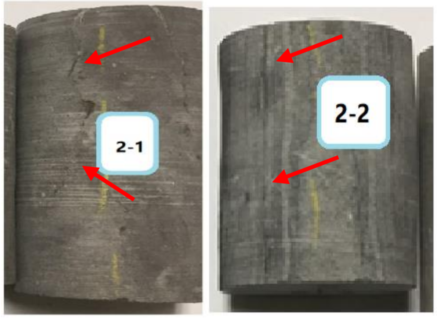


Fig. 18 Core 2-1 & 2-2 Before Flooding Test

Oil recovery by surfactant flooding on Core 2-1 and Core 2-2 were 52.1% and 50.9%, respectively. Core 2-1with no initial water saturation (blue line in Fig. 19) showed 1.2% greater than the core with initial water saturation pre-exists (red line). The two cores had a similar level of fractures, resulted in a close oil recovery between Core 2-1 and 2-2. In addition, because of fractures within Core 2-2, the initial water had a positive effect on the wettability of this core (shifting the direction toward water-wet direction). The oil extraction rate showed a quick response in that the water cut in Core 2-2 also showed a greater response. However, since oil extraction rate is accelerated by an EOR process, the water cut rose back quickly to a high value (> 80%) in a short time (Fig.20). So that the duration of the EOR effect was short.

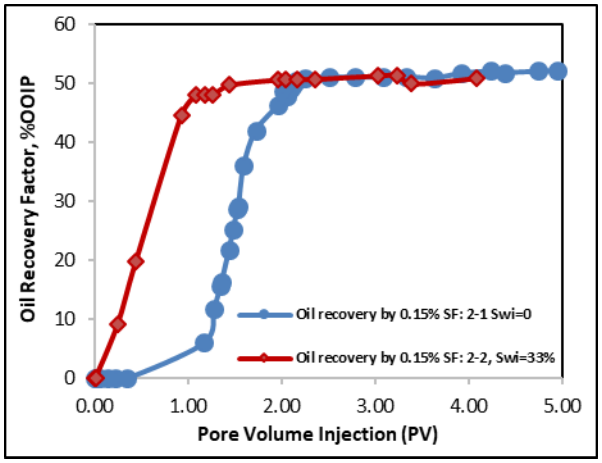


Fig. 19 Initial Water Saturation Effect on Oil Recovery Factor

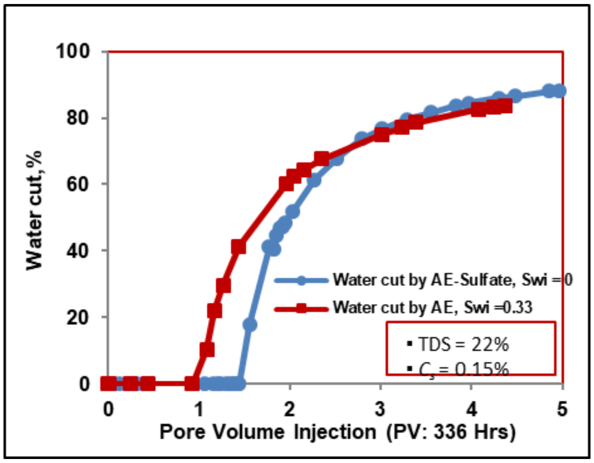


Fig. 20 Initial Water Saturation Effect on Water Cut

4.1.3 Effect of Salinity

The objective of the flooding tests with paired Cores 3-1 and 3-2 was to investigate the surfactant EOR potential under the optimum salinity we identified in previous study rather than at the formation salinity. Both core samples 3-1 and 3-2 were saturated with brine, then with crude oil to obtain a certain initial water saturation before flooding tests. The S_{wi} in Cores 3-1 and 3-2 were 45% and 43%, respectively. Then Core 3-1 was flooded with Surfactant AE (with 0.1 wt% at 10% salinity), and Core 3-2 was flooded with brine (at 10% salinity). The optimum salinity of10% was previously determined by spontaneous imbibition (Wang et al. 2016).

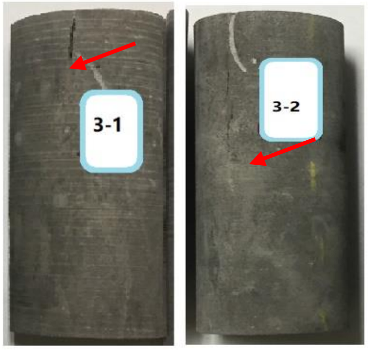


Fig. 21 Core 3-1 & 3-2 before Flooding Tests

Compared to the other core samples we discussed (2-1 and 2-2, 4-1 and 4-2), Cores 3-1 and 3-2 were less permeable. The permeabilities to water and oil of these two cores were 10^{-4} md (Table 1). From the exterior, only minor visible fractures were observed (Fig. 19). Under similar fracture presence, initial water saturation, and at the optimal salinity in solutions for two cores, the oil recovery by surfactant flooding from the Core 3-1 (green line in the Fig. 22) was 12.4% greater than that from Core 3-2 by flooding using only brine (purple line). In the same figure, oil extraction rate during brine flooding was slow by about 0.3 PV than surfactant flooding did. In Fig. 23, water cut rose quickly during the latest stage of water flooding. After 4.79 PV, high water cuts (over 90%) were achieved (in Cores 3-1 and 3-2) both by water flooding and surfactant flooding.

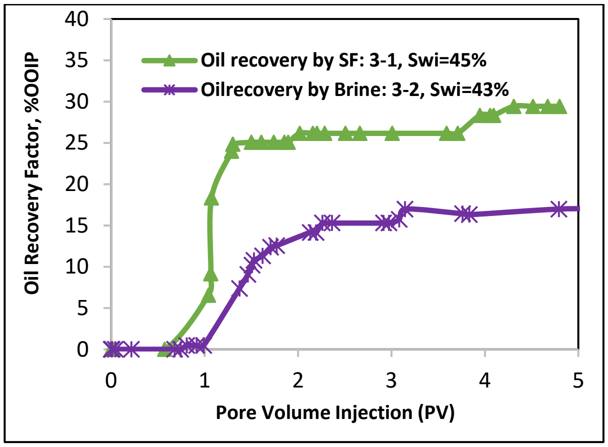


Fig. 22 Effect of Brine and Surfactant Flooding on Oil Recovery at Optimal Salinity

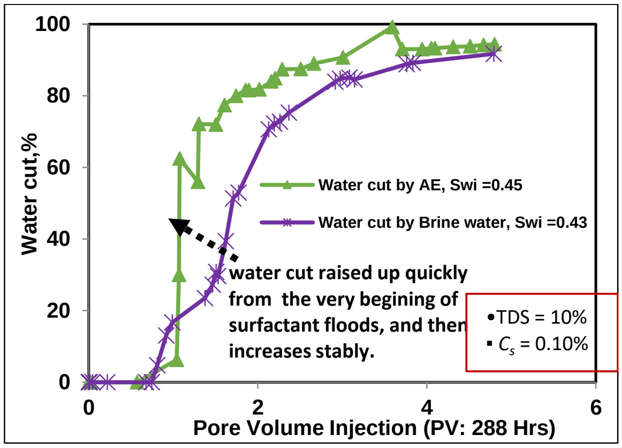


Fig. 23 Optimal Salinity Effects on Water Cut

The comparison of optimal salinity effects on oil recovery also involved Cores 3-1 and 4-2. The initial water saturations of these two cores were 45%, and 49%, respectively. Both cores were flooded with surfactant formulations, but with 10% salinity and 18.2% salinity, respectively. The oil recovery factor for Cores 3-1 and 4-2 were 29.4% and 58.0%, respectively (Fig. 24). Here, the permeabilities to water and oil of Core 3-1 were 0.0003 md, and 0.0005 md, respectively; and the permeabilities to water and oil of Core 4-2 were much higher: 0.657 md and 1.020 md, respectively (because the fractures were more developed in this core, see Fig. 25).

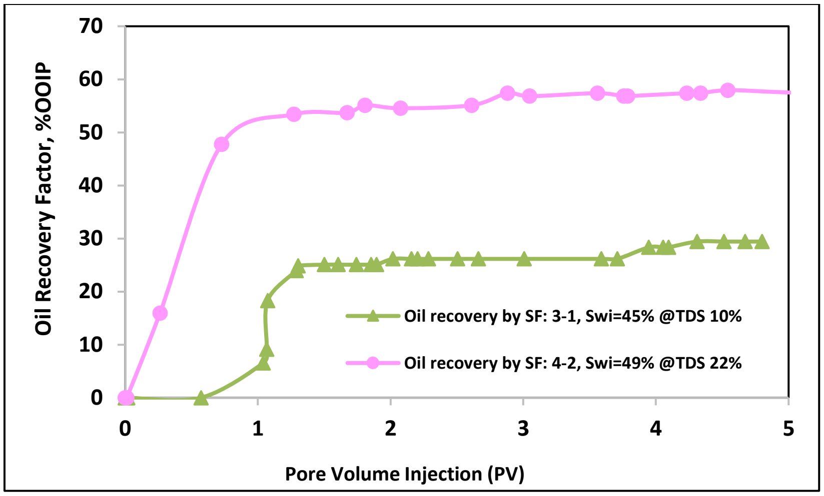


Fig. 24 Optimal Salinity Effects on Oil Recovery

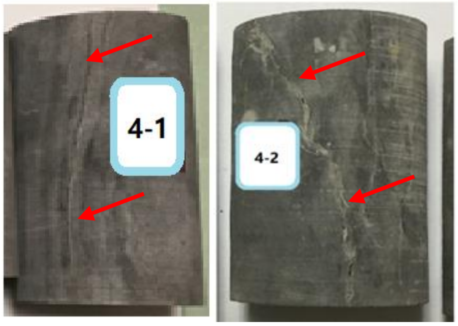


Fig. 25 Core 4-1& 4-2 before Flooding Tests

4.1.4 Effect of Surfactant Concentration

The objective of the tests with two pairs of core samples (Cores 2-1 and 2-2 and Cores 4-1 and 4-2) was to investigate surfactant EOR potential on surfactant concentrations. Cores 2-2 and 4-2 were saturated with brine, then with crude oil before surfactant flooding. The S_{wi} values were 33% and 49% in Cores 2-2 and 4-2, respectively. Then, they were flooded with Surfactant AE with 0.15% and 0.1% concentrations at 22% salinity. In contrast, Cores 2-1 and 4-1 were only saturated by crude oil, then flooded with surfactant at the same formation salinity. The S_{wi} value were zero both in Cores 2-1 and 4-1.

Compared to the other core samples we discussed above, Core 4-1 & 4-2 exhibited much higher permeability than the other cores (Table1). Especially Core 4-2 exhibited multiple fractures throughout the core. Therefore, the oil recovery was higher than in the other cores.

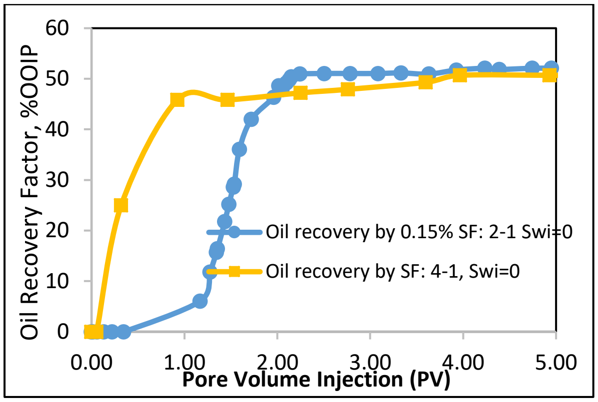


Fig. 26 Surfactant Concentration Effect on Oil Recovery, S_{wi}=0

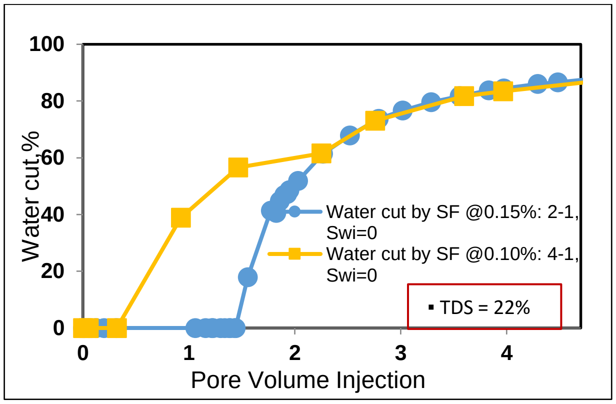


Fig. 27 Surfactant Concentration Effects on Water Cut, S_{wi}=0

Theoretically, as the surfactant concentration increases, more oil could be recovered. However, When the initial water saturation was zero, the final oil recovery of Core 2-1(blue line in Fig. 26) with surfactant concentrations of 0.15% was just 1% greater than Core 4-1(orange line in Fig. 26) with surfactant concentrations of 0.1 %. When a certain initial water saturation exists before surfactant flooding ($S_{wi} \neq 0$), the final oil recovery of Core 2-2 (red line in Fig. 28) with surfactant concentrations of 0.15% was 7% less than Core 4-2 (pink line in Fig.28) with surfactant concentrations of 0.1 %. These results indicated that (1) fractures apparently played an important role in oil recovery (higher permeabilities to oil and water, about 10^3 magnitude than the other cores, and (2) the pore throat or the rock might be blocked by higher concentration surfactant molecules with ultra-low permeability, so that the oil recovery was low.

On the other hand, the water cut changes with the $S_{wi} = 0$ trended normally (Fig. 29). Core 4-1 with surfactant concentrations of 0.1% had a quick response and higher water cut than Core 2-1 with higher surfactant concentrations until 2.27 PV injection, then both increased gradually. When a certain initial water saturation existed in the cores, the water cut with the higher surfactant concentration maintained a stable low level (red line in the Fig. 29).

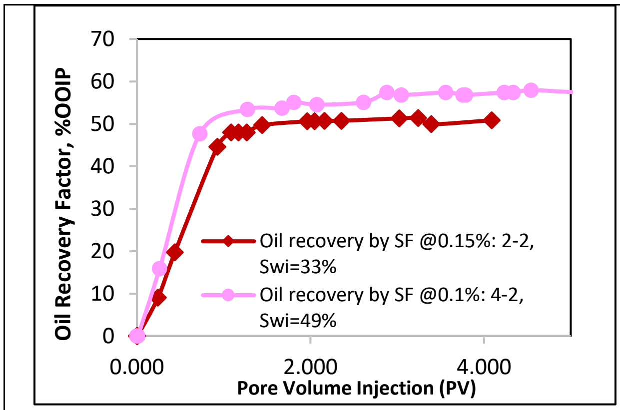


Fig. 28 Surfactant Concentration Effects on Oil Recovery, Swi≠0

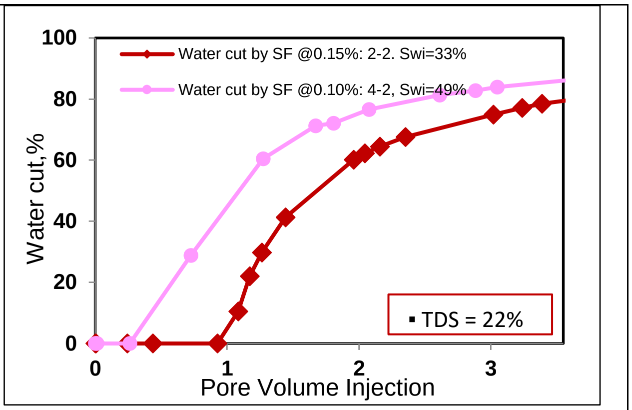


Fig. 29 Surfactant Concentration Effects on Water Cut, Swi≠0

4.1.5 Oil Recovery Rate

The shape of oil recovery curve in the Fig. 17 is an indication of the oil recovery rate change. In most cases of surfactant flooding, the phenomena of oil recovery increased fast within the pore volume of 1.5 PV and then getting stable indicates the surfactant penetration was improved by surfactant driving process.

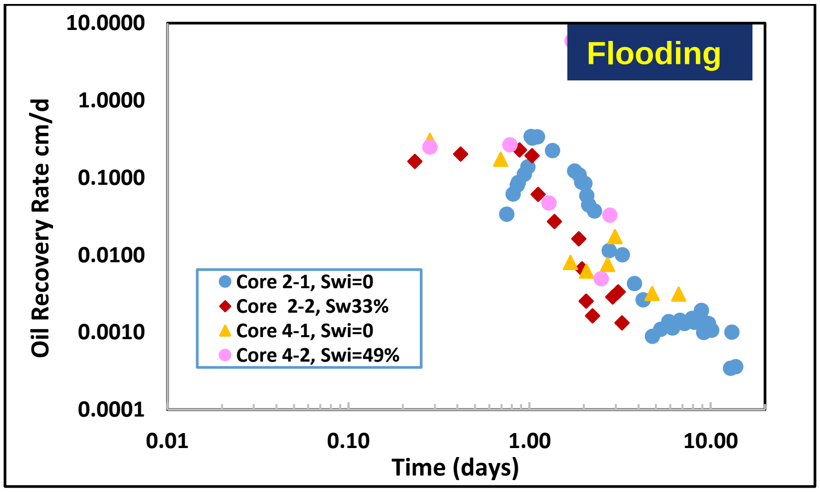


Fig. 30 Oil Recovery Rate by Surfactant Flooding

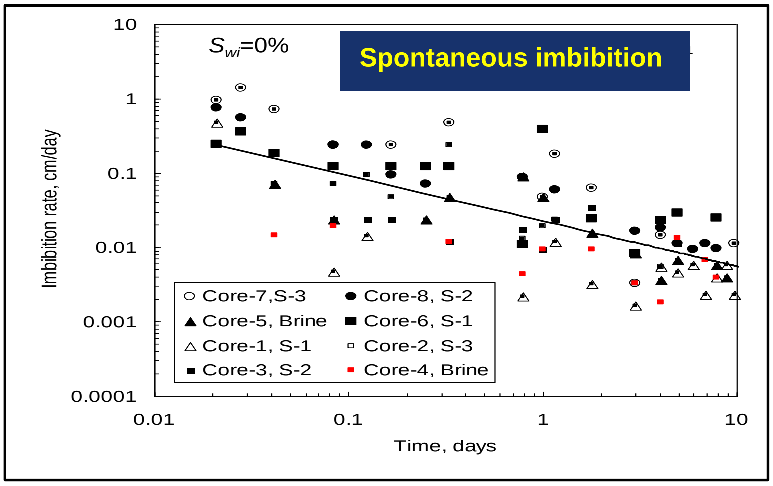


Fig. 31 Oil Recovery Rate by Spontaneous Imbibition
Wang, Zhang, and Butler (2015)

The recovery rate change also can be depicted by oil recovery rate vs. time as shown in Fig. 30. From the laboratory observation, the flooding process needs some time (1-2 days in this study) to push the oil out with overburden pressure existence at the beginning, with the penetration of surfactant formulation through rock matrix, the oil recovery rate reached the peak quickly, then decreased rapidly within a certain time. On the contrary, in our previous study (Wang, Zhang, and Butler 2015), the oil recovery rate of surfactant spontaneous imbibition showed a different trend (Fig. 31). During the spontaneous imbibition, the oil recovery was driven by capillary force and gravity drainage, it responded quickly at the beginning (in 24 hours). However, imbibition rate is inversely proportional to a square characteristic length. It took a longer time to recover the oil out. Therefore, the forced imbibition/flooding could speed up the oil recovery.

4.2 Surfactant Flooding Coupled with Acidizing Treatment

The results in this part consist of four sections. The mineralogy of the rock is described in the first section. The acid reaction and rock solubility are present in the following section. The third section demonstrates the chemical formulation aging test. The chemical formulation flooding coupled with acidizing is discussed in the fourth section.

4.2.1 Rock Mineralogy Study

The mineralogy of 16 rock samples at different depths from two wells was examined by XRD. As Table 4 shows, the rock matrix was made of 26.9 - 69.7wt% of carbonate minerals with an average of 37.6 wt%. In which, dolomite is 8.5 -36.0wt% with an average of 21.8 wt%, calcite is 5.4 - 55.2wt% with an average of 15.8%. Other minerals include: quartz 15.4-38.0 wt%, clay and mica were in range of 5.8-26.4 wt%, feldspar 4.9 -17.7 wt%. Total organic carbon (TOC) was measured by Weatherford SRA Source Rock Analyzer. Based on the measurement, the TOC of the samples was ranged from 0.42 – 1.48 wt%. The above measurement and analysis results are consistent with the literature reported previously (Meissner 1978; Pitman, Price, and LeFever 2001). As reported, the Middle Bakken is a light to medium-gray, interbedded sequence of siltstones and sandstones with small amount shale to dolomitic fine-grained siltstone and sandstone to silty dolomite.

Table 4 Mineralogy of 16 Middle Bakken Samples (wt%)

NO.	**Depth (ft.)**	**Quartz** SiO_2	**Dolomite** $CaMg(CO_3)_2$	**Calcite** $CaCO_3$	**Clay+Mica**	**Feldspar**	**Other minerals**	**Total Carbonate**
1	10466.5	16.9	8.5	41.7	5.8	17.7	9.4	**50.2**
2	10479.5	38.0	25.0	5.4	13.5	14.2	3.9	**30.4**
3	10482.0	36.0	15.6	13.3	9.3	15.4	10.4	**28.9**
4	10615.5	27.0	36.0	7.1	18.0	9.5	2.4	**43.1**
5	10622.6	30.0	25.0	12.0	17.8	9.0	6.2	**37.0**
6	10623.0	15.4	14.5	55.2	8.0	5.7	1.2	**69.7**
7	10623.9	26.8	26.6	14.3	16.3	7.4	8.6	**40.9**
8	10624.2	28.9	25.1	12.3	20.5	4.9	8.3	**37.4**
9	10629.0	23.5	22.3	7.0	25.3	17.6	4.3	**29.3**
10	10630.4	23.0	11.7	36.0	18.3	7.5	3.5	**47.7**
11	10632.9	37.5	24.4	6.5	11.3	14.5	5.8	**30.9**
12	10632.9	32.6	28.2	6.8	18.3	11.1	3.0	**35.0**
13	10636.3	29.0	25.0	6.1	10.6	15.0	14.3	**31.1**
14	10639.5	31.0	19.9	7.0	26.4	13.9	1.8	**26.9**
15	10641.5	35.0	19.3	8.1	21.8	14.8	1.0	**27.4**
16	10644.5	33.0	21.1	14.2	14.3	15.4	2.0	**35.3**

4.2.2 Acid Reaction and Solubility Study

In order to study the solubility of the acidic solution, rock sample was pulverized into fine grains. The powdered sample was used in this study contains an average of 31.1wt% of carbonate minerals (sample #13 in Table 4). Based on the experimental result, we observed that the reaction between acid and carbonate caused a weight loss of rock (powder sample) and produced other compositions include CO_2, Ca^{2+}, and Mg^{2+}. As Table 5 shows, acid dissolved 26.0 wt%-28.0 wt% of the rock based on ICP-MS measurement. The total dissolved powder sample was 31.2 wt% - 33.4 wt%. Therefore, the dissolved carbonate mineral accounted for 78.8-88.9 % of the total dissolved sample. It suggests that the rock rich in carbonate can be dissolved in acidic solution, and the weight loss caused mostly by acidizing treatment. Furthermore, Fig. 32 shows the chemical formulations of acid and surfactant solution had higher dissolution than the acid alone when acid content was 0.5 wt% and 1.0 wt%. However, when acid content was 2.0 wt% (Case 3 & 6), the solubility of chemical formulations (acid and surfactant solution) and acidic solution alone were very close and lower than that of acid content of 0.5% or 1.0%. As the results, we will use 0.5-1.0 wt% acid to perform the experiments in the following section.

Table 5 Acid Reaction and Weight Loss

Case	**Chemical components**	**Weight Loss by carbonate dissolution**	**Total weight loss**	**Carbonate dissolution/ Total weight loss**	**PH (initial)**	**PH (final)**
1	0.5% OA	26.0%	31.2%	83.2%	2.52	4.47
2	1.0% OA	26.0%	33.0%	78.8%	2.31	3.86
3	2.0% OA	27.5%	32.0%	86.0%	2.13	3.47
4	0.5% OA + 0.1% AES	28.0%	31.5%	88.9%	2.62	4.66
5	1.0% OA + 0.1% AES	27.7%	33.4%	83.1%	2.43	3.9
6	2.0% OA + 0.1% AES	27.6%	31.6%	87.2%	2.22	3.52
7	4% NaCl (Blank/control)	1.5%	9.0%	16.8%	6.65	8.08

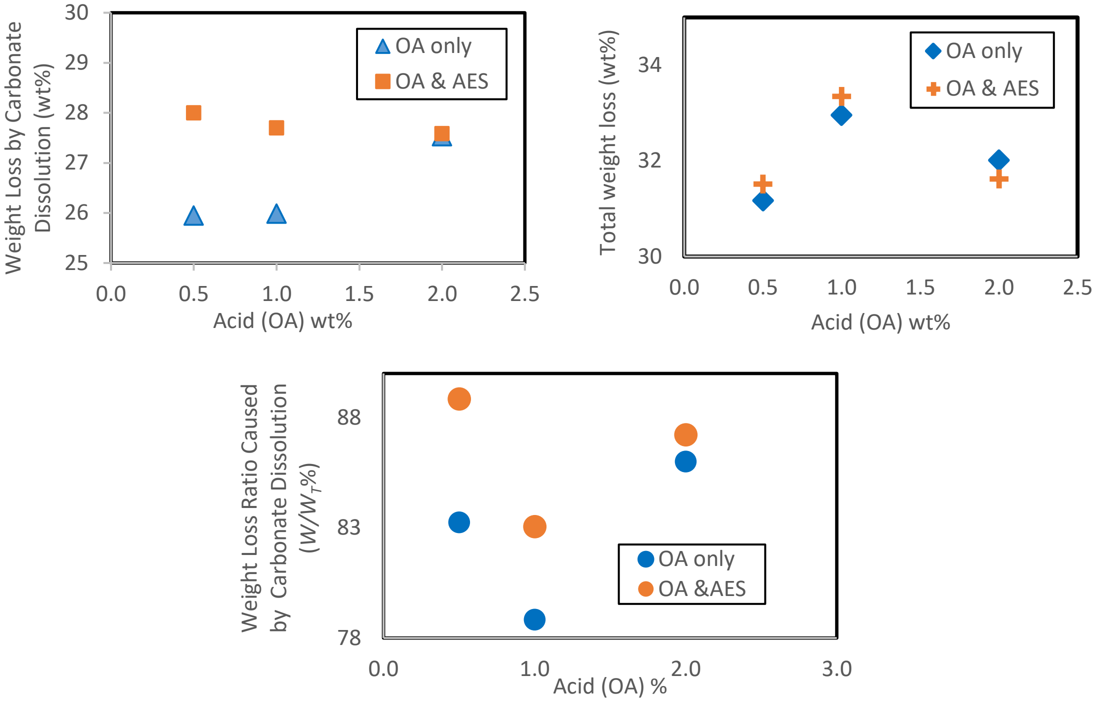


Fig. 32 Rock Weight Loss by Different Acid Concentration
(a) weight loss by carbonate dissolution (wt%) (b) total weight loss (wt%)
(c) weight loss ratio caused by carbonate dissolution (w/w_T%)

Other interesting phenomena also were observed: when we centrifuged the reacted mixture of rock powder and acidic solution at 5000 rpm for 1 hour, we observed that for those mixtures without surfactant AES (case 1-3), the solid phase and liquid phase could not be separated, need an additional centrifuge at 10000 rpm for 10 min. On the contrast, the mixture with surfactant AES (Case 4-6) could be completely separated (Fig. 33). The mixture does not contain neither acid nor surfactant has a slightly turbidity between the above two groups.

In a summary, the Middle Bakken is a carbonate-rich formation, in the studied sample, carbonate minerals account 31.1 wt% of the rock matrix. The selected organic acid (0.5-1.0 wt%) can dissolve 32.3±1.1 wt% of the Bakken powder sample, in which 83.8±5.0 % are dissolved carbonate minerals. It suggests that the rock rich in carbonate can be dissolved by acidic solution quickly if they can contact adequately. Furthermore, the chemical formulations of acid and surfactant have higher dissolution than the acid alone.

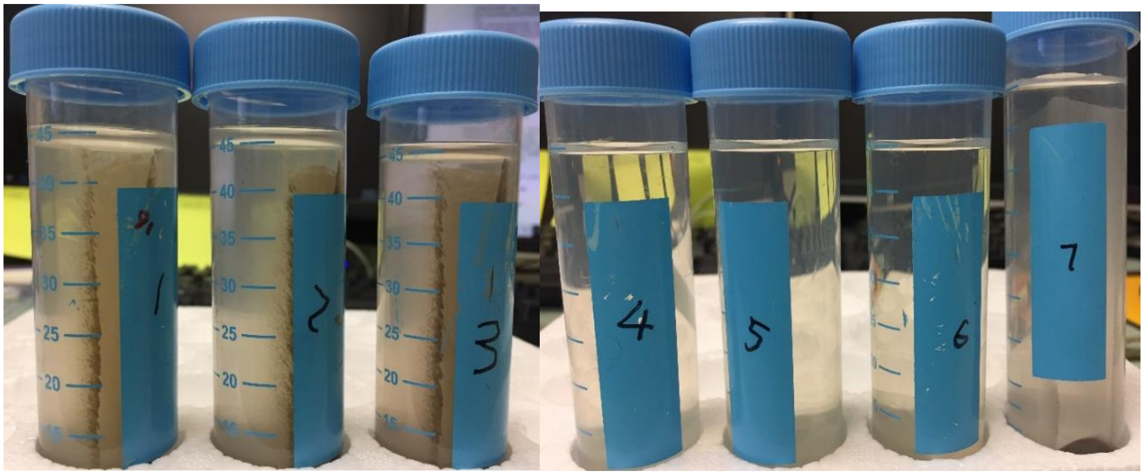


Fig. 33 After Acid Reaction- to separate the mixture by centrifuge

4.2.3 Rock Segments Aging Test

4.2.3.1 Aging Test Analysis.

Five rock segments were cut from a same rock slab, with which the carbonate content was 31.1%. These rock segments were put into pressure cells with brine, acidic solution or chemical formulations, then placed into oven at 115°C for 5 days aging. The aging test before and after the treatment, as Fig. 34 demonstrated, cases: 1) rock segment was aged with brine alone (18.24 wt%). After then, the solution was clear before and after treatment. No oil produced. 2) Rock segment was aged with OA (0.5 wt%) solution. The result showed the solution was clear before and after treatment. No oil produced. 3) Rock segment was aged with the AES (0.1 wt%) solution. Solution hazed before and clearer after treatment as seen. An oil rim produced on the top of solution. No acid reaction. 4) Rock segment was aged with a blend solution of OA (1.0 %) and AES (0.1 wt%). After aging, the solution hazed before and clearer after treatment. An oil rim produced on the top of solution indicated acid reaction occurred. 5) Rock segment aged at a blend solution of OA (1.0 %) and AES (0.1 wt%). Solution was hazed before and clearer after treatment. The result also demonstrated the acid reaction was occurred due to the phenomena of an oil rim produced on the top of solution. 6) Control of chemical formulation. A blend of OA (1.0 %) and AES (0.1 wt%) in brine without the rock segment. Solution hazed before and clearer after treatment.

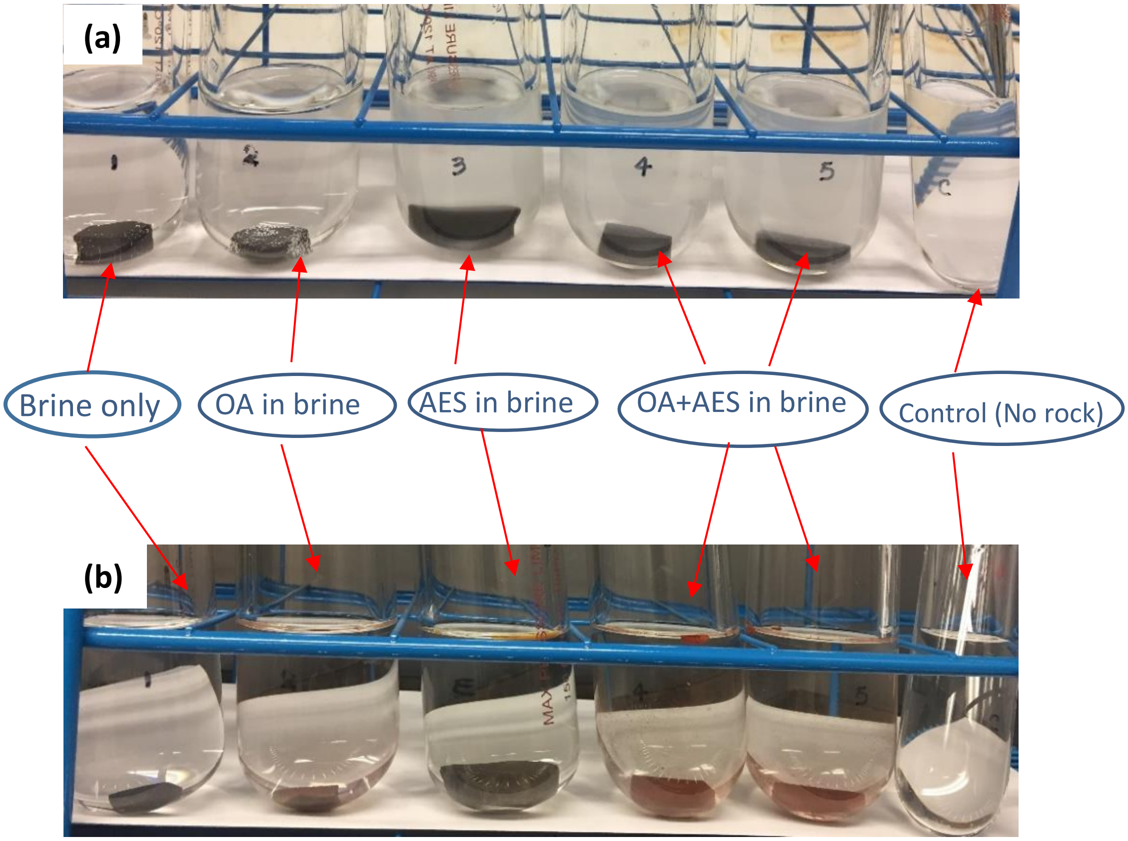


Fig. 34 Rock Segments Aging Test
(a) Rock segments with solutions before aging test (b) rock segments with solutions after aging test

Table 6 Carbonate Dissolution at Different Conditions

Case	Chemical Components	Produced Oil	Acid reaction	Weight loss by Acidizing	Total weight loss	Carbonate dissolution/ Total weight loss	PH (Initial)	PH (Final)
1	Brine (18.24%)	No	No	NA	1.1%	NA	6.16	6
2	0.5% OA	No	Yes	5.3%	10.1%	52.5%	1.89	4.75
3	0.1 % AES	Yes	No	NA	2.4%	NA	7.84	5.8
4	1.0% OA + 0.1% AES	Yes	Yes	3.5%	8.8%	39.8%	1.9	4.27
5	1.0% OA + 0.1% AES	Yes	Yes	5.5%	10.5%	52.4%	1.87	4.27
6	1.0% OA + 0.1% AES (no rock sample)	No	No	NA	NA	NA	1.9	1.63

As Table 6 showed, in the case of 18.2% brine only (case 1), there is no oil produced and the rock segment weight loss is just 1.1 wt%; in the case of 0.5 wt% organic acid (Case 2), there is acid reaction, the weight loss is 10.1 wt%, but no oil produced; in the case of 0.1 wt% AES (Case 3), there is oil produced, but no acid reaction, and the weight loss is only 2.4 wt%; in the case of chemical formulations (case 4&5), oil produced, there is acid reaction, and the weight loss are 8.8 wt% and 10.5 wt% respectively. The results suggest that with the surfactant presence, oil can be produced from the rock segments, and with the presence of organic acid, carbonate minerals can dissolve in the solution. Compared with powdered sample weight loss of 26.0-28.0 wt% by acidizing, the aging test weight loss by acidizing was only 3.5-5.5%. Furthermore, the powdered sample weight loss by acidizing was accounted 78.8-88.9 % of the total weight loss, while the aging test was 39.8-52.5% (Cases 3 to 5). The above results indicated that the acid reaction level depends on the rock homogeneity (permeability distribution and mineral composition distribution). In other words, this acid reaction was affected by the depths of acidic solution be delivered into the rock matrix.

4.2.3.2 SEM Images and EDS Mapping Analysis.

Theoretically, acid reaction with carbonate in rock will result in microstructural changes: creation of pores and cavities, increase in surface roughness, and channel development. In order to compare these changes from the pre- and post-treatments, the rock segments were carefully positioned and marked before treatment. With these markers, we could easily relocate the same image area in the post-treatment samples. Figs. 35-38 showed direct visual comparison of rock surface at the times of pre- and post-treatments in the same area at various conditions. The SEM images for the same area demonstrated the changes of microstructures at the times of pre- and post-treatments, and this was consistent with the observations in the aging test.

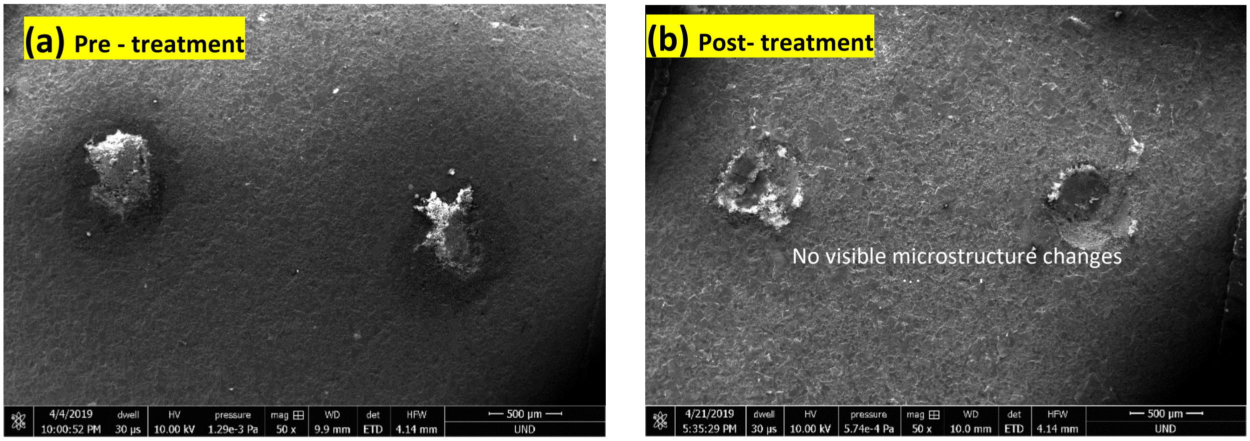


Fig. 35 In-situ SEM Comparison of case 1 (Brine only): microstructures of rock segment at the times of pre and post-treatments in the same area. (a) Pre-treatment; (b) Post-treatment. Brine did not change the rock microstructures.

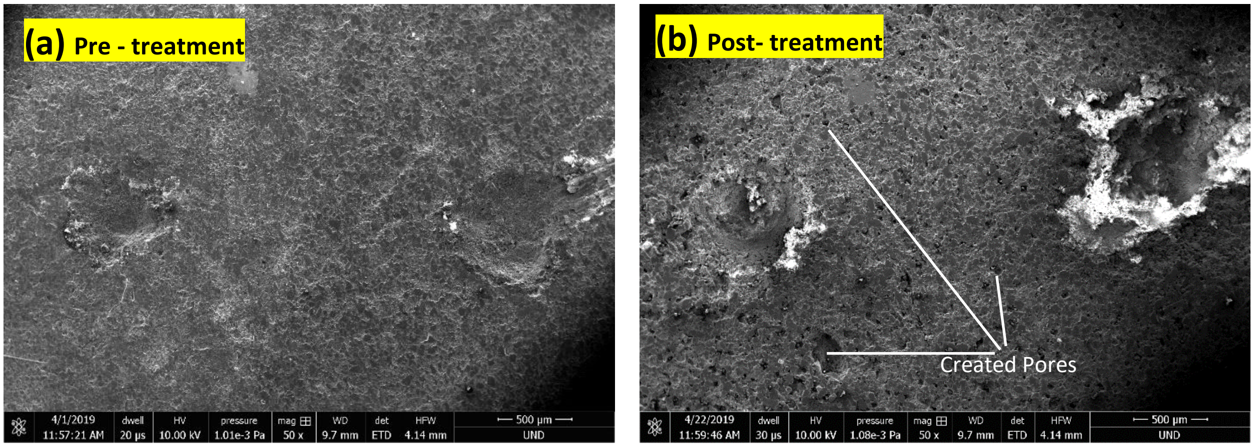


Fig. 36 In-situ SEM Comparison of case 2 (OA 0.5 wt%): microstructures of rock segment at the times of pre and post-treatments in the same area. (a) Pre-treatment; (b) Post-treatment. Acid solution creates cavitiew and roughness at the rock surface.

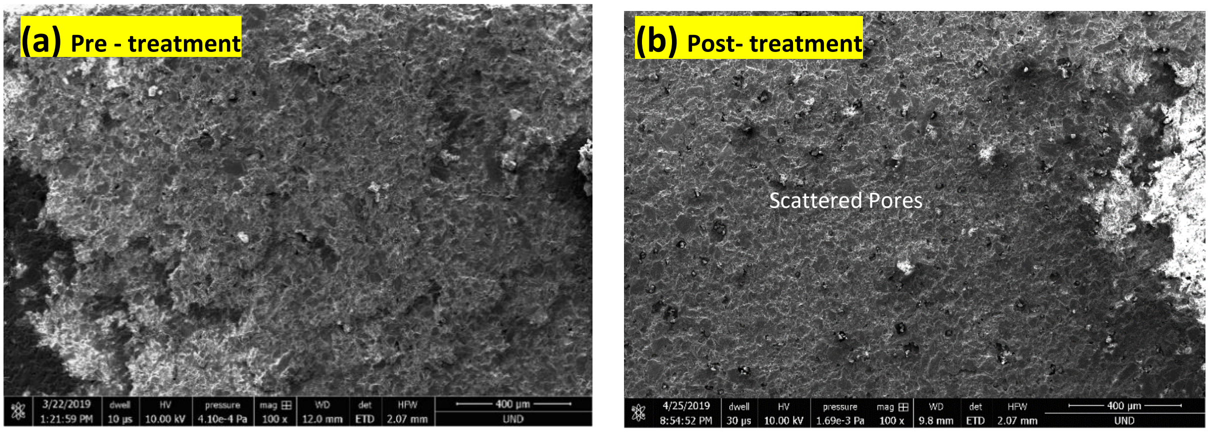


Fig. 37 In-situ SEM Comparison of case 3 (AES 0.1 wt%): microstructures of rock segment at the times of pre and post-treatments in the same area. (a) Pre-treatment; (b) Post-treatment. Surfactant solution alone removes some soluble fine grains, left scattered small holes.

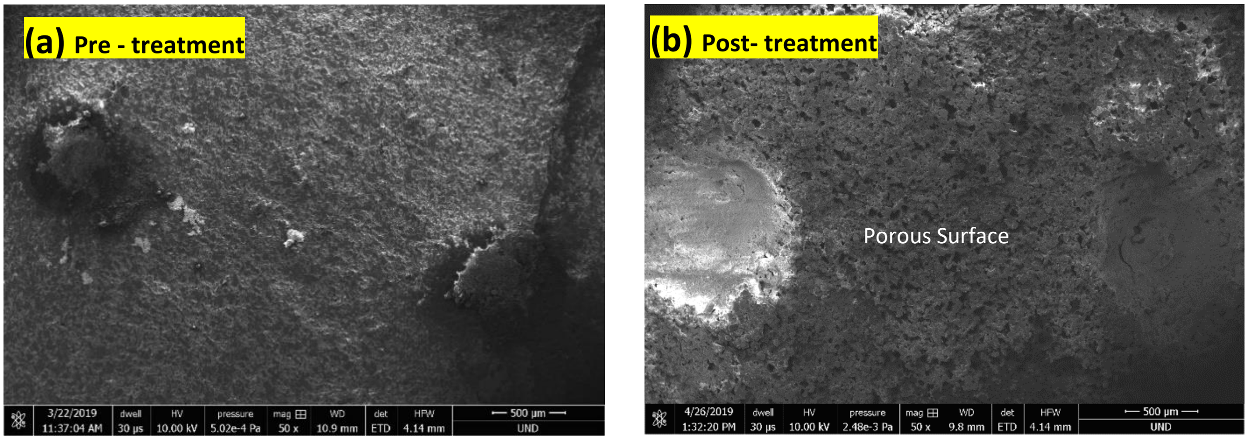


Fig. 38 In-situ SEM Comparison of case 4 (chemical formulation): microstructures of rock segment at the times of pre and post-treatments in the same area. (a) Pre-treatment; (b) Post-treatment. Chemical formulation dissolves the carbonate minerals, creates cavities and roughness

In order to have a close visual comparison on the changes of microstructure, a rock segment treated with chemical formulation in the aging test (case 4) was presented here. Figs. 39-41 showed the view of the same area at the times of pre- and post-treatment at 50, 500 and 10,000 magnification. In the images of 50x (Fig. 39.), the surface of the rock segment became very porous after the aging test. In the images of 500x (Fig. 40), cavities, channels, and roughness of the rock segment were observed after the aging test. Images of 5000x, the SEM image (Fig. 41a) and EDS mapping (Fig. 41c) before treatment clearly displayed a carbonate-rich (CB-rich) area and a silicate area. In the same areas after treatment (Fig. 41b), silicate area retained the original shape, but the acid etched surface and displayed more roughness due to the scattered carbonate mineral dissolution. The CB-rich area was completely altered due to the reaction with acid. Cavities, channels, and roughness were created as observed in the images. However, a negative result when the surrounding carbonate minerals dissolved, the inert minerals or some of them may be moved and relocated, and then block the channels, for example.

The analysis of SEM images and EDS mapping indicated: carbonate-rich reservoir rocks reacted with acid, pores, cavities, channels and roughness were created by carbonate mineral dissolution. These microstructure changes may increase porosity and permeability in the rock matrix, thereby increasing fracture conductivity. The studied results agreed with research findings of Wu and Sharma (2017).

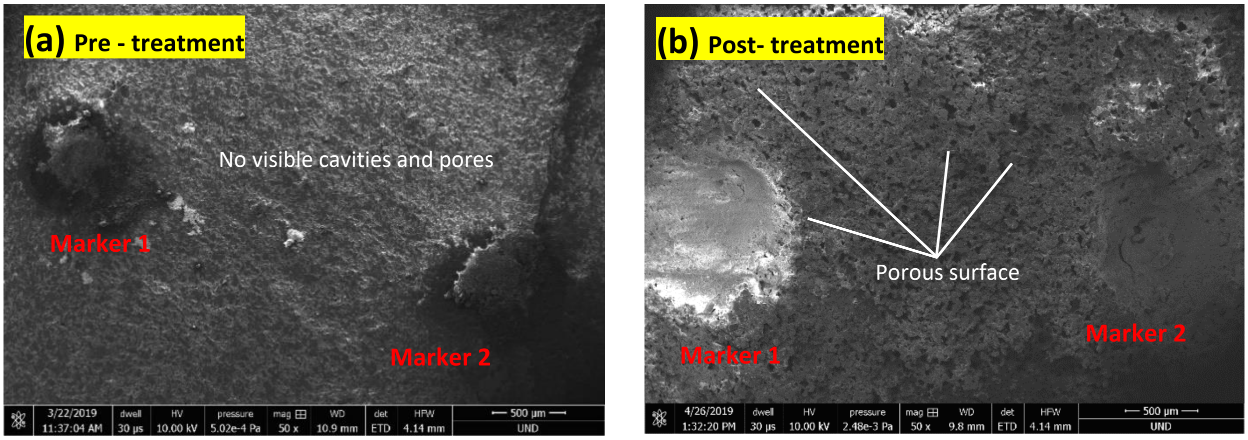


Fig. 39 SEM Comparison of Rock Eegment at 50x

The two dots were the markers used to position the studied area: (a) Pre-treatment: the surface is relatively plain. No visible pores and cavities. (b) Post-treatment: the surface became very porous.

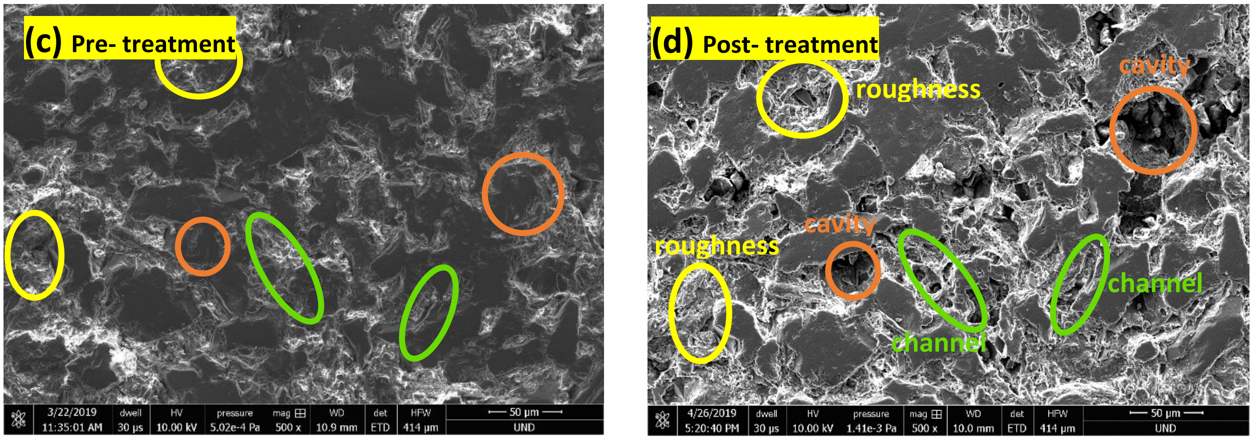


Fig. 40 SEM Comparison of Rock Segment at 500x

(a) Pre-treatment: the surface was polished and no obvious cavities. (b) Post-treatment: the surface became porous and rough. Visible pores, cavities, roughness, and channels can be noticed in the same areas.

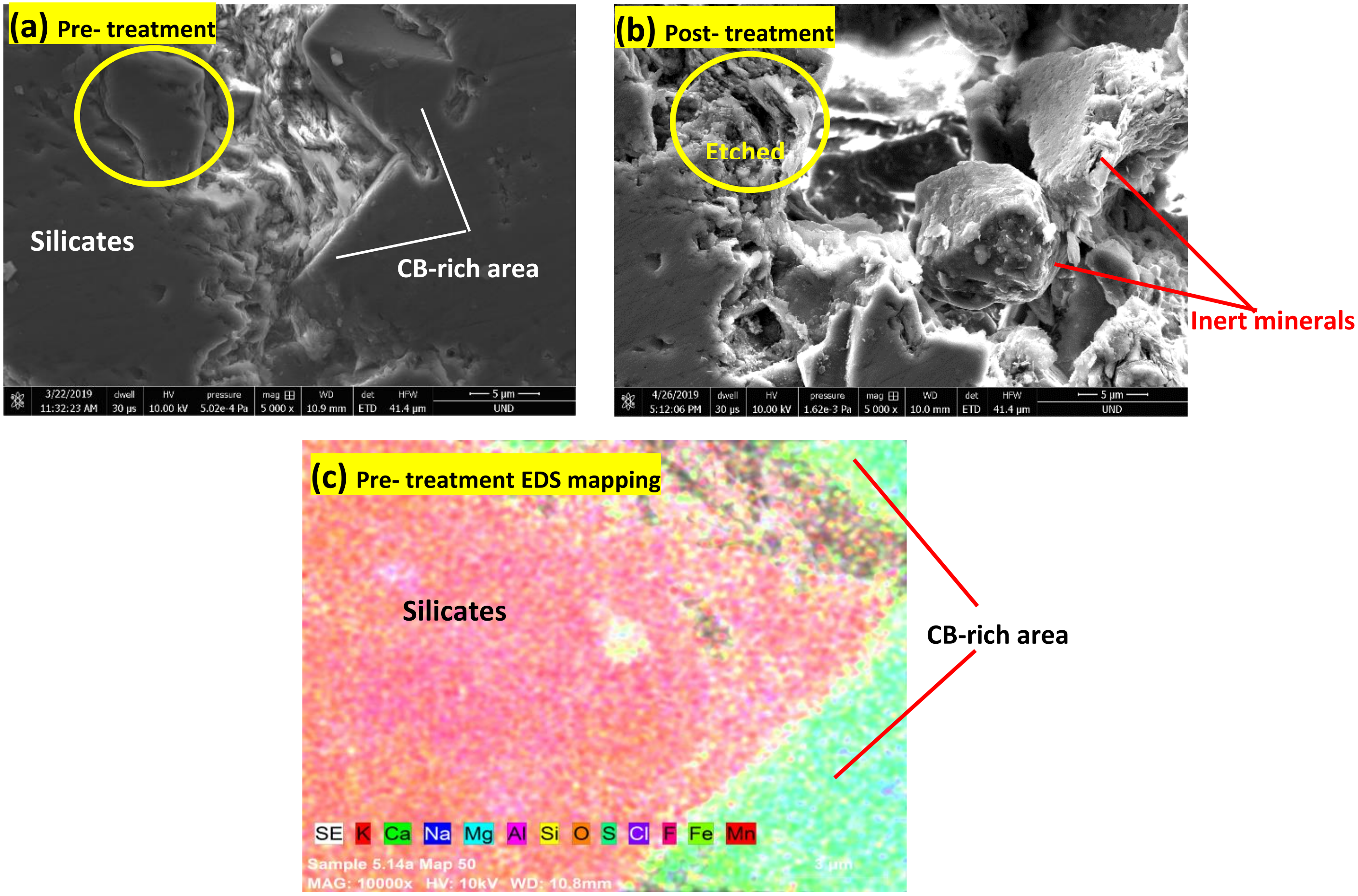


Fig. 41 SEM & EDS Mapping Comparison of Rock Segment at 5000x
(a) Pre-treatment: the light spot was consisted of a CB-rich area and silicates area, and some transition area. (b) Post-treatment: carbonate dissolution created cavities and channels on the carbonate-rich area, and also etched the silicates area on the left. (c) Pre-treatment mapping: EDS mapping shows the right side was a CB-rich area, while left side was silicates.

4.2.4 Chemical Formulation Flooding Study

Chemical formulation flooding was conducted to study the interaction of rock plug with acidic solution coupled with surfactant formulation by flooding test, as well as the effects on porosity, permeability, and oil recovery. Four core samples used for these experiments came from the Middle Member of the Bakken Formation in Well #18226 and well #23285 in North Dakota. The images of rock plugs were shown in Fig. 42. Except sample 4, all other three rock plugs contained visible fractures. Description of rock plugs were listed in Table 7. Test conditions for each sample were shown in Table 8. All the cores plugs were cleaned by Dean-Stark with toluene and methanol, dried and vacuumed before core flooding.

Table 7 Description of Rock Plugs

Sample ID	Well #	Depth ft.	Diameter mm	Length mm	Porosity % (to water)	Total Carbonate %	Clay %
1	18226	10622.6	1”	55.5	8.95	37.0	12.0
2	18226	10629.0	1”	67.0	6.94	29.3	21.1
3	18226	10636.3	1”	67.6	9.06	31.1	10.6
4	23285	10479.5	1”	49.4	6.71	30.4	10.7

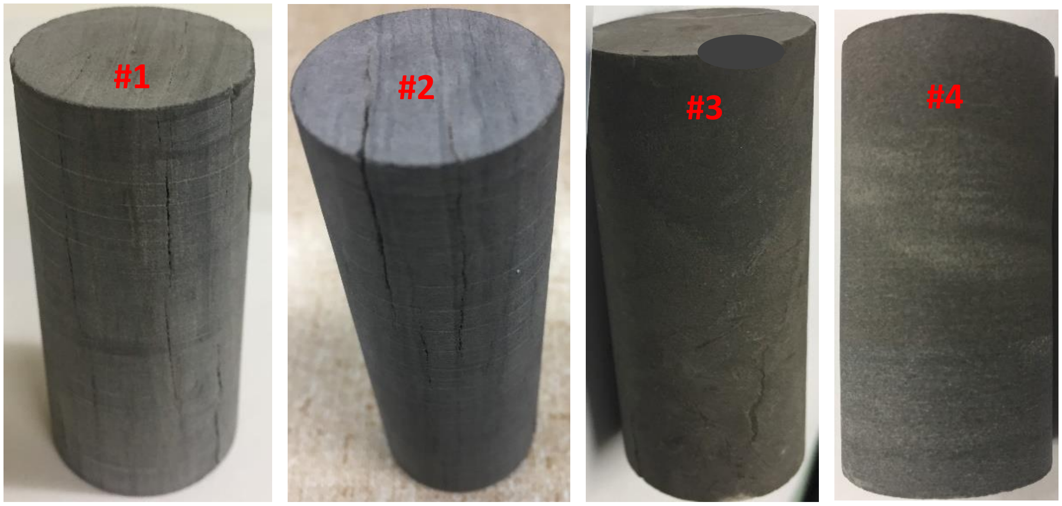


Fig. 42 Images of Rock Plugs for Chemical Formulation Flooding

Table 8 Chemical Formulation Flooding Conditions

Sample ID	Procedure	Flush Fluid	Chemical Formulation
1	Brine pre-flush → CF flooding → Brine post -flush (no oil involved)	4% brine	1.0 % OA + 0.1% AES in 4% brine
2	Brine pre-flush → Oil Saturation → CF flooding → Brine post -flush	4% brine	1.0 % OA + 0.1% AES in 4% brine
3	Brine pre-flush → Oil Saturation → CF flooding → Brine post -flush	4% brine	1.0 % OA + 0.1% AES in 18.2% brine
4	Brine pre-flush → Oil Saturation → CF flooding → Brine post -flush	4% brine	1.0 % OA +0.1% AES in 18.2% brine

4.2.4.1 Flooding Effluent

Effluent of sample #1 during the CF flooding was analyzed to study the interaction of rock plug with acidic solution. Chemical formulation was injected at 0.505 ml/hr. through the core plug in the Hassler coreholder. The pore volume (PV) of the sample #1 is 2.58 ml. Effluent was collected when the injected fluid at times of 4.7 PV, 8.6 PV and 13.5 PV, respectively. The PH value and concentration of Ca^{2+} and Mg^{2+} before and after the flooding are listed in Table 9 and Fig. 43 shows the concentration of Ca^{2+} and Mg^{2+} in the effluent. Because there were no Ca^{2+} and Mg^{2+} injected during the process, the Ca^{2+} and Mg^{2+} should come from the fluid-rock interaction by carbonate dissolution during flooding process. In addition, calcite was more active than dolomite to react with the acid. This Bakken core consisted of 25.0% dolomite, and 12.0% calcite. However, the concentration of Ca^{2+} in the effluent was much higher than Mg^{2+}.

Table 9 Ca^{2+} & Mg^{2+} Concentration in Flooding Fluid & Effluent

Injected PV	pH		Ca^{2+} (ppm)		Mg^{2+} (ppm)	
	Initial	Effluent	Initial	Effluent	Initial	Effluent
2.95 - 4.7	2.35	4.52	33.53	2467.02	2.01	377.32
4.7 - 8.6	2.35	4.93	33.53	2831.95	2.01	434.65
8.6 - 13.5	2.35	4.75	33.53	2747.59	2.01	439.40

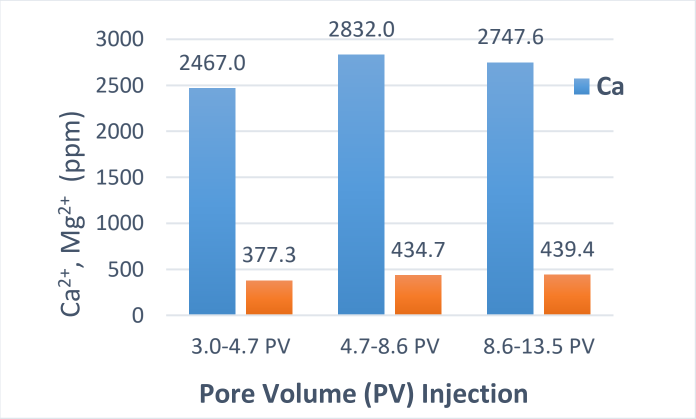


Fig. 43 Concentration of Ca^{2+} and Mg2+ in Effluent

4.2.4.2 NMR Porosity Study

The goal of this experiment was to evaluate the effect of chemical formulation on rock porosity by flooding test. The results are listed in Table 10. The initial porosities ranged from 6.71% to 9.06%. After chemical formulation flooding, NMR porosities went up to 7.51%-10.03%. The increment was 7.6%-13.3%. The porosity and pore distribution of each sample had been discussed individually.

Table 10 Effect of CF Treatment on NMR Porosity

Sample ID	NMR Porosity %		increment
	Pre-treatment	Post-treatment	
1	8.95	9.63	7.6%
2	6.94	7.74	11.5%
3	9.06	10.03	10.7%
4	6.71	7.51	11.9%

1. Core sample #1

As NMR tested result shows, the initial porosity was 8.95%, and the post-treatment porosity went up to 9.63%. There was a 7.6% increment after the chemical formulation flooding process. In Fig. 44, only one peak was observed in pre-treatment NMR T2 spectrum (dashed blue line). The T2 relaxation time was mainly distributed between 0.1ms and 10ms indicates the small pore throats present in the rock sample. After the chemical formulation flooding process, the NMR T_2 spectrum (red line) demonstrated an adjacent bimodal peak. The left wing moved slightly toward left indicates that some smaller pores were formed. In addition, the new right peak was mainly distributed between 10ms to 100ms. This indicates that the medium pores were created, or the small pores were connected to larger pores during the flooding process.

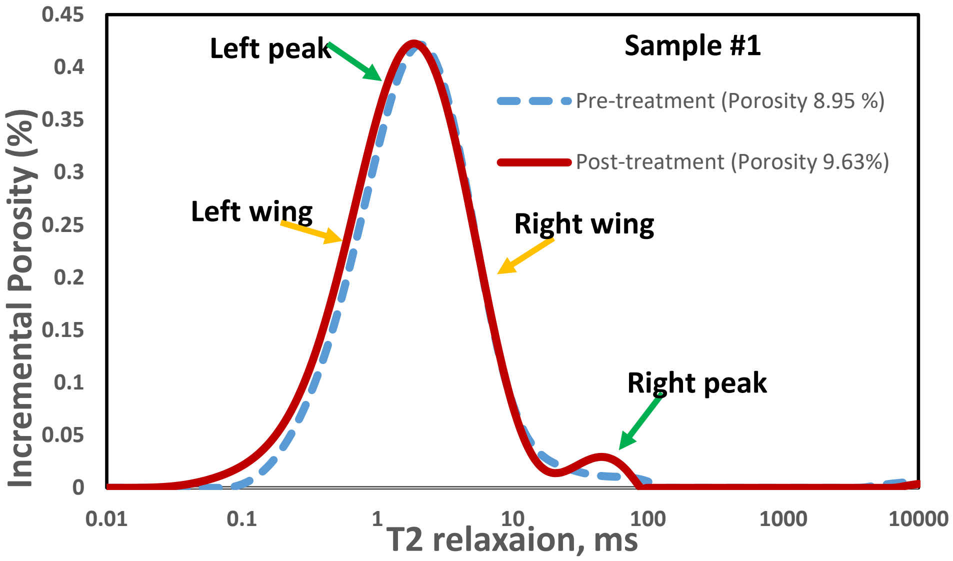


Fig. 44 NMR T2 spectrum of Core plug #1

2. Core sample #2

The NMR tested result shows the porosity was 6.94% by pre-treatment, and the porosity was 7.86% using post-treatment. There was a 11.5% increment after the chemical formulation flooding process. As Fig. 45 shown, the NMR T2 spectrum (dashed blue line) of pre-treatment was an adjacent bimodal peak. The left peak T2 relaxation time was mainly distributed between 0.1ms and 10ms indicates the small pore throats present in the rock sample. The right peak T2 time was distributed between 10ms to 100ms implies the larger pore throats present in the rock sample. The larger area of the left peak suggests small pores are dominant in the sample. After the chemical blend flooding process, the NMR T_2 spectrum (red line) became an isolated bimodal peak. The left peak of NMR T_2 spectrum (red line) moved toward left and a higher peak between 1-10 ms indicate new smaller pores present or primary pores were compacted or destroyed. The small isolated right peak suggested the medium pores were compacted or destroyed during the flooding process.

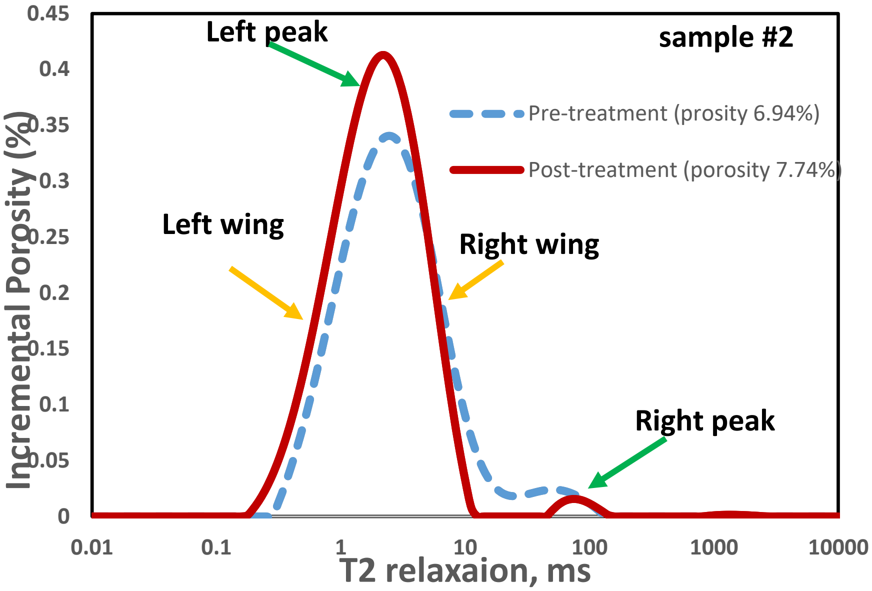


Fig. 45 NMR T2 spectrum of Core plug #2

3. Core sample #3

As NMR tested result shows, the initial porosity was 9.06%, and the post-treatment porosity went up to 10.03%. There was a 10.7% increment after the chemical formulation flooding process. In Fig. 46, the isolated bimodal peaks were observed in pre-treatment NMR T2 spectrum (dashed blue line). The left peak T2 relaxation time was mainly distributed between 0.1ms and 10ms indicates the small pore throats present in the rock sample. The right peak T2 time was distributed around 100ms implies the larger pore throats or micron crackers present in the rock sample. The larger area of the left peak suggests small pores are dominant in the sample. After the chemical blend flooding process, the NMR T_2 spectrum (red line) has only one peak with the left wing overlapped with that of the pre-treatment spectrum (blue dashed line). However, the right wing of the peak stretched from 10ms to 100ms. The results indicate that the medium pores were created, or the small pores were connected to the larger pores during the flooding process. But the maximum T_2 time was still less than 200ms.

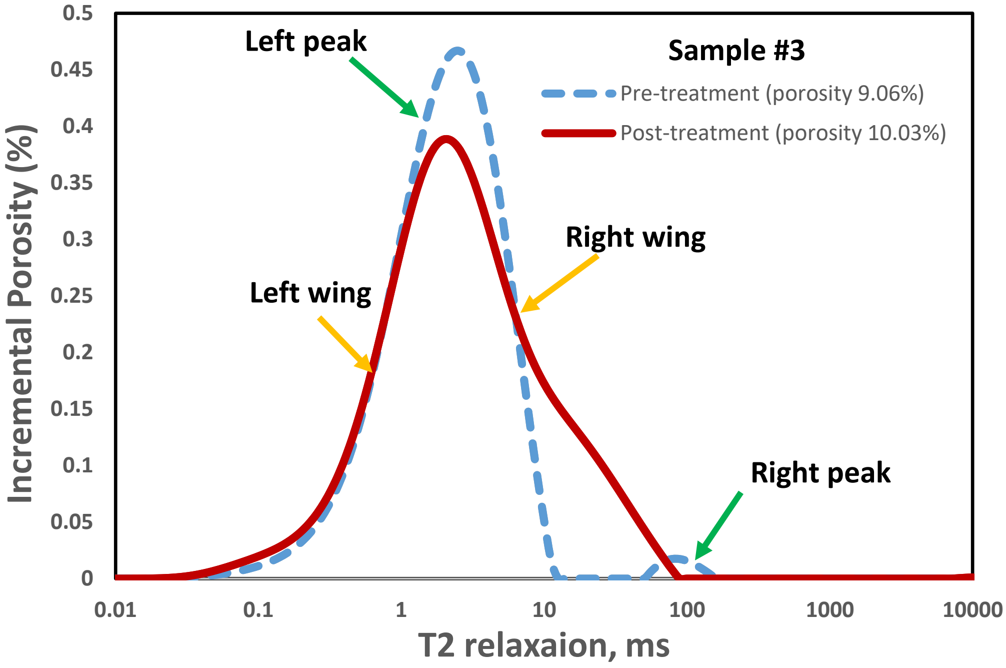


Fig. 46 NMR T2 spectrum of Core plug #3

4. Core sample #4

The NMR test result shows the porosity was 6.71% by pre-treatment, and the porosity was 7.51% using post-treatment. There was 11.9% increment after the chemical formulation flooding process. As Fig. 47 shows, the NMR T2 spectrum (dashed blue line) of pre-treatment had only one peak which distributed between 0.1ms and 20ms. After the flooding process, the T2 spectrum became to an adjacent bimodal peak which left peak moved toward left and a lower peak implies that more small pores formed. In addition, the new right peak suggests the medium pores were created, or the small pores were connected to the larger pores during the flooding process.

In a summary, the NMR porosities of all four core plugs increased after the chemical formulation flooding. The increment was 7.6%-13.3%. From the discussion above, we concluded that the increased porosity resulted from the interaction of core samples and chemical formulation. During the flooding process and acidizing, small pores were generated in rock sample and in some way small pores were connected to form larger pores or micro fractures.

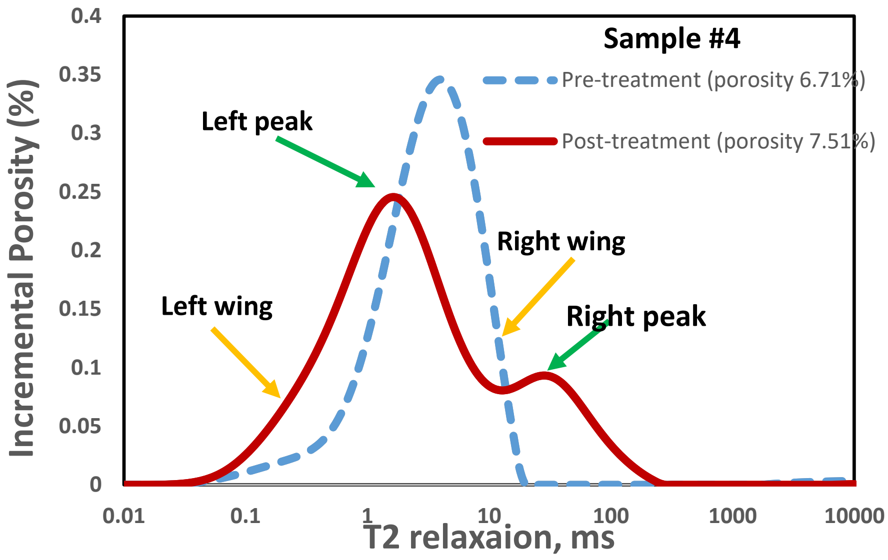


Fig. 47 NMR T2 spectrum of Core plug #4

4.2.4.3 Permeability Study

The goal of this experiment was to evaluate the impact of chemical formulation on rock permeability by flooding test. The pre and post-treatment permeability to brine were calculated by Darcy's Law (Eq.3):

$$Q = \frac{kA\Delta P}{\mu L} \tag{3}$$

permeability *k* was defined in Eq. 4:

$$k = \frac{Q\mu L}{A\Delta P} \tag{4}$$

where

k, permeability, darcy

Q, flow rate, mL/s

μ, fluid viscosity, cP

L, length of core plug, cm

A, cross-section area of core sample, cm^2

ΔP, pressure gradient, atm.

The results are listed in Table 11.

Table 11 Effect of CF Treatment on Permeability

Sample ID	Pre-treatment permeability μD	Post-treatment permeability μD	Increment
1	2.06	2.40	16.5%
2	3.28	2.08	-36.6%
3	0.64	0.74	15.6%
4	0.074	0.15	102.7%

As table 11 shows, after the chemical formulation flooding, the permeability increased in sample #1, #3 and #4. However, there was a decrease in sample #2. The permeability decreased from 3.28 μD to 2.08 μD. This may be explained by the discussion of NMR porosity in Fig. 45. After the chemical formulation flooding process, the NMR T_2 spectrum (red line) became an isolated bimodal peak. The left peak of NMR T_2 spectrum moved toward left and a higher peak between 1ms-10ms present indicated new smaller pores occurring or primary pores were compacted or destroyed. The small isolated right peak suggested the medium pores were compacted or destroyed during the flooding process. And this may be related to the higher clay content in sample #2. As shown in Table 7, Compare to sample #1 (clay of 12.0%), #3 (clay of 10.6%), and #4 (clay of 10.7%), sample #2 had a clay content of 21.1%. The higher clay content may result in swelling to compact or destroy the rock matrix pores.

4.2.4.4 Oil Recovery Study

The oil was recovered during the CF flooding process. Sample #1 was excluded in this experiment because it was used for flooding effluent analysis, there was no oil involved. Fig. 48 shows the oil recovery factor by time for different samples. It was observed that for the higher permeability cores (sample #2 and #3), the peak oil recovered was relatively quick. Sample #2 began produceing oil after 18 hr. of flooding/1.3 pore volume (PV) injection; sample #3 began recovering oil after 42 hr. of flooding/0.70 PV injection. However, with the lower permeability core (sample #4), the peak oil produced was relative slow, core plug began producing oil after 98 hr. of flooding/4.6 PV injection. The oil recovered by CF flooding for sample #2, #3, and #4 was 81.1%, 77.3% and 27.4%, respectively. Fig. 49 demonstrates the oil recovery rate by flooding process and spontaneous imbibition process. The chemical formulation flooding needs some time to push the oil with overburden pressure existence at the beginning, with the penetration of surfactant formulation into rock matrix, the oil recovery rate reached the peak quickly. Compared with surfactant spontaneous imbibition process in our previous research (Wang, Zhang, and Butler 2015), the oil recovery was driven by capillary force and gravity drainage, it responded quickly at the beginning. However, the imbibition rate is inversely proportional to a squared characteristic length, it took a longer time to recover the oil out. Surfactant flooding on a core level does speed up oil recovery a little. But surfactant flooding on a field scale can make oil recovery more efficient.

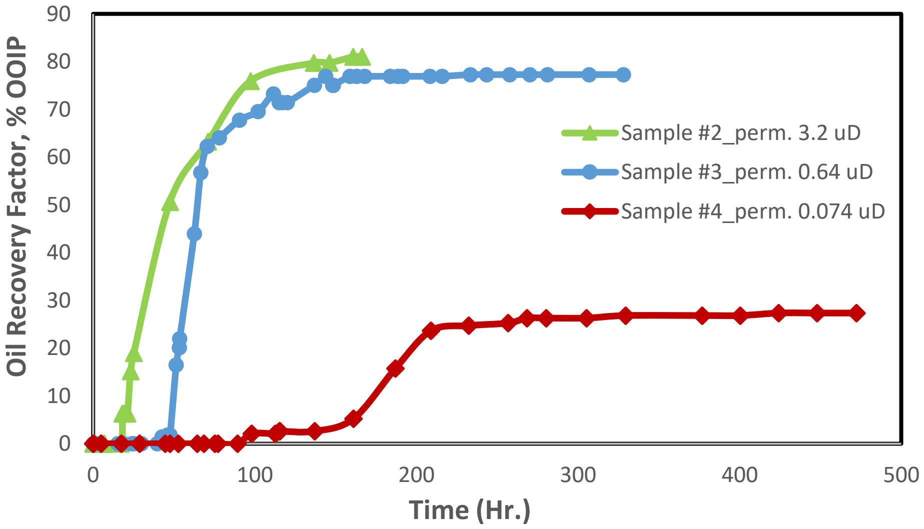


Fig. 48 Oil Recovery Factor with Time by CF Flooding

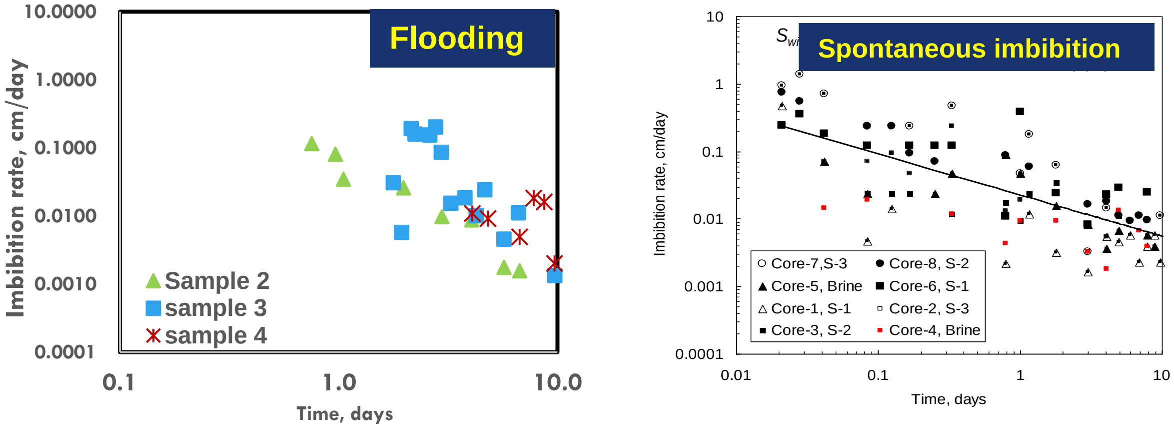


Fig. 49 Oil Recovery Rate by CF Flooding & Spontaneous Imbibition

5. CONCLUSIONS AND FINGDINGS

The forced surfactant imbibition and the combination of surfactant flooding and acidizing treatment were investigated in this study to evaluate the potential of a new approach to improve oil recovery from the Bakken Formation and tight formations. The significant findings and conclusions are summarized as below.

5.1 Forced Surfactant Imbibition

5.1.1 Oil Recovery by surfactant flooding Vs. Brine Flooding

1. In this study, surfactant flooding tests were conducted with three-paired Bakken cores in six cases. The surfactant flooding process for tight rocks with low permeability (10^{-4} md) at various conditions were carefully studied for the first time.
2. Permeability significantly determined the oil recovery in the flooding process. It was observed that the higher permeability cores, the peak oil produced was quick, while with a relative low permeability cores, the peak oil recovered was relative slow. However, the flooding of surfactant formulation benefited the oil recovery. The oil recovery by surfactant flooding ranged from 29.4% to 57.9% of OOIP, while by brine flooding alone was 17.0%. The incremental oil recovery by surfactant flooding was ranged from 12.4 to 40.9%.
3. Our observation shows forced surfactant imbibition (surfactant flooding) for tight rocks with low permeability (10^{-4} md) has good potential for oil recovery enhancement at various conditions.

5.1.2 Effect of initial Water Saturation, salinity, and surfactant concentration

The two cores used for initial water saturation test had a similar level of fractures resulted in a close oil recovery. The initial water had a positive effect (shifting the direction toward water-wet direction) on the wettability of core 2-2 ($S_{wi}\neq0$). So both of the oil extraction rate and the water cut response in Core 2-2 showed a greater response. However, since oil extraction rate is accelerated by an EOR process, the water cut rose back quickly to a high value (> 80%) in a short time. So that the duration of the EOR effect was short.

The comparison of optimal salinity effects on oil recovery were conducted between two cores had similar initial water saturations. The optimum salinity of 10% was previously determined by spontaneous imbibition. However, the core 4-2 flooded with 18.2% salinity recovered higher oil recovery factor than Cores 3-1 with 10% TDS. Here, the permeabilities of Core 3-1 to water was 0.0003 md; and the permeabilities to water of Core 4-2 was much higher: 0.657 md.

Two pairs of core samples (Cores 2-1 & 2-2 and Cores 4-1 & 4-2) were used to investigate surfactant EOR potential on surfactant concentrations. Before surfactant flooding, group one (Cores 2-1 & 4-1) was saturated with brine ($S_{wi\neq}0$), while group two (Cores 2-2 & 4-2) was not ($S_{wi}=0$). Then they were flooded with surfactant at concentration of 0.15% and 0.1%, respectively. Theoretically, as the surfactant concentration increases, more oil could be recovered. However, in group one ($S_{wi=}0$), the ultimate oil recovery of Core 2-1 with AES of 0.15% was just 1.4% greater than Core 4-1with AES of 0.1 %.

These results indicated that (1) fractures apparently played an important role in oil recovery; (2) The ultimate oil recovery was dominated by the permeability distribution heterogeneity or lithology differences in the rock matrix.

5.1.3 Oil Recovery Rate

From the laboratory observation, the flooding process needs some time (1-2 days in this study) to push the oil out with overburden pressure existence at the beginning, with the penetration of surfactant formulation through rock matrix, the oil recovery rate reached the peak quickly, then decreased rapidly within a certain time. On the contrary, during the spontaneous imbibition, the oil recovery was driven by capillary force and gravity drainage, it responded quickly at the beginning (in 24 hours). However, imbibition rate is inversely proportional to a square characteristic length. It took a longer time to recover the oil out. Surfactant flooding on a core level does speed up oil recovery a little. However, on a field scale, surfactant flooding can make oil recovery more efficient.

5.2 Surfactant Flooding couple with Acidizing Treatment

5.2.1 Acid reaction and solubility with Bakken sample

1. The mineralogy study of 16 samples from the Middle Bakken indicated that the studied rocks were rich in carbonate (dolomite and calcite) which accounts 37.6 wt% of rock matrix in an average. The diluted acid solution can dissolve 32.3±1.1 wt% of the Bakken powder sample, in which 83.8±5.0 % are dissolved carbonate minerals. It suggests that the acidic solution is capable of dissolving carbonate minerals quickly if they can contact adequately.
2. The chemical formulations have higher dissolution than the acid alone when acid content was 0.5 wt% and 1.0 wt%, and very close at 2.0 wt%.

5.2.2 Aging Test of rock segments

The solution contain acid reacted with rock segments at reservoir temperature. However, no oil produced when the sample only aged in acid and brine. Oil was produced but no acid reaction when the solution contained only surfactant (AES) in brine. Both acid reaction and recovered oil were observed in the chemical formulation aging test. This indicated that chemical formulation consisted of a surfactant and an organic acid in brine had a synergistic effect on the Bakken samples. In addition, the acid reaction level may depend on the rock homogeneity (permeability distribution or mineral composition distribution).

5.2.3 Effect of Chemical Formulation on the Rock Surface Microstructure

The analysis of SEM images and EDS mapping before and after treatment demonstrated that the carbonate-rich Bakken rock segments reacted with acid. The changes of microstructure were found and visually compared. Pores, cavities, channels and roughness were created by carbonate mineral dissolution on the surface. In other words, the chemical formulation penetrated in and interacted with rock matrix close to the fracture surface enhanced the contact area for the fluid with the rock matrix. However, this contact area enhancement method by acidizing was determined by the homogeneity (permeability distribution and mineral composition distribution).

5.2.4 Effect of Chemical Formulation on the Porosity during the Flooding Process

The NMR porosities of all four core plugs have been improved after the chemical formulation flooding. The increment was 7.6%-13.3%. The increased porosity resulted from the interaction of core samples and chemical formulation. During the flooding process and acidizing, small pores were generated in rock matrix and in some way small pores were connected to form larger pores or micro fractures.

5.2.5 Effect of Chemical Formulation on the Permeability during the Flooding Process

After the chemical formulation flooding, the permeability of three Bakken cores were improved by 5.6% - 102.7%. However, there was a decrease in one core sample. The permeability decreased from 3.28 μD to 2.08 μD. This is related to the higher clay content in this sample. The higher clay content may result in swelling to compact or destroy the rock matrix pores, which could lead to a loss of permeability.

5.2.6 Oil Recovery and oil recovery rate by CF flooding coupled with acidizing treatment

The oil recovery tests were conducted with core plugs at low permeability (~ 10^{-2} μD) during the CF flooding process. The CF flooding process coupled with acidizing were capable of recovering oil ranged from 27.4% to 81.1%. It was observed that for the higher permeability cores the oil recovered was relatively quick, while the lower permeability core produced oil was relative slow. Similar to the forced surfactant imbibition, the CF flooding coupled with acidizing treatment oil recovered gradually at the beginning, because it needs some time to push the oil with overburden pressure existence and go through the rock, with the penetration of surfactant formulation into rock matrix, the oil recovery rate reached the peak quickly.

5.3 Recommendations for the Future Work

The chemical formulation flooding has a synergic effect on the carbonate-rich tight formations to extract oil, it can be used as the fracturing fluid, treatment fluid, or the restimulation treatment fluid (refract fluid, for example). For the field application, an analysis model needs to be developed and the laboratory data of chemical formulation flooding needs to be scaled to the field.

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