DETERMINING OSMOTIC PRESSURE IN NIOBRARA CHALK AND CODEL SANDSTONE USING HIGH-SPEED CENTRIFUGE

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Petroleum Engineering).

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ABSTRACT

Low salinity waterflooding is an emerging enhanced oil recovery (EOR) technique that has attracted the attention of the oil industry. However, the classical application of waterflooding in unconventional shale reservoirs is impractical because of the nanoscale dimension of the matrix pores. Salinity contrast across shale matrix blocks leads to osmotic pressures which expels oil from tight shale. This thesis exploited this phenomenon to measure osmotic pressure in shale core plugs.

Typically, all the unconventional shale reservoirs produce hydrocarbon after hydraulic fracture stimulation. The stimulation treatment is performed using slick water and some gel components. A large percentage of this injected fluid is trapped inside the pores and cannot be produced. The findings and results of this thesis can be used to investigate the osmotic effect of the hydraulic fracturing fluids in tight shale formations.

This thesis includes measurement of osmotic pressure using ultra-high-speed centrifuge experiments and calculation of membrane efficiency for unconventional Niobrara chalk and Codell sandstone formations. The laboratory experiments show that the low-salinity brine is imbibed into the core samples in greater quantities compared to that of high-salinity brine. The brine imbibition is measured by displacement and production of resident oil in the core. Measured membrane efficiency of Niobrara B-Chalk, with permeability of 0.0022-0.0099 md, is 75 % of perfect membrane. Accounting for chalk solubility in brine within the pores should reduce the membrane efficiency to about 50%. Similarly, measured membrane efficiency of Codell sandstone, with permeability of 0.0085-0.0105 md, is 2.4 % of the perfect membrane.
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LIST OF SYMBOLS - ENGLISH

\( B \) constant for each solvent that is related to the deviations of the system from the ideal solution laws
\( c \) Molar concentration
\( I \) ionic strength
\( l \) length of the sample
\( M \) molality of the electrolyte
\( MW \) Molecular weight of solvent
\( n \) rotation speed
\( n \) Number of moles
\( p \) Pressure
\( p_c \) Capillary pressure
\( p_{nw} \) Non-wetting phase pressure
\( p_w \) Wetting phase pressure
\( R \) Gas constant
\( r \) distance from the center of rotation
\( r_2 \) distance from the center of rotation to outer face of the core
\( s \) Solvent
\( S_o \) Saturation of oil
\( S_w \) Saturation of water
\( S_{w,irr} \) Irreducible water saturation
\( T \) Temperature, \( T \)
\( x \) Mole fraction
\( z_i, z_j \) valences of ions
## LIST OF SYMBOLS - GREEK

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>Constant</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Constant</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Activity coefficient</td>
</tr>
<tr>
<td>( \delta )</td>
<td>The change in ions</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Constant</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>( \mu^* )</td>
<td>Standard state where the chemical potential of pure liquid solvent at system temperature and at zero pressure</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Number of positive and negative ions</td>
</tr>
<tr>
<td>( \pi )</td>
<td>Osmotic pressure</td>
</tr>
<tr>
<td>( \Delta \rho )</td>
<td>Density difference between the phases</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Sigma function</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Molar volume</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Angular velocity</td>
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## LIST OF SYMBOLS – SUBSCRIPT AND SUPERSCRIPT

<table>
<thead>
<tr>
<th>Subscript/Superscript</th>
<th>Description</th>
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<tr>
<td>1</td>
<td>Solvent</td>
</tr>
<tr>
<td>2</td>
<td>Solute</td>
</tr>
<tr>
<td>( A, B )</td>
<td>Phase</td>
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ACKNOWLEDGEMENTS

I want to express my sincere gratitude to my advisor Dr. Hossein Kazemi for his guidance and insight throughout the thesis study and during my studies in Colorado School of Mines. He inspired me to become an independent researcher and experimentalist. It has been a great privilege and pleasure to work with him. Without his expert advice and support it would not have been possible to finish this work. I would also like to thank to my committee members, Dr. Erdal Ozkan and Dr. Azra Tutuncu who helped me to understand the reservoir engineering concept and enrich my ideas. I would like to extend my gratitude to my minor advisor Dr. Steve Sonnenberg whose technical expertise greatly contributed to improve and broaden my scientific knowledge in petroleum geology.

I am also thankful for my company, Schlumberger, for granting me educational leave of absence to pursue my MS degree. I am thankful to all my colleagues in MCERS with special thanks to Denise Winn-Bower for her support and assistance throughout my MS study.

I would also like to thank my friends who helped me to cheer up and get through the hard times; Jason Carey, Sergio Suarez-Fernandez, and many others.

Needless to say, I am very grateful to my parents, my sister Ilkay and brother-in-law Erdinc, it would not be possible without your love and source of energy.
CHAPTER 1 INTRODUCTION

This thesis presents a practical technique to measure osmotic pressure in Niobrara chalk and Codell sandstone cores using an ultra-high-speed centrifuge. In this chapter, I will present the research objective, a brief description of methodology, and research contributions.

1.1 Problem Statement

Hydrocarbon recovery from unconventional reservoirs is very low; that is, maximum of ten percent. Therefore, improved methods to increase the oil production from shale reservoirs are needed. Classical waterflooding in unconventional reservoirs is not plausible because of the pore sizes; however, creating osmotic pressure by salinity contrast can cause a counter-current flow of oil and water by imbibing water to expel oil. Despite this apparent and potential benefit of osmotic pressure to make waterflooding feasible in shale reservoirs, waterflooding shale reservoirs is essentially impossible because of the tight matrix. The latter is the motivation for the research in this thesis.

Large salinity contrasts between stimulation fluids and formation lead to large osmotic pressures. This could improve the extraction of oil from the tight matrix of unconventional shale reservoirs. Thus, the potential of osmotic pressure created as a function of salinity contrast in such formations should be investigated. A related issue is gas trapping in many water drive gas reservoirs. This thesis also documents the use of the centrifuge to measure trapped gas saturation.

The aforementioned notions could lead to standard laboratory techniques for measuring osmotic pressure for use in shale reservoirs and trapped gas saturation in water drive gas reservoirs.

This thesis embarks on two different ideas: (1) Determining osmotic pressure in shale core samples, and (2) Enhancing oil recovery by low-salinity brine osmotic force to displace oil.

1.2 Objectives

The objectives of this research are:

(i) Investigate the potential of oil production improvement using the osmotic pressure concept for unconventional shale reservoirs.
(ii) Investigate the trapped gas saturation using standard trapped gas saturation measurements.

1.3 Methodology

Experimental work was performed using ultra-high-speed centrifuge with formation brine and low salinity brine for cores from Niobrara chalk and Codell sandstone formations to examine the effect of salinity contrast. Initially, CMS-300 device was used to estimate the pore volume, porosity and permeability values of the cores. Then, the centrifuge was used to saturate the cores with formation brine. Following core saturation, the cores were drained using decane in a drainage setup and then forced imbibition process was performed with low salinity brine using an imbibition setup. In between drainage and forced imbibition processes, spontaneous imbibition was performed with low salinity brine.

Trapped gas measurements were performed using ultra-high-speed centrifuge with formation brine and air by using cores from Bulo Bulo Field, Robore-III formation, Bolivia to examine the trapped gas saturation. Initially, the CMS-300 system was used to estimate the pore volume, porosity and permeability values of the cores. Then, the centrifuge was used to saturate the cores with formation brine. In contrast to osmosis experiments, for the drainage process, the formation brine saturated core was drained with air followed by forced imbibition process, in which the formation brine was injected. In between drainage and forced imbibition processes, the spontaneous imbibition was performed with formation brine using the under weighting balance setup.

1.4 Research Contributions

In this research, the osmotic pressure created via salinity contrast in unconventional shale reservoirs was measured using ultra-high-speed centrifuge experiments. High-speed centrifuge is a novel technique to rapidly measure osmotic pressure in very low permeability cores. Furthermore, it was observed that the osmotic pressure could improve the oil production from such tight matrix formations. Consequently, the imbibition force to determined the EOR fraction was quantified. Moreover, the membrane efficiency was calculated.
In addition to quantifying osmotic pressure and the EOR by osmosis, I also embarked on quantifying the magnitude of trapped gas saturation when water enters a core.

1.5 Thesis Organization

This thesis has eight chapters.

Chapter 1 states the purpose, motivation, objectives, methodology, and the contributions of the research.

Chapter 2 presents the relevant publications that focus on the effects of low salinity brine on conventional reservoirs and theories on the effect of low salinity brine on production.

Chapter 3 presents an overview of the osmotic pressure, focusing on the semi-permeable behavior of clays.

Chapter 4 presents a geological overview of the Niobrara chalk and Codell sandstone formations.

Chapter 5 discusses the experimental methods. Core cleaning process, porosity and permeability measurements using CMS-300, drainage, and imbibition process using ultra-high-speed centrifuge are explained.

Chapter 6 presents the literature review on trapped gas saturation, a geological overview of Robore III formation, and discusses the experimental methods for trapped gas measurements.

Chapter 7 presents results of osmotic pressure experiments. The discussion of the results is also included in this chapter.

Chapter 8 presents the conclusions and recommendations of this research.
CHAPTER 2 EFFECT OF LOW SALINITY BRINE

The investigation on the effect of low salinity concentration brine on production dates back to the 1940s. However, it did not attract the attention of researchers on the EOR/IOR aspect until the 1990s. During the 90’s Morrow’s research on the effect of wettability on oil recovery led him and his colleagues to focus on the effects of salinity on oil recovery. Their research on Berea sandstone cores and cores from Prudhoe Bay, Alaska demonstrated the effect of brine salinity on the wettability of the rock and oil recovery. Tang and Morrow (1999) generalized the necessary conditions for the effect of low salinity to take place as; the presence of connate brine and initially resided clay content in rock along with mixed wettability. These can be accepted as the first screening efforts for low salinity mechanisms. However, further studies revealed that these conditions are not sufficient to explain the effect of low salinity. Later on, various other laboratory studies proved the possibility of oil recovery with low salinity flooding on oil recovery with promising results which followed by the discussions on the original driving mechanism for the technique.

This chapter presents the overview of the main theories of the effect of low salinity.

2.1 Overview of the Effect of Low Salinity Contrast

The main theories behind the effect of salinity contrast can be gathered under five mechanisms; fines migration, pH increase, multicomponent ion exchange, double layer expansion, and osmosis.

2.1.1 Fines Migration

Fines migration was the first mechanism that was proposed as a mechanism for oil recovery with salinity contrast. Bernard (1967) performed experiments for injecting NaCl brine to Berea sandstone cores and an outcrop core from Wyoming which had 1.2 % clay. According to this study, the increase in recovery was due to the improved microscopic sweep efficiency induced by clay swelling and plugging of pore throat by fines migration.

Fines migration also observed in the core samples during the low salinity flooding experiments conducted by Tang and Morrow (1999). In these experiments, it was observed that water took different flow paths due to the permeability reduction and increased differential
pressure. As a result, the sweep efficiency was improved. In addition to that, poorly cemented clay particles detached during the water flow, especially with low salinity water flow, which also assisted in the oil recovery by reducing the oil saturation, and therefore altering the wettability to more water-wet condition (Figure 2-1). The effect of permeability reduction and an increase in oil recovery with low salinity water flooding seen more on clay-rich sand samples rather than clean sandstone samples.

However, many other core flood studies, especially the ones carried out for BP by Lager et al., (2008) that used sandstone cores from oil reservoirs, showed that this mechanism could not be generalized as the primary driving mechanism as their experiments did not show fines migration or significant permeability decrease in the presence of increased oil recovery.

![Figure 2-1](image)  Fines migration in crude oil, brine, and rock interaction.

### 2.1.2 pH Increase

The pH increase was first proposed as the main driving mechanism for low-salinity effect by McGuire et al. (2005). An increase in oil recovery was observed when a sandstone core was flooded with low salinity water (1,500 ppm and 150 ppm) compared to a high salinity flood (15,000 ppm). The increase in pH of the effluent from 8 to 10 with low salinity flooding compared to high salinity flooding, similar to alkaline flooding by generating in-situ surfactants, caused a reduction in interfacial tension (IFT). The reduction in IFT will result in the mobilization of the capillary trapped residual oil.

Austad et al. (2010) proposed wettability alteration to the more water-wet side due to the pH increase. The interaction between the brine initially adsorbed inorganic cation Ca++, and an
organic compound to the clay would be disturbed when low saline water with low ionic concentration was injected. This low saline water would cause desorption and replacement of cations $\text{Ca}^{++}$ with proton $\text{H}^+$ and release $\text{OH}^-$ (Figure 2-2). Therefore, a local increase in pH would be created. Then, the local increase in pH close to the clay surface created a reaction between basic and acidic materials.

![Initial situation](image1)

<table>
<thead>
<tr>
<th>Initial situation</th>
<th>Low salinity flooding</th>
<th>Final situation</th>
</tr>
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<tbody>
<tr>
<td><img src="image2" alt="Diagram" /></td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
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</tbody>
</table>

Figure 2-2  Low salinity EOR effects with pH increase (The initial pH at reservoir condition may be around 5). Upper: Desorption of basic material. Lower: Desorption of acidic material. (Austad et al. 2010).

### 2.1.3 Multicomponent Ion Exchange

Polar compounds of the oil phases are bonded to multivalent cations at clay surfaces forming organometallic complexes or adsorbed to the rock, therefore increasing the oil-wetness of the rock surface. When low salinity brine was injected, multicomponent ion exchange (MIE) will take place by replacing the organic polar compounds from the rock with simple cations. Depending on the organic function of the organic matter and the condition of the clay surfaces, cation exchange, ligand bonding, cation and water bridging are affected by cation exchange during a low salinity brine injection (Figure 2-3).
Oil molecules are bound to clay particles by bridges of divalent cations such as Mg$^{++}$ and Ca$^{++}$. In high salinity water which has high ionic concentration, these bridges are compressed to the clay surface by electrical forces. By reducing the salinity, these forces are reduced, and the bridges can expand. This expansion allows non-bridging monovalent ions like Na$^+$ to access and replace the divalent cations. Therefore, the oil molecules are then free to be swept towards the production (Figure 2-4).
2.1.4 Double Layer Expansion

When an electrically charged surface contacts water it generates an electrically neutral layer which is created by the surface charge and the opposite charge within the brine which is called electrical double layer (EDL) shown in Figure 2-5. The thickness of this layer oppositely varies with the salinity, which means in high salinity solutions this layer will be compressed whereas in low salinity solutions it will thicken. This will result in a reduction in clay-clay attraction and change the wettability to more water-wet side and increase in oil detachment (Sheng 2014; Nasralla and Nasr-el-Din 2014).

The effect of the double layer was first introduced by Ligthelm et al. (2009) after a series of core flood experiments on Berea sandstone, Middle Eastern sandstone, and Middle Eastern limestone. An increase in the oil recovery was observed when the injection brine containing both Na\(^+\) and Ca\(^{2+}\), Mg\(^{2+}\) was changed to a brine containing Na\(^+\) only. It was concluded that under low salinity water condition, the number of Ca\(^{2+}\) and Mg\(^{2+}\) were not enough to act as bridges between negatively charged clay minerals and negatively charged oil-brine interface. Therefore, the repulsive forces exceeded the binding forces through the multivalent cation bridges and the polar oil components may be desorbed from the clay surfaces.

![Figure 2-5 A schematic of EDL (Subtech 2017).](image)
Later, Nasralla and Nasr-El-Din (2014) showed the effects of low salinity by measuring the zeta potential, which is the potential at the shear plane of EDL. The negatively-charged oil-water interface and clay surfaces have associated double layers (Figure 2-6a). Because of the interaction between the oil and the clay with the active oil components where the double layer thickness is small due to the high ionic strength of brine, the wettability of the rock will change into oil-wet. During low salinity, the double layers will expand and overlap (Figure 2-6b). This causes desorption in the binding between similarly charged oil-water interface and clay surface and resulting in repulsion and wettability alteration to the more water-wet surface (Figure 2-6c). Moreover, increasing the pH of the low salinity brine increases the repulsion forces between the oil components and the mineral surface.

![Figure 2-6](image)

**Figure 2-6** Hydrocarbon release mechanism through double layer expansion (Redrawn from Kuznetsov et al. 2015).

### 2.1.5 Osmosis

Recently, osmosis proposed as a possible mechanism for oil recovery for low salinity applications by Fakcharoenphol et al. (2014), Sandengen and Arntzen (2013) and Sandengen et al (2016). Even though these studies suggested that osmotic pressure is the driving force behind the
low salinity effect, they differ on the proposed semi-permeable membrane for osmosis to take place. Fakcharoenphol et al. (2014) suggested that the rock matrix, in particular, the shales, behaves as a semi-permeable membrane. The experiment carried out as low and high salinity imbibition using sandstone core samples from Middle Bakken formation. In addition to the experiments, a mathematical model was presented for a multi-phase, chemical osmosis flow model for hydrocarbon bearing shale formations by defining osmotic pressure as a function of salt concentration and the mathematical model was tested by validating the osmotic pressures measured in a shale sample experiment conducted by Takeda et al. (2012).

Sandengen et al. (2016) proposed that oil behaves as a semi-permeable membrane that transports water but not the ions based on the description of Su et al. (2010) on the behavior of oil. The driving force is the activity of the water, and water is thought to be passing through the oil and encounter with connate water which has higher salinity, and therefore connate water will swell and move the surrounding oil. The enclosure of water filled cavities with oil is required so that oil saturation would be high. Also, a wide pore size distribution would be beneficial. As a result, water will be moved from the water transporting large pores and into the less conductive network of small pores.

The focus of this research is the measurement of osmotic pressure. Therefore, osmosis and osmotic pressure will be covered in more detail in Chapter 3.
CHAPTER 3 OSMOSIS

Osmosis is the movement of solvent particles across a semipermeable membrane from a dilute solution into a concentrated solution. The solvent moves to dilute the concentrated solution and equalize concentration on both sides of the membrane.

This chapter includes (1) overview of osmosis concept and historical background, (2) clay mineralogy, and (3) semi-permeable behavior of clays.

3.1 Overview of Osmosis Concept

The spontaneous flow of a solvent through a semi-permeable membrane that separates two solutions having different solvent activity is called osmosis. Osmosis can be best explained with the classical experiment setup that consists of an open U-tube where two aqueous solutions having different concentrations (phase A and phase B) separated by a semi-permeable membrane with no initial hydraulic pressure difference. In this experiment, water will be transported to the higher concentration side until a hydraulic pressure difference is established (Figure 3-1). This hydraulic difference is equal to the theoretical osmotic pressure between the two solutions. So, unlike the name suggests, osmotic pressure is not a real pressure that is exerted within the solution. It is instead an abstraction that represents the pressure difference that has to be established at equilibrium.

![Figure 3-1 Osmotic pressure in a U-tube.](image)
3.1.1 Historical Background of Osmosis

The osmotic pressure was first described by Abbe Nollet in 1748. However, first direct measurements were conducted more than a century later by a botanist, Pfeffer in 1877 by using sugar solutions. He noted that membranes appeared to permit passage of water while restraining the passage of solutes. In 1861, Thomas Graham documented that transfer of certain substances is slower in diffusion while he was working on dialyzers. He called these substances colloids. He formulated the theory that these dissolved substances exert a pressure which is analogous of gas under certain conditions. After analyzing the results of the experiments of Pfeffer, Van’t Hoff also noted the analogy between the data and the perfect gas law (Farrington and Daniels 1979).

In Figure 3-1, the semi-permeable membrane is permeable to solvent 1 but impermeable to solute 2. Phases A and B are at the same temperature. The pressure on phase A is \( p \), while the pressure on phase B is \( p + \pi \) at equilibrium. The equation of chemical equilibrium is (Prausnitz et al. 1999),

\[
\mu_1^A = \mu_1^B \quad (3-1)
\]

Where, \( \mu \) is the chemical potential that is given by

\[
\mu_1^A = \mu_{\text{pure1}}^A(T, p) \quad (3-2)
\]

\[
\mu_1^B = \mu_{\text{pure1}}^B(T, p + \pi) + RT \ln a_1 \quad (3-3)
\]

Where, \( a \) is the activity which is related to the composition of through \( a_i = \gamma_i x_i \), in here \( \gamma \) is the activity coefficient, and \( x \) is the mole fraction.

For a pure fluid, \( \left( \frac{\partial \mu}{\partial p} \right)_T = \nu \) where, \( \nu \) is the molar volume. Assuming that the molar volume does not vary with pressure (incompressible fluid), we have

\[
\mu_{\text{pure1}}(p + \pi) = \mu_{\text{pure1}}(p) + \pi \nu_{\text{pure1}} \quad (3-4)
\]
Equation 3-2 can be rewritten as

$$-ln a_i = \frac{\pi \nu_{\text{pure}}}{RT}$$  \hspace{1cm} (3-5)$$

If the solution in phase $B$ is dilute, $x_i$ is close to unity; in that event $\gamma_i$ is also close to unity and Eq. 3-5 becomes,

$$-ln x_i = \frac{\pi \nu_{\text{pure}}}{RT}$$ \hspace{1cm} (3-6)$$

When $x_2 \ll 1, ln x_i = ln(1 - x_2) \approx -x_2$, Eq. 3-6 becomes

$$\pi \nu_{\text{pure}} = x_2 RT$$ \hspace{1cm} (3-7)$$

Because $x_2 \ll 1, n_2 \ll n_1 and x_2 \approx \frac{n_2}{n_1}$ Eq. 3-7 becomes,

$$\pi V = n_2 RT$$ \hspace{1cm} (3-8)$$

Where, $V = n_1 \nu_{\text{pure}}$ is the total volume available to $n_2$ moles of solute.

Equation 3-8 is termed as ideal osmotic pressure equation or Van’t Hoff equation. The ideal osmotic pressure relation was derived for systems where membrane permeability is not ion selective or for solutions of non-electrolytes. However, the osmotic pressure relation becomes more complex in case of the presence of aforementioned conditions. This condition can be described by a U-tube setup consisting of a chamber that is divided into two parts by a membrane that is ion selective, which means the membrane allows some of the ions to flow through while inhibiting others (Figure 3-2). In this case, it is necessary to satisfy the electrical neutrality criteria for each of the phases in the chamber in addition to the usual Gibbs equations for equality of chemical potentials (Praustnitz et al. 1999).
Now, consider an aqueous system in a chamber that is divided into two equal parts as phase A and phase B by a membrane as shown in Figure 3-2. The membrane is ion-selective and aqueous solution contains three ionic species: Na\(^{+}\), Cl\(^{-}\), and R\(^{-}\), where R\(^{-}\) is an anion which is larger than Cl\(^{-}\). The ion-selective membrane is permeable to water, Na\(^{+}\) and Cl\(^{-}\) but it is impermeable to R\(^{-}\).

In initial condition phase A contains only water, Na\(^{+}\) and R\(^{-}\) at molar concentrations \(c_{Na}^{i}\) and \(c_{R}^{i}\), and phase B contains only water and Na\(^{+}\) and Cl\(^{-}\) at molar concentrations \(c_{Na}^{i}\) and \(c_{Cl}^{i}\). In this initial condition, electroneutrality requires that,

\[
c_{Na}^{A,i} = c_{Na}^{B,i} \quad \text{and} \quad c_{Cl}^{A,i} = c_{Cl}^{B,i} \quad \text{(3-9)}
\]

To achieve equilibrium the ions will move through the ion-selective membrane. In this state, now let \(\delta\) represent the change in the concentration of Na\(^{+}\) in phase A. Because R\(^{-}\) cannot move through the membrane from one side to the other, the change in Cl\(^{-}\) concentration in phase B is \(-\delta\).

At equilibrium, the final concentrations are:

In phase A:
\[
\begin{align*}
    c_{Na}^{A,f} &= c_{Na}^{A,i} + \delta \\
    c_{Na}^{B,f} &= c_{Na}^{B,i} - \delta \\
    c_{Cl}^{A,f} &= c_{Cl}^{A,i} \\
    c_{Cl}^{B,f} &= c_{Cl}^{B,i} - \delta \\
    c_{R}^{A,f} &= c_{R}^{A,i} \\
    c_{R}^{B,f} &= 0
\end{align*}
\quad \text{(3-10)}
\]

In phase B:
\[
\begin{align*}
    c_{Na}^{B,f} &= c_{Na}^{B,i} - \delta \\
    c_{Na}^{A,f} &= c_{Na}^{A,i} + \delta \\
    c_{Cl}^{B,f} &= c_{Cl}^{B,i} \\
    c_{Cl}^{A,f} &= c_{Cl}^{A,i} - \delta \\
    c_{R}^{B,f} &= c_{R}^{B,i}
\end{align*}
\quad \text{(3-11)}
\]
The equation of chemical equilibrium for the solvent is,

$$\mu_s^A = \mu_s^B$$

(3-12)

Where, $s$ represents solvent.

The relationship between the chemical potential, pressure, and activity can be denoted by

$$\mu_s^A = \mu_s^* + p_A^s \nu_A + RT \ln a_A^s$$

(3-13)

$$\mu_s^B = \mu_s^* + p_B^s \nu_B + RT \ln a_B^s$$

(3-14)

Where, $\mu_s^*$ is the standard state where the chemical potential of pure liquid solvent at system temperature and zero pressure.

Substituting Equations 3-13 and 3-14 into Equation 3-12 yields,

$$\pi = p^A - p^B = \frac{RT}{\nu_s} \ln \left( \frac{a_s^B}{a_s^A} \right)$$

(3-15)

The activity coefficient of water in an aqueous Potassium Chloride ($KCl$) solution using Debye-Huckel limiting law,

$$\ln(x_{H_2O} y_{H_2O}) = -MW_{H_2O} v M_{KCl} \left[ 1 + \frac{\alpha}{3} z_+ z_- \sqrt{I} \sigma(\beta a \sqrt{I}) + \frac{\delta I}{2} \right]$$

(3-16)

Where,

$$\sigma(y) = \frac{1}{y^3} \left[ 1 + y - 2 \ln(1 + y) - \frac{1}{1 + y} \right]$$

(3-17)

Here, $MW$ is the molecular weight of the solvent, $v$ the number of positive and negative ions, $M$ molality of the electrolyte, $z_+ z_-$ valences of ions, $I$ ionic strength, $\sigma$ sigma function, and $\alpha$, $\beta a$, $\delta$ constants.

The measured osmotic pressure obtained from an experiment by using a nonideal membrane is different from the thermodynamically predicted value by using Equation 3-15 (Staverman 1952). The comparison of the theoretical and measured values of osmotic pressure will display the membrane efficiency of the media that is used as a semipermeable membrane.
Here, the membrane efficiency defines the ability of the media to deter ion movement when interacting with ionic fluids. The membrane efficiency will be equal to one if all ionic movement is stopped. Therefore, the media is a perfect semi-permeable membrane. The earlier studies to determine the membrane efficiency of shale samples showed that this value ranges between 0.18% to 4.23% (Zhang et al. 2008).

First laboratory studies on geological materials and the effect of osmosis were done by De Sitter (1947). He suggested that argillaceous sediments have the ability to act as a semi-permeable membrane to explain the salinity changes in subsurface waters in depth. Also, White (1957) proposed that the connate water salinities are the result of the filtering of salt ions by semi-permeable membranes.

In 1959, Berry determined the reason for the apparent hydrodynamic sink in the San Juan basin as osmosis. Kemper (1960), and also in another study by McKelvey and Milne (1962) showed the exclusion of the salt ions by using a clay membrane. On a follow-up study, Milne et al. (1964) conducted experiments to show the inhibition of salt transmission by applying a pressure gradient and using bentonite membranes. In 1961, Hill proposed that subsurface pressure anomalies in the San Juan basin of New Mexico and the pressure anomalies in Alberta, Canada, are the result of osmosis. Also, Zen and Hanshaw (1964) suggested that high pore pressures related with osmotic pressure may trigger the overthrust faulting. They proposed that in specific areas where the negative charge on the walls of colloidal sized pores which anions are entering restricts the transfer of dissolved salts but allowing the water to pass. Therefore, in this system, the colloidal sized small pores are acting as a semi-permeable membrane to allow the osmosis to occur.

Membrane behavior of clays has been known for a long time. Kharaka and Berry (1973) have shown that the hyperfiltration efficiency is a function of pressure and concentration gradients, temperature, membrane porosity, and type of ion. Another study by Wood (1976) suggested that the some of the dominant ionic species in the aquifer system of Saginaw, Michigan may be controlled by hyperfiltration by the help of the clay minerals in the formation.

Therefore, the theory of clays acting as semi-permeable membranes is used to explain the salinities and the chemical compositions of formation waters that cannot be explained solely by water-rock interactions. Thus, the mineralogy of clays is a crucial aspect to consider when discussing the semi-permeable membrane behavior of clay platelets.
3.2 Clay Mineralogy

Clay minerals are a combination of two units of atomic lattices, octahedron and silica tetrahedrons. They are characterized by the arrangement of the sheets that are formed by these atomic lattices and isomorphous substitution within the crystal’s structure. They occur in small sizes, and they have negative charges which are balanced by the adsorption of cations from the solutions (Mitchell and Soga 2005, Grim 1968).

The octahedron is made up of two sheets of tightly packed oxygen or hydroxyls where aluminum (Al), iron (Fe), or magnesium (Mg) are bounded to them in octahedral coordination (Figure 3-3). In the presence of aluminum, the formula for the octahedron will be as \( [Al_2(\text{OH})_6]_n \) that resembles gibbsite. Therefore it is also called as gibbsite layer in its sheet form. In the presence of magnesium or iron, the formula will become as \( [\text{Mg}_3(\text{OH})_6]_n \) or \( [\text{Fe}_3(\text{OH})_6]_n \). The magnesium bearing octahedron resembles brucite mineral, so it is also termed as brucite sheet in clay mineral structures. The theoretical thickness of an octahedron is 5.05 Angstrom (Mitchell and Soga 2005, Grim 1968).

![Octahedron Unit and Sheet Structure](Figure 3-3)

**Figure 3-3** Octahedral unit and sheet structure.
The silica tetrahedrons are composed of a silicon atom which is in the center having an equal distance from the four oxygen atoms that are in tetrahedral coordination (Figure 3-4). Three of the oxygen atoms are shared with the adjacent tetrahedron and forming a hexagonal net which is furthermore connected in a sheet structure. The general formula for the sheet that is formed by this silica tetrahedrons is $\text{Si}_4\text{O}_{10}$. The electrical charge of this sheet is balanced by the replacement of oxygen atoms by hydroxyls, therefore, making the general formula as, $\text{Si}_4\text{O}_6(\text{OH})_4$, or combining with a positively charged sheet that has a different composition. The theoretical thickness of a tetrahedron is 4.65 Angstrom (Mitchell and Soga 2005, Grim 1968).

![Figure 3-4 Tetrahedron unit and sheet structure.](image)

Clay minerals are formed by two, three, or four sheets depending on their type. These sheets can be closely stacked, or they may have a water layer in between (Figure 3-5). In some clay minerals, different cations occupy the tetrahedral and octahedral spaces other than the ones in their ideal structure without changing the crystal structure, which is defined as an isomorphic substitution. The typical examples of isomorphic substitution are aluminum replacing silicon, magnesium replacing aluminum, and ferrous iron replacing magnesium. The isomorphic substitution defines the type of mineral in clay subgroups.
Kaolinites consist of a strongly bonded one tetrahedral sheet that is combined with an alumina octahedral sheet. Octahedral sheets are sharing the atoms on one of their planes with the silica tetrahedra that are positioned as tips downward (Figure 3-6). The electrically neutral structural formula for the kaolinites is \((\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}\). The different members within the kaolinites are produced by the variations in the stacking of layers and the position of aluminum ions in octahedral sheets, such as dickite and nacrite. Out of these two members, dickite is the most common mineral in sandstones. Particles of kaolinite have a net negative charge related to the substitution of \(\text{Al}^{3+}\) with \(\text{Si}^{4+}\) in silica tetrahedral or octahedral sheets. Also, this can be related to the broken bonds around the edges which are leading to adsorption of cations to be balanced. The second theory is coherent with the behavior of clay particles in different pH environments. In the
low pH environment, the edges of the kaolinite particle are positively charged, but in high pH environment, they are negatively charged. This can be considered as a verification for the existence of isomorphous substitution in kaolinites. The thickness of a well-crystallized kaolinite mineral is 0.05 – 2 μm. This thickness decreases in poorly crystallized minerals (Mitchell and Soga 2005, Grim 1968).

![Kaolinite structure diagram](image)

**Figure 3-6** Kaolinite structure diagram.

Smectites, such as montmorillonite, consist of two silica tetrahedral sheets that have their tips pointed toward the center of the unit where an alumina octahedral sheet exists resembling a sandwich-like structure. The oxygen atoms at the tips of the tetrahedral sheets are shared with the octahedral sheet (Figure 3-7). The electrically neutral structural formula for the smectites is $(\text{OH})_4 \text{Si}_x\text{Al}_4\text{O}_{20-n}\text{H}_2\text{O}$.

Smectites have high cation exchange capacity because of the unbalanced substitutions which are caused by the extensive isomorphous substitution in them that the aluminum in their octahedral sheet may be substituted by magnesium, iron, zinc, nickel, lithium, or other cations, and silicon in their tetrahedral sheets may be replaced by aluminum ions. The resulting unbalanced net charge from the isomorphous substitution is balanced by the exchangeable cations that are
present between different units. Their thickness is generally around 1 nm (Mitchell and Soga 2005, Grim 1968).

Figure 3-7 Montmorillonite structure diagram.

Illites such as muscovite have a similar structure to the smectites. However, some of its silicon is replaced with aluminum, and the unit charge is balanced by potassium ions (Figure 3-8). Their electrically neutral structural formula is \((\text{OH})_4 \text{K}_2 \text{Si}_{6-2} \text{Al}_2 \text{Al}_4 \text{O}_{20}\). The cation exchange capacity of illites is less than the smectites. The thickness of illites can be as thin as 3 nm (Mitchell and Soga 2005).
3.3 Semi-Permeable Behavior of Clays

The negatively charged clay minerals attract the cations in the formation water to preserve their electrical neutrality. While preserving their neutrality, clay surfaces along with the attracted cations formed a layer which is termed as a diffusive double layer. The highly concentrated adsorbed cations will try to diffuse into the water to equalize the concentration in the pore space. However, this tendency to escape and diffuse to the water is opposed by the electrostatic attraction that is increasing close to the negatively charged clay surfaces. Thus, the ion distribution of the cations decreases with the increasing distance from the clay surface, which is analogous to the gas molecules in the atmosphere where gravitational attraction of the Earth keeps the gas molecules
from escaping. The idealized ion distribution adjacent to a single clay surface is shown in Figure 3-9.

![Figure 3-9](image)

Figure 3-9  Distribution of cations and anions adjacent to a clay platelet.

The theory of the description of the ionic distributions adjacent to the charged surfaces is first proposed by Gouy (1910) and Chapman (1913). Later, their theory developed and extended to describe the repulsive energies and forces of interaction between colloidal particles by Derjaguin and Landau (1993), and Verwey and Overbeek (1948).

In a high porous clay-bearing sediment water and the dissolved salts can pass through the relatively large channels between the grains. The output in such sediment will be equal to the input side of the clay membrane because the distance between the adjacent clay membranes is high. However, due to compaction, this distance will decrease so that the negative charges on the clay minerals inhibit the anions that are attempting to pass through by repelling them (Figure 3-10). This effect is termed “negative adsorption” (Donnan 1924). Cations can still move through the membrane; however, their movement will seize due to the electrical imbalance between the two sides of the membrane in later time. Uncharged water molecules will continue to pass through and increasing the salinity on the input side of the clay membrane. The experiments that are conducted by McKelvey and Milne (1962) by using compressed bentonites showed that the salinity ratio between input and output sides of the membranes ranging from 8:1 to 1.7:1. In compressed shale
that has a low content of cation exchanging clays the salinity ratio is 1.7:1 to 1.3:1, which represents that even with low content of cation exchanging clays, shale can effectively inhibit the movement of dissolved salts.

3.3.1 Geological Studies on Semi-Permeable membrane behavior of Clays

The semi-permeable membrane behavior of clays and shales has been researched by several scientists to explain the abrupt salinity and chemical compositions that are found in some formation waters. In 1947, De Sitter suggested that fine-grained sediments have a salt-sieving act that prevents the passage of salt ions but permitting the water molecules, resulting in a saline brine.

Figure 3-10 Overlap of double layers.
concentration. Hanshaw (1962) and Hanshaw and Coplen (1973) studied filtrated NaCl solutions using compacted montmorillonite and illite membranes. Kharaka (1971) and Kaharaka and Berry (1973) showed that the efficiency of a membrane is increased with the increase of compaction pressure.

Biochemists suggested using osmotic pressure equations to determine the particle size and molecular weight of particles in a protein solution separated by a semi-permeable membrane. A modified Van’t Hoff equation (Eq. 3-18) is used to quantify the results of the experiments conducted on protein solutions:

\[ p = RT \left( \frac{c}{MW} + Bc^2 \right) \]  \hspace{1cm} (3-18)

Where, \( p \) is the osmotic pressure, \( R \) molar gas constant, \( T \) absolute temperature, \( c \) concentration, \( MW \) average molecular weight, and \( B \) constant for each solvent that is related to the deviations of the system from the ideal solution laws.

In later studies, it has been seen that there are osmotic force changes due to the movement of ions that are added to the solution through the semi-permeable membrane. This phenomenon is defined by Donnan. Thus it is called Donnan Membrane Equilibrium.

White (1965) made an analogy between the membrane behavior of clays, aforementioned organic protein solutions and the Donnan membrane experiment. In Donnan membrane experiment, the membrane has large pores that allow the passage of small ions but not permitting the large ionized colloidal particles until an equilibrium is reached on both sides of the membrane. Donnan conducted an experiment where he used a solution of a dye sodium salt called Congo Red, that is used as a colloidal electrolyte, which is soaked into a NaCl solution but separated by a semi-permeable membrane (Figure 3-11). The semi-permeable membrane that is used is impermeable to Congo Red anions but permeable to all other ions that are present. It is observed that the Na\(^+\) and Cl\(^-\) ions diffuse to the Congo Red solution until equilibrium is reached, later he used his results to modify the Van’t Hoff equation to quantify this behavior (Hartman 1947).
Donnan also conducted the same experiment using Congo Red solution against pure water. In this case, some of the \( Na^+ \) ions diffuse through the membrane from the Congo Red solution side to the pure water side. This diffusion causes an electrical instability on both sides of the membrane. Therefore, water molecules ionize and H+ ions pass through the membrane to the Congo Red solution side until the electrical balance is formed and an equilibrium state is reached (Hartman 1947).

White (1965) suggested that the behavior of clays on anions can be compared to the Donnan Membrane experiments. He concluded that in a high porosity clay-bearing sedimentary rock with abundant channels between the pore spaces, salts dissolved in water and water would pass through the grains. The experiments used cation-exchanging clays as semi-permeable membranes.

Broken bonds at the mineral surface along with the substitution of low-valance cations within the mineral valance causes the clay minerals to have negative surface charge (White 1965, and Grim 1968). This negative surface charge attracts the cations in an electrolyte solution which covers the surface of these clays. However, the concentration of these cations decreases moving...
away from the mineral surface into the pore. The double layer is composed of this negatively charged layer of the mineral surface and cation that is attached to it.

The double layers in sandstones have little to no effect due to their relatively large sizes of pore spaces compared to the thicknesses of the double layers. However, in clay-rich rocks, the thickness of the double layers is comparable to the pore sizes, mainly due to the decrease of pore spaces by compaction. The solutions in the pore spaces of a clay-rich rock that is compacted are all influenced by the double layer as they start to overlap. This occurrence leads to the repel of the anions to enter the clay pore but attract the cations in the solution. In later time, when cations that are adjacent to clay surface become dominant ion species in the solution, they will start to repel the cations from entering the clay pores as well. In this time, only electrically neutral water molecules can pass through the pores. Hence, clays act as a semi-permeable membrane allowing solvent components to pass but inhibiting the solutes. In this case, sandstones are not effective membranes as they permit the passage of solutes as well. However, this is not the case for tight sandstones due to their small pore sizes.

White (1965) describes that initially there is no perfect shale membrane in sedimentary rocks, that they continue to allow some of the anions to escape through larger interconnected openings. However, these interconnections sizes decrease in time as the compaction continues, resulting in a nearly perfect membrane, and increasing the salinity on the input side of the membrane. However, not all the pores are the same size, so in this case, the effect of still imperfect membranes because of the escape routes due to larger pore spaces is the decrease of salinity at some parts of the sedimentary rocks where larger pores exist. So, the salinity of brine in pore spaces of shale may differ in salinity depending on the amount of adsorbed low salinity water.

In sedimentary basins, salinity increases with age. However, when the sedimentation is uplifted after the end of the burial, the decrease in porosity will stop and even can be reversed as compaction decreases. In this case, the system is not dominated anymore by the overburden stress, but with hydrostatic pressure. Then, in this system, meteoric water flushes out the existing high saline brines. However, it is also noted that the higher parts of the hydrologic system may provide the energy needed for the salt-sieving. Therefore, the salinity in some parts of the system may continue to increase.
Another discussion on the literature states that sediments are not equally permeable to all constituents of the solutions at the same degree. While some cations move through membranes of fine-grained sediments easier, the others cannot. The radius of the ions can have an impact on this effect that when the pore throat radii decrease significantly due to compaction, some ions cannot pass through. Marshall (1949) and McKelvey and Milne (1962) proposed that due to this effect membranes have different permitting rates for different cations.

In recent years, the studies on the effect of osmotic pressure on the abrupt salinity and chemical compositions that are found in some formations lead to researches on the effect of osmotic pressure on oil production.
CHAPTER 4 GEOLOGICAL DESCRIPTION

The core samples used in this study were from the Niobrara chalk and Codell sandstone of the DJ Basin. Thus, the regional setting in DJ Basin and Niobrara petroleum systems are presented in this chapter.

4.1 Regional Setting in DJ Basin

The Denver Basin extends more than 70,000 square miles across eastern Colorado, southeastern Wyoming, and southwestern Nebraska (Figure 4-1). Boundaries of the Denver basin are the Front Range of the Rocky Mountains on the west, Hartville uplift on the northwest, Chadron arch on the northeast, Las Animas arch on the southeast, and Apishapa uplift on the southwest (Higley and Cox 2007). It is an asymmetrical Laramide foreland-style structural basin that is stretched north to south, with a steeply dipping (>10-degree dips) folded and faulted western flank and a gently dipping east flank (<0.5 degrees) (Weimer 1996; Sonnenberg 2017).

Figure 4-1 Cross-Section of Denver Basin (Sonnenberg 2016).
4.2 Niobrara Petroleum System

The Niobrara Formation and Codell sandstone are active plays in the Denver Basin (Figure 4-3). The Codell sandstone occurs between the primary Cretaceous carbonate producing sections, Niobrara and Greenhorn. Both of these carbonate sections are deep water depositions consisting of chucks and marls. In between these deep-water depositions, The Codell sandstone is thought to represent a lowering of sea level between two of the highest sea levels during Cretaceous. The thickness of Codell averages between 15 to 20 ft in this area. It has a low resistivity due to the clay and pyrite content. The source rocks for the Codell are the Graneros, Greenhorn, Carlile, and also the adjacent Niobrara Formation. The source beds are marine Type II (oil prone) kerogen. This type of source bed can generate both oil and gas (Sonnenberg 2014).

The Niobrara formation is one of the nine horizons that are productive in the Wattenberg area of Colorado, which produces oil, gas, and gas condensate. The Niobrara formation contains approximately 0.512 billion barrels of proved reserves as of 2014 (EIA). Stratigraphically, it consists of four chalk intervals with three intervening marl intervals, and a limestone interval. The aforementioned units are referred to in descending order as A chalk and A marl, B chalk and B marl, C chalk and C marl, D chalk-marl, and the Fort Hays Limestone. Below these stratified units there lies the Codell Sandstone (Figure 4-2).

Figure 4-2 A typical stratigraphic column in the Wattenberg Field includes multiple reservoirs and source rock intervals covering a vertical depth from 4,300 to 7,800 feet (Sonnenberg 2015).
Figure 4-3  Denver Basin Map (Kent and Porter 1980).
Four transgressive cycles occurred during the Niobrara cyclotherm, resulting in the deposition of the Fort Hays Limestone, C chalk, B chalk, and A chalk intervals. During the transgressive cycles, higher relative sea level allowed for carbonate-rich waters from the south to invade the area of the CWIS which is now Colorado. Three regressive cycles took place during the Niobrara cyclotherm, resulting in the deposition of the D chalk-marl, C marl, B marl, and A marl intervals (Longman et al. 1998; Kauffman 1997). Figure 4-4 shows a schematic of these transgressive-regressive cycles of the Niobrara cyclotherm.

Figure 4-4  Schematic of the transgressive-regressive cycles of the Niobrara Cyclotherm and the stratigraphy (Longman et al. 1998).
The typical log responses of Niobrara Formation from the various chalk and marl intervals and the Codell sandstone are shown in Figure 4-5. The crossovers at the B chalk, C chalk, Fort Hays limestone and Codell sandstone shows the hydrocarbon content in these intervals.

![Figure 4-5](image)

Figure 4-5  The characteristic log responses of the Niobrara Formation (Kamruzzaman 2015).

The thickness of D chalk is about 45 feet. GR values lie around 75 gAPI units and resistivity around 12 ohm-m, neutron porosity 12%, and density porosity 5%. The gradual increase of GR value with decreasing depth is an indication of formation change from chalk to marl. The mineralogy obtained from XRD data shows an average of 47% carbonates, 24% clays, 19% quartz, and 0.76% TOC. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.13% and 460 °C respectively.

The thickness of C marl is over 50 feet. It has varying log responses as GR values ranging between 75-210 gAPI, and resistivity ranging between 8-30 ohm-m. However, neutron porosity
and density porosity show more or less close values as, 15-25%, and 12-20% respectively and overlying and crossing each other in different segments suggesting the presence of hydrocarbon and most probably oil. The varying log response values may be related to transition between chalk and marl at the edges of the interval. The mineralogy obtained from XRD data shows an average of 61% carbonates, 15% clays, 11% quartz, and 3.7% TOC. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.2% and 465 °C respectively. The high TOC value makes C marl the best hydrocarbon source rock in the Niobrara Formation interval in the DJ Basin (Longman et al. 1998).

The thickness of C chalk is about 45-50 feet. It has varying log responses as GR values ranging between 70-200 gAPI but a sharp change from the underlying C marl. The resistivity is ranging between 25-55 ohm-m. The neutron porosity is showing values of 10-15% and density porosity values showing values of 12-18% with a significant cross-over suggesting the presence of gas in here. It has a sharp GR transition from underlying C marl. The XRD data shows an average of 74% carbonates, 11% clays, 6.8% quartz, and 2.5% TOC. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.2% and 464 °C respectively.

The thickness of B marl is about 40 feet with parallel-laminated marls with chalky-marl units. GR response ranges between 125-200 gAPI with a higher GR response near the middle of the unit, suggesting an increase in shale content. The resistivity is ranging between 12-25 ohm-m and neutron and density porosity values ranging in between 10-20% and 8-15% respectively. The values of neutron porosity are higher than the above and below chalk units, showing a divergence between density porosity and neutron porosity curves suggesting no hydrocarbon content in this interval. The XRD data shows an average of 62% carbonates, 18% clays, 9.5% quartz, and 2.9% TOC. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.25% and 467 °C respectively. Even if the TOC of this unit is lower than the C marl, it still possesses a good potential to be a source rock.

The thickness of B chalk is about 40 feet interbedded with chalky-marl and marl rock units (Longman et al. 1998). The GR gradually decreases when the depth gets shallower from the edge of B marl and ranging between 70-120 gAPI. This interval shows the highest resistivity response compared to the underlying units where it ranges between 20-200 ohm-m. The neutron porosity is showing values of 10-12% and density porosity values showing values of 15-19% with a
significant cross-over suggesting the presence of gas in here. The XRD data shows an average of 65% carbonates, 15% clays, 14% quartz, and 1.6% TOC. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.17% and 463 °C respectively.

The thickness of A marl is about 35 feet. The GR is gradually increased when the depth gets shallower and reaching its maximum value at the transition between Sharon Spring Member. The overall GR values range between 95-225 gAPI and resistivity ranging between 10-30 ohm-m. The neutron porosity ranges between 12-15% and density porosity ranging between 13-17%. Both porosity curves are crossing over at different depths showing small gas-crossovers, therefore the presence of hydrocarbon in here. The XRD data shows an average of 49% carbonates, 23% clays, and 14% quartz. The vitrinite reflectance (Ro) and Tmax values from the studied core samples were found to be 1.27% and 469 °C respectively. TOC content is high, 3.2%, which makes this interval one of the best source rock in Niobrara Formation (Longman et al. 1998).

Figure 4-6   XRD Mineralogy data for each interval (Kamruzzaman 2015).
The experiments were conducted in the high-speed centrifuge. 1.5-inch diameter core plugs were used in this study. This chapter addresses the details of the experimental setup.

This chapter includes (1) core cleaning, (2) equipment used for porosity and permeability measurement, (3) equipment used for capillary pressure measurement, and (4) the fluids and the cores used in the experiments.

5.1 Core Cleaning

Core plugs are extracted from core samples as long cylinders of 1-inch or 1.5-inch diameter. Then, they were cut to appropriate lengths for the needs of further experiments. The majority of reservoir core samples are either poorly reserved or not preserved at all. To perform and get accurate results from porosity, permeability, and fluid saturation experiments they need to be cleaned. The cleaning process is performed to clean the core plug samples from mud filtrates from the drilling mud, native oil, and connate water.

API RP40 (1998) provides a list of methods for cleaning the core samples:

- Solvent Flushing by Direct Pressure
- Flushing by centrifuge
- Gas driven solvent extraction
- Distillation extraction (Soxhlet Extraction)
- Liquefied gas extraction

Cores should be cleaned by using at least two solvents of the non-polar and polar-type to remove all the residual fluids that might affect further parameter measurements and experiment procedures. Non-polar solvents dissolve the light components of oil whereas polar solvents dissolve the heavy components of oil along with water and precipitated salts from formation brine. For cleaning procedures, toluene, xylene, chloroform are the most common non-polar solvents, and methanol, ethanol, dichloromethane are the most common polar solvents. Usually, a non-polar solvent is the first to be used to clean the core in the cleaning procedure, which is followed by a polar solvent.
In this research, Soxhlet extractor is chosen as the cleaning method because it is the cheapest and the quickest method out of the aforementioned methods. Also, several cores can be placed in the same chamber, and if delicate samples which can be damaged from high pressure or high temperature can be cleaned by using cool Soxhlet extractor.

Soxhlet extractor can be used to clean a large number of cores depending on the size of the core samples and the chamber of the apparatus. Firstly, the round bottomed flask which sits on a heating mantle is filled with the solvent. When the solvent reaches the boiling point, it evaporates. The evaporated sample travels up to the condenser unit, which is filled with continuously circulated cold water. The solvent condenses in this unit and drips down to the chamber which holds the core samples. As the solvent fills the chamber, it submerges the core samples, and it is soaked through the pore spaces of the samples and dissolves the residual fluids and precipitated salts. When the level of the solvent reaches the siphon level, the solvent and the dissolved fluids in the chamber will reflux to the round bottom flask beneath it. Then, the cycle will repeat but leaving the dissolved fluids in the bottom flask because of the boiling point difference. Therefore, cores will be exposed to fresh evaporated and condensed solvents each time. Through the cleaning process, the color change in the bottom flask is checked regularly, and the solvent will be refreshed or changed if needed.

5.1.1 Cleaning Procedure

All the cores that are used in this study are cleaned with Soxhlet extractor (Figure 5-1). Solvents that are used are toluene, methanol, and chloroform. Prior to cleaning, all cores that are selected for cleaning are weighed to see how many residual fluids and precipitated salt be removed.

Firstly, toluene is used to clean the cores. The boiling point of toluene is 110.6°C (Table 5-1). Toluene removes the heavy components of oil, and as it has a high boiling point, it also removes the residual water (McPhee et al. 2015). However, as toluene has a very high boiling point and potential to damage the clay minerals as it can also remove the clay-bound water, the hot toluene extraction kept running only for 2-3 days. The cores kept submerged with toluene in the chamber for 1-2 weeks more without continuously boiling the solvent but refreshing the solvent regularly depending on the discoloration. With this method, I try to mimic the effect of cool Soxhlet extraction. The discoloration occurred every 3-4 hours at the beginning of the cleaning but the rate decreased after 4-6 days. The decrease on rate was quicker on Niobrara chalk samples
compared to Codell sandstone samples. The cores kept in toluene until the discoloration is minimized. However, the process was stopped after two weeks not to create further damages inside the core that cannot be seen by the naked eye.

At the end of toluene cleaning stage, core samples will contain precipitated salts because of the extracted formation water. Also, some of the heavy oil components will be present as well. Chloroform-methanol azeotrope with 65% and 35% ratio is used for the next stage to complete the cleaning procedure. An azeotrope is a mixture of two or more solvents. The proportions of the components are not altered in the distillation process because when boiled, the vapor has the same proportion as the unboiled mixture. However, this mixture has a significantly lower boiling point than the individual components. Individually chloroform has a boiling point of 61°C, and methanol has 64.7°C. However, the azeotrope of chloroform and methanol with a ratio of 65% to 35%, the boiling point will be decreased to 53.5 °C (Table 5-1). The decrease in the boiling point is also needed not to damage the clay minerals in the cores. The cores were cleaned with the azeotrope for a week until the discoloration ceases. It is observed that the cease of discoloration was quicker on the chalk samples because of their tighter pore structure compared to sandstones. However, the process stopped after one week of cleaning not to create further damages inside the core that cannot be seen by naked eye.

<table>
<thead>
<tr>
<th>Table 5-1</th>
<th>Properties of cleaning solvents (McPhee et al. 2015).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Boiling Point (°C)</td>
</tr>
<tr>
<td>Toluene</td>
<td>110.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61</td>
</tr>
<tr>
<td>Chloroform/Methanol</td>
<td>53.5</td>
</tr>
<tr>
<td>Azeotrope (65/35)</td>
<td></td>
</tr>
</tbody>
</table>

5.1.2 Core Drying

After cleaning the cores, they are placed in an oven with constant temperature to remove the residual solvents by drying them. The clay minerals within the cores are most delicate at this stage, and extensive care should be taken. A high temperature (over 100°C) oven drying may lead to the destruction of the clay minerals, especially the fibers of illites, thus increasing the permeability on later stages. Due to this issue regarding the clay minerals, the temperature of the oven is kept at below 60-65°C at all times. The weight of the plugs was monitored regularly until a constant weight that is within the +/- 0.01 g range reached. The drying stage takes 6-8 days depending on the type of the cores.
5.2 Porosity and Permeability Measurements

Porosity, permeability, and pore volume was measured using CMS-300 (Figure 5-2). The core plug is loaded to the core holder by the carousel and initially set net confining pressures were applied to the core plugs. Net confining pressure was arranged as 1000-1500-2000 psi for Niobrara and Codell core plugs. The experiment was performed as first increasing order followed by a decreasing order to identify the hysteresis.

CMS-300 uses nitrogen to apply net confining stress by a rubber sleeve. Porosity was measured by allowing the helium gas to expand through the core plug with the outlet valve closed. Helium gas was injected into the core plug at 250 psi after the target net confining stress is reached. Klinkenberg permeability was determined by using the mass flow rate from the Helium gas on a pressure decay curve which is based on Jones (1972)’s method. Air permeability was back-calculated from the Klinkenberg permeability (McPhee et al. 2015).

Figure 5-2  Core Laboratories CMS-300 unsteady-state permeameter/porosimeter (McPhee et al. 2015).
5.3 Capillary Pressure Concept and Measurements

Capillary pressure is the pressure difference between the adjacent phases of a wetting and a non-wetting phase at equilibrium. Thus, the capillary pressure can be defined as in Eq. 5-1:

\[ P_c = P_{nw} - P_w \]  

(5-1)

In a pore space that is occupied with oil and water, as non-wetting and wetting phases respectively, the fluid saturations are defined as:

\[ S_w + S_o = 1 \]  

(5-2)

The knowledge of capillary effects, which control the distribution of the saturation gradients of different phases in a pore network, is essential in multi-phase flow through porous media. The relationship between the capillary pressure and the saturation is vital to understand the characteristics of the porous medium and how the phases behave when replacing one another. The relationship between fluid saturation and capillary pressure in a porous medium that is occupied by oil and water is defined in a sketch in Figure 5-3. In this figure, line 1 represents the drainage curve, where the non-wetting phase (oil) is displacing the wetting phase (water). The point reaches maximum capillary pressure, and minimum saturation is irreducible water saturation \( S_{w,irr} \). Line 2 represents the spontaneous imbibition curve where water is displacing oil without the direction of the water. Line 3 is forced imbibition where water saturation increases with increasing capillary pressure until it reaches the residual oil saturation.

There are three main methods currently used in laboratories to determine the capillary pressure curves; mercury methods, porous plate methods, and centrifuge method. Mercury method is a quick method that is used to obtain capillary pressure data, pore throat distribution and pore level heterogeneity. Porous plate method is used to determine the capillary pressure curves and saturation relationships by using a plate in ambient conditions or confining stress of up to 10,000 psi. The samples that are used for this method should have a permeability above 1 md.
The centrifuge is a widely used method in conventional laboratories for the determination of capillary pressures since the early 1950s. Experiments can be performed on cores that are saturated with one or more fluid. The rotation of the rotor creates a centrifugal force on the buckets towards the center of rotation which causes the denser fluids will be pushed away from the center of rotation and replaced by lighter fluids by the centrifugal forces (Figure 5-4). The fluid production is recorded during the experiment and transformed into saturation values. The saturation values versus capillary pressure values are calculated at the inlet face of the core sample at various angular speeds.
The capillary pressure ($p_c$) at a distance, $r$ from the center of rotation, is defined in Eq. 5-3 (Ayappa et al. 1989):

$$p_c = \frac{1}{2} \Delta \rho \omega^2 (r_2^2 - r^2)$$

(5-3)

Where, $\Delta \rho$ is the density difference between the phases, $\omega$ angular velocity, $r_2$ distance from the center of rotation to the outer face of the core, and $r$ distance from the center of rotation.

The centrifuge capillary pressure is measured at the inlet face of the core with the primary assumption stating that capillary pressure is zero at the outer face of the core. Therefore, the Eq. 5-3 can be rewritten as (Bentsen and Anli 1977):

$$p_{c, in} = 1.578 \times 10^{-7} \Delta \rho n^2 l (r_2 - \frac{l}{2})$$

(5-4)

Where, $n$ is the rotation speed and $l$ length of the sample.
5.3.1 Ultra-High-Speed Centrifuge

Beckman ultra-fast centrifuge (ACES200) with a 3-rotor system that is used for 1.5-inch diameter cores plugs was used for the centrifuge experiments (Figure 5-4). Maximum speed for imbibition and drainage cycle are 16,500 rpm and 15,500 rpm respectively. Drainage and imbibition cycles are done by using a different bucket, receiver cup, and core holder assemblies. A complete cycle of centrifuge experiment consists of initial saturation, drainage cycle, and forced imbibition.

![Image of centrifuge](image)

Figure 5-5 Core Laboratories ACES-200 ultra-high-speed centrifuge.

5.3.1.1 Centrifuge Calibration Procedure

The centrifuge has to be calibrated for each drainage and imbibition cycles to make sure the camera captures the interfaces correctly. Calibration is done by adding a small volume of brine and decane on each receiving cup. To enhance the capture rate of the interface by the camera an opaque disc that floats between the brine and decane is used. The buckets are balanced to an accuracy of +/-0.003 g. After the rotor is assembled and appropriate parameters are input to the “cup data”, “test parameters”, and “testing” tabs, the “fluids run” will be started (Figure 5-5). For
each desired rpm, production curves are needed to be stabilized and later on pixel height is calculated by using the values from this stabilized section of the calibration.

![Parameter input windows on centrifuge software.](image)

**Figure 5-6** Parameter input windows on centrifuge software.

### 5.3.1.2 Initial Saturation

All cores were initially saturated with the formation brine. The initial saturation of the core samples was performed by using the imbibition setup of the centrifuge to overcome the difficulty of saturating tight cores with a conventional vacuum. The receiving cups were filled with formation brine for the saturation cycle, and the cores kept spinning at 7,000 rpm for two days. The weight difference between before saturation and after saturation was used to calculate the initial saturation of the cores.

### 5.3.1.3 Drainage Cycle

After the calibration procedure, drainage setup was loaded with the initially saturated core plugs, and the core holder and receiving cup are filled with decane (Figure 5-7). The weight of the drainage buckets was balanced to an accuracy of +/- 0.003 g. The centrifuge software provides the
production data plotted versus time on the production window. Speed was selected as starting from 1,000 rpm to 13,000 rpm with an increment of 1,000 rpm for capillary pressure experiments. The experiments was run for each RPM until the brine production ceases, then moving to the next RPM. The tolerance for the production cease was 0.01 cm$^3$ change in the last 12-24 hours which gave a flat curve on the production window.

![Figure 5-7 Drainage bucket setup.](image)

After completing the experiment, collected data was processed. Water saturation for each RPM was calculated by dividing the difference of the production and the pore volume to the total pore volume that is measured by CMS-300. This procedure was repeated for each RPM until the residual water saturation was reached.

For trapped gas experiments similar procedure was followed, but instead of using decane, cups were not filled with any fluid and leaving the core plugs without any fluid surrounding them. The gas saturation was calculated for each speed at the end of the experiment by dividing the brine
production to the pore volume that will be measured by CMS-300. This procedure was repeated for each RPM until the residual water saturation was reached.

5.3.1.4 Forced Imbibition Cycle

Forced Imbibition cycle with centrifuge follows the spontaneous imbibition cycle which is described on the following section 5.3.2. The centrifuge was calibrated again for imbibition cups in a similar way that is done prior to drainage cycle. The receiving cups were filled with brine with a small amount of decane (1-3 cm³ depending on the size of the cup), and small space of air to produce contrast between the interfaces that are to be captured by the centrifuge camera (Figure 5-8).

The weight of the imbibition buckets was balanced to an accuracy of +/- 0.003 g. After assembling the rotor inside the centrifuge and start the imbibition cycle, the light and heavy interfaces were immediately captured by the camera. Similar to the drainage cycle the RPM increase was selected as increments of 1,000 RPM starting from 1,000 RPM to 13,000 RPM. The

![Figure 5-8 Forced Imbibition bucket setup.](image)
tolerance for the production cease was 0.01 cm³ change in the last 12-24 hours which gave a flat curve on the production window.

After completing the imbibition cycle, water saturation at each RPM was calculated by adding the percentage of production to the pore volume to the water saturation that was measured on the spontaneous imbibition cycle. This is also repeated for each RPM, and the maximum speed provided the residual oil saturation.

For trapped gas experiments similar procedure is followed, but instead of using decane, cups were filled with the brine, and the opaque disc that is floating above the brine used to enhance the interface captured by the camera.

5.3.2 Spontaneous Imbibition

Spontaneous Imbibition was measured by using an under-weighting balance (Figure 5-9). In this method, the core-plug is hung to a balance from below with a fishing line, and it is submerged into the brine that is stored in a beaker below the system. The change in weight due to the imbibition is recorded every minute on the computer that is connected to the balance. The core sample should be immersed into the brine, and it should be centralized in the beaker not to touch the sides. Otherwise, buoyancy forces may lead to inaccurate results.

![Figure 5-9 Schematic of spontaneous imbibition setup in the laboratory.](image-url)
5.4 **Fluids and Cores**

The fluids and the cores that were used in this study are presented in this section.

5.4.1 **Fluids**

Brine was prepared by using various amounts of KCl as a salt ingredient regarding the target brine concentration considering Niobrara formation brine salinity (40,000 ppm). Thus, in the experiments, the formation brine salinity was used as the control measures, and the low salinity brine was selected as 5,000 ppm to compare the effect of low salinity brine. For the drainage cycle, decane was used due to its lower density and viscosity values. For visualization and creating a contrast between brine and decane during centrifuge experiments, a red dye (Sigma Aldrich Oil Red-O), which is only soluble in decane, was used.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Salinity, ppm</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Saline Brine</td>
<td>40,000</td>
<td>1.0314</td>
</tr>
<tr>
<td>Low Saline Brine</td>
<td>5,000</td>
<td>1.0134</td>
</tr>
</tbody>
</table>

Table 5.3 Properties of decane

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Red dye concentration, ppm</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane</td>
<td>15</td>
<td>0.734</td>
</tr>
</tbody>
</table>

5.4.2 **Cores**

Four cores were used in this study. Two cores were from B chalk member of Niobrara formation, and two cores were from Codell sandstone member of Carlile formation (Figure 5-10). The IDs, depths, and dimensions of the cores were presented in Table 5-4.

<table>
<thead>
<tr>
<th>Core ID</th>
<th>Formation</th>
<th>Depth, ft</th>
<th>Weight, g</th>
<th>Length, in</th>
<th>Diameter, in</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-19</td>
<td>B chalk</td>
<td>5,605.35</td>
<td>88.051</td>
<td>1.329</td>
<td>1.495</td>
</tr>
<tr>
<td>3-19A</td>
<td>B chalk</td>
<td>5,605.55</td>
<td>124.630</td>
<td>1.863</td>
<td>1.490</td>
</tr>
<tr>
<td>4-138A</td>
<td>Codell sandstone</td>
<td>5,829.90</td>
<td>123.358</td>
<td>1.880</td>
<td>1.486</td>
</tr>
<tr>
<td>4-139</td>
<td>Codell sandstone</td>
<td>5,830.10</td>
<td>125.418</td>
<td>1.927</td>
<td>1.487</td>
</tr>
</tbody>
</table>
Figure 5-10  Cores from Codell formation.
An important topic for gas-condensate reservoirs is quantifying the trapped gas saturation which cause the gas production to be left behind. When an aquifer is underlying a gas reservoir, water will imbibe into the gas-saturated zone and traps the gas molecules. This chapter includes (1) geological overview of Bulo Bulo Field Robore III formation and (2) description of fluids and cores used in the experiment and results.

6.1 Geological Overview of Bulo Bulo Field Robore III Formation

The cores that are used for trapped gas experiments are from Robore III reservoir in the Bulo Bulo field, Bolivia. The reservoir formation consists of naturally fractured interbedded shales and sandstones. The Bulo Bulo field is an anticline located in the Carrasco Province. The reservoir formation Robore is divided into three as Robore I, II, and III, and Limoncito formation overlies the Robore I to act as a hydrodynamic seal for the reservoir. According to Navarro (2012) Robore formation is deposited in a shallow sea platform, and Robore III in particular deposited in a marginal marine environment dominated by storm waves. The formation is fine to very fine-grained low porosity sandstones which has quartz as a dominant mineral.

The typical log responses of Robore-III Formation are shown in Figure 6-1, that is logged from the same well that the core plugs are acquired. Robore III formation is categorized as very-fine to fine-grained sub-feldspathic sandstones with sharp and subangular clasts. The cement consists of quartz, feldspar, and calcite. Chlorite and illite are the clay minerals found in the formation. The dominant pore throat size falls to the range of micropores (less than 0.02-0.06 mm), but mesopores and macropores are also present.
Robore III is an overpressured reservoir with an initial pressure gradient of 0.77 psi/ft (Figure 6-2). Natural fractures in the system are macropore sized, and they are the main channels to allow the fluid to flow even though partial mineralization is present. However, it is observed that during production the reservoir pressure decreases significantly and leads to the collapse of the natural fractures and stops the production.
6.2 Description of Fluids and Cores Used in the Experiment and Results

For the trapped gas saturation experiments, formation salinity brine was selected as 30,000 ppm. Air was used to mimic the hydrocarbon gas. KCl was used as a salt ingredient to reach the target salinity for the brine. Food color was used as a dye to create a contrast between the brine and air during centrifuge experiments.

6.2.1 Experimental Procedure

Trapped gas experiments followed a similar procedure as osmotic pressure experiments, but instead of using decane, cups were not filled with any fluid and leaving the core plugs without any fluid surrounding them. The gas saturation calculated for each speed at the end of the experiment by dividing the brine production to the pore volume that will be measured by CMS-300. This was repeated for each RPM until the residual water saturation was reached. For forced imbibition cycle, cups were filled with the brine, and the opaque disc that is floating above the brine used to enhance the interface captured by the camera.
6.2.2 Results

One core sample from Bulo Bulo Field was used for trapped gas measurements. The core that is used in this study had minor fractures on it prior to the experiment.

The core was initially saturated with 30,000 ppm KCl brine by using an ultra-high-speed centrifuge for two days at 6,000 rpm, and maximum water saturation ($S_w = 94.8\%$) was reached. Next, the air was used for the drainage cycle for the core sample. Air started to enter into the cores at 1,000 rpm ($p_c = 5.04\text{ psi}$). Irreducible water saturation, $S_{w,\text{irr}}$, of 73.61\% was reached at 11,000 rpm ($p_c = 601.103\text{ psi}$). At the end of the drainage cycle, there was no damage on the core sample. During the spontaneous imbibition, some air bubbles seen on the core sample. The water saturation change at the end of spontaneous imbibition was 13.9\%. Finally, the core was put into the centrifuge for the forced imbibition cycle to acquire the final capillary pressure curve after spontaneous imbibition.

Figure 6-3 presents the full cycle of capillary pressure curves for 4-6-104 core sample.

Figure 6-3  Capillary Pressure Curve for trapped gas core sample (4-6-104).
CHAPTER 7  RESULTS AND DISCUSSION

In this study, the procedure to measure osmotic pressure was to measure the apparent spontaneous imbibition of lower salinity brine and the forced imbibition capillary pressures at in cores saturated with decane and high salinity irreducible brine saturation. Four cores were used in this study, two cores from Niobrara chalk and two cores from Codell sandstone. In this chapter, the results of the experiments will be presented.

7.1 Measurement of Osmotic Pressure Experiments

The properties of the cores were measured directly by using CMS-300. The properties are reported in Table 7-1. The cores from Niobrara formation have natural fractures.

Table 7-1 Porosity and permeability measurements of core samples

<table>
<thead>
<tr>
<th>Core ID</th>
<th>Formation</th>
<th>Porosity, %</th>
<th>Pore Volume, cm$^3$</th>
<th>Permeability, md</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-19</td>
<td>B chalk</td>
<td>12.73</td>
<td>4.863</td>
<td>0.0099</td>
</tr>
<tr>
<td>3-19A</td>
<td>B chalk</td>
<td>10.91</td>
<td>5.806</td>
<td>0.0022</td>
</tr>
<tr>
<td>4-138A</td>
<td>Codell sandstone</td>
<td>10.75</td>
<td>5.730</td>
<td>0.0085</td>
</tr>
<tr>
<td>4-139</td>
<td>Codell sandstone</td>
<td>14.28</td>
<td>7.828</td>
<td>0.0105</td>
</tr>
</tbody>
</table>

All the cores were saturated with 40,000 ppm KCl brine by using the centrifuge. However, 100% saturation was not established in most of the cores. The initial water saturation values for each core is reported in Table 7-2.

Table 7-2 Initial Water Saturations of core samples

<table>
<thead>
<tr>
<th>Core ID</th>
<th>Formation</th>
<th>Initial Water Saturation, fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-19</td>
<td>B chalk</td>
<td>0.842</td>
</tr>
<tr>
<td>3-19A</td>
<td>B chalk</td>
<td>0.958</td>
</tr>
<tr>
<td>4-138A</td>
<td>Codell sandstone</td>
<td>1.000</td>
</tr>
<tr>
<td>4-139</td>
<td>Codell sandstone</td>
<td>0.838</td>
</tr>
</tbody>
</table>

After the initial saturation, drainage cycle was performed by using the drainage setup of the ultra-high-speed centrifuge with increasing rpm to establish the drainage portion of the capillary pressure curves. When irreducible water saturation was reached, cores were transferred to spontaneous imbibition setup and kept submerged into the specific brine until equilibrium was reached. Following the spontaneous imbibition, the cores were prepared for the final cycle to
establish the capillary pressure curves, forced imbibition. As the lengths presented in Table 5-4 for each core is different, the resulting capillary pressures are different on each speed stage for each core on both forced imbibition and drainage cycles.

### 7.1.1 Codell Sandstone

The Codell sandstone is a member of the Carlile formation. There are two core samples, Codell 4-138A and Codell 4-139, used in the experiments. Both Codell sandstone cores that are used in this study were initially intact without a visible natural fracture (Figure 7-1).

![Codell 4-138A](image1.png) ![Codell 4-139](image2.png)

(a) Codell 4-138A  (b) Codell 4-139

Figure 7-1 Initial state of the Codell sandstone cores.

Both of the cores were initially saturated with 40,000 ppm KCl brine by using an ultra-high-speed centrifuge for two days at 7,000 rpm, and maximum water saturation \( S_w = 100\% \) was reached for Codell 4-138A core and \( S_w = 83.8\% \) for Codell 4-139 core.

Next, decane was used for the drainage cycle for each core sample. Decane started to enter into the cores at 6,000 rpm \( (p_c=50.131\text{psi}) \) and 6,000 rpm \( (p_c=50.895\text{psi}) \) for the Codell 4-138A and Codell 4-139 core samples, respectively. Irreducible water saturation, \( S_{w,irr} \) of 49.65% was reached at 13,000 rpm \( (p_c=235.264\text{psi}) \), and 45.77% was reached at 13,000 rpm \( (p_c=238.849\text{psi}) \) for the Codell 4-138A and Codell 4-139 core samples, respectively. At the end of the drainage cycle, there was no damage on either of the core samples.
For the imbibition process, Codell 4-138A core sample was used for low salinity case, and Codell 4-139 core sample was used for high salinity case. Therefore, the salinity of 5,000 ppm KCl brine was used for Codell 4-138A core sample and 40,000 ppm of KCl brine was used for Codell 4-139 core sample.

During the spontaneous imbibition, extensive decane droplets seen on the core sample Codell 4-138A. The bubbles were more than what was observed on chalk core plugs. Figure 7-2 shows the core after six days of spontaneous imbibition. The water saturation change at the end of spontaneous imbibition was 7.4% for 4-138A core sample.

![Figure 7-2 Spontaneous imbibition on Codell sandstone 4-138A for low salinity, 5,000 ppm brine, surrounding a core saturated with 40,000 ppm brine.](image)

During the spontaneous imbibition, fewer decane droplets occurred on the core Codell 4-139 compared to Codell 4-138A. Figure 7-3 is showing the core after six days of spontaneous imbibition. The water saturation change at the end of spontaneous imbibition was 6.3%.
Figure 7-3  Spontaneous imbibition on Codell sandstone 4-139 for high salinity, 40,000 ppm brine, surrounding a core saturated with 40,000 ppm brine.

Finally, both of the cores put into the centrifuge for the forced imbibition cycle to acquire the final capillary pressure curve after spontaneous imbibition.

Figure 7-4 presents the full cycle of capillary pressure curves for Codell 4-138A core sample.

Figure 7-4  Capillary Pressure Curve for low salinity core sample (Codell 4-138A).
The capillary pressure curve for the Codell 4-139 core sample is shown in Figure 7-5.

![Capillary Pressure Curve for high salinity core sample (Codell 4-139).](image_url)

**Figure 7-5** Capillary Pressure Curve for high salinity core sample (Codell 4-139).

### 7.1.1.1 Comparison of Codell Sandstone Core Samples

Figure 7-6 shows the comparison of the capillary pressure curves from the two Codell sandstone core plugs. Red curves represent the capillary pressure curves for the case of low saline brine, and black curves represent the high saline brine. As it was mentioned previously, the water saturation difference at the end of spontaneous imbibition was higher on low saline brine case (Codell 4-138A). The difference was approximately 1.1%. The difference between the two cases increases continuously in the following capillary pressure data points on the forced imbibition curve.
The effect of osmotic pressure can be quantified using the data from these two core plugs. To show this effect, the curves are modified so that the irreducible water saturation, $S_{w,irr}$, points will coincide; the drainage curves are not shown in this plot (Figure 7-7). The capillary pressure for high salinity case (Codell 4-139) at the same water saturation value is higher than the low salinity case (Codell 4-138A). The only difference in both cases was the salinity of the brine that was used in the imbibition cycles. Therefore, this difference in pressure can be reported as osmotic pressure.

The osmotic pressure in this experiment is measured as 8.2 psi. The theoretical osmotic pressure using the Eq. 3-15 and Eq. 3-16 was found as 336.51 psi for the KCl brines that has 40,000 ppm and 5,000 ppm concentration respectively. The input parameters are shown in Table 7-3.
Table 7-3  Input values for theoretical osmotic pressure calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration,  $C_{KCl}$</th>
<th>Molecular weight $MW_{KCl}$</th>
<th>Number of moles, $N_{KCl}$</th>
<th>Molality: $M_{KCl}$</th>
<th>Activity, $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>40,000</td>
<td>74.5513</td>
<td>0.536543</td>
<td>0.536543</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5,000</td>
<td>74.5513</td>
<td>0.0671</td>
<td>0.0671</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The ratio of the measured value to the theoretical value is calculated to quantify the membrane efficiency of Codell sandstone samples.

$$\text{Membrane Efficiency} = \frac{\pi_{\text{measured}}}{\pi_{\text{theoretical}}} = \frac{8.2 \text{ psi}}{336.51 \text{ psi}} = 0.024 = 2.4\%$$

Figure 7-7  Capillary Pressure Curves for High and Low Salinity Codell Sandstone Core Samples.
7.1.2 B-chalk

There were two core samples, B-chalk 3-19 and B-chalk 3-19A, used in the experiments. Both B-Chalk cores that are used in this study were initially intact with some visible natural fracture.

Both of the cores were initially saturated with 40,000 ppm KCl brine by using an ultra-high-speed centrifuge for two days at 7,000 rpm, and maximum water saturation \( S_w = 84.2\% \) was reached for B-chalk 3-19 core and \( S_w = 95.8\% \) for B-chalk 3-19A core.

Next, decane was used for the drainage cycle for each core sample. Decane started to enter into the cores at 5,000 rpm \( (p_c = 27.275 \text{ psi}) \) and 6,000 rpm \( (p_c = 49.865 \text{ psi}) \) for the B-chalk 3-19 and B-chalk 3-19A core samples, respectively. Irreducible water saturation, \( S_{w,irr} \), of 38.05\% was reached at 12,000 rpm \( (p_c = 184.298 \text{ psi}) \), and 37.29\% was reached at 12,000 rpm \( (p_c = 199.399 \text{ psi}) \) for the B-chalk 3-19 and B-chalk 3-19A core samples, respectively. At the end of the drainage cycle, both of the cores were cracked. The cracks occurred from the natural fractures (Figure 7-8).

![Image of B-chalk cores at the end of drainage cycle](image)

(a) B-chalk 3-19  
(b) B-chalk 3-19A

Figure 7-8 B-chalk cores at the end of drainage cycle.

For the imbibition process, B-chalk 3-19A core sample was used for low salinity case, and B-chalk 3-19 core sample was used for high salinity case. Therefore, the salinity of 5,000 ppm
KCl brine was used for B-chalk 3-19A core sample and 40,000 ppm of KCl brine was used for B-chalk 3-19 core sample.

During the spontaneous imbibition, the amount of decane droplets were less than that was observed on the Codell sandstone core samples. Figure 7-9 shows the B-chalk 3-19A core after six days of spontaneous imbibition. The water saturation change at the end of spontaneous imbibition was 34.89% for 3-19A core sample.

Figure 7-9  Spontaneous imbibition on B-chalk 3-19A core sample for low salinity, 5,000 ppm brine, surrounding a core saturated with 40,000 ppm brine.

During the spontaneous imbibition, less decane droplets occurred on the core B-chalk 3-19 compared to B-chalk 3-19A. Figure 7-10 is showing the core after six days of spontaneous imbibition. The water saturation change at the end of spontaneous imbibition was 31.99% for 3-19 core sample.
Finally, both of the cores put into the centrifuge for the forced imbibition cycle to acquire the final capillary pressure curve after spontaneous imbibition.

Figure 7-11 presents the full cycle of capillary pressure curves for B-chalk 3-19A core sample.

Figure 7-11  Capillary Pressure Curve for low salinity core sample (B-chalk 3-19A).
The capillary pressure curve for the B-chalk 3-19 core sample is shown in Figure 7-12.

![Capillary Pressure Curve](image)

**Figure 7-12** Capillary Pressure Curve for high salinity core sample (B-chalk 3-19).

### 7.1.2.1 Comparison of B-chalk Core Samples

Figure 7-13 shows the comparison of the capillary pressure curves from the two Niobrara B-chalk core plugs. Red curves represent the capillary pressure curves for the case of low saline brine, and black curves represent the high saline brine. As it was mentioned previously, the water saturation difference at the end of spontaneous imbibition was higher on low saline brine case (B-chalk 3-19A). The difference was approximately 2.9%. The difference between the two cases increases continuously in the following capillary pressure data points on the forced imbibition curve.
Figure 7-13 Capillary Pressure Curves for High and Low Salinity B-chalk Core Samples.

The effect of osmotic pressure can be quantified using the data from these two core plugs. To show this effect, the curves are modified so that the irreducible water saturation, $S_{w,irr}$ points will coincide; the drainage curves are not shown in this plot (Figure 7-14). The capillary pressure for high salinity case (B-chalk 3-19) at the same water saturation value is higher than the low salinity case (B-chalk 3-19A). The only difference in both cases was the salinity of the brine that was used in the imbibition cycles. Therefore, this difference in pressure can be reported as osmotic pressure.

The osmotic pressure in this experiment is measured as 252 psi. The theoretical osmotic pressure using the Eq. 3-15 and Eq. 3-16 was found as 336.51 psi for the KCl brines that has 40,000 ppm and 5,000 ppm concentration respectively. The input parameters are shown in Table 7-3.
Table 7-4  Input values for theoretical osmotic pressure calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration, $C_{KCl}$</th>
<th>Molecular weight $MW_{KCl}$</th>
<th>Number of moles, $N_{KCl}$</th>
<th>Molality: $M_{KCl}$</th>
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<tr>
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<td>ppm</td>
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<td>74.5513</td>
<td>0.536543</td>
<td>0.536543</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>g/mol</td>
<td>5,000</td>
<td>74.5513</td>
<td>0.0671</td>
<td>0.0671</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The ratio of the measured value to the theoretical value is calculated to quantify the membrane efficiency of Codell sandstone samples.

$$Membrane\ Efficiency = \frac{\pi_{measured}}{\pi_{theoretical}} = \frac{252\ psi}{336.51\ psi} = 0.749 = 74.9\%$$

Figure 7-14  Capillary Pressure Curves for High and Low Salinity B-chalk Core Samples.
CHAPTER 8 CONCLUSIONS

In this thesis, the potential for incremental oil recovery for unconventional shale reservoirs because of the osmotic pressure created via salinity contrast was evaluated. It has been difficult and time-consuming to measure osmotic pressure in cores. In this thesis, I have introduced a novel laboratory technique to measure osmotic pressure in very low permeability cores using a high-speed centrifuge. Specifically, I measure spontaneous and forced imbibition characteristics of fluids at several salinities in cores saturated with decane at irreducible brine saturation. The experiments were conducted using Codell sandstone and Niobrara B-chalk core samples. The 40,000 ppm represented the high salinity brine which is the formation brine, and 5,000 ppm represented the low salinity brine. The following are the main conclusions of this thesis.

- Osmotic pressure in a permeable porous material is the external pressure to be applied to the fluid inside the porous material so that there is no net transfer of solvent across the core surface. Osmotic pressure is a colligative property meaning that the osmotic pressure is a function of the molar concentration of the solute particles but not their identity (for instance, dissolved sodium chloride will be represented at two sets of particles—chlorine and sodium ions). It should be noted that capillary pressure is dependent on the wettability of the internal surfaces of pores and the magnitude of the phase saturations in the pores. On the other hand, osmotic pressure is function of contrast between particle concentrations outside and inside the pores of the core.

- Measured osmotic pressure of Niobrara B-chalk, which has a permeability of 0.0022-0.0099 md was 74.9 % of the calculated osmotic pressure in a perfect membrane using activity coefficient. Accounting for chalk solubility in brine within the pores should reduce the calculated osmotic pressure to about 50% of that in perfect membrane.

- Measured osmotic pressure of Codell sandstone, which has a permeability of 0.0085-0.0105 md was about 2.4 % of the calculated perfect membrane.
REFERENCES


