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THE EFFECT OF MINERAL COMPOSITION ON SHALE OIL RECOVERY

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THE EFFECT OF MINERAL COMPOSITION ON SHALE OIL RECOVERY

By
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A thesis submitted in partial fulfillment of the
requirements for the degree of

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Abstract

Identifying contact angles in porous media is essential for characterizing multiphase flow of fluids in reservoirs. Traditional methods to measure contact angles assume a homogenous structure of reservoir rock; however, microscale pictures by Scanning Electron Microscopes (SEM) show that rock composition varies even inside a single pore. In addition, the preferentiality of oil layer formation is different according to the minerals constituting the reservoir rock. As a result, contact angles have heterogeneous behavior at the pore-scale.

For the purpose of this research, contact angles are measured on the pure minerals that make up the main components of a Bakken reservoir rock. Investigations of different minerals show that each mineral has a different contact angle from the other minerals at the same medium properties. Altering medium properties also shows different contact angle behavior according to the mineral tested. The results from the experimental work shows that contact angles decrease with low salinity media. In addition, these results were used in a pore-scale network model to study the behavior of these minerals combined with each other.

In general, this research gives more attention to mineral properties of reservoir rock which leads to a better understanding and characterization of the reservoir. It became clear that the mineralogical content plays a significant role in low salinity flooding where contact angles generally decreases with water compared to contact angles measured in brine. The pore-scale network model is built to simulate the flow of fluids in heterogeneous rock formation. This work has allowed the calculation of relative permeability curves, which are difficult to obtain for unconventional reservoirs. These results will lead to better understanding of heterogeneous reservoir behavior, as well as the effect of Improved Oil Recovery (IOR) projects, such as waterflooding, on oil production in shale formations.

Keywords: Mineral composition, shale oil, shale mineral composition, shale improved oil recovery

Dedication

I would like to dedicate this work to my God and Lord. To my father, mother, sister, brother-in-law and the new family member, John.

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I would like to acknowledge the great technical and financial support I got from the Petroleum Engineering Department at Montana Tech. Special thanks to my advisor, Todd Hoffman and my committee members, Burt Todd and Gary Wyss.

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Introduction

In 2015, the average monthly oil production from shale in North Dakota, US reached 1.18 million barrels per day (NDIC Oil and Gas). Moreover, the estimated reserve for the Bakken and Three Forks was 8 billion bbl (USGS, 2013). However, the recovery factor of shale oil does not exceed 15% in most cases. In other words, the oil production declines fast and most of the resources remain trapped in shale formations. At this point, Improved Oil Recovery (IOR) techniques should be applied, which requires good knowledge of fluid/fluid and fluid/rock interactions in the reservoir. Macroscale implementation of reservoir properties is used to predict shale oil reservoir performance. However, the results from macroscale models are neither accurate nor efficient when applied to shale reservoirs. Compared to conventional reservoirs (e.g. sandstone and limestone/dolomite reservoirs), Bakken formations are characterized with high heterogeneity in rock composition and microscale pores. These two features (i.e. heterogeneity and micro-pores) causes the unexpected behaviors of Bakken formations when macroscale models are applied. Pore-scale network models can account for heterogeneity and micro-pores when structuring a model, thus it can be more effective in predicting Bakken formation performance. However, pore-scale network models are too small to model field scale behaviors (e.g. well recovery and water cut). Microscale models, however, can provide macroscale models with some reservoir properties, which can be extracted from microscale models and then implemented in macroscale models.

In order to better understand the Bakken reservoir formation, Scanning Electron Microscope (SEM) images were used to analyze the composition of obtained Bakken rock samples. These images showed a high heterogeneity in the rock composition which mainly contains quartz, calcite, dolomite, feldspar and pyrite. These minerals were identified as the main constituents of the microscale pore spaces. However, the interactions between reservoir fluids and

these minerals were never explained in prior literature. For this purpose, a captive bubble device was constructed to study how the Bakken reservoir minerals interact with reservoir fluids through contact angle measurements. In addition, a pore-scale network model was constructed to study the effect of mineral heterogeneity on reservoir behaviors.

1.1. Literature Review

Fatt (1959) first defined fractional wettability as the fraction of reservoir rock that has a contact area with water. He proposed that the multiphase flow properties are different in different reservoir rocks, assuming identical pore geometry, due to the difference in fractional wettability. Earlier in 1956, Fatt suggested that contact angle measurements cannot be used to identify rock wettability due to the heterogeneity of reservoir rock. For this purpose, Fatt et al. (1956) used nuclear magnetic relaxation method to measure fractional wettability in reservoir rock. They observed that some surface areas in the tested rocks are water wet while others are oil wet which causes a variation in wettability among the rock samples. They related this variation in wettability to fractional wettability phenomena.

Denekas et al. (1960) related rock wettability to imbibition rates. They tested the rate of water imbibition into sandstone and limestone samples after being saturated with oil. It was observed that water wet samples have higher imbibition rates than slightly water wet samples. The authors also indicated that surfactants can effectively change imbibition rates of water into rock samples, hence changing their wettability.

However, in 1973, Salathiel proposed that pores that are exposed to oil, after a certain period of time, becomes oil wet due to the formation of oil layer on their surfaces. He also stated that mixed wettability (defined as the tendency of a fluid to adhere on rock surface preferentially

due to surface film formation) gives paths of flow for reservoir fluids even with very low saturations.

Although some authors use the terms interchangeably, fractional wettability and mixed wettability are different. Fractional wettability is when reservoirs have local areas of strongly oil wet but most of the reservoir is strongly water wet. This often occurs when reservoir rock has variable mineral composition and surface chemistry. Mixed wettability occurs when pore size impacts wettability. In larger pores, where oil has displaced water and became in contact with the rock surface, the polar organic compounds attach to the rock surface and cause the surface to become more oil wet (Crain, 2013).

According to Buckley et al. (1998), there are different mechanisms through which oil adsorbs on the mineral surfaces at the molecular scale. These mechanisms are polar, surface precipitation and acid/base. Polar mechanism results from the interactions between polar functional groups of oil with other polar properties on the mineral surface. These functional groups attached to hydrocarbon molecules affect the adhesion preferences of oil to mineral surfaces. Based on their polarity characteristics, functional groups can be either hydrophobic or hydrophilic.

In surface precipitation mechanism, the ability of oil to solvate asphaltenes is dependent on oil density. For poor solvents, asphaltenes precipitate on mineral surfaces creating oil wet surfaces. However, good solvents keep high oil components attached to oil structure and precipitation can be ignored (Buckley et al., 1998).

Acid/base interaction happens only in the existence of water layer between oil surface and mineral surface. The functional groups in mineral and oil behaves either as acids or bases (Buckley et al., 1998). As a result, wettability is affected by either of the following ways:

- (1) Water film stability: With low brine salinity of monovalent ions, pH value can be the only variable influencing acid and base equilibria, hence affecting the stability of water film.
- (2) Adsorption on acidic and basic mineral sites: At certain pH values, a mineral surface can be either positively or negatively charged and hence, coulombic interactions take place (Buckley et al., 1998).

Sorbie et al. (1995) developed a pore-scale network model to simulate fluids flow in fractionally wet reservoirs. In waterflooding, water may invade oil-occupied pores while ignoring others depending on the mineralogical content of each pore. As a result, each pore will have different advancing and receding angles, hence different invading pressure. In other words, invading pressure does not depend only on each pore size, it also depends on the contact angle in each individual pore.

Aghaei et al. (2015) measured in-situ contact angle in a sandstone rock sample. Their measurements show a difference in contact angle values in a single pore up to 2 degrees and a difference of 20 degrees in different pores (Figure 1). Although this big variation in contact angle measurements can be referred to surface roughness, it can also be related to the variation in mineral content in different pores and even in a single pore.

McCaffery (1972) built a high pressure (up to 10,000 psi) high temperature (up to 160 °C) pendant drop apparatus to study different fluid properties in porous media. The view cell designed for this experiment was capable of containing a rock piece to measure contact angles as well. He also studied the effect of lowering interfacial tension on enhanced oil recovery. His lab work proved that IFT increases as pressure increases and decreases as temperature increases. McCaffery also showed that the advancing contact angle of hydrocarbons measures on the surface of quartz decreases as temperature increases at constant pressure.

Figure 1: Contact angles measured at microscale (Aghaei et al., 2015)

Mirchi et al. (2015), developed a pendant/sessile drop experiment under reservoir conditions to test the effects of anionic and nonionic surfactants on oil production. They tested two shale samples: Shale A and Shale B. Shale A has a porosity 1.3% and organic content 8.3% while Shale B has a porosity 1.5% and organic content less than one. Their investigations led to the conclusion that surfactants lowered the interfacial tension under different temperature and pressure conditions, hence surfactants can change wettability in shale system.

1.2. Geological Background

For the purpose of this study, some core rock and fluid samples from Middle Member of the Bakken formation will be used in this study. The Bakken formation of the Williston basin covers a total area of 300,000 square miles across Montana, North Dakota and South Dakota in the US and Saskatchewan and Manitoba in Canada (Figure 2).

Figure 2: Locations of Elm Coulee and Parshall Fields (modified from Pitman et al., 2001).

1.2.1. Bakken Formation

Bakken Formation was deposited during the late Mississippian and early Devonian geological time where it overlies the Three Forks Formation and overlain by the Lodgepole Formation. Figure 3 shows a cross sectional area of the Bakken Formation which consists mainly of three members: Lower Member, Middle Member and Upper Member. The lower and upper members are source rock black shales with a maximum thickness of 56 ft and 65 ft respectively while the middle member is either silty dolostone or sandy limestone with maximum thickness of 90 ft (Marra, 2013). In addition, the middle member is the oil storage unit in the Bakken Formation System where oil migrates from the upper and lower members and it also has higher porosity and permeability than the upper and lower members (Marra, 2013).

Moreover, Bakken is a formation in Williston Basin where a number of fields produce from today (e.g. Elm Coulee and Parshall fields). The Elm Coulee field exists in the southwest margin of the Williston basin, while Parshall field exists in the eastern part of the basin, as shown in Figure 2. Elm Coulee was first discovered in 2000, which is considered the beginning of the shale boom. Oil production from the Elm Coulee field is mainly from the middle Bakken member of the reservoir at depths ranging from 8,500 to 10,500 ft (Sonnenberg et al., 2009). On the other side of Williston Basin, Parshall field was discovered in 2006 and it is considered the main reason for the boost in oil production in North Dakota. The middle Bakken member of the reservoir in Parshall field is an oil-rich zone and it lies at depths between 9,000 and 10,500 ft (Simenson, 2010).

Figure 3: Cross-section of the Bakken Formation through the Williston Basin

2. Composition Analysis

Composition analysis can identify the basic constituents of any rock or mineral sample. In this study, some Bakken samples were analyzed for the purpose of exploring the main components of the Bakken formation. In addition, some pure minerals were collected from different locations inside and outside the United States. These macroscale mineral samples are considered to be representative of the microscale pore minerals that exist inside the observed rock samples. The Scanning Electron Microscope (SEM) LEO 1430VP was used to test both rock and mineral samples. In addition, energy dispersive X-ray (EDS) using EDAX was used to analyze the mineralogical content of these samples. Figure 4 shows the SEM while warming up before performing tests on some minerals.

Figure 4: Scanning Electron Microscope used in this study (LEO 1430VP)

2.1. Rock Composition Analysis

Bakken Shale consists mainly of quartz, dolomite and calcite. Other traces and accessories that exist in shale formations are pyrite, feldspar, apatite, and rutile (Figure 5). Some hydrocarbon traces can also be seen trapped inside some microscale pores (Figure 5b). Note that this oil droplet is in contact with multiple grains that are made of different minerals. As a result, the flow of these microscale oil drops depends on the mineral composition of the pores, in addition to some other factors such as the interconnection of the micro pores, and reservoir fluids properties. Wettability is not a uniform function at microscale; some pores can be oil wet, water wet or intermediate wet which is called fractional wettability. In addition, an oil layer may be formed on the surface of some minerals which in return increases oil adhesion to this surface and change the mineral behavior to increase its preferentiality to oil. When oil forms a continuous path of oil layer through a number of pores, this phenomenon is called mixed wettability. However, this study is more concerned about fractional wettability due to the high heterogeneity of Bakken Shale formation.

Figure 5: Rock sample under SEM at a resolution 20 μm
(a) Different mineral composition, (b) Micro oil traces

2.2. Mineral Composition Analysis

The heterogeneity of Bakken shale formation raises the concern about the interaction of reservoir fluids with different minerals that exist in the reservoir rock. Figure 6 shows the minerals used in this study where (1) is calcite, (2) is dolomite I, (3) is dolomite II, (4) is feldspar I, (5) is feldspar II, (6) is pyrite and (7) is quartz. The hypothesis of studying dynamic contact angle behavior in the microscale is achievable, yet requires significant resources. For this study, pure minerals are used to investigate the behavior of different fluid system in the macroscale. The common properties of these minerals are first explained in the following sections.

Figure 6: Mineral samples used in this study.

2.2.1. Calcite

Calcite structure is analogous to the halite structure with the Na and Cl ions replaced with Ca and $(\text{CO}_3)^{2-}$ ions. These ions are arranged in a rhombohedral cell which results from the distortion of the cubic shape which is necessary to contain the large CO_3 ion group. According to Mohs scale, calcite has a defined value of hardness equal to 3 and a specific gravity of 2.715. In

general, calcite is the main component of limestones which is a good candidate as a reservoir rock. Limestone is a sedimentary rock that is deposited from marine organisms. It consists of bedding planes and some fractures. When these planes and fractures are connected, limestone becomes permeable. Sample 1 is a pure calcite mineral with apparent cleavages and joints. Figure 7 shows a microscale image of calcite surface.

Figure 7: Cleavages and joints in calcite structure with mineral composition analysis.

2.2.2. Dolomite

Dolomite is mostly a sedimentary rock that is formed as a result of diagenesis of limestones. It resembles two layers of CaCO_3 and MgCO_3 combined together. Pure dolomites are colorless; however, small iron intrusions can cause yellow to brownish color. In other cases, manganese and sometimes fluorite intrusions give dolomites a pink color. In addition, dolomite has an average value of hardness ranges between 3.5 to 4 according to Mohs scale and an average specific gravity of 2.86. Moreover, one of the special features of dolomite is that it is hardly soluble in cold diluted hydrochloric acid (HCl).

2.2.2.1. Dolomite I

Sample 2 is all dolomite with minor isomorphous substitution of Fe. However, this sample is colorless. Figure 8 shows a microscale image of sample 1 surface with mineral composition analysis.

Figure 8: Pure dolomite surface with mineral composition analysis.

2.2.2.2. Dolomite II

Sample 3 is another dolomite sample with more angular voids in addition to some fluorite inclusions. As a result, this sample has a light pink color. Figure 9 shows a microscale image of sample 4 surface with mineral composition analysis.

Figure 9: Dolomite surface with some fluorite inclusions and mineral composition analysis.

2.2.3. Feldspar

Feldspars are composed of three end members: albite ($\text{NaAlSi}_3\text{O}_8$), orthoclase (KAlSi_3O_8) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Feldspars have two groups: plagioclase and alkali. In other words, solid solutions between albite and anorthite are called plagioclase feldspars while solid solutions between orthoclase and albite are called alkali feldspar. Figure 10 shows the ternary phase diagram of feldspar that indicates the wide variations in feldspar composition. In addition, orthoclase feldspar has a defined value of hardness equals to 6 according to Mohs scale and an average specific gravity of 2.6.

Figure 10: Ternary phase diagram of feldspar modified after Greenwood et al. (1998)

2.2.3.1. Feldspar I

Sample 4 is bytownite plagioclase feldspar mineral which is a mix of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{NaAlSi}_3\text{O}_8$ (70-90% of Anorthite). The mineral surface is colorless with brownish color inside the sample. Figure 11 shows a microscale image of sample 2 surface with mineral composition analysis.

Figure 11: Bytownite plagioclase feldspar surface with mineral composition analysis.

2.2.3.2. Feldspar II

Sample 5 is an alkali feldspar sample (albite) which is a mix of $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 . It also has minor apatite inclusions which gives it a light greenish color. Figure 12 shows a microscale image of sample 5 surface with mineral composition analysis.

Figure 12: Albite feldspar surface with minor apatite intrusions and mineral composition analysis.

2.2.1. Pyrite

Pyrite is the most common mineral in the sulfide minerals group. It exists in different sedimentary, igneous and metamorphic rock compositions. The main composition of pyrite is FeS_2 ; However, limited substitution by nickel (Ni), cobalt (Co) or copper (Cu) can occur. It is usually formed in a cubic crystal shape which is attached to other minerals. Pyrite also has a pale yellow color which gives it a very close looking of gold. In addition, pyrite has an average value of hardness ranges between 6 to 6.5 according to Mohs scale and an average specific gravity range of 4.95 to 5.02. Sample 6 is a pure pyrite crystal sample. Figure 13 shows a microscale image of pyrite surface with mineral composition analysis.

Figure 13: Pure pyrite surface with mineral composition analysis.

2.2.2. Quartz

Quartz is the most common naturally occurring SiO_2 polymorph. It can be found in different types of rock either sedimentary, igneous or metamorphic. Pure quartz is colorless and ranked as 7th hardest mineral on Mohs scale. The two forms of quartz exist are α -quartz and β -quartz. α -quartz is stable in temperature range of 21 °C to 573 °C while β -quartz is stable in

temperature range of 573 °C to 870 °C. The transformation from α -quartz to β -quartz at elevated temperatures causes the induction of fractures between the pores of a certain rock types. In addition, quartz is the main constituent of sandstone because it is more resistant to weathering conditions. Small grains of quartz are cemented with other mineral grains to form sandstones which are usually identified as high porous and high permeable media. As a result, sandstones have the ability to store different fluids such as water, oil and gas in rock formations at different depths. Sample 7 is a pure quartz showing euhedral crystal faces. Figure 14 shows a microscale image of quartz surface with mineral composition analysis.

Figure 14: Pure quartz surface with mineral composition analysis.

Dolomite, feldspar, calcite, quartz and pyrite are all common constituents of sedimentary rocks. For example, sandstones are mainly composed of quartz and/or feldspar with some calcite, which acts as a cementing material. As a result, the pore spaces in sandstones are made of either one single mineral or a mix of two or more minerals. Bakken samples, when examined by SEM-

EDS, showed this variation in mineral composition. Table I shows a summary of minerals used in this study and their properties.

Table I: Mineral properties

Sample Number	Sample Name	Mineral Composition	Color
1	Calcite	CaCO_3	White
2	Dolomite I	$\text{CaMg}(\text{CO}_3)_2$, Fe substitution	Colorless
3	Dolomite II	$\text{CaMg}(\text{CO}_3)_2$, CaF_2 intrusions	Light pink
4	Feldspar I	$\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$	Colorless
5	Feldspar II	$\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8	Light green
6	Pyrite	FeS_2	Golden
7	Quartz	SiO_2	Colorless

3. Experimental Work

The captive bubble experiment is used to measure the contact angle of the interface of two fluids and a solid surface. It is important to note that contact angle not only depends on the properties of the fluids but it also depends on the solid surface properties which varies according to the surface mineralogy and surface roughness. In this study, minerals and rock samples were placed in resin molds and polished to eliminate surface roughness effects. Samples were then tested for its mineralogical composition using SEM-EDS. Afterwards, captive bubble experiment was used to identify contact angles of minerals and rock samples in RO water (filtered) and brine. The results of this experimental work show the effect of rock matrix heterogeneity on reservoir wettability and the effect of medium change on oil production.

3.1. Experimental Theory

Figure 15 shows the oil/water, oil/rock and water/rock interactions. Using the interfacial tension relationships, the contact angle (θ) can be found as follow:

$$\cos \theta = \frac{\sigma_{so} - \sigma_{sw}}{\sigma_{wo}} \quad (1)$$

Where:

σ_{so} = Interfacial tension between rock/mineral and oil

σ_{sw} = Interfacial tension between rock/mineral and water

σ_{wo} = Interfacial tension between water and oil

Figure 15: Relationship between contact angle and interfacial tension.

In addition, adhesion tension (A) which is defined as the difference between rock/oil and rock/water interfacial tension is calculated as follow:

$$A = \sigma_{so} - \sigma_{sw} = \sigma_{wo} \cos \theta \quad (2)$$

In case $0 < \theta < 90$, the adhesion tension is positive, hence the system is water wet

In case $90 < \theta < 180$, the adhesion tension is negative, hence the system is oil wet

In case $\theta = 90$, the adhesion tension is zero and the system is identified as neutral wet

In case $\theta = 0$, the adhesion tension becomes equal to the interfacial tension between oil and water and the system is identified as strong water wet

3.2. Device Structure

The device used in this study is built from scratch to measure contact angles of different mineral and rock samples. The basic structure of this device is composed of a camera, syringe, fluid cell and a diffuser. Figure 16 shows the device parts where (a) is the camera, (b) is the lens,

(c) is the syringe and needle behind the post, (d) is a positioning tool, (e) is the fluid cell and (f) is a light diffuser.

Figure 16: Contact angle measurement device structure.

3.2.1. Camera

The camera used in this experiment is a monochrome 1.3 MP camera equipped with Sony IMX035 Flea3 USB3 Vision. The producer of this camera is FLIR, which is previously known as PointGrey. Monochrome camera is preferred over a colored camera because monochrome sensors are more sensitive to high details and capable of producing higher resolution. In addition, this camera can captures 35 frames per second which gives the advantage of closely monitoring

the bubbles until full stabilization. The camera is equipped with a 35mm f1.7 2/3" CCTV lens. Moreover, an extension tube is used to increase the magnification of the camera. The pictures obtained from the camera are analyzed using FlyCap software. Figure 17 shows an example of a picture taken from the camera.

Figure 17: A captured picture from the camera.

3.2.2. Fluid Cell

The fluid cell is designed to contain the medium fluid which is water for the captive bubble method or oil in case of pendant drop method. This cell has an opening on top to allow immersing the samples inside the medium fluid and a small capillary tube to allow inserting the needle inside the cell. This capillary tube is covered with a rubber stopper to prevent any liquid leakage during the experiment. Figure 18 shows a schematic 3D design of the cell and a close up picture of the cell with a sample inside.

(a)

(b)

Figure 18: Schematic 3D design of fluid cell**(a) Schematic,****(b) Actual design**

In addition, the fluid cell is fixed inside two plastic brackets which are mounted on posts (Figure 18b). These two brackets were designed specially with the cell dimensions and printed with a 3D printer. This design is shown in Appendix C.

3.2.3. Syringe

The syringe pump is 100 μL gastight luer lock obtained from Hamilton Company equipped with either 18g or 25g needles. This pump can dispense fluid as low as 3 μL which facilitates the process of measuring the advancing and receding contact angles. Figure 19 shows a picture of the syringe. In addition, a special positioning tool was designed to hold the syringe pump and precisely move it upwards and downwards. The main idea of this tool is converting rotational motion into linear motion in the vertical direction using a screw rod and a fixed bolt. In addition, this positioning tool can move the needle as low as a few μm . A schematic of this tool is shown in Appendix C.

Figure 19: The syringe used in the experiment.

3.2.4. Light Diffuser

The diffuser is composed of 1500 grit ground glass which is made of very fine sandblast. In addition, it has a high area of diffusion for the incoming light. A small cylindrical tube contains the ground glass and a light source. This light source is a warm white 3000-3200K GY6.35 base LED source. A 12V adapter is used to convert regular 110V electric source to 12V needed to operate the LED light.

3.2.5. Other Components

The camera, fluid cell, positioning tool and light diffuser are mounted to a breadboard through mounting posts. These mounting posts are fixed on a rail to allow a free movement of the camera and diffuser through the x direction and the fluid cell and positioning tool through the y direction. The breadboard measures 6" x 12" and is made of aluminum. It has four Sorbothane Feet to isolate any noise from the experiment and absorb any shocks. All of these tools are obtained from Thorlabs.

3.3. Experimental Procedures

The experimental procedures are divided into four main sections: sample molding, sample polishing, fluids preparation and finally contact angle measurement. The first two sections aim to

prepare the samples for contact angle measurements. Placing the samples in molds was necessary to test them with the Scanning Electron Microscope. In addition, molds fit better with other components in the contact angle measuring device. Polishing also is important to assure a smooth surface, which is essential for precise contact angle measurements. Fluids preparation aims to prepare and test the properties of the fluids used in the experiment and finally contact angles are measured following the procedures given in section 3.3.4.

3.3.1. Samples Molding

The mineral samples are cut using a rock-cutting saw and pieces with a bigger flat surface area are chosen for the experiment. These pieces are then placed in a 1-inch mold. The casting materials are epoxy and resin which are mixed at a ratio of 1:25 respectively. This mixture is stirred well and poured inside the mold holder to cover the whole sample. Finally, the molds were left for 24 hours to completely hard.

3.3.2. Samples Polishing

The samples are placed in samples holder which is then connected to the polishing machine. The polishing disc is set at 200 revolutions per minute and the force that the sample holder exerts on the polishing disc is 5 N. In addition, the samples holder rotates in an opposite direction to the polishing disc. The following sanding papers are used for polishing in sequence: 60, 180, 240, 320, 400, 600, 800, 1000, 1200 grits. Each polishing cycle took 7 minutes to assure a smooth surface. Regular water is used to displace the cuttings from the sanding papers during the polishing process.

3.3.3. Fluids Preparation

The fluids used in this experiment are RO water, brine and oil. The RO water was filtered to 0.45 μm , and it has a specific gravity of 0.96. The brine and oil properties and preparations are presented in the following two sections.

3.3.3.1. Brine Preparation

Brine was prepared using deionized and filtered water to 0.45 μm mesh grid filter. Four components are added to the water to resemble naturally formed brine: Sodium Chloride (NaCl), Potassium Chloride (KCl), anhydrous Calcium Chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and anhydrous Magnesium Chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The four components are mixed together using a magnetic stirring device (VWR VMS-C4) for 15 mins. The composition of the synthetic reservoir brine is shown in Table II.

Table II: Brine Composition

Salt	Concentration (g/L)
NaCl	21.3
KCl	0.2
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.45
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.2

3.3.3.2. Oil Preparation

The oil used in this study is dead oil extracted from the Bakken formation in North Dakota. At room temperature and pressure, the oil density is 0.83 g/cm^3 (38.88 °API) and viscosity is 2.04 cP. For this research, oil is filtered to 0.45 μm . The composition of this oil at room pressure and temperature is shown in Table III.

Table III: Oil Composition

Component	Mole Percentage (14.7 psi)
N₂	0.456
CO₂	0.125
C₁	3.057
C₂	7.338
C₃	11.948
iC₄	2.811
nC₄	8.882
iC₅	4.898
nC₅	8.231
C₆	10.826
C₇	14.458
C₈	12.53
C₉	7.229
C₁₀₊	7.211

3.3.4. Contact Angle Measurements

Three types of contact angle measurements are conducted during the length of this experiment: Advancing Contact Angle (ACA), Receding Contact Angle (RCA) and Static Contact Angle (SCA). These measurements are done under ambient conditions with RO water and brine.

The steps of this experiment are as follow:

- 1- RO/brine water is poured inside the fluid cell and the syringe is charged with oil.
- 2- Mineral sample is immersed inside the fluid cell on the same vertical plan as the syringe needle.
- 3- The diffuser and the camera are turned on and adjusted to give a clear image.

- 4- The positioning tool is used to set the needle at an appropriate distance from the sample. This distance is in a range of 1 – 2 cm.
- 5- Oil is pumped from the syringe to form an oil bubble on the mineral surface. Pumping continues just before the bubble starts to move. A picture is captured at this instance.
- 6- Oil is pumped back to the syringe. The drop shape starts to shrink and a picture is captured just before the oil drop is released from the needle tip.
- 7- Oil is pumped again to the mineral surface until the drop has an appropriate volume. The drop is left for 15 mins until it stabilizes and then a picture is taken.
- 8- The mineral sample is removed from the device and cleaned using toluene. The sample is then washed with fresh water and dried with high pressure air.
- 9- The fluid cell is washed with fresh water and dried with high pressure air.
- 10- The pictures taken during the experiment are analyzed using ImageJ to determine the ACA, RCA and SCA.

3.3.5. Contact Angle Measurement Limitations

Contact angle is defined as the angle between the horizontal plane on the mineral surface and the tangent line to the bubble edges. Hence, determining the contact line is critical in contact angle measurements. However, contact lines for strongly water/oil surfaces cannot certainly be determined which causes significant errors in contact angle measurements (Saraji, 2013).

In this study, the camera is tilted 2-4 degrees to capture the bubble reflection on the mineral surface as shown in Figure 20. This reflection facilitates determining the contact line. In addition, contact angle images are magnified to precisely determine two hinging contact points which construct the contact line.

Figure 20: Contact line determination

Another limitation to contact angle measurement is when the contact angle approaches 90° (Figure 21). In this case, the bubble shape becomes connected to its reflection on the rock/mineral surface, hence contact line cannot be determined.

Figure 21: Receding contact angle approaching 90° .

3.4. Results

Contact angles are measured in two different media: RO water and brine. The minerals tested shows different behavior as a result of medium change. Table IV shows the results of ACA, RCA and SCA measurements in RO water.

Table IV: Contact angle measurements in RO water

#	Mineral	Advancing Contact Angle	Standard Deviation	Receding Contact Angle	Standard Deviation	Static Contact Angle	Standard Deviation
1	Calcite	36.752	±5.186	78.685	±4.504	41.358	±4.541
2	Dolomite I	25.1	±2.63	86.205	±6.349	44.505	±0.897
3	Dolomite II	37.2	±2.9	87.4	±3.737	39.6	±3.737
4	Feldspar I	56.61	±1.902	N/A	N/A	61.378	±1.264
5	Feldspar II	42.344	±0.855	59.104	±7.919	58.891	±6.992
6	Pyrite	32.543	±3.097	69.529	±2.822	40.87	±1.022
7	Quartz	51.811	±0.54	N/A	N/A	60.5	±3.674

Some contact angles were not measured due to failures while running the experiment. These failures are based on the measurement limitations discussed in section 3.3.5. In addition, the accuracy of these measurements depends on the quality of pictures taken from the camera. The camera is affected by many factors such as the focal length adjustment between the lens and the oil drop, the surrounding light reflections and oil bubble vibrations. These factors lead to the variation in the standard deviation (SD) shown in Table IV.

Some minerals are more water wet than others. Dolomite II, for example, shows the most water wet behavior among the seven samples while Feldspar I shows the most oil wet behavior. The same minerals are tested in brine medium and the results are shown in Table V.

Table V: Contact angle measurements in brine

#	Mineral	Advancing Contact Angle	Standard Deviation	Receding Contact Angle	Standard Deviation	Static Contact Angle	Standard Deviation
1	Calcite	35.454	±1.11	N/A	N/A	41.518	±0.259
2	Dolomite I	62.674	±0.474	94.861	±0.154	83.904	±2.41
3	Dolomite II	43.24	±2.419	74.151	±7.756	70.38	±4.856
4	Feldspar I	95.114	±3.749	126.036	±3.244	114.704	±1.4
5	Feldspar II	49.275	±0.441	75.156	±2.611	61.647	±0.073
6	Pyrite	60.047	±1.403	91.801	±3.673	85.761	±4.548
7	Quartz	51.175	±3.458	77.583	±5.527	69.12	±0.775

Some minerals, such as calcite and quartz, did not show a significant change in contact angle measurements when tested with RO water and brine. However, other contact angles (e.g. Dolomite I, Dolomite II, Feldspar I, Feldspar II and pyrite) increased when tested in brine. Feldspar I showed a strong oil wet behavior when tested in brine medium (Figure 22). In addition, some minerals, like pyrite, showed water wet behavior in water and intermediate wet behavior in brine.

Figure 22: SCA of feldspar I in brine.

These results show that decreasing the salinity of the medium can significantly reduce the contact angle measurements (Figure 23). As a result, oil recovery is affected by the medium fluid. When performing waterflooding, low salinity water decreases the contact angle and minerals become more water wet, hence recovering more oil. This is likely due to polar interactions between the low salinity water and mineral surface. Similar results were shown in previous literature (Morrow et al., 2013) but this work indicated that these results are based on the mineralogy of rock matrix.

Figure 23: Variations in CA measurements due to medium change.

In addition, contact angles were measured for a shale rock sample in both RO water and brine as shown in Table VI. These results further proves that contact angles increase when the medium changes from water to brine. In other words, reservoir system becomes more water wet in case of low salinity waterflooding.

Table VI: Contact angle measurements for a shale rock sample

Medium	Advancing Contact Angle	Standard Deviation	Receding Contact Angle	Standard Deviation	Static Contact Angle	Standard Deviation
RO	27.248	±4.757	N/A	N/A	31.958	±0.204
Brine	29.791	±2.208	64.513	±4.422	38.214	±3.473

Based on the mineral contact angle measurements, it was expected that the shale rock sample will have a static contact angle in the range of 40° to 60° in water; however, the measured static contact angle for the shale sample is 31.958°. This hypothesis would have been true if the contact surface is solid bulk with no voids. The pores that exist on the sample surface are filled with water which is the same as the water exists in the medium, hence these pores become analogous to a mineral with contact angle that is smaller than the mineral contact angles. Moreover, surface roughness is possibly another reason. In order to calculate the average contact angle of a rock sample based on its mineralogy, surface areas of each mineral and pore spaces should be calculated.

4. Pore-scale Network Model

It was noticed from the experimental work that each mineral has a different contact angle from the other minerals. However, these separate contact angles do not tell how this heterogeneous mineral composition affects the reservoir. Therefore, a pore-scale network model is utilized to study the effect of heterogeneity of mineralogical content on oil recovery.

In this model, pores are assumed to have a triangular shape (Figure 24a) which are initially filled with water. Oil then invades some pores due to oil migration, representing primary oil drainage (Figure 24b). Relative permeability curves are constructed based on this primary drainage process. Waterflooding is then studied as an improved oil recovery method. In the waterflooding model, water completely invades some pores while other pores are left with some oil traces which is mainly dependent on the rock wettability. Using area calculations, water and oil saturations are calculated. In addition, conductance calculations are used to calculate relative permeabilities of water and oil.

Figure 24: Overview of pore shape (a) Three grains cemented to each other forming a triangular pore in between, (b) Triangular pore with domination of oil and water traces at the corners

Fractional wettability is implemented in this model such that each pore is assigned randomly to a certain mineral where the minerals used are calcite, dolomite, feldspar, pyrite and quartz and their contact angles are obtained from the results of the captive bubble experiment. Each pore has also a random pore size based on Hui and Blunt (2000) model. In addition, each pore is assigned different contact angle based on its mineralogical structure. As a result, the threshold capillary pressure for each pore is calculated based on its mineral contact angle and pore size.

The oil layer adhesion on different minerals affects the hinging contact angle at the edges of invaded pores. However, this study is more concerned about the overall heterogeneity effect of rock formation so oil layer formation is not considered. In other words, wettability is determined only based on the contact angle of each mineral.

Pores are arranged according to their threshold capillary pressure and pores invasion is simulated at the invasion of each pore following a bundle of capillary tubes flow mechanism, where the tubes are triangular in shape. Based on pore size and wettability, some pores are not invaded and remains virgin pores throughout the whole simulation. The threshold capillary pressure of these pores is higher than the invasion pressure of oil during the primary drainage. These pores represents the connate water saturation in a macroscale reservoir model. During waterflooding model, some pores are left with an oil layer, which is not producible. These oil layers represent the irreducible oil saturation in a macroscale model.

4.1. Model Theory

The theoretical approach of this model is based on parameters such as: pore space, threshold capillary pressure, saturation calculations and conductance calculations. These calculations are based on the equations described in Hui and Blunt (2000) with some modifications

to implement the effect of fractional wettability. This model is chosen for its simplicity while applying the basic governing rules of a pore-scale network model.

4.1.1. Pore Space

An accurate representation of the pore space can be done using microscopic X-ray tomography. These pore spaces can then be implemented into the model. However, a random distribution of pore spaces can be used to generate pores network with predetermined minimum and maximum pore sizes. For the purpose of this study, Hui and Blunt (2000) model is followed to propagate random pore sizes. The pore sizes are calculated based on the following equation:

$$R = (R_{max} + R_{min})(-\delta \ln[x(1 - e^{-1/\delta}) + e^{-1/\delta}])^{1/\gamma} + R_{min} \quad (3)$$

Where R is pore radius, x is a random number between 0 and 1, δ and γ are exponents and equal to 0.8 and 1.6 respectively. R_{min} is the radius of the smallest pore while (R_{max}) is the radius of the largest pore in the model.

The pore shape is simulated as an equilateral triangle where the half angle (α) is equal to 30° . In addition, each pore is assigned a mineral type with a specific contact angles.

4.1.2. Threshold Capillary Pressure

Capillary pressure is defined as the pressure difference between two different fluids at their interface. In the microscale, capillary pressure is the dominant parameter in the fluid/fluid and fluid/rock interactions. For this model, all the pores are initially filled with water which represents the primary status of a reservoir rock. Oil then migrates to the formation and invades some of the pores which were already occupied with water. However, this invasion does not happen until the pressure of oil phase exceeds the threshold capillary pressure of the invaded pores. The threshold capillary pressure is defined as the minimum pressure required for the invading phase to penetrate

pores which contains invaded phase. During primary drainage, oil is the invading phase while water is the invaded phase. For triangular shaped pores, the capillary pressure is calculated as follow:

$$P_{cow} = \frac{\sigma_{ow}}{R} \left[\cos \theta + \sqrt{\frac{\tan \alpha}{2} (\sin 2\theta - 2\theta + \pi)} \right] \quad (4)$$

Where P_{cow} is the threshold capillary pressure, σ_{ow} is the interfacial tension between oil and water, R is the pore inscribed radius, θ is the contact angle for primary drainage and α is the half angle.

In case of waterflooding, water becomes the invading phase while oil becomes the invaded phase. Figure 25 shows the possible configurations of pores during waterflooding. Case (a) shows a virgin pore which was not invaded during primary drainage. Case (b) shows a water wet pore where oil occupies the center of the pore and water occupies the corners. Case (c) shows an oil wet pore where oil occupies the center of the pore and water occupies the corners. Case (d) shows an oil film sandwiched between the corner and center waters.

Oil/water capillary pressure decreases during waterflooding because the pressure of wetting phase (water) increases. The oil/water/solid contact is pinned with hinging angle θ_h that increases from θ_{owD} in primary drainage to θ_{owF} in waterflooding. When $\theta_h = \theta_{owF}$, the arc meniscus (AM) starts moving. Waterflooding only ceases when oil saturation reaches irreducible oil saturation (S_{oi}). In addition, waterflooding changes from spontaneous imbibition to forced imbibition when a critical angle (θ_c) is reached. This critical angle is calculated as follow:

$$\theta_c = \arccos \left(\frac{-\sin(\alpha + \theta_{owP}) \sin \alpha}{\frac{RP_{cow}^{max}}{\sigma_{ow}} \cos \alpha - \cos(\alpha + \theta_{owP})} \right) \quad (5)$$

Figure 25: Different case scenario of pore configurations in case of waterflooding

According to Blunt and Hui (2000), critical angle values are compared with the values of θ_{owF} in waterflooding. The threshold capillary pressure is calculated based on this comparison for the three following situations:

In case of spontaneous imbibition ($\theta_{owF} < \theta_c$):

1. r (curvature) is first assumed to be equal R (inscribed radius)
2. b (distance between corner and oil/water interface) is calculated using the following

$$\text{equation: } b = \frac{\sigma_{ow} \cos(\alpha + \theta_{owP})}{P_{cow}^{max} \sin \alpha}$$

3. β is calculated. $\beta = \arcsin\left(\frac{b \sin \alpha}{r}\right)$

4. A_{eff} is calculated. $A_{eff} = \frac{R^2}{2 \tan \alpha} - \frac{rb \sin(\alpha + \beta)}{2} + \frac{r^2 \beta}{2}$

5. Ω_{eff} is calculated. $\Omega_{\text{eff}} = \left(\frac{R}{\tan \alpha} - b \right) \cos \theta_{owF} + r\beta$
6. r is calculated. $r = \frac{A_{\text{eff}}}{\Omega_{\text{eff}}}$
7. These calculations are repeated till the value of r stabilizes
8. P_{cow} is calculated. $P_{\text{cow}} = \frac{\sigma_{ow}}{r}$

In case of intermediate CA ($\theta_{owF} \geq \theta_c$ but $\theta_{owF} \leq \frac{\pi}{2} + \alpha$):

$$P_{\text{cow}} = \frac{2\sigma_{ow} \cos \theta_{ow}}{R} \quad (6)$$

In case of forced imbibition ($\theta_{owF} > \frac{\pi}{2} + \alpha$):

$$P_{\text{cow}} = \frac{\sigma_{ow}}{R} \left[\cos \theta_{owF} - \sqrt{\frac{\tan \alpha}{2} (-\sin 2\theta_{owF} + 2\theta_{owF} - 2\alpha - \pi)} \right] \quad (7)$$

4.1.3. Saturation and Permeability Calculations

Area calculations are used to determine water and oil saturations at each single invasion percolation cycle. Water and oil saturations are calculated for each case of the ones shown in Figure 25 where the ratio between the total area of a fluid phase and the total area of the pore is the fluid saturation in this pore.

4.1.3.1. Pores Filled with Only One Fluid

Those pores are either virgin pores (i.e. pores which are originally filled with water and have not been invaded with oil during primary drainage) or pores which are completely invaded with oil during primary drainage. Figure 26 shows how these pores configuration during waterflooding.

Figure 26: Configuration of pores which are filled with only one fluid

In case of virgin pores in primary drainage or pores which are completely filled with water during waterflooding (Figure 26a), water area (A_w) is equal to the total area of the pore (A_t) and calculated as follow:

$$A_t = A_w = n_c R^2 \cot \alpha \quad (8)$$

Where n_c is the number of corners (which is equal to 3 in case of equilateral triangle), R is the inscribed radius and α is the half angle (which is equal to 30° in case of equilateral triangle). In case of a pore which is fully invaded with oil (Figure 26b), the area of oil is equal to the total area of the pore and calculated as follow:

$$A_t = A_w = n_c R^2 \cot \alpha \quad (9)$$

Conductance is also calculated in a similar manner. In case of pores represented in Figure 26a, water conductance (g_w) is equal to total conductance (g_t) and calculated as follow:

$$g_w = g_t = \frac{\pi \left(\sqrt{\frac{A_t}{\pi}} + R \right)^4}{128} \quad (10)$$

While in case of a pore which is fully invaded with oil represented in Figure 26b, the conductance of oil is equal to the total conductance of the pore and calculated as follow:

$$g_o = g_t = \frac{\pi \left(\sqrt{\frac{A_t}{\pi}} + R \right)^4}{128} \quad (11)$$

4.1.3.2. Pores with Corner Water

The hinging contact angle increases until the invasion percolation pressure reaches the threshold capillary pressure of the given pore and it becomes completely filled with water. As a result, the water and oil area and conductance change with the change in hinging contact angle. This hinging contact angle (θ_h) is calculated as follow:

$$\theta_h = \arccos \left(\frac{P_{cow}^{max} b \sin \alpha}{\sigma_{ow}} \right) - \alpha \quad (12)$$

Where P_{cow}^{max} is the invasion percolation pressure and b is the distance between the corner point and the hinging point.

Figure 27: Configuration of pores with water in the corners

Figure 27 shows the possible pore configurations during waterflooding where case (a) represents a water wet pore while case (b) represents an oil wet pore. The water corner area in both cases is calculated as follow:

$$A_w = n_c r_{ow}^2 \left[\cos \theta_h (\cot \alpha \cos \theta_h - \sin \theta_h) + \theta_h + \alpha - \frac{\pi}{2} \right] \quad (13)$$

Where r_{ow} is the radius of the arc meniscus between the two fluids and is equal to $\frac{\sigma_{ow}}{p_{cow}}$. In addition, the total pore area is calculated as follow:

$$A_t = n_c R^2 \cot \alpha \quad (14)$$

And hence the center oil area can be simply calculated as the difference between the total pore area and corner water area as follow:

$$A_o = A_t - A_w \quad (15)$$

Conductance is also calculated in a similar manner as area calculation. The corner water conductance is first calculated as follow:

$$g_w = \frac{A_w^2 (1 - \sin \alpha)^2 (\varphi_2 \cos \theta_1 - \varphi_1) \varphi_3^2}{12 n_c \sin^2 \alpha (1 - \varphi_3)^2 (\varphi_2 + \varphi_1)^2} \quad (16)$$

Where,

$$\varphi_1 = \frac{\pi}{2} - \alpha - \theta_h \quad (17)$$

$$\varphi_2 = \cot \alpha \cos \theta_h - \sin \theta_h \quad (18)$$

$$\varphi_3 = \left(\frac{\pi}{2} - \alpha \right) \tan \alpha \quad (19)$$

Oil conductance is then calculated as follow:

$$g_o = \frac{\pi \left(\sqrt{\frac{A_o}{\pi}} + R \right)^4}{128} \quad (20)$$

And finally the total conductance of the pore is calculated as follow:

$$g_t = \frac{\pi \left(\sqrt{\frac{A_t}{\pi}} + R \right)^4}{128} \quad (21)$$

4.1.3.3. Pores with an Oil Film

During waterflooding, it is possible that an oil layer is left sandwiched between the corner water and center water. This layer is not stable and collapses if the invasion percolation pressure decreases to a certain collapse pressure ($P_{collapse}$) given as follow:

$$P_{collapse} = \frac{\sigma_{ow} [\cos \alpha \sin \alpha (2 \sin \alpha + \cos \theta_{ow}) + \sin^2 \alpha \sqrt{4 \cos^2 \alpha - 3 - \cos^2 \theta_{ow} - 4 \sin \alpha \cos \theta_{ow}}]}{b(3 \sin^2 \alpha + 4 \sin \alpha \cos \theta_{ow} + \cos^2 \theta_{ow})} \quad (22)$$

When oil layer collapses, the pore configuration goes back to a pore completely filled with water. This process is shown in Figure 28.

Figure 28: Configuration of pores with oil layer and water in the center and corners

In the presence of oil layer, the corner area is calculated as follow:

$$A_c = n_c r_{ow}^2 \left[\cos(\pi - \theta_{ow}) (\cot \alpha \cos(\pi - \theta_{ow}) - \sin(\pi - \theta_{ow})) + (\pi - \theta_{ow}) + \alpha - \frac{\pi}{2} \right] \quad (23)$$

While the corner water area is given as:

$$A_{wc} = n_c r_{ow}^2 \left[\cos \theta_h (\cot \alpha \cos \theta_h - \sin \theta_h) + \theta_h + \alpha - \frac{\pi}{2} \right] \quad (24)$$

Hence, the oil layer area is calculated as:

$$A_o = A_c - A_{wc} \quad (25)$$

The total area of the pore (A_t) is calculated as given in Equation 15. From this equation, the center water area is calculated as follow:

$$A_{w_center} = A_t - A_c \quad (26)$$

Conductance is also calculated in a similar manner as area calculation. The corner water conductance is calculated as given in equations 16 – 19. The center water conductance is then calculated and added to the corner water conductance to give total water conductance. Center water conductance is calculated as follow:

$$g_{w2} = \frac{\pi \left(\sqrt{\frac{A_{w_center}}{\pi}} + R \right)^4}{128} \quad (27)$$

And oil layer conductance is calculated as follow:

$$g_o = \frac{A_o^3 (1 - \sin \alpha)^2 \tan \alpha \varphi_3^2}{12n_c A_c \sin^2 \alpha (1 - \varphi_3) \left[1 + \varphi_3 - (1 - \varphi_3) \sqrt{\frac{A_w}{A_c}} \right]^2} \quad (28)$$

Where φ_3 is calculated from Equation 20

Finally, in each invasion percolation cycle, the total area and conductance of water in all pores is calculated and divided by the total area and total conductance of pores respectively to give water saturation and water relative permeability. Similarly, the total area and conductance of oil in all pores is calculated and divided by the total area and conductance of pores to give oil saturation and oil relative permeability. These data are constructed to create the relative permeability curves at the given modeling conditions.

4.2. Model

In this section, the model is built based on the previously mentioned mechanisms. The data used in building the model are presented and the model results are shown in the following two sub-sections.

4.2.1. Data

The model assumes pore sizes in the range of 0.1 μm to 1 μm . The pores are assigned minerals randomly based on the percentages shown in Table VII. The minerals contact angles are obtained from the experimental work results in Section 3.4. The interfacial tension between oil and water is assumed to be 0.048 N/m and kept constant regardless of medium change because it is not the point of study in this research. The irreducible oil saturation was assumed to be 0.2 and the number of pores used to build this model is 2000 following Hui and Blunt (2000).

Table VII: Mineralogical content used in the model

Calcite	Dolomite	Feldspar	Pyrite	Quartz
0.2	0.2	0.125	0.125	0.35

4.2.2. Results

Two pore-scale network models were built based on the previously mentioned mechanisms, one for primary drainage and the other for waterflooding. The relative permeability curves for the primary drainage model is shown in Figure 29. These relative permeability curves are based the behavior of each mineral inside the pores. These curves can be compared to the relative permeability curves obtained from mixed wettability (Figure 30). With the given values of contact angle measurements, the relative permeability curves obtained from fractional wettability behaves as an average oil wet system, while the mixed wettability model assumes a uniform system which can behave either as a water wet or oil wet system.

Figure 29: Relative permeability curves for primary drainage model using fractional wettability.

Figure 30: Relative permeability curves of primary drainage assuming mixed wettability (Hui and Blunt, 2000).

The permeability curves for waterflooding model is shown in Figure 31. The system behavior is very close to that of primary drainage because the same contact angles were assumed in both models. However, these contact angle values can be changed according to the reservoir structure and experimental results to generate a more relevant model. In addition, the model was set to stop as it reaches an irreducible oil saturation of 0.2 which can also be configured while building the model. A complete code for this model is shown in Appendix B.

Figure 31: Permeability curves for primary drainage model.

4.3. Sensitivity Analysis

A sensitivity analysis is used to test the effect of some parameters used in building the model to the results. These parameters are pore size, minerals contact angles, reservoir medium (brine or water) and mineralogical content. This analysis uses the primary drainage model to compare different runs.

4.3.1. Pore Size

Two runs were used to test the effect of pore sizes on relative permeability curves obtained from the model. The pore sizes were changed to the values shown in Table VIII.

Table VIII: Pore sizes used in sensitivity analysis.

	$R_{\min}$ (μm)	$R_{\max}$ (μm)
Run 1	1	10
Run 2	0.1	1

The result of these two runs is shown in Figure 32. The two relative permeability curves are almost identical; however, Run 2 resulted in high capillary pressures because smaller pore sizes were used. Shale oil reservoirs are characterized with small pore sizes; however, they can have the same relative permeability curves as conventional reservoirs. The only difference is that shale oil reservoirs move slowly through this curve compared to conventional reservoirs.

Figure 32: Sensitivity analysis based on pore size.

4.3.2. Contact Angle Changes

Four additional runs are used to analyze the effect of minerals' contact angles on relative permeability curves. The first two runs (Run 3, Run 4) are based on primary drainage model while the two other runs (Run 5, Run 6) are based on waterflooding model. The contact angles used in primary drainage are the advancing contact angles while the contact angles used waterflooding are receding contact angles. These contact angles are shown in Table IX and they are based on the contact angle measurements in Section 3.4 with a difference of ± 10 degrees between each run.

Table IX: Contact angles used in the sensitivity analysis.

	Calcite	Dolomite	Feldspar	Pyrite	Quartz
Run 3	26.752	15.1	32.344	22.543	41.811
Run 2	36.752	25.1	42.344	32.543	51.811
Run 4	46.752	35.1	52.344	42.543	61.811
Run 5	68.685	77.4	49.104	59.529	67.583
Run 6	78.685	87.4	59.104	69.529	77.583

The effect of contact angle changes is shown in Figure 33 and Figure 34. These two figures show the same response to increasing contact angles. The reservoir becomes more oil wet as the result of increasing contact angles of each individual mineral. The non-uniformity of the curves in case of waterflooding model is due to the numeric instability of the model especially with small pore sizes used in the model.

Figure 33: Sensitivity analysis based on contact angle measurements in primary drainage.

Figure 34: Sensitivity analysis based on contact angle measurements in waterflooding.

4.3.3. Medium Change

In this analysis, water is tested against brine as a medium. Run 2 is used as the water medium case while Run 7 is used as the brine medium case. The contact angle measurements used in Run 7 are obtained from contact angle measurement results presented in Section 3.4. These contact angles are shown in Table X.

Table X: Contact angles used in the sensitivity analysis for medium change.

	Calcite	Dolomite	Feldspar	Pyrite	Quartz
Run 2	36.752	25.1	42.344	32.543	51.811
Run 7	35.454	62.674	49.275	60.047	51.175

The results of this analysis (Figure 35) shows that the rock shows more water wet behavior in case of water than brine. This result is related to the increase in contact angles of minerals measured in brine, and is consistent with low salinity flooding recovery mechanisms.

Figure 35: Sensitivity analysis based on contact angle measurements in water and brine.

4.3.4. Mineralogy Changes

Two runs are used in this section to indicate the change in mineralogy. Run 8 represents a rock where quartz is the dominant mineral while Run 9 represents a rock where calcite is the dominant mineral. Table XI shows the percentage of mineralogical content of the two runs.

Table XI: Mineralogical composition used to identify the effect of mineralogy change.

	Calcite	Dolomite	Feldspar	Pyrite	Quartz
Run 8	10%	10%	5%	5%	70%
Run 9	70%	10%	5%	5%	10%

The model results are shown in Figure 36. These results shows that the rock shows more water wet behavior in case of calcite that quartz.

Figure 36: Sensitivity analysis based on mineralogy change.

4.3.5. Fractional and Mixed Wettability

Two final runs are used to compare between fractional and mixed wettability models. Run 2 represents the base case that was used in previous sections and run 10 represents the mixed wettability model where only one contact angle is assumed to all the minerals as shown in Table

XII. The contact angle used in the mixed wettability model is the advancing contact angle obtained from the experimental measurements in chapter 3.

Table XII: Contact angles used in the sensitivity analysis for medium change.

	Calcite	Dolomite	Feldspar	Pyrite	Quartz
Run 2	36.752	25.1	42.344	32.543	51.811
Run 10	27.248	27.248	27.248	27.248	27.248

The model results are shown in Figure 37. These results shows that the mixed wettability model assumes a more water-wet system than the fractional wettability model.

Figure 37: Sensitivity analysis based on fractional and mixed wettability models.

5. Conclusions

Reservoir models are used to predict reservoir performance and study the potential of improved oil recovery techniques; however, many models do not implement some factors such as wettability parameters and mineral composition. These factors can be neglected in reservoirs with high porosity and permeability and uniform rock composition. However, tight reservoirs with heterogeneous mineral composition like the Bakken show high deviation from conventional reservoirs. These kinds of reservoirs are poorly modeled when using conventional reservoir modeling techniques. The purpose of this research was studying the effects of wettability on different mineral compositions and use the study results in building a microscale model. The outcomes of this research are presented in the next two sections.

5.1. Contact Angle Measurements

The contact angle measurement experiment aimed to test the wettability of different minerals in different media. The experiment showed that some minerals are highly affected with medium change and others do not show any significant difference. These results lead to the following conclusions:

- 1- The pores inside reservoir rocks have different mineralogy. As a result, the reservoir does not behave in a uniform way. Bakken is an example of a heterogeneous reservoir rocks, hence non-uniform wettability should be included in the Bakken reservoir rock simulation.
- 2- When medium changes due to waterflooding or gas injection, each mineral inside the reservoir responds to this change differently. In other words, the wettability of pores changes according to the mineral that constitutes these pores. As a result, some pores

- (e.g. Pores composed of calcite, Feldspar II or quartz) remains water wet while other pores (e.g. Pores composed of Dolomite I or Pyrite) change to oil wet.
- 3- According to Morrow et al. (2011), low salinity waterflooding is capable of increasing oil recovery from reservoir rock. This behavior was seen within some of the minerals tested in this research. Low salinity water leads to a decrease in contact angles of four tested mineral samples while the other two remained constant. In other words, the wettability of pores inside the reservoir changes to be more water wet when low salinity water is used in waterflooding instead of brine.
 - 4- Bakken can be better represented following the fractional wettability model while considering the formation of oil layer on minerals surface and the stability of this layer.

5.2. Pore-scale Network Model

A pore-scale network model was constructed to study the applicability of fractional wettability model. This model was applied by assigning pores different mineralogy according a certain ratio representing the percentage of these minerals in a reservoir rock. The results obtained from this model lead to the following conclusions:

- 1- Mixed wettability models should be compared to fractional wettability models when the composition of the reservoir is highly heterogeneous as in the case of Bakken. The pore-scale network model used in this study showed how the rock behavior changes according to the rock mineral content.
- 2- A pore-scale network model that considers the pore structure and reservoir rock composition is capable of producing relevant relative permeability and capillary pressure curves that represents the behaviors of reservoir rock. This is important because it is difficult to measure these parameters for unconventional reservoirs.

- 3- Pore-scale network model can be used to illustrate pore properties which are not considered (or partially considered) in macroscale models. In addition, macroscale models can implement some of the properties obtained from pore-scale network models.
- 4- When the medium changes from water to brine, reservoir rock shows more oil wet behavior. As a result, low salinity can be more effective in waterflooding projects.
- 5- Minerals contact angle, medium and mineralogical content are the main reasons of the reservoir behavior to be water wet or oil wet.
- 6- Relative permeability curves for two identical reservoirs, except in pore size, can be the same. The difference is that the reservoir with low pore sizes advances slowly through the relative permeability curves.
- 7- Pore-scale network model requires high computing resources especially if there is any plans of upscaling the model to a core-scale model.

6. Future Work

This study is a conceptual work aiming to better understand heterogeneous reservoirs behavior. Future development of this research is crucial to obtain more representative models of shale oil reservoirs. Some of this work is:

- 1- Calculating the average contact angle of reservoir rock surfaces based on measured void and surface areas as well as the mineralogical content of that surface.
- 2- Conducting contact angle and interfacial tension measurements under high pressure and high temperature conditions which are relevant to the studied reservoir conditions.
- 3- Using CT scanner to accurately measure pore spaces of the studied core samples.
- 4- Developing a microscale network model to consider other pore-scale flow mechanisms such as snap-off and pore filling.
- 5- Studying the adhesion tension of different crude oil samples to determine the stability of oil layer on different minerals.

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8. Appendix A: Source Code

```

program FP
implicit none

real :: x, Sigma_ow, Sigma_go, Sigma_gw, sf, Thita_ow, Thita_go, Thita_gw, p, Half_Angle
real :: Pmax, b, Hinging_Angle, Pcollapse, Soi, Po, Pw, Pcow, Pcgw, Pcgo, row, rgw, rgo, Ro,
Rco, Rw, Rcw, z, Swi
real :: Quartz, Calcite, Feldspar, Dolomite, Pyrite, Total_Area, Area
integer :: i,j,n,k, l,t, Rmin, Rmax
double precision::pi
real, dimension(:,,:), allocatable :: NT,WF, WF_fnl, GI, GI_fnl

pi=3.1415926536d0
Half_Angle=30
Rmin = 0.1
Rmax = 1.0

n = 2000
Sigma_ow = 0.048  !N/m

Thita_ow = 60
Soi=0.2
Swi=0.02

!-----Mineral Composition-----!
Quartz = 0.1
Calcite = 0.1
Feldspar = 0.05
Dolomite = 0.7
Pyrite = 0.05
!-----Primary Drainage(Blunt)-----!

allocate(NT(n,20))
allocate(WF(n,15))
allocate(GI(n,15))
allocate(WF_fnl(n/5,10))
allocate(GI_fnl(n/5,10))

!Calculating Pcow and R
Total_Area = 0
do i=1 , n
call random_number(x)
NT(i,1) = i
! #

```

```

NT(i,2) = 0.000001*((Rmax-Rmin)*((-0.8*log(x*(1-exp(-1/0.8))+exp(-1/0.8))))*(1/1.6)) +
Rmin) !R    (m)
NT(i,5) = At(NT(i,2))!At
Total_Area = Total_Area + NT(i,5)
end do

```

```

!Quartz
Area = 0
do i=1,n
    NT(i,18) = 51.811
    Area = Area + NT(i,5)
    if ((Area/Total_Area) >= Quartz) exit
    z=i
end do

```

```

!Calcite
Area = 0
do i=z,n
    NT(i,18) = 36.752
    Area = Area + NT(i,5)
    if ((Area/Total_Area) >= Calcite) exit
    z=i
end do

```

```

!Dolomite
Area = 0
do i=z,n
    NT(i,18) = 25.1
    Area = Area + NT(i,5)
    if ((Area/Total_Area) >= Dolomite) exit
    z=i
end do

```

```

!Feldspar
Area = 0
do i=z,n
    NT(i,18) = 42.344
    Area = Area + NT(i,5)
    if ((Area/Total_Area) >= Feldspar) exit
    z=i
end do

```

```

!Pyrite
Area = 0
do i=z,n
    NT(i,18) = 32.543

```

end do

!Calculating threshold capillary pressure

do i=1,n

NT(i,3) =

$$(\text{Sigma_ow}/(\text{NT}(i,2))) * (\cos(\text{NT}(i,18) * \pi / 180d0) + \sqrt{(\tan(30.0 * \pi / 180d0) / 2) * (\sin(2 * \text{NT}(i,18) * \pi / 180d0) \& \\ - (2 * \text{NT}(i,18) * \pi / 180d0) - (2 * 30 * \pi / 180d0) + \pi)}))$$

! Pcow (pascal) for
drainage
end do

!Arranging Pcow and R

do k=1,n

do j=1,n-1

if (NT(j,3) > NT(j+1,3)) then

!Arranging Pcow

sf = NT(j,3)

NT(j,3) = NT(j+1,3)

NT(j+1,3)=sf

!Arranging R

sf = NT(j,2)

NT(j,2) = NT(j+1,2)

NT(j+1,2)=sf

!Arranging Contact Angle

sf = NT(j,18)

NT(j,18) = NT(j+1,18)

NT(j+1,18)=sf

end if

end do

end do

! Creating the TxT file

open(unit=1 , file='mineral.txt')

do i=1,n

write(1,*) NT(i,1),NT(i,2),NT(i,3),NT(i,18)

end do

close(unit=1)

do i=1,n

NT(i,4)=0.0 !Status

NT(i,5) = At(NT(i,2))!At

NT(i,8)=gt(NT(i,5),NT(i,2))!gt

end do

!Invasion Percolation

do i=1,n

```

NT(i,4)=1.0 !Status
p=NT(i,3) !P
row=Sigma_ow/p
do j=1,n
  if (NT(j,4)==1.0) then
    NT(j,6)=Aw(row,NT(j,18))!Aw
    NT(j,7)=NT(j,5)-NT(j,6)!Ao
    NT(j,9)=gw_1(NT(j,6),NT(j,18))!gw
    NT(j,10)=go(NT(j,7),NT(j,2)) !go
  else if (NT(j,4)==0.0) then
    NT(j,6)=NT(j,5)!Aw=At
    NT(j,7)=0.0
    NT(j,9)=NT(j,8)!gw=gt
    NT(j,10)=0.0 !go
  end if
end do
NT(i,11)=sum(NT(1:n,6))/sum(NT(1:n,5))!Sw
NT(i,12)=sum(NT(1:n,9))/sum(NT(1:n,8))!Krw
NT(i,13)=sum(NT(1:n,10))/sum(NT(1:n,8))!Kro
z=i
! if (NT(i,11) < Swi) exit
end do

Pmax= NT(z,3)
do i=1,n
  NT(i,19)=(sigma_ow*(1/tan(Half_Angle*pi/180d0)*cos(NT(i,18)*pi/180d0)-
sin(NT(i,18)*pi/180d0))/Pmax) !b
end do

! Creating the TxT file
open(unit=1 , file='PD.txt')
do i=1,n
write(1,*) NT(i,11),NT(i,12),NT(i,13), NT(i,3)
end do
close(unit=1)

!-----Water Flooding(Blunt)-----!

! Calculating Threshold Capillary Pressure
do i=1,n
  NT(i,14)= Thita_c(NT(i,2), NT(i,18)) !Thita_C
  if (NT(i,18) < NT(i,14)) then
    NT(i,3)= p_1(NT(i,2), NT(i,18))
  else if (NT(i,18) > NT(i,14) .and. Thita_ow <= (90+Half_Angle)) then
    if (NT(i,18) >= 90) then
      NT(i,3)= p_2(NT(i,2), NT(i,18))
    end if
  end if
end do

```

```

    else if (NT(i,18) < 90) then
        NT(i,3)= - p_2(NT(i,2), NT(i,18))
    end if
    else
        NT(i,3)= (Sigma_ow/(NT(i,2)))*(cos(NT(i,18)*pi/180d0)-sqrt((tan(30.0*pi/180d0)/2)*(-
sin(2*NT(i,18)*pi/180d0) &
        + (2*NT(i,18)*pi/180d0) - (2*30*pi/180d0)-pi)))
        !NT(i,3)= p_3(NT(i,2),NT(i,5))
    end if
end do

! Rearranging the pores
do k=1,n
do j=1,n-1
    if (NT(j,3) < NT(j+1,3)) then
        !Rearranging R
        sf = NT(j,2)
        NT(j,2) = NT(j+1,2)
        NT(j+1,2)=sf
        !Rearranging P
        sf = NT(j,3)
        NT(j,3) = NT(j+1,3)
        NT(j+1,3)=sf
        !Rearranging Status
        sf = NT(j,4)
        NT(j,4) = NT(j+1,4)
        NT(j+1,4)=sf
        !Rearranging At
        sf = NT(j,5)
        NT(j,5) = NT(j+1,5)
        NT(j+1,5)=sf
        !Rearranging gt
        sf = NT(j,8)
        NT(j,8) = NT(j+1,8)
        NT(j+1,8)=sf
        !Rearranging go
        sf = NT(j,14)
        NT(j,14) = NT(j+1,14)
        NT(j+1,14)=sf
        !Rearranging CA
        sf = NT(j,18)
        NT(j,18) = NT(j+1,18)
        NT(j+1,18)=sf
        !Rearranging b
        sf = NT(j,19)
        NT(j,19) = NT(j+1,19)
    end if
end do
end do

```

```

NT(j+1,19)=sf
end if
end do
end do

```

```

!Necessary to check for Soi
do i=1,n
  NT(i,11)=0.0
  NT(i,12)=0.0
  NT(i,13)=0.0
end do

```

```

do i = 1,n
  if (NT(i,18) <= 90+Half_Angle .and. NT(i,4) /= 0.0) then
    NT(i,4) = 4.0
  else if (NT(i,18) > 90+Half_Angle .and. NT(i,4) /= 0.0) then
    NT(i,4) = 3.0
  end if
  p= NT(i,3)
  row= Sigma_ow/p
  do k = i+1,n
    NT(k,20) = Thita_h(p, NT(k,19))
    if (NT(k,20) > NT(k,18)) then
      NT(k,20) = NT(k,18)
    end if
  end do
  do j = i+1,n
    if (NT(j,20) < 90 - Half_Angle) then
      NT(j,4) = 1.0
    else if (NT(j,20) >= 90 - Half_Angle) then
      NT(j,4) = 2.0
    end if
    if (NT(j,4) == 3.0 .and. p < p_col(NT(j,18))) then
      NT(j,4) = 4.0
    end if
  end do
  do t= 1,n
    if (NT(t,4)==0.0 .or. NT(t,4)==4.0) then
      NT(t,6)=NT(t,5)!Aw=At
      NT(t,7)=0.0
      NT(t,9)=NT(t,8)!gw=gt
      NT(t,10)=0.0 !go
    else if (NT(t,4)==1.0) then
      NT(t,6)=Aw(row,NT(t,20))!Aw
      NT(t,7)=NT(t,5)-NT(t,6)!Ao
    end if
  end do
end do

```

```

        NT(t,9)=gw_1(NT(t,6),NT(t,20))!gw
        NT(t,10)=go(NT(t,7),NT(t,2)) !go
    else if (NT(t,4)==2.0) then
        NT(t,6)=Aw(row,NT(t,20))!Aw
        NT(t,7)=NT(t,5)-NT(t,6)!Ao
        NT(t,9)=gw_2(NT(t,6))!gw
        NT(t,10)=go(NT(t,7),NT(t,2)) !go
    else if (NT(t,4)==3.0) then
        NT(t,15)=Aw(row,180.0-NT(t,18))!A_corner
        NT(t,16)=Aw_2(row,NT(t,20))!A_corner_water
        NT(t,17)=NT(t,5) - NT(t,15)!A_center_water
        NT(t,7)= Aol(row, NT(t,18)) !Ao
        NT(t,6)= NT(t,5) - NT(t,7)!Aw
        NT(t,9)= gw_2(NT(t,16)) + gt(NT(t,17),NT(t,2))!g_corner_water + g_center_water
        NT(t,10)=go_2(NT(t,7),NT(t,15),NT(t,16),1.0,1.0)!go
    end if
end do
NT(i,11)=sum(NT(1:n,6))/sum(NT(1:n,5))!Sw
NT(i,12)=sum(NT(1:n,9))/sum(NT(1:n,8))!Krw
NT(i,13)=sum(NT(1:n,10))/sum(NT(1:n,8))!Kro
if (NT(i,11) > 1-Soi) exit
end do

```

```

! Creating the TxT file
open(unit=2 , file='WF.txt')
do i=1,n
write(2,*) NT(i,11),NT(i,12), NT(i,13), NT(i,3)
end do
close(unit=2)

```

!-----Functions-----!

CONTAINS

FUNCTION Aw(r,m)

real :: Aw

real, intent(in) :: r,m

Aw = 3*(r**2)*(cos(m*pi/180d0)*((1/tan(Half_Angle*pi/180d0))*cos(m*pi/180d0)-

sin(m*pi/180d0)) &

+ m*pi/180d0 + Half_Angle*pi/180d0 - pi/2)

END function Aw

FUNCTION Aw_2(r,m)

real :: Aw_2

real, intent(in) :: r,m

Aw_2 =

3*(r**2)*(((cos(m*pi/180d0)*cos((m+Half_Angle)*pi/180d0))/(sin(Half_Angle*pi/180d0))) &


```

      -((pi/2)*(1-(((m+Half_Angle)*pi/180d0)/(90*pi/180d0))))))
END function Aw_2

```

```

FUNCTION Aol(r,m)
real :: Aol
real, intent(in) :: r,m
Aol = 3*(r**2)*(((cos(m*pi/180d0)*cos((m-
Half_Angle)*pi/180d0))/(sin(Half_Angle*pi/180d0))) &
      -((pi/2)*(-1+(((m-Half_Angle)*pi/180d0)/(90*pi/180d0))))))
END function Aol

```

```

FUNCTION At(r)
real :: At
real, intent(in) :: r
At = 3*((r)**2)*(1/tan(30.0*pi/180d0))
END function At

```

```

FUNCTION gw_1(r,m)
real :: gw_1, phi_1, phi_2, phi_3
real, intent(in) :: r,m
phi_1 = (90-Half_Angle-m)*pi/180d0
phi_2 = ((1/tan(Half_angle*pi/180d0))*cos(m*pi/180d0))-sin(m*pi/180d0)
phi_3 = ((90-Half_Angle)*pi/180d0)*tan(Half_Angle*pi/180d0)
gw_1 = ((r**2)*((1-sin(Half_Angle*pi/180d0))**2)*(phi_2*cos(m*pi/180d0)-
phi_1)*(phi_3**2)) &
      / (12*3*(sin(Half_Angle*pi/180d0)**2)*((1-
phi_3)**2)*((phi_2+phi_1)**2)) ! gw
END function gw_1

```

```

FUNCTION gw_2(r)
real :: gw_2, phi_1, phi_2, phi_3
real, intent(in) :: r
phi_3 = ((90-Half_Angle)*pi/180d0)*tan(Half_Angle*pi/180d0)
gw_2 = ((r**2)*((1-
sin(Half_Angle*pi/180d0))**2)*tan(Half_Angle*pi/180d0)*(phi_3**2)) &
      / (12*3*(sin(Half_Angle*pi/180d0)**2)*(1-phi_3)*((1+phi_3)**2))
! gw
END function gw_2

```

```

FUNCTION gt(a,c)
real :: gt
real, intent(in) :: a,c
gt = (pi*(sqrt(a/pi)+c)**4)/128
END function gt

```

```

FUNCTION go(a,c)

```

```

real :: go
real, intent(in) :: a,c
go = (pi*(sqrt(a/pi)+c)**4)/128
END function go

```

```

FUNCTION Thita_c(radius, thetaPD)
real :: Thita_c
real, intent(in) :: radius, thetaPD
Thita_c = (acos((-sin((Half_Angle+thetaPD)*(pi/180d0))*sin(Half_Angle*pi/180d0))/ &
    ((radius*Pmax/sigma_ow)*cos(Half_Angle*pi/180d0)&
    -cos((Half_Angle+thetaPD)*(pi/180d0)))))*(180d0/pi)
END function Thita_c

```

```

FUNCTION p_1(R, Thita)
real :: p_1, f, a, b, c, d, e
real, intent(in) :: R, Thita
f=R
do j=1,4
    a = sigma_ow/f ! Pcow (Pa), f=r
    b = (sigma_ow*(1/tan(Half_Angle*pi/180d0)*cos(Thita*pi/180d0)-
sin(Thita*pi/180d0))/Pmax) ! b (m)
    c = (asin(b*sin(Half_Angle*pi/180d0)/R))*(180d0/pi) ! Beta
    d = ((R**2)/(2*tan(Half_Angle*pi/180d0))) - &
        (0.5*(f*b*sin((Half_Angle+c)*pi/180d0))) + &
        (0.5*(f**2)*(c*pi/180d0)) ! A_eff
    e = (((R/tan(Half_Angle*pi/180d0))-b)*cos(Thita*pi/180d0)) + &
        f*(c*pi/180d0) ! O_eff
    f = d/e ! r
end do
p_1= a
END function p_1

```

```

FUNCTION p_2(a, Thita)
real :: p_2
real, intent(in) :: a, Thita
p_2 = (2*Thita*cos(Thita*pi/180d0))/a
END function p_2

```

```

FUNCTION p_3(R,At,m)
real :: p_3, L, a, b, c, row, row_1, row_2
real, intent(in) :: R, At,m
L= (2*At)/R
a= 3*((pi/2)+(Half_Angle*pi/180d0)-(m*pi/180d0)+ &
    ((cos(m*pi/180d0)*cos((m-Half_Angle)*pi/180d0))/(sin(Half_Angle*pi/180d0))))
b= -L*cos(m*pi/180d0)
c= At

```

```

row_1=(-b+sqrt((b**2)-(4*a*c)))/(2*a)
row_2=(-b-sqrt((b**2)-(4*a*c)))/(2*a)
if (row_1 > row_2) then
row= row_2
else if (row_1 < row_2) then
row= row_1
end if
p_3= Sigma_ow/row
END function p_3

```

```

FUNCTION Thita_h(a,length)
real :: Thita_h
real, intent(in) :: a,length
Thita_h = ((acos((a*length*sin(Half_Angle*pi/180d0))/(Sigma_ow)))-
(Half_Angle*pi/180d0))*(180d0/pi)
END function Thita_h

```

```

FUNCTION p_col(m)
real :: p_col, f, y, z, p_1, p_2
real, intent(in) :: m
!real, intent(in) :: a
!do f=0.0,180.0,1
!y= (Thita_ow*pi/180d0) + (f*pi/180d0) - pi - ((cos(Thita_ow*pi/180d0)*cos((Thita_ow-
Half_Angle)*pi/180d0))/(sin(Half_Angle*pi/180d0)) &
! + ((2*cos(Thita_ow*pi/180d0)-
cos(f*pi/180d0))*((cos((f+Half_Angle)*pi/180d0))/(sin(Half_Angle*pi/180d0))))
!if (y>0.0000001) exit
!end do
!z= (b*sin(Half_Angle*pi/180d0))/(cos((f+Half_Angle)*pi/180d0))!row
!p_col= Sigma_ow/z
p_col=
(Sigma_ow*((cos(Half_Angle*pi/180d0)*sin(Half_Angle*pi/180d0)*(2*sin(Half_Angle*pi/180
d0) &
+cos(m*pi/180d0)))+(((sin(Half_Angle*pi/180d0))**2)*(sqrt(4*((cos(Half_Angle*pi/180d0))**
2) &
-3-((cos(m*pi/180d0))**2)-4*sin(Half_Angle*pi/180d0)*cos(m*pi/180d0)))))/ &
(b*(3*((sin(Half_Angle*pi/180d0))**2)+4*sin(Half_Angle*pi/180d0)*cos(m*pi/180d0) &
+((cos(m*pi/180d0))**2)))
!p_2=
(Sigma_ow*cotan(Half_Angle*pi/180d0)*(2*sin(Half_Angle*pi/180d0)+cos(Thita_ow*pi/180d
0))-sqrt(((sin(Thita_ow*pi/180d0))**2)- &
! 4*((sin(Half_Angle*pi/180d0))**2)-
4*sin(Half_Angle*pi/180d0)*cos(Thita_ow*pi/180d0)))/(b) ! Geometrical Collapse
END function p_col

```

```

FUNCTION go_2(a,b,c,d,e)
real :: go_2, phi_3
real, intent(in) :: a,b,c,d,e
    phi_3 = ((90-Half_Angle)*pi/180d0)*tan(Half_Angle*pi/180d0)
    go_2 = ((a**3)*((1-
sin(Half_Angle*pi/180d0))**2)*(tan(Half_Angle*pi/180d0))*((phi_3)**2))/ &
    (12*3*b*((sin(Half_Angle*pi/180d0))**2)*(1-phi_3)*((1+(d*phi_3)-((1-
(e*phi_3))*(sqrt(c/b))))**2))
END function go_2
end program FP

```

9. Appendix B: Parts Used in the Experiment

Fluid cell design

Fluid cell holder

Positioning tool

Samples holder

SIGNATURE PAGE

This is to certify that the thesis prepared by Andrew Fakhry entitled "The Effect of Mineral Composition on Shale Oil Recovery" has been examined and approved for acceptance by the Department of Petroleum Engineering, Montana Tech of The University of Montana, on this 1st day of December, 2017.

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