LABORATORY STUDY OF THE EFFECT OF CHEMICAL OSMOSIS
ON THE ELASTIC ROCK PROPERTIES OF PIERRE SHALE
AND IMPLICATION FOR OIL RECOVERY

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 Doctor of Philosophy (Petroleum Engineering).

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ABSTRACT

The main objective of this research is to experimentally (1) measure the effect of chemical osmosis on elastic properties of shale, (2) determine chemical osmosis membrane efficiency under in-situ stress, and (3) evaluate the swelling tendency of Pierre shale resulting from chemical osmosis and its implication on oil production. Three relevant tri-axial experiments were conducted on Pierre shale core samples, before and after fluid invasion at reservoir pressure and temperature conditions, to determine rock properties and behavior.

To accomplish the tasks, a new tri-axial cell was built to accommodate coupled acoustic and static measurements attributed to swelling during water intrusion into the Pierre shale matrix. Bulk modulus, Poisson’s ratio, and shear failure envelope of Pierre shale were determined from measurements on several shale samples with varying clay content. The membrane efficiency of the shale samples was experimentally determined to be in the range of 10 to 30% depending on clay content and stress level. Swelling strains of the samples were determined from experiments to be 1% in high smectite content samples and 0.07% in a 3.5 wt.% TOC sample from Pierre shale. For the PI-LC-WY-H-01 Pierre shale sample with low smectite and high TOC, we obtained an internal friction angle of 48.4 degrees. The shale samples containing high swelling clays indicated a decreasing trend in Young’s modulus when low salinity brine imbibed into the pore space by chemical osmosis. For relatively low smectite content and high TOC, the Young’s modulus increased when water saturation increased during osmosis pressure build up. The aforementioned results were included in the numerical model to account for osmosis and clay swelling characteristics on oil recovery from the rock matrix. The correlation of the membrane efficiency with stress is dependent on the formation mineralogy, particularly clay content.

A coupled mass transport-geomechanical mathematical model was developed (1) to simulate mass transport between the fracture and rock matrix amidst the occurrence of clay
swelling, and (2) to evaluate how fluid and rock interactions could affect oil recovery from the rock matrix in unconventional reservoirs. The model was used to evaluate oil recovery from a single matrix block while accounting for the change of membrane efficiency with stress, swelling, and mechanical property of shales. Based on our laboratory observations, I recommend investigating the swelling tendencies of shale formations before any water injection operations, especially for low salinity water injection. I also recommend determining the increase in effective stress with clay content resulting from low salinity water injection.
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LIST OF SYMBOLS

absorption coefficient ........................................... $\alpha_c$
Cross-sectional area of the sample ................................ $A$
Slope representing the membrane coefficient ......................... $Ac_b$
Water activity ....................................................... $a_w$
Water activity of injected fluid .................................... $a_{w1}$
Native fluid water activity of the sample ............................ $a_{w2}$
Skempton’s coefficient ............................................... $b$ value
Residue adsorption capacity ........................................ $C$
Cohesion .............................................................. $C_o$
Elastic coefficient of the rock matrix ................................ $C_{ij}$
Stiffness tensor ...................................................... $C_S$
Scale factor ......................................................... $c$
bulk compressibility .................................................. $c_b$
Fracture permeability proportionality coefficient .................. $c_{fk}$
Fracture porosity proportionality coefficient ....................... $c_{fp}$
Native salinity ....................................................... $c_{initial}$
Injected brine salinity ............................................... $c_{inj}$
Oil compressibility .................................................. $c_o$
Solute concentration in matrix ....................................... $c_{sm}$
Water compressibility ............................................... $c_w$
Pore compressibility .............................................. $c_\phi$
Bulk diffusivity ................................................. $D_{eff}$
Elevation .......................................................... $D_m$
Diffusivity in free solution .................................. $D_o$
Dynamic Young’s modulus ................................... $E_{dyn}$
Young’s modulus in the minimum horizontal stress direction ........... $E_h$
Static Young’s modulus ....................................... $E_{stat}$
Young’s modulus in the vertical stress or overburden direction .......... $E_v$
External force vector .......................................... $F$
Constant ($0 \leq f^{-1} \leq 1$) ................................. $f$
Acceleration due to gravity .................................. $g$
Expansion coefficients determined from moisture injection and swelling relationship from experiment ........................................... $K_1, K_2$
Elastic coefficient determined from moisture injection and change in Young’s modulus from experimental data ........................................... $K_3$
Permeability ....................................................... $k$
Air permeability ............................................... $k_a$
Boltzmann constant, absolute temperature, and gas molecular collision diameter . . $k_b, T_0, d_c$
Effective permeability ....................................... $k_{eff}$
Initial fracture permeability at mean effective stress ................... $k_{fi}$
Gas permeability ............................................... $k_g$
Matrix permeability .......................................... $k_m$
Permeability of oil in the matrix ................................. $k_{om}$
Permeability of water in the matrix ............................. $k_{wm}$
Liquid permeability $k_1$

Equivalent liquid permeability $k_\infty$

Length of sample $L$

Decay time constant (slope of $\ln[\Delta P(t)]$ vs $t$) $m$

Average pressure of core inlet and outlet $P$

Pore pressure $P_p$

Gas pressure $p$

Atmospheric pressure $p_a$

Water-oil capillary pressure of the matrix $p_{cwom}$

Constant related to desorption speed and the heat of adsorption $p_d$

Pressure of phase i in matrix $p_{im}$

Langmuir pressure $p_L$

Upstream pressure $p_1$

Outlet pressure $p_2$

Deviatoric stress $q$

Gas flow rate at atmospheric pressure $q_a$

Specific rate of phase i (oil, solute, water) in matrix $\dot{q}_{im}$

Gas flow rate at atmospheric pressure $q_1$

Universal gas content $R$

Radius of pore $r$

Saturation of phase i in matrix $S_{im}$

Fluid temperature in the matrix $T_m$

Time $t$
Displacement vector for rock particles \( u \)
Adsorption volume when gas pressure decreases to \( p \) \( V_a \)
Bulk volume \( V_b \)
Maximum desorption capacity \( V_d \)
Langmuir volume or maximum adsorption capacity of shale \( V_L \)
Partial molar volume of water \( V_m \)
Pore volume \( V_p \)
Shale adsorption capacity \( V_s \)
Upstream and downstream reservoir volumes \( V_1, V_2 \)
Velocity of matrix \( v_m \)
Biot’s coefficient tensor \( \alpha \)
Compressibility of fluid \( \beta \)
Specific gravity of phase \( i \) \( \gamma_i \)
Pressure pulse \( P(0) \)
Pressure drop \( \Delta p \)
Change in water content of the bulk sample \( S_{w} \)
Change in fluid pore pressure \( \delta p \)
Change in applied stress \( \delta \sigma \)
Incremental effective stress \( \Delta \sigma_{e,f} \)
Total strain tensor \( \varepsilon \)
Elastic strain \( \varepsilon_e \)
Swelling strain \( \varepsilon_s \)
Swelling strain in the \( i \) – direction \( \varepsilon_{si} \)
Vertical swelling strain captured from the experimental system \( \varepsilon_{sv} \)

Horizontal swelling strain in the axial direction \( \varepsilon_{sh} \)

Increment of fluid content \( \varsigma \)

Failure criterion \( \eta \)

Effective solute porosity ratio of the connected porosity to the total porosity \( \theta \)

Gas molecular mean free path \( \lambda \)

Fluid viscosity at temperature and mean pore pressure \( \mu \)

Air viscosity \( \mu_a \)

Oil viscosity \( \mu_o \)

Water viscosity \( \mu_w \)

Liquid viscosity \( \mu_l \)

Poisson’s ratio \( \nu \)

Osmotic potential \( \pi \)

Density of phase \( i \) \( \rho_i \)

Matrix density \( \rho_m \)

Oil density \( \rho_o \)

Solute density \( \rho_s \)

Axial stress \( \sigma_a \)

Deviatoric stress \( \sigma_a - \sigma_r \)

Net mean stress \( \frac{(\sigma_a + 2\sigma_r)}{3} - Pp \)

Effective stress \( \sigma_{eff} \)

Minimum horizontal stress \( \sigma_h \)

Effective stress tensor \( \mathbf{\sigma}_{m,eff} \)
Normal stress \( \sigma_n \)
Radial stress \( \sigma_r \)
Vertical stress \( \sigma_v \)
Tortuosity \( \tau \)
Porosity \( \phi \)
Initial porosity at mean effective stress \( \phi_{fi} \)
Matrix porosity \( \phi_m \)
Friction coefficient \( tan \varphi \)
Membrane coefficient/efficiency of the shale matrix \( \omega \)
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>3-D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>AIPEA</td>
<td>Association Internationale Pour l'Etude des Argiles</td>
</tr>
<tr>
<td>CD</td>
<td>Consolidated Drained</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
</tr>
<tr>
<td>CMS</td>
<td>Core Measurement System</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CRC</td>
<td>Core Research Center</td>
</tr>
<tr>
<td>CU</td>
<td>Consolidated Undrained</td>
</tr>
<tr>
<td>DJ</td>
<td>Denver Julesburg</td>
</tr>
<tr>
<td>EIA</td>
<td>U.S. Energy Information Administration</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced Oil Recovery</td>
</tr>
<tr>
<td>EUR</td>
<td>Estimated Ultimate Recovery</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>HST</td>
<td>Highstand System Tract</td>
</tr>
<tr>
<td>HI</td>
<td>Hydrogen Index</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>IOR</td>
<td>Improved Oil Recovery</td>
</tr>
<tr>
<td>JNC</td>
<td>Joint Nomenclature Committees</td>
</tr>
<tr>
<td>LVDT</td>
<td>Linear Vertical Displacement Transducer</td>
</tr>
<tr>
<td>Term</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Low Salinity Water</td>
<td>LSW</td>
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<tr>
<td>Low Salinity Water Injection</td>
<td>LSWI</td>
</tr>
<tr>
<td>Oxygen Index</td>
<td>OI</td>
</tr>
<tr>
<td>Production Index</td>
<td>PI</td>
</tr>
<tr>
<td>Practical Salinity Units</td>
<td>PSU</td>
</tr>
<tr>
<td>Nondestructive Testing</td>
<td>NDT</td>
</tr>
<tr>
<td>Proportional, Integral, Derivative</td>
<td>PID</td>
</tr>
<tr>
<td>Pore Pressure Intrusion</td>
<td>PPI</td>
</tr>
<tr>
<td>Pore Pressure Penetration</td>
<td>PPP</td>
</tr>
<tr>
<td>Parts per million</td>
<td>ppm</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>PR</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>SSA</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>TDS</td>
</tr>
<tr>
<td>Tetrahedral Octahedral</td>
<td>TO</td>
</tr>
<tr>
<td>Tetrahedral Octahedral Tetrahedral</td>
<td>TOT</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>TOC</td>
</tr>
<tr>
<td>Transgressive System Tract</td>
<td>TST</td>
</tr>
<tr>
<td>Unconfined Compressive Strength</td>
<td>UCS</td>
</tr>
<tr>
<td>Unconventional Natural Gas and Oil Institute</td>
<td>UNGI</td>
</tr>
<tr>
<td>United States Geological Survey</td>
<td>USGS</td>
</tr>
<tr>
<td>Weight percent</td>
<td>wt.%</td>
</tr>
<tr>
<td>Western Interior Seaway</td>
<td>WIS</td>
</tr>
</tbody>
</table>
X-ray Diffraction .......................................................... XRD
Young’s modulus ......................................................... YM
ACKNOWLEDGMENTS

Most certainly, the embodiment of this dissertation been a monumental journey for me made possible due to my faith in God and the people that I shared many memorable moments with through this entire process. I will like to express my deepest gratitude to my late advisor, Dr. Azra N. Tutuncu for putting me through my program by encouraging me, fueling my curiosity and providing me with the insights to pursue pioneering endeavors. Special thanks to Dr. Ramona Graves for inspiring me to take on the challenge of a Ph.D. degree and sponsoring the initial phases of my research.

I will be remiss if did not recognize the contributions of my committee members in molding my resolve into striving for this great accomplishment. My co-advisor, Dr. Hossein Kazemi has always being a source of knowledge and inspiration that I tap into ceaselessly. Dr. Erdal Ozkan always sparked my interest and understanding of the subject scope with conceptual applications of my research that always got me thinking beyond my knowledge horizon. Dr. Stephen Sonnenberg has always been supportive and with my geological interpretations leading into my investigations and a huge motivational source. Dr. Bruce Trudgill has been nothing but patient in my transition to a hybrid a petroleum engineer armed with geological prowess. Dr. Xiaolong Yin for being gracious to step into my committee and offer relevant suggestions to complement my thesis. I am indeed grateful for all the mentorship and support I obtained during this time.

There are no words to express my gratitude to Dr. Daisuke Katsuki for offering his time and insight regarding experimental procedures and ensuring the authenticity of my laboratory results. Dr. Binh Bui generously gave modeling expertise and assisted me with the development of a robust model in my research. His daily eye-opening advice surely kept my eye on the prize. And of course, I am appreciative of the past and current members of my beloved UNGI consortium, for all the constructive and enlightening conversations. I am
thankful to the entire petroleum engineering faculty and administration who at one point or the other have helped me to my destination.

I am eternally grateful to my mom, dad, and brothers; Olatunde Adekunle, Oyeyemi Adekunle and Ayoola Adekunle foremost for their unconditional love and support through all the challenging times. My magnanimous friendships with Midowa Gbededo, Tan Ngo, Cedric Sedjro and Koko-ete Obott will always be a source of strength and joy for me. I will forever be grateful for their unending encouragement and motivation.

Many thanks to Dr. Mark Miller, Dr. Manika Prasad, Dr. Jennifer Miskimins, Dr. Yu-Shu Wu, and Dr. Fleckenstein for their cheerful stories and bringing out the professionalism embodied in my dissertation. Denise Winn-Bower, Joe Chen and Terry Snyder for making every hurdle along the way a lot smoother to pass. Thanks for the memories and for always believing in me.
In loving memory of Dr. Azra Tutuncu
CHAPTER 1
INTRODUCTION

The amount of trapped oil in hydrocarbon-rich shale reservoirs recoverable through Enhanced Oil Recovery methods has been an ongoing study in the oil and gas industry. The success of low salinity water injection in conventional reservoirs such as sandstones has warranted the same approach to be considered for unconventional reservoir systems. Applying low salinity water floods in shale reservoirs to improve hydrocarbon recovery is debatable due to uncertainties surrounding the feasibility of water injectivity into the extremely tight matrix. Advantageously, the same tight shale matrix has been characterized as a leaky membrane that can facilitate the flow of water and solute molecules across distinct chemical potential environments. The flow direction of water can be controlled by generating chemical osmosis within the shale formation by introducing varying salinity fluids other than the native interstitial water present in the pore spaces. Mass transport in unconventional reservoirs has been receiving a lot of attention. The influence of rock-fluid interactions inherent in source rock and reservoir rock formations has been studied extensively in order to understand and control the mechanisms for optimal development of oil and gas. Shale formations have largely become the target for extraction of these hydrocarbons but the low permeability nature of the shale matrix presents its unique challenges for fluid flow within these potential source rocks. Multi-lateral well placement along with hydraulic fracturing performed within the extensive shale depositional environment has propelled US shale plays into leading producers of oil and gas across the globe in recent decades. Consequently, the technological frontier for shale development is constantly being pushed. Previous research studies indicate that higher cation exchange capacities and lower permeabilities correlate well with the increased membrane efficiencies. Reservoir shales typically have relatively lower amounts of swelling clays and in theory, can be exposed to a higher chemical poten-
tial difference between the native and injected fluid salinity before detrimental permeability reduction is experienced through the volumetric expansion of swelling clays. This fluid flux into the pore spaces of the rock matrix acting as a semi-permeable membrane is significant enough to promote additional recovery from the extremely low permeability rock. Thus, the development of unconventional reservoirs requires a better understanding of mass transport in the reservoir and the mechanical interaction between fluid and rock. Correlating the impacts of generated osmotic potential and physicochemical effects on formation mechanical properties and strength will ultimately provide better strategies for shale field development.

1.1 Objectives and Scope

In summary, the objectives of my research are to

1. Experimentally measure the effect of chemical osmosis on elastic properties of Pierre shale membrane efficiencies under varying stress conditions, and to further determine how the membrane behavior influences the flow of fluids.

2. Account for clay swelling and rock deformation under chemical osmosis in a numerical model capturing the nature of fluid flow driven by chemical osmosis within the Pierre shale matrix.

3. Develop a predictive mathematical model to evaluate oil recovery from a single matrix block accounting for the change of membrane efficiency with stress, swelling, as well as the variation of mechanical property of shales.

The primary focus of this research study was to investigate the impact of osmosis rock-fluid interaction on the geomechanical and failure properties of Pierre shale. This research study also extends beyond observing the effects of wellbore stability in seal shales having high swelling clays and considers the associated impact on production optimization in liquid-rich reservoir shales. The second objective observes the impact of osmosis on the mass transport in shale formations because of these geomechanical alterations. Drilling through
shale formation having high clay content can be quite problematic. Drilling programs are often optimized within these active shale intervals using high salinity fluids to stabilize or dehydrate the clays. Hydration of smectite can cause swelling of shale up to 20 times its original volume. Thus, controlling the flow of water molecules within both drilling and formation fluid is important for maintaining borehole stability while drilling through clay-rich shales. The impact of this induced osmotic potential can also be beneficial for production enhancement in reservoir shales thereby instigating the experimental studies on high organic content Pierre shale.

In this research study, pore pressure penetration under tri-axial measurements have been conducted using varying salinity fluids to understand the contribution of the osmotic pressure inflow, geomechanical properties, acoustic and resistivity characteristics in shale formations. Pierre shale core samples with 65 wt.% smectite were utilized as a reference to investigate the role of a high percentage of swelling clay on osmosis. Coupled geomechanics, osmotic, acoustic and resistivity measurements were conducted to develop a relationship between osmosis and clay composition in Pierre shale. Varying salinity pore fluids have been injected at in situ reservoir stress conditions, elevated pore pressure, and at constant temperature conditions.

The permeability, resistivity, acoustic and geomechanical properties were measured prior to the core samples being exposed to various brine concentration fluids in order to understand the role of the osmotic effects on the changes observed in permeability, resistivity, acoustic, geomechanical properties and associated effective stress state acting on the formation. SEM and FESEM scans were collected prior to and after completion of the experiments to determine the pore structure changes during the experiments as well as to obtain the pore size distribution of the core samples used in this study. Ultimately, this data captures fluid flow intricacies within such low permeability reservoirs caused by salinity differences in the formation and injected fluid that will be advantageous for fluid formulation for improved hydrocarbon recovery.
1.2 Background and Motivation

The advancement in technology of the United States unconventional resource development has largely influenced the rise in oil production since 2010. The occurrence of the oil and gas industry downturn in 2014 slowed down activity but for the most part, production has continued to rise to the present day (EIA 2019b) as shown in Figure 1.1. According to the EIA (2019a), the proven reserves of crude oil in the United States increased by 12% (about 4.6 billion barrels) to 43.8 billion barrels. A similar rise in proven reserves were also reported for condensates and natural gas production in the same year. For instance, the U.S. Geological Survey released an updated oil and gas resource assessment of the Bakken and Three Forks formations in 2013. The technically recoverable continuous resources were defined for six assessed geologic units within these formations to have 7,375 million barrels of oil, 6,723 billion cubic feet of gas and 527 million barrels of natural gas liquids (USGS 2013).

The typical recovery factor for unconventional assets ranges from about 2 to 10% and this recovery can be attributed mainly to the application of multilateral wells in the development of shale formations. The combination of horizontal wells extending up to two miles in lateral length and multi-stage hydraulic fracturing technology has greatly contributed to the overall primary drive mechanism, thereby unlocking the remaining stored hydrocarbon potential from these extremely tight source rocks. Most of the prolific shales, deposited in marine or lacustrine environments, serve as source rocks to many conventional reservoirs that have already been developed. The deposition of these shale formations was created under low energy conditions, resulting in the typical low permeabilities of the shales occurring in the microdarcy and nanodarcy ranges. Fortuitously, these source rocks still have vast amounts of hydrocarbons in place depending on the level of maturity, hydrocarbon generation and expulsion from within the source rocks. The process of source rock fracturing is a mechanism associated with the primary migration of hydrocarbons and cause for permeability increment in the source rocks. The observed fractures are commonly horizontal with oblique and perpendicular fractures to bedding occurring regionally (Sonnenberg 2014).
Producing wells usually start with favorable production but soon afterward experience a steep decline in production. It is understood that this decline in production, arising from the depletion of stored hydrocarbons primarily from the natural fractures existing within the formation, is attributed to the slow recharge of existing hydrocarbons within the rock matrix. Particularly for unconventional resources, these recovery factor numbers keep improving with rising IOR and EOR technology. Studies implemented for the application of unconventional EOR technologies have been limited to mostly numerical and experimental investigations. Field pilot tests are rare and in these few cases, have conflicting results in comparison to laboratory and simulation studies (Alfarge et al. 2017).

Figure 1.1: Weekly U.S. field production of crude oil. Source: U.S. Energy Information Administration (EIA 2019b).

Miscible gas injection using CO$_2$, produced gases or a combination of both seems to be the most favorable unconventional EOR approach from a research perspective (Balasubramanian
et al. 2018). Laboratory studies have shown that miscible gas injection is favorable for EOR applications due to the low permeability of the shale formations. In the miscible gas injection, huff and puff has enabled further production for oil reservoirs where injected gas is allowed to diffuse with the oil in the tight matrix and mobilize the oil upon production after a certain period of soaking. Altering the wettability through chemical EOR such as surfactant injection follows as the next best approach to EOR in unconventional reservoirs.

Implementing typical water floods does not seem feasible due to low sweep efficiencies resulting from more severe viscous fingering and capillarity in the micropores and nanopores of the shale formations. Hoffman and Evans (2016) propose methodologies for implementing second-generation pilots for unconventional reservoirs after studying seven pilot tests from 2008 to 2014 showing that early breakthrough times and poor sweep efficiencies to be associated with fluid injectivity. In the U.S. region of the Bakken formation, injectivity of water and gas did not appear to be the issue. However conformance control, which measures the uniformity of a flooding operation vertically and aerially, was determined to be more of a factor. Canadian Bakken pilot tests performed around the same time proved more successful probably because of the relatively higher permeabilities and porosities experienced in the region. In addition, the implementation of innovative technologies in injection strategy by placing injector wells perpendicular to the producers and gas detection devices to detect and isolate breakthrough contributed to the success.

Another popular approach that has proven successful in EOR operations for conventional reservoirs is low salinity water injection (Chandrashegran 2015). This concept is investigated in this study as a favorable means of recovering more hydrocarbons in unconventional resources. This approach takes advantage of the difference in the chemical potential of the native fluid existing in the formation and an injected fluid possessing lower salinity. The different salinity creates a driving mechanism for water molecules to flow to the region of higher saline concentration. This effect ultimately builds up osmotic pressure, which is an added force that drives residual oil trapped in the matrix pores. The level of recovery will
depend largely on the difference in salinity between the two fluids, mineralogy - specifically the clay content, and permeability under injectivity conditions.

Considering low salinity water injection in unconventional reservoirs, the prolific shale formations have varying characteristics in terms of their mineralogy. It takes proper analysis of these unique plays to fully understand the underlying mechanical behavior that exists governing fluid flow through the matrix. Shale formations containing above a critical amount of clay present significant rock-fluid interactions that affect drilling, completion, stimulation, production and economic viability of the operations. Shales are typically considered to behave as semi-permeable or leaky membranes. Therefore, correlating the impacts of generated osmotic potential and physicochemical effects on formation mechanical properties and strength will provide better efficiency of the drilling and completion operations in shale formations whether they are sealing reservoir formations or are an organic-rich source rock that is produced. Within the platy surfaces of clay minerals, exist negatively charged oxygen ions (aluminosilicates) held together by cations. The oxygen ions are usually organized into a hexagonal network or the hydroxyl ions are organized into a closely packed network. A unique feature of these clays is their ability to swell when water is absorbed between the layers. Swelling will occur differently depending on the amount of exchangeable cations on the surfaces of the clays. The concept of cation dissociation can be used to explain the relationship between clay composition and swelling. For instance, when a clay belonging to the montmorillonite group is dispersed in water, the cations present between the sheets tend to dissociate simultaneously pulling the particles apart and leaving the structure with more negatively charged ions. Ultimately, strong repulsive forces are created amongst the negative ions that cause the clays to assume the appearance of swelling (Sheng and Morsy 2014).

Therefore, the type of fluid that shale formations contacts changes their mechanical properties and strength characteristics. For example, static Young’s modulus increases when the Pierre shale outcrop core samples containing up to 65 wt.% smectite having larger specific surface area are exposed to high salinity brine solution of 257,000 ppm NaCl (Adekunle...
et al. 2018). Alternatively, water imbibition from low salinity injection adversely alters the structure of the same formation containing swelling clays. While there have been many research studies conducted on the effect of exposure to various fluids, the effect of this exposure on geomechanical properties of shales has not been sufficiently investigated under in-situ reservoir stress, elevated pore pressure, and temperature conditions. Computationally, oil recovery is less than 5% for shale formations having less than 10% membrane efficiency (Bui and Tutuncu 2017). The impact of improved membrane efficiency on oil recovery will be investigated under elevated stress conditions also.

The late Cretaceous Pierre shale formation possesses varying total organic carbon (TOC) content, yet distinctively has high TOC within the Sharon Springs member of the same formation. The Sharon Springs member serves as the source rock for hydrocarbons migrating into vertical fractures within the Pierre shale while underlying Niobrara formation in the Powder River and Denver-Julesburg (DJ) basins is also a source of the hydrocarbons produced from the Pierre shale. It is important to distinguish the mineralogical properties of these various formations to understand the impact of the fluid salinity on the physicochemical behavior of the rock formation. Source rock analysis in the Sharon Springs in Fremont county in DJ basin presents relatively high TOC to range from 2.96 – 7.37 wt.% and having Type II oil-prone kerogen characteristics as shown in Table 1.1. The hydrocarbons within the source rock are mature in the oil window. The Sharon Springs member in other basins does not necessarily contain the same level of TOC as in the Fremont county, DJ basin. For example, TOC values in the Sharon Springs member in the Powder River basin vary between 1.27 and 2.72 wt.% with Kerogen Type and Kerogen Quality graphs putting the Sharon Springs Member as Type III kerogen suggesting gas prone organic matter within the member (Kaykun 2013).

The distinct sensitivity of shale formations to fluid composition and their semi-permeable membrane behavior has been well recognized for minimizing wellbore stability issues during drilling and completion operations. The advent of production from organic-rich shale forma-
tions within the past decade has also brought opportunities benefiting their fluid sensitivity in EOR operations, as mobilization of free as well as trapped oil within the rock matrix is supported by the osmosis process impacting the improved estimated ultimate recovery. The higher the amount of the swelling clay in the formation, the larger the contribution from the osmosis resulting in further permeability reduction in the shale formation. Clay swelling can be triggered through ionic exchange between the native formation fluid and the fluids injected during the completion, stimulation and/or EOR operations if the fluid compositions are not compatible with the formation and the native fluid. The efficiency of the semi-permeable membrane can be increased by limiting the ion selectivity and transfer of solute. The chemical potential difference between the injected and native fluids can cause imbibition of water molecules into the shale matrix or dehydration of the shale that in turn increases or decreases the osmotic pressure created, respectively.

Table 1.1: Total organic carbon and programmed pyrolysis data from Sharon Springs member (Core chip) of the Pierre shale (Allred 2017)

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Top Depth (ft)</th>
<th>TOC</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>Tmax (°C)</th>
<th>HI</th>
<th>OI</th>
<th>S2/S3</th>
<th>S1/TOC</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bull 42-4</td>
<td>2963.5</td>
<td>2.96</td>
<td>1.94</td>
<td>8.80</td>
<td>0.16</td>
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Evidence supports the occurrence of chemical osmosis within the stratigraphic sections in marine shales and evaporate depositional environments in sedimentary basins. This is
one of the processes directly related to the chemical compositional and pore fluid pressure distributions in the basins. Supporting evidence is reported by Graf et al. (1966). They illustrate the distribution of subsurface brine concentrations through a stratigraphic interval in the upper Mississippian section of the Illinois basin. In general, salinity is observed to increase with depth within the basin, yet this increase in salinity rate decreases near the structural low of the basin. Moderate amounts of water from lower formations pass through the existing shales emerging with lower dissolved solids and diluting the encountering brine.

The lower concentration is evidence that the filtration of the saline water or dilution process is occurring at a significant burial depth interval up to 5,500 ft in the Pierre shale depositional environment, ensuring the presence of hydro-static pressure through the shale micropores. Further analysis of brine cations presents that the relative concentration of calcium and sodium ions (Ca\textsuperscript{++}/Na\textsuperscript{+}) at the same depths of the geographical area is reversed indicating the active selectivity of shale pores to different salts ions (Graf 1983). The microporosity of the shale allows more Na\textsuperscript{+} to pass upward through the bed than Ca\textsuperscript{++} due to the smaller atomic radius of the sodium ion. The anion ratios of chlorine and bromine within the brine in the Michigan basin are shown to have expected values of concentrated seawater owing to their smaller atomic radii relative to cations. This phenomenon can be related to isotopic fractionation, which is the relative partitioning of the heavier and lighter isotopes between two coexisting phases in a natural system. More details on the topic of isotopic fractionation is discussed in Tiwari et al. (2015). Essentially, this isotopic fractionation occurs during the flow of seawater through the micro (and nano) pores in shale. (Magara 1974) reported increasing salinity of formation water in the Gulf Coast with decreasing shale porosity. The passage of water through the shales during compaction leaves behind most of the salt ions. The efficiency of the ion filtration causes the salinity of the water expelled from the shale to lose salt ions converting the water to about 33\% of the formation water. Under compacted regions with low salinity would have other governing processes to explain the salinity such as montmorillonite dehydration (clay diagenesis) and reverse osmosis to be
further discussed in the research study presented here.
CHAPTER 2
LITERATURE REVIEW

This chapter provides an extensive geological analysis of the Pierre shale formation of study supporting its suitability for chemical osmosis investigations.

2.1 Pierre Shale Oil Production

Historically, 15.5 million barrels of oil have been produced in the Pierre shale formation from over 1,000 wells since the 1860s. More recently, natural gas has been extracted in the Raton basin in Southern Colorado primarily from the naturally fractured regions of the formation. This concept applies consistently within the Pierre shale where hydrocarbon extraction in low TOC environment has been known to be associated with highly naturally fractured zones. Because the Sharon Springs member is a high TOC source rock (up to 6 wt.%), hydrocarbons migrate from it to existing natural fracture systems. With the right mix of TOC and clay percentage in the formation, the osmotic efficiencies could be influential towards oil production or formation stabilization. Incorporating the osmotic efficiency into flow models gives us an indication of the improved EUR when low salinity water is injected as an EOR methodology in the Pierre shale.

The Pierre formation is located within the late Cretaceous and is the host formation for commercial oil deposits in Florence and Cañon City oil field in Fremont county, Colorado and Boulder oil field in Boulder county, Colorado. More recently, the Pierre shale within the Raton basin of Southern Colorado has been associated with natural gas extraction despite very low permeabilities that are typically unfavorable for hydrocarbon extraction. Production occurs in naturally fractured regions of the Raton consistent with early production from within the Pierre shale in the 1860s. The hydrocarbon production from the Pierre shale has been misunderstood until quite recently. Early wells drilled in the shallow regions of the
Pierre shale intersected natural fractures containing migrated hydrocarbons from underlying source rocks. It has become common knowledge to target these naturally fractured regions of hydrocarbon accumulations and produce utilizing gravity drainage. Figure 2.1 illustrates the tactics from Fremont Petroleum Corporation to maximize the oil production in a producing well from the Pierre shale formation (Hart 2017). Combining 3D seismic and horizontal well drilling to identify and target the hydrocarbon filled natural fractures contributes to the success of wells drilled in Fremont county. Studies have shown that the most likely source of oil produced out of the Florence field is the Sharon Springs member of the lower Pierre shale. Further description of the Pierre shale and its members are discussed in the following section.

Figure 2.1: Fremont Petroleum Corporation Pierre shale hydrocarbon extraction technology (Hart 2017).

2.2 Geologic Setting

The Pierre shale is of marine origin and was deposited during the existence of the Western Interior Seaway (WIS), a large, shallow, epicontinental seaway extending from the Boreal Sea to the emerging Gulf of Mexico (Allred 2017). It is correlative with other marine shales
that occur farther west, such as the Bearpaw shale, Mancos shale and the Lewis shale (Izett et al. 1971). Overlain by marginal marine deposits, the Pierre shale is of early Campanian to early Maastrichtian age, evident from numerous fossil marine mollusks within several concretion levels within the formation that are useful for regional correlation. Although not exactly known, it is stipulated that the Maastrichtian period is when the earliest initiation of the basement in evolved thrust faulting known as the Laramide Orogeny took place in the Western Interior basin (Dickinson et al. 1988). During the Laramide deformation, much of the Pierre shale was removed by erosion prior to the deposition of the Middle Park Formation of late Cretaceous and Paleocene age leaving the maximum remaining thickness of about 5,000 ft. From regional correlation estimates, about 3,000 to 4,000 ft in the upper part of the Pierre shale formation was eroded during Laramide time.

Ammonite zones exist all through the distinct sections of the Pierre shale. Ammonites are ammonoids that are an extinct group of marine mollusk animals in the subclass Ammonoidea of the class Cephalopoda. The Pierre shale both within the Kremmling area of Grand county, Colorado and the Powder River basin has similar descriptions and correlations of their member formations. In the Kremmling area, the Pierre shale can be divided into three main sections, namely the lower, middle and upper sections.

The lower section, about 1,500 ft thick, consists of dark-gray to black non-sandy marine shale. The Sharon Springs member which is heavily fractured and possesses high TOC content is about 45 ft thick. Lying 1,100 ft above the base of the lower part, the Sharon Springs member distinctively contains at least eight bentonite beds with gray Septarian limestone concretions visible in many places. The Sharon Springs member is stratigraphically unique as it differs from the rest of the Pierre shale because of its dark color, resistance to erosion, richness in organic material, and high radioactivity readings. The member derives its name from the town of Sharon Springs in Wallace county near the west boundary of Kansas (Gill et al. 1972). The lower shale unit of the Pierre near Kremmling correlates with the Mancos shale from Fish Creek to near Hamilton having strong agreement with the
units containing *B. asperiformis* ammonites. The same lower shale part of the Pierre near Kremmling correlates with about the lower 1,000 ft of the shaly unit near Boulder.

The middle section of the Pierre consists of alternating sandy shale and several named sandstone members. This sandy section is about 3,300 ft thick with the lower 400 ft of the middle sandy part of the Pierre consisting of silty shale with a few interbedded sandstone beds (Izett et al. 1971). The entirety of the middle section (3,300 ft) of the Pierre near Kremmling correlates with about the upper 600 ft of the lower shale unit, the middle sandy 2,400 ft thick unit and about the lower 100 ft of the upper shaly unit near Boulder. The middle sandy part of the Pierre correlates with about the upper 1,000 ft of the Mancos and the Iles and Williams Fork formations. The Kremmling Sandstone member and the Muddy Buttes sandstone both depict a strong correlation to the stratigraphic units of the Mancos shale near the Fish Creek and Hamilton area respectively. The individual members and their thicknesses in ascending stratigraphic order are: Kremmling sandstone (20 - 70 ft), Muddy Buttes sandstone (5 - 30 ft), Hygiene sandstone (50 - 120 ft), Carter sandstone (30 - 65 ft), and Gunsight Pass (150 - 170 ft).

The upper section of the Pierre remaining in the Kremmling area consists of about 200 ft of uniformly dark marine shale having distinctive gray dense limestone concretions. Fossil records within the area correlates the Pierre shale to the east near Boulder and with the Mesaverde group to the west near Hamilton. The upper shale part of the Pierre shale near Kremmling also correlates well with the same upper shaly unit near Boulder and the lowermost part of the Lewis shale west of the Park Range shale (Izett et al. 1971).

### 2.2.1 Lower Pierre shale sequence stratigraphy of the Powder River basin

Another perspective on the stratigraphic variability of the Sharon Springs can be observed further north in the southern part of the Powder River basin, Wyoming. In this region of the Sharon Springs (Figure 2.2), multiple occurrences of disconformities and erosive periods exist suggesting periods of complex tectonic events within this area of the WIS. It is apparent from the large areal distribution of the Sharon Springs from the west to east
of Colorado (Figure 2.3) that structural and stratigraphic complexities can exist along the unit. Figure 2.4 shows the nature of deposition to be characterized as part of the Highstand System Tract (HST) in the south and a part of the Transgressive Systems Tract (TST) in the north (Bertog 2010) modified from Asquith (1970). This is justified from reports that conformable facies in the southern regions become disconformable in the north. The simultaneous occurrence of tectonic events with the transgressive system, of deposition in place in Wyoming further complicates the apparent nature of the deposition.

Figure 2.2: Generalized stratigraphic column of the upper Cretaceous section of the Powder River basin (Kaykun 2013).
Studies focused on the sequence stratigraphy within the southern Powder River has explored the varying mechanism of deposition of the sandstone and shale members of the lower Pierre shale. Kaykun (2013) emphasized understanding the mechanisms that lead the deposition of the two sandstone members within a study interval far away from the synchronous shoreline deposits. The Shannon sandstone member was interpreted to be deposited as tide-dominated marine deltas in a subaqueous environment whereas the Sussex sandstone was interpreted to be deposited under a wave-dominated environment. The depositional environment of the sandstone members here indicates a close shoreline position suggesting rapid relative sea-level fall. Understanding the source rock potential of the organic-rich Sharon Springs member that was continuous within the area was another focus of the study. Kaykun
(2013) research study showed that the Sharon Springs member of the lower Pierre shale is indeed continuous throughout the lower Pierre shale area. TOC values of the member differ between 1.27 and 2.72 wt.% with kerogen type and kerogen quality graphs putting the Sharon Springs member as Type III kerogen suggesting gas prone organic matter within the member. It was concluded that members in the Powder River basin did not have significant source rock potential and most likely did not contribute as the source to oil accumulation in the Shannon and Sussex sandstone members of the lower Pierre shale.

2.2.2 Members of the lower Pierre shale

Numerous well logs are available in the southern portion of the Powder River basin which provides a robust dataset for building the sequence stratigraphy framework. From Kaykun (2013) study, eight different formation tops were picked in 1,490 wireline well logs utilized to create the 3-D surface maps and isopach maps for each member of the lower Pierre shale. The depositional environment and correlation of members have been extensively described
in previous studies. The Sharon Springs is the focal point of this study and a brief summary of the sequence of the members in the lower Pierre shale will be discussed to provide some context. The uppermost horizons of the progradational Gammon Ferruginous member, which is the lowermost member of the lower Pierre shale, show truncation patterns towards its upper boundary located between the Gammon Ferruginous member and the Shannon sandstone. The Gammon Ferruginous member is directly overlain by the Ardmore Pedro bentonite beds on the east and is overlain by the Shannon sandstone with a sharp erosional basal contact which is interpreted to be the forced regressive surface of erosion on the west. The Shannon sandstone pinches out eastward with a downlapping pattern.

The unnamed member of the lower Pierre shale lies above the Shannon sandstone on the east and directly above the Gammon Ferruginous member at the central area where Shannon sandstone pinches out. This member is characterized by an eastward progradation evident by downlaps gotten from electric log correlations. The Sussex sandstone member was deposited following the deposition of the unnamed member and it shows a pinching out geometry eastward with a downlapping pattern above the unnamed member. The Ardmore Pedro bentonite beds lies above the Sussex sandstone on the western half of the study area and directly on the Gammon Ferruginous member on the eastern half. The member is characterized by an onlapping pattern towards the west which indicates the transgressional nature of the member. The member ceases to exist along a corridor and the absence is interpreted as the consequence of local erosion which has taken place along the corridor where there is a regional topographic relief.

The Sharon Springs member overlying the Ardmore Pedro bentonite beds covers the eroded corridor located at the center of the basin. The deposition of the Sharon Springs took place during the early Campanian, at which stage the WIS was no longer at its maximum transgression but had experienced a significant fall in sea level (Allred 2017). Also, a combination of relatively low sea levels experiencing high sediment supply and the migrating zone of maximum subsidence that instigated the intrusion of sediments into the basin
portraying its downlap nature onto the Niobrara formation (Figure 2.4). The onlapping patterns depict transgressional behavior more noticeable on the eastern side. Typical well log response for the member shows a slightly to distinctly fining upward trend with some irregular peaks. It reaches its greatest thickness values along the corridor where the Ardmore Pedro bentonite beds member does not exist, and it directly overlies theUnnamed member of the lower Pierre shale along this corridor with series of onlaps. The Mitten Black shale member lies above the Sharon Springs member showing progradational pattern from westward onlaps on the slightly east-dipping region in the central area of the study area. The Red Bird silty member directly overlies the Mitten Black shale member and was deposited as the last member of the lower Pierre shale interval also depicting progradational patterns (Kaykun 2013). Progradation can be seen to gradually slowdown from the absence of downlapping horizons towards the upper boundary of the Mitten Black shale member. The member depicts an eastward progradation not as distinct as the Mitten Black shale member.

2.2.3 Geochemistry

The source rock analysis (SRA) data on the Sharon Springs obtained from U.S. Geological Survey (USGS) was performed by Weatherford labs using a Rock-Eval VI analyzer. Table 1.1 shows the analysis of the Sharon Springs member from Well Bull #42-4 (Figure 2.5). Pyrolysis data was utilized to determine the free hydrocarbons, kerogen type, level of maturity and remaining hydrocarbon potential. TOC was measured with a Leco carbon analyzer upon combustion and measurement of produced carbon dioxide. Rock-Eval analysis for both hydrogen index (HI) and oxygen index (OI) were calculated using the S2 and S3 peaks in relation to TOC from the produced program (Allred 2017). S1 represents the free hydrocarbons already present in the sample and it increases with depth. The free hydrocarbons may be distilled out of the sample initially by heating up to 350°C. S2 represents the amount of hydrocarbons generated through thermal cracking of non-volatile organic matter when the sample temperature is increased to 550°C which is an indication of the quantity of
hydrocarbons that the rock may potentially produce should burial and maturation continue. S2 normally decreases with depths greater than one km. Typical S1 and S2 minimum values for good source rocks are 1.0 and 5.0 mg HC/g dry rock respectively. S3 is the trapped CO$_2$ released during pyrolysis up to a temperature of 390°C.

Figure 2.5: A. Cored section images of the Sharon Springs member from Well Bull #42-4 (Core Research Center (USGS), Denver Federal Center). B. Erosional bentonite base from Bull #42-4 core. C. Grain orientation from thin section (Allred 2017).
The HI is a measure of the hydrogen richness of the source rock and when the kerogen type is known it can be used to estimate the thermal maturity of the rock. The availability of hydrogen is an indication of the level of hydrocarbons that can be generated from the kerogen.

\[ HI = \frac{S_2}{TOC} \times 100 \]  (2.1)

The OI measures the oxygen richness of the source rock and can be used in conjunction with the hydrogen index to estimate the quality and thermal maturity of source rocks. OI values greater than 50 mg/g are characteristic of immature hydrocarbons. The amount of oxygen in the rock can provide an indication of the kerogen type.

\[ OI = \frac{S_3}{TOC} \times 100 \]  (2.2)

The Production Index (PI) is a ratio of the already generated hydrocarbon to potential hydrocarbons. Low ratios indicate immaturity or extreme post mature organic matter. High ratios indicate a mature stage or contamination by migrated hydrocarbons or drilling additives. PI also increases steadily with depth and associated hydrocarbon generation.

\[ PI = \frac{S_1}{(S_1 + S_2)} \]  (2.3)

Cross-plots of HI vs OI and HI vs Tmax can be seen in Figure 2.6(a) and Figure 2.6(b) respectively. The Van-Krevelen diagram comparing HI and OI classifies the kerogen type. Further analysis of the Van-Krevelen diagram from HI vs Tmax determines the kerogen type as well as the thermal maturity of the rock. Analysis from both plots shows that the Sharon Springs member of the Bull #42-4 well is most likely marine and in the oil window of maturity depicting type II kerogen.

2.3 Osmosis Pressure

Osmotic pressure is the pressure applied by a solution to prevent the inward flow of water across a semipermeable membrane. Osmosis is the process in which a liquid passes through a membrane, which allows the passage of solvent molecules but is too small for the larger
solute molecules to pass through. Because the molecules are in random motion, there will be more molecules moving from the high concentration region to the low concentration region. The motion of a substance from a high concentration region to a low concentration region is called diffusion. In the absence of a hydraulic pressure gradient, the movement of fluid into the shale matrix is mainly governed by the chemical potential difference between the pore fluid and the injected fluid. This results in the osmotic transport of water into the rock matrix (Ewy and Stankovich 2000).

2.3.1 Lithological role in basin-wide osmotic potential gradients

Berry (1959) reported the osmotic flow of water in the cretaceous section of the San Juan basin having transgressive and regressive deposits partly separated and interbedded.
by various facies inclusive of marine shale. Consistent potentiometric sinks coinciding with increased salinity of the formation water occur in and around the inner basin, especially in the cretaceous aquifers. Kelley et al. (2014) depicted the symbolized geologic units of the San Juan basin in chronological order which are listed in Figure 2.7. Water flows gravitationally due to differences in head and osmotically due to salinity differences between formations separated in some fashion by a shale or claystone member serving as the semi-permeable membrane. Most notably, the Entrada sandstone in the middle Jurassic represents a high transmissibility zone. Evaporite from the gypsum and limestone facies member in the Todilto formation of the middle Jurassic is believed to be the source of the high saline waters from 130,000 to 270,000 ppm present in the Entrada formation. Osmotic pressure most likely built up within the fresh waters of the Dakota owing to the potentiometric drawdown experienced within the formation. The brushy basin claystone in the late Jurassic portion of the Morrison formation that separates the late Cretaceous members of the Dakota, serves as the semi-permeable membrane promoting drawdown of the potentiometric surface from the overlying fresh waters aquifers in the Dakota leaving concentrated residual waters. This drawdown effects transition upwards less progressively into a similar system of sandstone with intervening shale members as in the case of the Gallop sandstone and Mancos shale in the Mesa Verde group and the Pictured Cliff sandstone and Lewis shale.

Further evidence of water flowing osmotically through 130,000 ppm evaporate blocks and redistributing salinity across underlying and overlying strata in the presence of shales is reported by Berry (1959) within the San Juan basin. The cycle of water flow experienced in the saline core is shown in Figure 2.8. Potentiometric drawdown from overlying formations (Dakota) depicts the flow of freshwater into the saline core being fed by the evaporite facies in the Todilto formation from point 1. The saline core is believed to be trapped hydrodynamically within the inner basin due to the tilt of the steeply dipping syncline close to the bottom of the basin. Simultaneously, saline water from the Estrada formation flows osmotically through the saline core through point 2. The flow of water proceeds to transition
upward around the basin margins redistributing the brine concentrations in upper layers from the saline core. Osmotic pressures are created primarily through salinity differences in depositional beds where the major sources of the salinity in the formation water come from evaporite beds. Theoretically, maintaining the salinity differences across beds entails losing portions of the evaporite for a finite amount of time at which point the osmotic pressure created would dissipate. The finite amount of time represented in geologic time scale can take as long as 25 million years as in the postulated case of the San Juan basin.

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<td>Sandstone, a few shales and coals</td>
<td>Regressive marine to coastal deposit</td>
<td>Oil, gas, water</td>
<td>Kg</td>
</tr>
<tr>
<td>Mancos Shale</td>
<td>Shale, thin sandstones</td>
<td>Offshore marine</td>
<td>Oil, gas</td>
<td>Km</td>
</tr>
<tr>
<td>Dakota Sandstone</td>
<td>Sandstone, shale and coals</td>
<td>Transgressive coastal plain to marine shoreline</td>
<td>Oil, gas, water</td>
<td>Kd</td>
</tr>
<tr>
<td><strong>Jurassic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morrison Formation</td>
<td>Mudstones, sandstone</td>
<td>Continental rivers</td>
<td>Uranium, oil, gas, water</td>
<td>Jm</td>
</tr>
<tr>
<td>Wyndah/Cow Springs/Bluff</td>
<td>Siltstone, sandstone</td>
<td>Alluvial plain and eolian</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entrada Sandstone</td>
<td>Sandstone</td>
<td>Eolian sand dunes</td>
<td>Oil, gas, water</td>
<td>Je</td>
</tr>
</tbody>
</table>

Figure 2.7: Generalized description of the Cenozoic, Cretaceous, and Jurassic rock units in the San Juan basin (after Kelley et al. 2014).
2.3.2 Well case

Marine (1974) calculated that the slight over-pressuring observed for two wells from a buried Triassic basin in South Carolina which matched the osmotic pressures that should result from the salinity differences. After considering several mechanisms, this over-pressuring that created a high head was determined to be mainly caused by osmotic membrane phenomena preserving the high head through the overall drive of water flowing towards the more saline Triassic basin.

Figure 2.8: Diagrammatic sketch showing the osmotic system controlled by saline waters in the Entrada and related stratigraphic units (Berry 1959).

2.3.3 Chemical osmosis, reverse chemical osmosis and ion filtration of the shale matrix

The very low permeability within the shale matrix enhances the membrane efficiency of the selectivity of solute particles in the formation of water. Reverse chemical osmosis, as well as filtration of solute ions, also takes place in shales. Chemical osmosis induces water molecular flow in the direction of lower water activity among fluids, naturally produces
an over-pressuring on the high-salinity side of the shale. Moreover, the process of reverse chemical osmosis under natural conditions requires a non-osmotic process to generate an over-pressuring on the high-salinity side of a shale that will overcome the over-pressuring produced by chemical osmosis. Such non-osmotic processes are the well demonstrated rapid deposition of fine-grained sediments (burial compaction), tectonic compression and temperature effects contributing to aqua thermal pressure occurring in sedimentary basins where this mechanism of over-pressuring will certainly vary regionally depending on the depositional environment. Thus, the occurrence of the aforementioned processes is sufficient to allow reverse osmosis to occur in shale formations lowering the high salinity of brine. Laboratory experiments have also captured this reverse osmotic behavior in compacted clays (Graf 1983; Mese 1995; Mese and Tutuncu 1996; Tutuncu and Mese 2011b). Brine fluid having low solute concentrations can, therefore, flow outward from overpressure zones during this process.

Notwithstanding, these naturally occurring processes have created variations in formation salinity where we observe salinity reversal and water freshening such as the case in the Eagle Ford shale. Generally, total dissolved solids (TDS) which is a measure of salinity created through rock – fluid interactions, increases with depth (Figure 2.9) due to mixing with deeper brines from evaporite or halite dissolutions. The Eagle Ford formation brine samples from Nicot et al. 2018 study does not follow this trend due to naturally occurring geologic features. The TDS ranges from as low as 18,000 ppm at greater depth of about 3.6 km up to over 200,000 ppm concentrations at shallower depths of about 2.5 km. Dilution from meteoric water and hydraulic fracturing water were ruled out as a possible explanation to the lower salinity experienced at greater depth from the observed water stable isotopes. The more likely cause was attributed to the natural dehydration of clays during the conversion of smectite to illite, a phenomenon very common in the Gulf Coast. This conversion is essentially clay diagenesis involving the expulsion of clay bound water typically freshwater, interspersed within the Si and Al structure layers, into intergranular porosity from within in the smectite clays under unstable conditions of higher temperatures and pressures. Higher
salinities are experienced in the Bakken play exhibiting TDS up to 300,000 ppm is most likely as a result of pore water trapped in the middle Bakken by low permeability of the lower and upper Bakken shale. Over-pressuring from burial compression at such depth caused the pore water to be forcefully expelled through the tight shales while simultaneously filtering ions leaving a highly concentrated brine solution within the fine-grained, dolomitic siltstone middle Bakken (Peterman 2014).

![Figure 2.9: Produced water TDS as a function of well depth (Nicot et al. 2018).](image)

Taking advantage of these chemical processes can be beneficial for enhanced oil recovery options within shales. The limit of the water drive will depend mainly on salinity differences across the shale barriers to reach an equilibrium condition. Therefore, some basins will benefit more from low salinity water injection over others. Areas with high salinity such as the Bakken will experience higher osmotic pressure build-up with low salinity water injection allowing the flow of water to be driven longer into the matrix and sweep more residual oil from the basin in the process. Thus, individual analysis of the geologic setting of the sedimentary basin has to be evaluated to determine the extent of water drive. On either side of a
permeable membrane represented as shale, variations in electrical potential, temperature, and chemical concentration will create the osmotic pressure gradient that will drive fluid flow (Graf 1983). The focus of this study will be limited to major contributory effects from the chemical osmotic processes related to the difference in fluid salinity.

2.3.4 Drilling activity

The process of osmosis has been used in drilling operations to stabilize problematic zones having swelling clays. High salinity fluid relative to the formation native water is used in the drilling fluid to restrict the flow of water out of the matrix this stabilizing the clays (Mese and Tutuncu 1996; Mese 1988). Oil-based muds reported relatively higher efficiencies up to 51.18% in shale samples (Zhang et al. 2008). It is believed that emulsion instability may cause the oil-based mud to lose its ability to restrict ionic flow preventing a perfect membrane of efficiencies up to 100% from occurring. Experiments from Al-Bazali et al. (2006) study in shales showed that the membrane efficiencies were low ranging from 0.18 to 4.23% using water-based muds having salt solutions. These reported efficiencies in salt solutions are very low compared to the theoretical osmotic potential and is greatly dependent on the experimental conditions. Studies have shown that higher Cation Exchange Capacities (CEC) and lower permeabilities correlate well with larger membrane efficiencies (Mese 1988; Tutuncu and Mese 2011a). CEC is a rough approximation of the capacity of the clay mineral surfaces present in the rock to exchange cations with water (Padin et al. 2018) that translates to the swelling or expansive nature of the clay. The extent of swelling will vary based on the mineralogical composition of the shale matrix. Membrane efficiency has also been proven to increase with increasing effective stress. Measurements on the Pierre shale sample have reported up to 29.6% membrane efficiency under elevated stress and high salinity difference conditions. In Adekunle et al. (2018) study, the membrane efficiency was observed to increase from 16.5 to 29.6% due to shale structural changes associated with an increase in pore fluid salinity relative to the native fluid and increase of the effective stress associated with the structural change. The salinity difference of the tested fluids in the experiments was 60,000
ppm to 257,000 ppm NaCl solution at elevated isotropic stress conditions up to 6,000 psi and 4,000 psi average pore pressures. The presence of 65 wt.% smectite signifies higher levels of CEC contributing to the relatively high membrane efficiency using an aqueous solution in the shale measurements of the earlier and current research study.

2.4 Low Salinity Water Injection (LSWI)

One of the first companies to pursue low salinity water injection as an EOR option was Eni Oil and Gas Company now Eni SpA. In 2006, Eni began low salinity EOR studies in sandstone reservoirs and performed their first field-scale development project on a West African field in 2008. Based on the knowledge acquired from the field studies, an internal workflow for low salinity evaluation and deployment (Rotondi et al. 2014) was developed and shown in Figure 2.10. The requirements for low salinity water fluid can be summarized with the following conditions;

- Injected fluid should have a salinity less than 6 g/l and the optimal range is 1 – 2 g/l
- Formation rock matrix should contain water-sensitive minerals such as clays and should not be strongly water wet
- The native formation brine should possess divalent ions such as calcium (Ca$^{++}$) and magnesium (Mg$^{++}$)
- Lastly, the reservoir oil should contain polar components.

The workflow implements an in-house code to perform an initial EOR screening based on the aforementioned conditions for LSWI along with operational and feasibility issues. After this screening process, the experimental observation of the formation follows. Most importantly, core flooding tests are done on plug samples to observe mechanisms occurring that are associated with the low salinity water injection. Permeability reduction arising from water interaction with existing clay particles, wettability alteration, and relative permeability changes are some of the conditions observed and implemented into geochemical models during these tests. Typically, modeling the fluid flow of the process comes next. Flow models addressing the crude oil, brine and rock interactions can then be used to simulate fluid
flow and the impact of the LSWI on production for evaluation purposes. Proceeding the feasibility of the LSWI, further EOR consideration such as surfactant and polymer floods can be studied for the most optimal development approach. Polymer floods may not be feasible for unconventional reservoirs due to extremely low permeability conditions.

BP energy company implements this concept in its operations since 2014. LOSAL water, which is part of their DESIGNER water technology, is their default option for all water flooding projects across the globe. First implemented in the North Sea at clear field 200 miles north of the UK mainland brought forth successful results that have since been applied in all the company’s waterflood operations for sandstone reservoirs. In these sandstone reservoirs, research shows that oil molecules are bound to clay particles on the rock surfaces by bridges of divalent cations such as Calcium (Ca^{++}) and Magnesium (Mg^{++}). In water having high ionic concentration, the bridges become compressed to the clay surface due to strong electrical forces. The introduction of low salinity water reduces these forces allowing the bridges to

Figure 2.10: Eni low salinity EOR workflow (Rotondi et al. 2014).
expand, thus giving monovalent ions such as sodium (Na\(^+\)) the opportunity to replace these divalent ions. Ultimately, this causes the breakup of the bridge, which frees up the oil molecules that can now be more easily mobilized to the producers. Applying this process to unconventional resources can be applicable with further understanding of the mechanism occurring in the tight reservoirs. Due to the permeabilities in the microdarcy and nanodarcy ranges, the idea of membrane selectively filtering formation brine water becomes an added mechanism for fluid flow in these geologic source rocks.

2.5 Clays

The scientific study of clay or clay science dates back to the mid-1930s following the ‘clay mineral concept’ that clays are composed of micro-crystalline particles of a small group of minerals, referred to as the clay minerals. This concept has since expanded over several disciplines having unique perspectives. The Joint Nomenclature Committees (JNC) of the Association Internationale Pour l’Etude des Argiles (AIPEA) define clay as a naturally occurring material composed primarily of fine-grained minerals which becomes plastic under the exposure of water and hardens when dried or fired. In geology, sedimentology, and geo-engineering, the size limit for clays is typically set to be less than 4 µm equivalent spherical diameter. A useful classification of clay minerals has also been reported by Bergaya et al. 2006 as the basis for outlining nomenclature and differences between the various clay minerals. Clay minerals, as defined by JNC is a class of hydrated phyllosilicates which has the characteristics of plasticity and harden upon drying or firing. The properties that characterize clay minerals are as follows:

1. A layer structure possessing one dimension in the nanometer range; the thickness of the 1:1 (TO) layer is about 0.7 nm, and that of the 2:1 (TOT) layer is about 1 nm

2. The anisotropy of the layers or particles

3. The existence of several types of surfaces
4. The ease with which the external, and often also internal, surface can be modified by adsorption or ion exchange

5. Plasticity

6. Hardening on drying or firing.

2.5.1 Structure

The atomic structure of the clay minerals consists of two basic units, a tetrahedral sheet, and an octahedral sheet. Ideally, phyllosilicates (silica tetrahedral layer) contain a continuous tetrahedral sheet and each tetrahedron consists of a cation, T, coordinated to four oxygen atoms. The tetrahedron is also linked to adjacent tetrahedral through the sharing three corners (basal oxygen atoms) to form an infinite two-dimensional hexagonal mesh pattern along the apical (a), basal (b) crystallographic directions (Bergaya et al. 2006). Common tetrahedral cations are Si++++, Al+++, and Fe+++. The silicon atom is equidistant from the four oxygen or possibly hydroxyl ions arranged in a tetrahedral form with the silicon atom positioned in the center. The silica tetrahedral sheet is formed from these tetrahedrons arranged to form a hexagonal network repeated infinitely in two directions (Figure 2.11(a)). For the octahedron structure, a cation, O is coordinated by six closely packed oxygen and hydroxyl atoms. Aluminum, iron and magnesium atoms make up the arranged octahedron coordination and are linked to a neighboring octahedral by sharing edges (Figure 2.11(b)). Both tetrahedral and octahedral sheets are joined by sharing the apical oxygen or hydroxyl atoms to form the clay mineral layer in either 1:1 ratio such as kaolinite or 2:1 ratio such as illite. The octahedral and tetrahedral sheets make up the building block for most industrial clays (e.g. kaolins, smectites) but the arrangement and composition of atoms account for the differences in their physical and chemical properties.
2.5.2 Layer charge

Structural layers consisting of joined tetrahedral and octahedral sheets can be either electrically neutral or negatively charged. The charge per formula unit is the net negative charge per layer expressed as a positive number. The negative layer charge is balanced by the positively charged interlayer of the structure. A negative layer charge can arise from three different scenarios:

1. Substitution of Al\(^{+++}\) for Si\(^{++++}\) in tetrahedral sites

2. Substitution of Al\(^{+++}\) for Mg\(^{++}\) or other lower charge cations in octahedral sites

3. The presence of vacancies in trioctahedral species.
2.5.3 Clay minerals

The basic kaolin mineral structure has a layer of a single tetrahedral sheet and a single octahedral sheet in which the tip of the silica tetrahedrons are joined with the octahedral sheet. Kaolin is the group name for the minerals kaolinite, dickite, nacrite, and halloysite. Kaolinite is the most common kaolin mineral whereas the latter three minerals formed by hydrothermal alteration are relatively rare in comparison. The single tetrahedral and octahedral sheet are joined by sharing a common layer of oxygens and hydroxyls which classifies the structure as a 1:1 layer clay. These layers are continues in the a and b-axis directions and are stacked above each other. Substitutions of other elements for the aluminum and silicon within the lattice structure are very little which accounts for the balanced but minimal charge on the kaolinite layer. The base exchange capacity and the sorptivity are low in comparison to smectites and palygorskite-sepiolite due to this reason. Kaolinite exhibits low absorption and adsorption properties, which is directly related to the low surface charge on the particle.

Smectite is the group name for several hydrated sodium, calcium, magnesium, iron, and lithium aluminum silicates. The industrially used bentonite, which is a rock term used for these minerals, comprises either sodium montmorillonite, calcium montmorillonite or to a much lower degree, hectorite (lithium). Smectites are three-layer minerals having two silica tetrahedral sheets joined to a central octahedral sheet. The smectite lattice experiences considerable substitution in the octahedral sheet of Fe$^{+++}$, Fe$^{++}$, and Mg$^{++}$ for Al$^{+++}$, which creates a charge deficiency in the layer. Similarly, some substitution of silicon by aluminum occurs in the tetrahedral sheet also creating a charge imbalance. This net positive charge deficiency is balanced out but exchangeable cations (either calcium, sodium or lithium) adsorbed between the unit layers and on the edges. Substitution within the lattice causes about 80% of the total cation exchangeable capacity while broken bonds around the edges of the particles account for the remaining 20%. Sodium montmorillonite and hectorite have a high base exchange capacity relative to calcium montmorillonite (See Table 2.1). This high
charge on the lattice structure gives both sodium montmorillonite and hectorite the ability to exchange interlayer water and associated cations with more polar organic molecules such as ethylene glycol, quaternary amine, and polyalcohols (Bergaya et al. 2006).

Table 2.1: General properties of Phyllosilicate clay mineral group

<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Structural formula</th>
<th>Main oxide Composition</th>
<th>Surface Area m²/g</th>
<th>Base exchange meq/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>Al₄SiO₁₀(OH)₈</td>
<td>SiO₂, 46.54 Al₂O₃, 39.5 H₂O, 13.96</td>
<td>8 - 15</td>
<td>1 - 5</td>
</tr>
<tr>
<td>Illite</td>
<td>(K,H₃O)(Al,Mg,Fe)₂</td>
<td>SiO₂, 54.01 Al₂O₃, 17.02 H₂O, 12.03</td>
<td>10 - 100</td>
<td>10 - 40</td>
</tr>
<tr>
<td></td>
<td>(Si,Al)₄O₁₀</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vermiculite</td>
<td>(Mg,Fe⁺⁺⁺,Fe⁺⁺⁺⁺)₃</td>
<td>SiO₂, 11.92 Al₂O₃, 43.48 H₂O, 17.87 MgO, 14.39 FeO, 12.82</td>
<td>760</td>
<td>100 - 150</td>
</tr>
<tr>
<td></td>
<td>[(Al,Si)₄O₁₀]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smectite</td>
<td>(OH)₄Si₈Al₄</td>
<td>SiO₂, 66.7 Al₂O₃, 28.3 H₂O, 5</td>
<td>40 - 800</td>
<td>80 - 120</td>
</tr>
<tr>
<td></td>
<td>O₂₀ₙH₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite Sodium</td>
<td>(Na,Ca)₀.₃₃(Al,Mg)₂</td>
<td>SiO₂, 43.77 Al₂O₃, 18.57 H₂O, 36.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(Si₄O₁₀)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>Palygorskite</td>
<td>Si₈O₂₀₄H₂O, 58.43 Al₂O₃, 6.20 H₂O, 19.71</td>
<td>190</td>
<td>30 - 40</td>
</tr>
<tr>
<td></td>
<td>(OH₂)₄(OH)₂Mg₅</td>
<td>SiO₂, 58.73 Al₂O₃, 30.8 H₂O, 12.0 MgO, 26.26</td>
<td>190</td>
<td>30 - 40</td>
</tr>
<tr>
<td></td>
<td>Si₁₂O₃₀₈H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Chlorite</td>
<td>SiO₂, 58.73 Al₂O₃, 17.61 MgO, 26.26</td>
<td>190</td>
<td>30 - 40</td>
</tr>
<tr>
<td></td>
<td>(OH)₄(SiAl)₈</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Mg-Fe)₉O₂₀</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the study of smectite swelling, clay chemists have found that 90 to 95% of water is absorbed is within its the interlayers with the external surfaces contributing minimally to the absorption of water (Bleam 2017). Sodium montmorillonite has characteristic very small thin flakes creating a very high surface area of about 150 to 200 m²/g. This high surface area in combination with the high layer charge gives sodium montmorillonite a high sorptivity
and a high swelling capacity up to an order of 15 times when in contact with water. In addition to the very fine particle of sodium montmorillonite, the swelling capacity and flaky shape give the clay mineral the ability to form impenetrable membranes to water movement. Calcium montmorillonites have a larger particle size than sodium montmorillonite creating a lower surface area of 50 to 80 m²/g, a lower base exchange capacity and a lower swelling index of 2 to 3 order.

Illite is a clay mineral mica that has a 2:1 layer structure in which the interlayer cation is potassium. The potassium ion is not readily exchangeable and thus, its size, charge and coordination number allows the atom to fit snugly in the hexagonal rings of oxygen and adjacent tetrahedral sheets. This gives the structure a stiff interlocking ionic bond between the interlocking layers that also prevents water molecules and other polar compounds from occupying the interlayer positions. Illite has a charge deficiency due to the occurrence of less substitution of Al³⁺ for Si⁴⁺ in the tetrahedral sheet. There can also be some replacement of Al³⁺ by Mg²⁺ and Fe²⁺ in the octahedral sheets. Palygorskite and sepiolite are hydrated magnesium aluminum silicate minerals. Sepiolite is structurally similar to palygorskite except that it has a slightly larger unit cell (Wypych and Satyanarayana, 2004). Both minerals have a double silica tetrahedral chain linked by octahedral oxygen and hydroxyl groups containing aluminum and magnesium ions in chain-like structures. Similarly, both minerals have 2:1 inverted structures where the apices of the silica tetrahedrons are regularly inverted along the a-axis. As a result, parallel channels exist throughout providing a high internal surface area of 190 m²/g. These structural and chemical attributes of palygorskite and sepiolite allow for high capacity absorption of various liquids to take place which is quite useful in industrial applications. Chlorites have variable chemical compositions classified as non-clay but commonly present in shales. Chlorites layers are stacked randomly in such a manner that preserves permeability and hydration by keeping large levels of irreducible water trapped (Kennedy 2015). The structure has a 2:1 layer with interlayer brucite sheet Mg(OH)². A range of cation substitution exists in chlorites, some of which are Mg²⁺,
Fe$^{++}$, Al$^{+++}$, and Fe$^{+++}$. Chlorites have been identified as a coating on grains in many sandstones and are generally intermixed with other clay minerals. Interstratified chlorite–smectite is can be associated with the alteration of basic igneous rock in sandstone (Huggett 2005). Mineral composition of common clays are mixed in some capacity. Mixed-layered clay minerals usually contain two clay species such as illite and smectite where the layers can be randomly or regularly ordered. Such examples of common clays are shales, underclays, lacustrine clays, and other clay-rich materials. The illite–smectite mixed clay frequently occurs during deep burial diagenesis during which smectite is progressively replaced by illite.

The reduction in water saturation (relative humidity) and lowering ionic salt concentration in a clay suspension with relatively high salt concentrations causes’ layer expansion or spacing as water molecules pervade the interlayers of the structure. This progressive increase in layer spacing can also be referred to as crystalline clay swelling. As shown in Figure 2.12, the $d_{001}$ parameter which is equivalent to a water molecule size increases during crystalline clay swelling (Norrish 1954). As salt concentrations become increasingly more dilute, clay swelling is experienced as water molecules are readily available to hydrate the interlayer cations. This continuous swelling is often referred to as osmotic clay swelling. The type of salt also plays a role in the swelling potential if the clay structure. Sodium ions promote continuous osmotic swelling in smectite whereas the potassium ions resist the osmotic swelling due to insufficient hydration energy (Bleam 2017).
Figure 2.12: Ionic strength influence on crystalline and osmotic swelling of smectite clays (modified from Norrish 1954).
CHAPTER 3
METHODOLOGY

This chapter summarizes the approach in carrying out the study as a whole.

3.1 Sample Preservation

PI-H-01 and PI-H-02 samples were 1.5-inch diameter outcrop samples core in South Dakota procured from TerraTek (TerraTek 2015) as shown in Figure 3.1. The sample arrived in sealed wrappednylons to prevent contamination from moisture. The typical properties of the South Dakota shale reported by TerraTek are as follows; 2.0 g/cm$^3$ bulk density, 2.6 – 2.7 g/cm$^3$ grain density, 31 – 40% porosity, and the gas permeability is less than 10$^{-9}$ md. The unconfined compressive strength (UCS) ranges from 500 – 1,000 psi. The unconfined Young’s modulus of the sample is 80,000 psi with a Poisson’s ratio of 0.38. The tested Pierre shale outcrop samples gotten from TerraTek company are classified as Pierre II. The samples are horizontally cored parallel to the bedding planes. X-ray Diffraction (XRD) results of sample from Mineral Lab are shown in Table 3.1 and reveals the smectite and illite content of the sample to be 65 wt.% and 7 wt.% respectively. Additionally, 20 wt.% quartz is present with a trace amount of calcite, feldspar, dolomite minerals.

PI-LC-WY-H-01 was cored and acquired from USGS Core Research Center with XRD data describing the mineralogy clearly defined in Table 3.2.

3.2 Sample Description

Studies have shown that higher Cation Exchange Capacities (CEC) and lower permeabilities correlate well with larger membrane efficiencies. CEC is a rough approximation of the capacity of the clay mineral surfaces present in the rock to exchange cations with water (Padin et al. 2018) that translates to the swelling or expansive nature of the clay. In soil mechanics, the CEC is the degree to which a soil can adsorb and exchange cations.
Table 3.1: PI-H-01 X-ray Diffraction (XRD) data from Mineral Lab

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectite</td>
<td>(Ca,Na)$_x$(Al,Mg,Fe)$_y$(Si,Al)$<em>z$O$</em>{20}$(OH,F)$_4$.nH$_2$O</td>
<td>65</td>
</tr>
<tr>
<td>Mica/Illite</td>
<td>(K,Na,Ca)(Al,Mg,Fe)$_2$(Si,Al)$<em>4$O$</em>{10}$(OH,F)$_2$</td>
<td>7</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>20</td>
</tr>
<tr>
<td>Plagioclase Feldspar</td>
<td>(Na,Ca)Al(Si,Al)$_3$O$_8$</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Ca(Mg,Fe)(CO$_3$)$_2$</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Unidentified</td>
<td></td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Table 3.2: Sharon Springs PI-LC-WY-H-01 (T404 8432’ - 35’) sample bulk X-ray Diffraction Data (XRD) obtained from Mineral Lab

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical formula</th>
<th>Approx wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-35’ -13’ -22’ -25’</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>23 22 22 23</td>
</tr>
<tr>
<td>Plagioclase Feldspar</td>
<td>(Na,Ca)Al(Si,Al)$_3$O$_8$</td>
<td>10 11 10 10</td>
</tr>
<tr>
<td>Mica/Illite</td>
<td>(K,Na,Ca)(Al,Mg,Fe)$_2$(Si,Al)$<em>4$O$</em>{10}$(OH,F)$_2$</td>
<td>18 25 17 23</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>10 15 11 13</td>
</tr>
<tr>
<td>Smectite</td>
<td>(Ca,Na)$_x$(Al,Mg,Fe)$_y$(Si,Al)$<em>z$O$</em>{20}$(OH,F)$_4$.nH$_2$O</td>
<td>- &lt;5 &lt;5 -</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>31 14 22 19</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Ca(Mg,Fe)(CO$_3$)$_2$</td>
<td>&lt;3 &lt;3? &lt;5 &lt;5</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>3 4 9 6</td>
</tr>
<tr>
<td>“Unidentified”</td>
<td></td>
<td>&lt;5 &lt;5 &lt;5 &lt;5</td>
</tr>
</tbody>
</table>

Cations are positively charged ions such as K$^+$, Ca$^{++}$, and Fe$^{++}$. The three main groups of clay are kaolinite, illite, and smectite (or montmorillonites). Kaolinites are formed by the decomposition of orthoclase feldspar. Illite is the most common clay minerals formed by the decomposition of some mica and feldspars predominant in marine clays and shales. Smectite is formed by the alteration of mafic igneous rocks rich in calcium and magnesium. The weak linkage in cations (e.g. Na$^+$, Ca$^{++}$) results in high swelling or shrinking potential. The most common swelling clays found in reservoir rock are smectite and mixed-layer illite.
Figure 3.1: TerraTek outcrop samples; Typical properties of sandstones, carbonates, and shales (TerraTek 2015).

In this study, the high smectite content of the Pierre shale sample is advantageous for determining the impacts of swelling to the membrane efficiency. The upper Eagle Ford samples used in Padin (2016) experiments were reported to have low CEC values from 5 to 7 meq/100 g of rock. These samples reportedly had low distributed amounts of mixed illite-smectite clay minerals as low as 2.8 wt.% and higher concentrations of kaolinite clay minerals up to 19.46 wt.%. Kaolinites have the least CEC out of all the clay minerals typically ranging from 3 to 15 meq/100 g. Smectites have the highest CEC ranging from 80 to 120 meq/100 g.
3.2.1 Scanning Electron Microscopy

Both Scanning Electron Microscopy, SEM and Field Emission Scanning Electron Microscopy, FESEM were performed on a vertical outcrop (cored perpendicular to bedding plane) sample termed PI-V-01 on both horizontal and vertical cut sections from the sample to determine the pore size distribution and to visually observe the mineralogy. The SEM scans mainly highlights the minerals in place and quantify the distribution of these minerals while the FESEM shows the similar images but provide higher visual resolutions. Figure 3.2(a) shows a 951 times magnified image of the sample showing pyrite (iron sulfide - FeS$_2$) presence and a few clay mineral associated elements (aluminium and oxygen). The spikes indicate the level of counts that the electron microspore picks up off each element within the focal study point of the rock sample. Figure 3.2(b) shows a 3,000 times magnified image of the same sample picking up more concentrations of elements making up clay minerals and quartz such as calcium, magnesium, oxygen, potassium, aluminum, and silicon. Figure 3.3 shows magnifications of over 2,400 times of the dominant minerals in the sample. FESEM scan sheds some light on the porosity distribution within the sample.

![Figure 3.2: SEM Scans of PI-V-01 Mineralogy.](image)

(a) 951x Magnification of Pyrite clusters  (b) 3000x Magnification of Quartz and Clay Minerals Clusters
3.2.2 Rock properties

Intrinsic anisotropy from layering and anisotropy resulting from both natural and induced fractures play a vital role in fluid flow on organic-rich shales. Mokhtari et al. (2013) report gas effective permeabilities to decline exponentially with increasing effective stress in both fractured and the unfractured Eagle Ford, Mancos, Bakken, Green River, and Niobrara shale
samples. CMS 300 results of porosity and permeability variations within the Pierre shale samples used in this study are shown in Table 3.3. Porosity values between the outcrop samples PI-H-02 and PI-H-03 are relatively close with up to 7.49% difference in porosity. Permeability values vary almost four orders of magnitude due to the presence of a clearly defined fracture such as in sample PI-V-01 as seen in Figure 3.4(a). The nano-sized pores can be seen to have inter-particle and clay platelet porosity in Figure 3.5(a) and Figure 3.5(b) respectively. The Sharon Springs member sample PI-LC-WY-H-01 from well 404 can be seen in Figure 3.4(b) to have a darker grey color. The locations of other wells in the Sharon Springs member where cores are obtained can be found in Table 3.4.

![Figure 3.4: Experimental Pierre shale samples.](image)

Table 3.3: CMS - 300 Measurements of outcrop Pierre shale samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Net stress, psi</th>
<th>Pore Vol, cm³</th>
<th>Porosity (φ), %</th>
<th>Permeability, µd</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-H-02</td>
<td>500</td>
<td>6.185</td>
<td>22.3</td>
<td>3.87</td>
</tr>
<tr>
<td>PI-H-02</td>
<td>800</td>
<td>6.119</td>
<td>22.15</td>
<td>2.93</td>
</tr>
<tr>
<td>PI-H-03</td>
<td>500</td>
<td>6.486</td>
<td>20.99</td>
<td>33,000</td>
</tr>
<tr>
<td>PI-H-03</td>
<td>800</td>
<td>6.291</td>
<td>20.49</td>
<td>10,900</td>
</tr>
</tbody>
</table>
Figure 3.5: FESEM scans of PI-V-01 (Vertical Scans) sample showing increasing levels of magnification.

Table 3.4: USGS Core Research Center sample well locations

<table>
<thead>
<tr>
<th>Library Number</th>
<th>State</th>
<th>County</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>T451</td>
<td>WY</td>
<td>Laramie</td>
<td>-104.71781</td>
<td>41.35359</td>
</tr>
<tr>
<td>T404</td>
<td>WY</td>
<td>Laramie</td>
<td>-104.69988</td>
<td>41.24061</td>
</tr>
<tr>
<td>T355</td>
<td>CO</td>
<td>Fremont</td>
<td>-105.10895</td>
<td>38.33916</td>
</tr>
<tr>
<td>S502</td>
<td>CO</td>
<td>Weld</td>
<td>-104.26090</td>
<td>40.60906</td>
</tr>
</tbody>
</table>

3.2.3 X-ray Diffraction data

The figure Figure 3.6 shows a diagrammatic representation of the mineral clay composition of the Pierre shale samples considered in this study. The disparity between the outcrop sample (in blue circle) and the other well samples is clearly seen. The outcrop sample P-V-01 has 90% smectite and 10% of mica/illite mix. The well core samples have less smectite with increasing concentration of mica, illite and kaolinite. Figure 3.7 show more general representation of the mineral composition grouped into clays, quartz and carbonates. Figure 3.7(a)
shows the bulk XRD data for the Pierre samples having less than 38% carbonates and less than 55% quartz. Figure 3.7(b) also show bulk XRD data but the clay group is merged with TOC content showing how the organic content and clay content make up the bulk mineral of the sample (Table 3.5).

Figure 3.6: Clay composition of the Pierre shale samples.

3.3 Comparative Study

Previous studies in the literature have shown that higher cation exchange capacities and lower permeabilities correlate well with increased membrane efficiencies. Yet, testing on similar outcrop Pierre shale cores have been reported to show unexpectedly low membrane efficiencies of about 1.21% at liquid permeabilities of 6.48 nd using NaCl as the test fluid. The Arco-China shale sample used in the experimental study by Zhang et al. (2008) yielded
Figure 3.7: X-ray Diffraction of the PI-LC-WY-H-01 Pierre shale sample.
Table 3.5: Sharon Springs XRD results for clay-size fractions of well samples obtained from Mineral Lab

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical formula</th>
<th>Approx. wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T355:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2961'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-62'</td>
</tr>
<tr>
<td>Mica/Illite</td>
<td>(K,Na,Ca)(Al,Mg,Fe)$_2$(Si,Al)$<em>4$O$</em>{10}$(OH,F)$_2$</td>
<td>49</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>17</td>
</tr>
<tr>
<td>Smectite</td>
<td>(Ca,Na)$_x$(Al,Mg,Fe)$_4$(Si,Al)$<em>8$O$</em>{20}$(OH,F)$_4$.nH$_2$O</td>
<td>26</td>
</tr>
<tr>
<td>Chlorite</td>
<td>(Mg,Fe,Al)$_6$(Si,Al)$<em>4$O$</em>{10}$(OH)</td>
<td>-</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Plagioclase feldspar</td>
<td>(Na,Ca)Al(Si,Al)$_3$O$_8$</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>-</td>
</tr>
<tr>
<td>Unidentified</td>
<td></td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

the highest membrane efficiency among a set of experiments on Pierre shale, C1 shale, and C2 shale samples. From Table 3.6 below, the low permeability of 0.45 nd and high cation exchange capacity of 24.5 meq/100 g provided the membrane efficiency of 3.95% and 4.23% using NaCl and CaCl$_2$ respectively. The highest membrane efficiencies measured in the C1, C2 and Pierre shale tests were 2.38% using KCOOH, 3.56% using CaCl$_2$ and 1.21% using NaCl respectively. Among the remaining shale samples, C2 membrane efficiency was highest understandably from its relatively lower permeability and higher CEC to the three other shale samples. Following the trend, the Pierre shale membrane efficiency result of 1.21% corresponds to the trend as the sample had the highest permeability of 6.48 nd and the lowest CEC of 10.5 meq/100 g among the four shale samples tested. Zhang et al. (2008) reported the highest membrane efficiency for the sample to be 1.78% when CaCl$_2$ was used as the test fluid. Interestingly, the native water activity of the Arco shale was the lowest having a 0.85 water activity which is about 22 wt.% NaCl concentration. This cannot be ignored as a significant factor in the higher membrane efficiency reported as the chemical potential gradient between the native fluid and injected fluid is much greater than the other tested shale samples. It will be beneficial to know how the Arco-China shale responded with
a native fluid comparable to the other shale samples. Additionally, the moisture content will affect the strength of the Pierre shale. Studies from Fooks and Dusseault (1996) show the strength of a Pierre shale sample, having mixed amounts of illite-smectite clay content, to increase with reducing native moisture content. Lower moisture content translates to increased strength characteristics. For my experiments, the sample is fully saturated with brine to mimic in-situ reservoir conditions. Thus, unlike the matrix block, the pore spaces have less grain to grain contact because they are filled with fluid.

Table 3.6: Properties of shale samples used to determine membrane efficiency (Zhang et al. 2008)

<table>
<thead>
<tr>
<th>Shale</th>
<th>Native moisture (%)</th>
<th>Water activity</th>
<th>Permeability (nD)</th>
<th>CEC (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pierre</td>
<td>13.03</td>
<td>0.98</td>
<td>6.48</td>
<td>10.5</td>
</tr>
<tr>
<td>Arco-China</td>
<td>9.88</td>
<td>0.85</td>
<td>0.45</td>
<td>24.5</td>
</tr>
<tr>
<td>C1</td>
<td>14.45</td>
<td>0.98</td>
<td>2.96</td>
<td>21.0</td>
</tr>
<tr>
<td>C2</td>
<td>5.53</td>
<td>0.94</td>
<td>0.83</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 3.7 shows results on membrane efficiency calculation conducted by Zhang et al. (2008) on the Pierre shale samples. As the chemical potential (derived from the difference in water activity) between the native fluid and the test fluid, there is a greater buildup of osmotic pressure. Although the osmotic pressure rises from increased potential, the membrane efficiency is seen to reduce in the case of most of the brine solutions except CaCl$_2$. This can be attributed to the leaky membrane nature of the shale matrix, which permits the flow of both solute and water molecules under higher pressures. Scanning Electron Microscopy, SEM was performed on a vertical outcrop (cored perpendicular to bedding plane) of the Pierre shale sample called PI-V-01. Nano-sized pores seen to have inter-particle and clay platelet porosity serving as pathways for fluid flow within the shale matrix as shown in Figure 3.5. These nano sized pathways will also serve as the membrane essential for the ion...
filtering mechanism to occur. Magnified images of PI-V-01 by 950 times and 4,300 times in the horizontal plane can be seen in Figure 3.8 to show avenues for the inter-particle porosity.

Figure 3.8: FESEM scans of PI-V-01 (Horizontal Layer Scans) sample showing increasing magnification levels of Inter-particle porosity.

Table 3.7: Membrane efficiency experimental results for Pierre shale during interaction with different salt solutions of varying water activities (Zhang et al. 2008)

<table>
<thead>
<tr>
<th>Salt solution (Test fluid)</th>
<th>Water activity (%)</th>
<th>Measured osmotic pressure (psi)</th>
<th>Membrane efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.93</td>
<td>12.4</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>25.6</td>
<td>0.92</td>
</tr>
<tr>
<td>KCl</td>
<td>0.93</td>
<td>2.9</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>5.0</td>
<td>0.18</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.93</td>
<td>11.9</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>49.8</td>
<td>1.78</td>
</tr>
<tr>
<td>KCOOH</td>
<td>0.93</td>
<td>4.0</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>6.2</td>
<td>0.22</td>
</tr>
</tbody>
</table>
CHAPTER 4
EXPERIMENTAL SYSTEM

The chapter discusses the entire experimental procedure and components utilized in conducting all the tests in this study. Coupled measurements of resistivity, acoustic, failure and permeability measurements have been conducted with two separate coupled tri-axial assemblies available at UNGI Geomechanics laboratory.

4.1 Brine Preparation

Salinity is the amount of dissolved solids in water. On average, seawater in the ocean has a salinity of roughly 35,000 ppm (parts per million) which equates to 3.5 wt.% of dissolved solids. Salinity may also be reported in Practical Salinity Units (psu) where one psu equates to roughly one ppt (part per thousand). Notwithstanding, sodium chloride, NaCl is usually the predominant salt type within the saltwater making up about 86% of the total salt by weight in seawater (Table 4.1). Seawater concentrations mostly include a variety of salts with varying concentrations. Similarly for formation fluids left behind mainly from the seawater during deposition, the salt type in each location varies with concentration and composition. Table 4.2 shows both flow back water and produced water from the Eagle Ford shale formation. Sodium and calcium are the prevalent ions in both fluid streams. Although the ionic size of the salt ions can affect the chemical osmosis process, the differing ionic sizes from each individual salt type and their influence of the effectiveness of osmosis in the Pierre shale is beyond the scope of the research. Padin et al. (2018) reported on the influence of potassium chloride (KCl), calcium chloride (CaCl₂) and sodium chloride (NaCl) on the chemical osmosis in the Eagle Ford shale. Each salt solution interacted differently with the Eagle Ford matrix affecting the level of osmotic pressure buildup in each case.
Table 4.1: Chemical composition of seawater (Glazer et al. 2019)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>% of total</th>
<th>mmol/kg</th>
<th>g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Chloride</td>
<td>55.29</td>
<td>546.0</td>
<td>19.353</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium</td>
<td>30.74</td>
<td>469.0</td>
<td>10.760</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Magnesium</td>
<td>3.69</td>
<td>53.0</td>
<td>1.292</td>
</tr>
<tr>
<td>SO⁴⁺⁺⁺⁺</td>
<td>Sulphate</td>
<td>7.75</td>
<td>28.0</td>
<td>2.712</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium</td>
<td>1.18</td>
<td>10.3</td>
<td>0.412</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium</td>
<td>1.14</td>
<td>10.2</td>
<td>0.399</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>99.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Initial water quality of a sample from the Eagle Ford formation (Rodarte and Smith 2014)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Produced water (mg/l)</th>
<th>Flowback water (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>12.70</td>
<td>5.51</td>
</tr>
<tr>
<td>Boron</td>
<td>56.40</td>
<td>119.00</td>
</tr>
<tr>
<td>Calcium</td>
<td>1950.00</td>
<td>849.00</td>
</tr>
<tr>
<td>Iron</td>
<td>64.10</td>
<td>91.50</td>
</tr>
<tr>
<td>Magnesium</td>
<td>168.00</td>
<td>65.80</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.56</td>
<td>5.15</td>
</tr>
<tr>
<td>Potassium</td>
<td>130.00</td>
<td>591.40</td>
</tr>
<tr>
<td>Sodium</td>
<td>1150.00</td>
<td>6910.00</td>
</tr>
<tr>
<td>Strontium</td>
<td>272.00</td>
<td>81.20</td>
</tr>
<tr>
<td>Iron, ferric*</td>
<td>40.20</td>
<td>52.00</td>
</tr>
<tr>
<td>Iron, ferrous</td>
<td>23.90</td>
<td>39.50</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>290.00</td>
<td>2560.00</td>
</tr>
</tbody>
</table>

*Calculated as iron minus iron, ferrous

Petersen et al. (2016) estimated the salinities of the WIS to be 29 - 35 psu for deep marine, 20 - 32 psu for shallow marine and 11 - 26 psu for estuarine environments of the WIS. Thus, the initial saturation fluid for the third sample having 4 wt.% TOC was made up to 35,000 ppm of NaCl solution to represent the in situ conditions of the formation fluid. Based on these estimates, 99.99% pure NaCl was chosen as the salt to closely simulate the formation brine used in the laboratory tests of the Pierre shale samples. For comparative purposes, the outcrop Pierre shale samples PI-H-01 and PI-H-02 were saturated with
similar NaCl salinity fluids as that of the Eagle Ford tested samples in Padin (2016) study. Chemical osmosis tests were also conducted in a similar fashion to observe the influence of high smectite content present in the Pierre shale outcrops on osmotic pressure buildup. A full description of the samples and experimental procedures are provided in the result section presented in Chapter 5.

The preparation of brine took place with the following steps;

- Vacuum deionized water for 24 hrs to remove dissolved air
- Place the vacuumed distilled water in a measurement beaker and determine the volume within the beaker
- Measure out the mass of 99.9% grade NaCl on a weighing scale that will result in the desired salinity
- Pure the measured NaCl into the water and stir the solution until complete dissolution occurs.

For example, to achieve a 35,000 ppm NaCl salt solution (3.5 wt.% salinity), 845.5 grams of vacuumed deionized water was measured out, and then 30.6658 grams of NaCl was measured out, poured into the water and stirred until fully dissolved into solution.

A similar preparation approach as described was done for 60,000 ppm and 1,000 ppm NaCl brine solutions.

\[
\text{Mass of NaCl salt} = \frac{\text{Desired Salinity (wt)}}{1 - \text{Desired Salinity (wt)}} \times \text{Mass of H}_2\text{O} 
\]

\[
= \frac{3.5}{1 - 3.5} \times 845.5 \text{ gH}_2\text{O} = 30.6658 \text{ g of NaCl salt}
\]

### 4.2 Temperature Dependence on the Solubility of Salts

The solubility of salts ions is temperature-dependent. Specifically for the saturated NaCl solution, the limit of saturated had to be carefully determined based on the temperature con-
ditions. Figure 4.1 shows the solubility curve of multiple salts with the curve representing their saturation conditions. The first set of experiments on sample PI-H-01 was conducted in an enclosure with heating fans that allowed for the temperature to be maintained at 40°C. The solubility of a fully saturated NaCl solution at 40°C is approximately 34.67 g NaCl/100 g H₂O. Thus, the brine solution was measured up accordingly to meet this saturation conditions for 257,448 ppm brine (about 257,000 ppm). The second and third set of experiments on PI-H-02 and PI-LC-WY-H-01 was done in laboratory conditions of 24°C average room temperature. Thus, the saturated NaCl brine solutions were prepared according to this condition. For instance, the solubility of NaCl at 24°C is approximately 30 g NaCl/100 g H₂O. Therefore, the mass of salt required to fully saturate the H₂O solution at this temperature amounted to roughly 235,000 ppm.

4.3 Theoretical Background

Osmotic efficiency in shales is obtained from the subjected hydraulic gradient and osmotic gradient. The presence of swelling clay signifying higher CEC contributes to membrane efficiency improvement. A schematic diagram of the osmotic potential gradient created between the two saline fluid separated by a semi-permeable membrane is shown in Figure 4.2 (Ampac 2016). J₁ represents the net flux of water molecules in the direction of freshwater whereas J₂ represents the net flux of water molecules in the direction of the higher concentration salt-water. The shale matrix represents a leaky membrane permitting the influx of both water and solute molecules in either direction across the membrane. Ideally, during the chemical osmosis process, there will be a net flow of water molecules driven from lower concentration fresh water to the region of higher concentration brine through the membrane. The influx of water molecules will be in the direction towards the higher concentration causing a buildup of osmotic pressure in that region (J₂ is greater than J₁). For reverse chemical osmosis to take place, there has to be a non-osmotic related pressure mechanism in place that will overcome the osmotic pressure built up in the high salinity region and forcefully drive the
net flow of water molecules in the direction of the lower salinity freshwater (J1 is greater than J2).

4.3.1 Membrane efficiency test description

Osmotic efficiency in shales is obtained from hydraulic and osmotic gradients applied to the sample. Typically drilling (water-based muds) or stimulation fluids can introduce the hydraulic gradients. The salinity of these fluids can create the osmotic potential between the injected fluid and the native fluid of the formation.

\[ \omega = \frac{\Delta p}{\pi} \]  

(4.2)
\[ \pi = \frac{RT_m}{V_m} \ln \left( \frac{a_{w2}}{a_{w1}} \right) \] (4.3)

where \( \pi \) is the osmotic potential from difference in water activities; \( \Delta p \) is the pressure drop across the shale sample; \( a_{w1} \) is the water activity of injected/drilling fluid; \( a_{w2} \) is the native water activity of the sample; \( R \) is the universal gas constant; \( T_m \) is the fluid temperature in the matrix; \( V_m \) is the partial molar volume of water.

The water activity typically describes the equilibrium amount of water available for the hydration of materials. A water activity of one \( (a_w = 1) \) is pure water) signifies that the entire water molecules are available while a water activity of zero \( (a_w = 0) \) signifies that none of the molecules are available (Barbosa-Cánovas et al. 2007). As the water activity drops, the level of TDS within the solution simultaneously occurs.

### 4.3.2 Water activity estimation

Different theoretical and empirical models have been developed to estimate water activity with considerations to solute types in the solution. For electrolyte or aqueous solution as in the case of seawater brines, the Pitzer Equation and Bromley Equation may be used to estimate the water activity. The Pitzer Equation was chosen as a means to estimate the
water activity in this study.

Pitzer Equation

\[ \omega - 1 = |z_m z_x| F + 2m \left( \frac{v_m v_x}{v} \right) B_{mx} + 2m^2 \left( \frac{(v_m v_x)^{1.5}}{v} \right) C_{mx} \]  \hspace{1cm} (4.4)

\[ F = \frac{-0.392 I^{0.5}}{1 + 1.2 I^{0.5}} \]  \hspace{1cm} (4.5)

\[ I = 0.5 \sum_i m_i z_i^2 \]  \hspace{1cm} (4.6)

\[ |z_m z_x| = \frac{\sum_i m_i z_i^2}{\sum_i m_i} \]  \hspace{1cm} (4.7)

\[ B_{mx} = B_{mx}(0) + B_{mx}(1) e^{-2.10.5} \]  \hspace{1cm} (4.8)

\[ a_w = e^{-0.01802 \sum_i M_i} \]  \hspace{1cm} (4.9)

where \( \omega \) is the osmotic coefficient; \( z_m \) and \( z_x \) are the charges of \( m \) (Na\(^+\)) and \( x \) (Cl\(^-\)) ions; \( I \) is the Ionic strength or concentration; \( v \) is the number of ions present; \( v_m \) and \( v_x \) are the respective number of ions; \( M \) is the solution molality; \( B_{mx}(0), B_{mx}(1), B_{mx} \) and \( C \) are the Pitzer coefficients; Pitzer coefficients for NaCl; \( B(0) = 0.0765 \) \( B(1) = 0.2664 \) \( C = 0.00127 \). The input parameters for molality calculations used in this study are presented in Table 4.3. The parameters in Table 4.4 are used to determine the osmosis potential and water activity of the solution used in the experiments.

**Table 4.3: Input parameters for molality calculations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>g/mol</th>
<th>Parameter</th>
<th>no</th>
<th>Parameter</th>
<th>no</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of sodium (m)</td>
<td>22.990</td>
<td>Charges</td>
<td>2</td>
<td>No of ions, ( v )</td>
<td>2</td>
</tr>
<tr>
<td>Molar mass of chlorine (x)</td>
<td>35.453</td>
<td>( z_{Na^+} )</td>
<td>1</td>
<td>( v_{Na} )</td>
<td>1</td>
</tr>
<tr>
<td>Molecular wt. of NaCl</td>
<td>58.443</td>
<td>( z_{Cl^-} )</td>
<td>1</td>
<td>( v_{Cl} )</td>
<td>1</td>
</tr>
<tr>
<td>Molar mass of hydrogen</td>
<td>1.008</td>
<td>(</td>
<td>z_{Na^+} z_{Cl^-}</td>
<td>)</td>
<td>1</td>
</tr>
<tr>
<td>Molar mass of oxygen</td>
<td>15.999</td>
<td>( B_{mx}(0) )</td>
<td>0.0765</td>
<td>Avogadro’s constant</td>
<td>( 6.022 \times 10^{23} )</td>
</tr>
<tr>
<td>Molecular wt. of water</td>
<td>18.015</td>
<td>( B_{mx}(1) )</td>
<td>0.2664</td>
<td>( C_{mx} )</td>
<td>0.00127</td>
</tr>
</tbody>
</table>
Table 4.4: Osmotic potential and water activity determination

<table>
<thead>
<tr>
<th>Brine Density</th>
<th>% NaCl (w/v)</th>
<th>Molality (mol/kg)</th>
<th>Ionic Strength</th>
<th>F</th>
<th>Osmotic Potential $B_{mx}$</th>
<th>Water Activity $a_w$</th>
<th>Salt Conc. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g/cm$^3$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.001</td>
<td>0.10</td>
<td>0.017</td>
<td>0.0171</td>
<td>-0.0443</td>
<td>0.2816</td>
<td>0.9605</td>
<td>0.9994</td>
</tr>
<tr>
<td>1.010</td>
<td>1.00</td>
<td>0.171</td>
<td>0.1711</td>
<td>-0.1084</td>
<td>0.1930</td>
<td>0.9247</td>
<td>0.9943</td>
</tr>
<tr>
<td>1.035</td>
<td>3.50</td>
<td>0.599</td>
<td>0.5989</td>
<td>-0.1573</td>
<td>0.1332</td>
<td>0.9229</td>
<td>0.9803</td>
</tr>
<tr>
<td>1.060</td>
<td>6.00</td>
<td>1.027</td>
<td>1.0266</td>
<td>-0.1793</td>
<td>0.1116</td>
<td>0.9366</td>
<td>0.9659</td>
</tr>
<tr>
<td>1.235</td>
<td>23.50</td>
<td>4.021</td>
<td>4.0210</td>
<td>-0.2308</td>
<td>0.0813</td>
<td>1.1167</td>
<td>0.8506</td>
</tr>
<tr>
<td>1.257</td>
<td>25.74</td>
<td>4.405</td>
<td>4.4051</td>
<td>-0.2339</td>
<td>0.0805</td>
<td>1.1454</td>
<td>0.8338</td>
</tr>
</tbody>
</table>

4.3.3 Membrane efficiency tests

Pore pressure alteration as a function of time and fluid type is typically measured using pore pressure transmission tests. The tests are conducted to observe the osmosis effect by monitoring upstream and downstream pressures from the core samples measured. The equilibrium pressure value reached is compared with the theoretical value for the osmotic potential to determine the membrane efficiency. The membrane efficiency is measured using the described pressure transmission techniques where hydraulic and osmotic gradients are subjected to a shale sample for various fluid ionic and concentration fluids. The pressure drop created across the sample is compared to the osmotic potential owing to the difference in activity between the native and test fluids as illustrated in Eq. 4.2 and Eq. 4.3.

4.3.4 Osmosis contribution to rock behavior and fluid transport in shale

Strengthening of shale formations having a significant amount of swelling clays (montmorillonite) will improve drilling time through these problematic zones. Significant strengthening has been observed with a fully saturated NaCl brine solutions up to 26 wt.% in 65 wt.% smectite Pierre II outcrop shale samples. On the other hand, within the same formation, shale-weakening occurring from water imbibition can adversely alter the structure of the matrix formation containing such high percentage swelling clays.
The research study presented here aims to minimize the uncertainties involved in the osmotic pressure component of the alterations observed by conducting precisely controlled coupled tri-axial measurements. High pore pressure penetration up to 4,000 psi applied in our experiments improves the shale sample saturation with the selected fluids tested. This procedure provides more reliable osmotic pressure data at high saturation pressures. In the high smectite content Pierre shale, a significant improvement to osmotic membrane efficiency is observed depending on the difference in fluid salinity. The membrane efficiency was observed to increase from 16.56 to 27.74% due to shale structural changes associated with an increase in pore fluid salinity relative to the native fluid and increase of effective stress. The changes in the membrane efficiency of Pierre shale as a function of the fluid salinity and stress have been investigated by coupling these changes with the geomechanical property changes. Measurement of the membrane efficiency, permeability, dynamic and static Young’s moduli, and shear strength under elevated confining stress and elevated pore pressure states at a constant temperature of 40°C was performed on intact samples (having no observable fractures) of Pierre shale to capture the intrinsic matrix properties. The permeability of the shale sample used has been determined to be 9.38 nd and 15.4 nd at net stress of 2,000 psi for low salinity and high salinity brine injection, respectively. The outcrop Pierre samples with higher clay content presented an increase in permeability from 9.38 to 15.4 nd during the imbibition stage implemented in our coupled tri-axial measurements. Reservoir shales typically show significantly higher tensile strength under induced swelling pressures which makes it more difficult to induce hydraulic fracture in reservoir shales. Studies have shown that higher concentrations of KCl increased the tensile strength of shales (Tutuncu and Mese 2011b). On the other hand, the lower tensile strength observed in seal shales allows the creation of fractures in seal shales with associated high residual strains implying the occurrence of plastic deformation and healing of fractures over time.
4.4 Methods

The nature of tri-axial tests conducted on shales involving water intrusion into the pores is very time-consuming. Coupled measurements were captured on each tested sample and further used for the interpretation of rock behavior. Having only a limited number of samples also makes each the experiments very critical where a lot of information on the sample is collected before any failure analysis is carried out. As such, there are time series effects on measured properties occurring in these experiments which requires a time-sensitive approach for accurate interpretation of data.

Essentially, the membrane efficiency measurements have been conducted under tri-axial testing conditions in combination with pressure pumps and an MTS loading frame. Three separate Pierre shale samples, PI-H-01 (1.993 g/cm$^3$), PI-H-02 (2.020 g/cm$^3$) and PI-LC-WY-H-01 (2.998 g/cm$^3$), horizontally drilled have been used to generate osmotic pressures in the presence of different salinity fluids. A pressure cell is placed underneath the loading frame where load is applied to the piston transferring over to the sample within the cell. The axial loading from the MTS represents the horizontal stress on the sample parallel to the bedding planes and the overburden stress is supplied front the radial confining stress of the cell. Confining stress is also applied to the sample within the cell by means of mineral oil surrounding the sample. The sample is completely isolated by means of a rubber sleeve where fluid injection can also be conducted under controlled pressures using ISCO syringe pumps to simulate the pore pressures. The PI-H-01 sample was tested at elevated net stress conditions up to 6,000 psi and pore pressures of 4,000 psi. This was performed in order to get a relationship with the membrane efficiency at high-stress conditions. The PI-H-02 sample membrane efficiency tests were conducted at relatively lower stress conditions of 1,500 psi net stress and 1,000 psi pressures. The second set of experimental tests on PI-H-02 was performed to mainly capture membrane efficiency at relatively lower stress conditions under slightly different salinity conditions and to obtain mechanical properties of the sample within a reasonable rock failure limit. Prior to the test, 10-micron porous filters place on
each end of the sample were calibrated to correctly account for no sample deformation and acoustic travel time properties. Force calibration of the loading frame was also performed to ensure that the vertical load applied was a true representation of the stress intended as the overburden. The radial stress acting within the cell acts as an upward force on the overlying piston. Thus, the vertical load/force applied was calibrated to ensure that the intended isotropic and anisotropic test conditions necessary for the test were met.

The 1.5 inch cell piston completely covers each of the tested samples having 1.0 inch in length and 1.5 inch in diameter. The dimensions were chosen to reduce the injection time required to fully saturate the low permeability shale samples. Both samples were within the range of 15 nd to 25 nd under high confining and pore pressure conditions. Using the pulse decay approach (unsteady state) for permeability test, PI-H-01 sample initially saturated at 60,000 ppm NaCl solution, measured 20 nd at 6,000 psi net stress and 4,000 psi average pore pressures during 257,000 ppm NaCl injection. Sample PI-H-02 was initially saturated with high salinity, 23.5% NaCl solution (235,000 ppm) under elevated pore pressures of 1,000 psi and isotropic confining stress conditions of 1,100 psi. The pulse decay permeability of the sample was determined to be 20.236 nd at 1,500 psi confining pressure and average pore pressure of 1,000 psi. The axial deformations were monitored precisely using a linear variable differential transducer (LVDT) attached to the body of the cell while tracking the movement of the piston. PI-LC-WY-H-01 was saturated with 35,000 ppm and injected with 10,000 ppm to initiate chemical osmosis pressure build-up. The modified tri-axial pressure cell used with the MTS loading frame for coupled measurements is shown in Figure 4.3.

4.4.1 Types of tri-axial tests

There are three main test variations as summarized in Table 4.5.

Unconsolidated Undrained (UU) Test – Here we have the most basic and fastest of the three procedures generally performed on cohesive soil specimens. The reason being that only total stresses are controlled and recorded which determines the undrained shear strength providing an indication of a soils short term stability such as during or directly following a
construction project. Cell pressure is applied without allowing drainage. Then keeping cell pressure constant, deviator load is increased to failure without drainage.

Table 4.5: Summary of test conditions during shearing

<table>
<thead>
<tr>
<th>Test type</th>
<th>Rate of axial strain</th>
<th>Drainage</th>
</tr>
</thead>
<tbody>
<tr>
<td>UU</td>
<td>Typically the fastest, reaching failure criterion in 5 – 15 minutes</td>
<td>Closed, no excess pore pressure measurement</td>
</tr>
<tr>
<td>CU</td>
<td>Slow enough to allow adequate equalization of excess pore pressures</td>
<td>Closed, record excess pore pressure</td>
</tr>
<tr>
<td>CD</td>
<td>Slow enough to result in negligible pore pressure variation</td>
<td>Open, record change in volume and maintain constant back pressure</td>
</tr>
</tbody>
</table>

Isotropically Consolidated Undrained (CIU) Test – This is the most common procedure allowing strength parameters (friction angle and cohesion) to be determined based on effective stresses while also shearing at a much faster rate in comparison to the CID test. Thus, the excess pore pressure change within the specimen shearing has to be monitored.
and recorded as the shearing takes place. Drainage is allowed during cell pressure application. Then without allowing further drainage, increase $q$ while keeping $\sigma_r$ constant as for UU test.

Isotropically Consolidated Drained (CID) Test – Characterizes long-term loading response by providing strength parameters determined under effective stress control (such as friction angle and cohesion) on cohesive soil. The test takes considerable time given that the shear rate form loading has to be slow enough to simulate negligible pore pressure changes. Similar to CIU except that as deviator stress is increased, drainage is permitted.

From soil mechanics perspective, Figure 4.4 show typical representation of the Mohr-Couloumb failure envelope plots for UU and CU tri-axial measurements.

![Figure 4.4: Typical Mohr-Coulomb plots of different tri-axial tests.](image-url)
4.4.2 Tri-axial cell experimental setup

The sketch view of the equipment is shown in Figure 4.5. The equipment consists of the type-A pressure cell (A), high pressure ISCO syringe pumps (B, C and D) connected with high pressure lines, two transfer vessels used to separate injected fluids from the pump fluids. The pumps all have the capability of regulating the flowing pressures and rates control panels (F).

Figure 4.5: First set of experiments conducted with this setup.
4.4.3 Pressure cell schematic used in Type-B experiments

Figure 4.6 and Figure 4.7 shows the side view and plan view respectively of the pressure cell internal structure designed for the type-B experiments. The spiral lines are a representation of the pore pressure lines connected to the sample and isolated from the hydraulic pressuring fluid that supplies the confining stress by a rubber sleeve. The 1.5 inch cell piston head contains the acoustic transducers used in measuring the P and S waves. A stainless steel spacer can be installed to accommodate for shorter sample lengths. Aluminium 1.5 inch to 1 inch converters can be installed when testing smaller diameter core samples from the piston diameter.

4.4.4 Porous filters description

The porous filters are placed on both ends of the sample within the pressure cell to avoid the sample from being contaminated with potential solids within the brine stream and to aid the even distribution of fluid flow across the sample. One side of the porous filter is in contact with the sample while the other side of the porous filter is either in contact with one of the cell piston ends or in contact with a stainless steel spacer (Figure 4.6). The porous filters are relatively more compressible to other components of the cell set up due to their porous nature. Thus, calibration of the porous filter deformation under isotropic and anisotropic stress load conditions needs to be performed for accurate measurement of the mechanical properties of the sample during the actual test. The calibration was carried out with an aluminium dummy sample having similar dimensions as the shale sample. The vertical deformation from the LVDTs and travel time from acoustic data under the stress conditions was obtained to calibrate the static and dynamic properties accurately. Thus calibration data comprising of the static and dynamic measurements are taken fully into consideration when calculation properties such as Young’s modulus, bulk modulus, and Poisson’s ratio. A correlation between static and dynamic properties can be seen in the result section of the
thesis. It is also important to note that the porous filter realizes some permanent deformation under significant compression.

Figure 4.6: Side view of internal components of the pressure cell.
Figure 4.7: Plan view of the internal components of the pressure cell.

Hysteresis in deformation is often observed during initial stress loading and unloading of the filters so as a good practice to ensure consistency during the tests; the porous filters are
initially subjected to a series of high vertical compression before calibration data for static and dynamic measurements are collected. Subsequently, the same porous filters are used during the actual experiment at which time, the compressibility of the filters becomes stable and repeatable. Figure 4.8 to Figure 4.10 show the porous filters that were used in each test. The diameter of the filters and rubber sleeve isolating the confining mineral oil from the sample varies with the sample diameter. Specifically for the 1.0-inch diameter 10-micron filter, the top surface has a descriptively rough (Figure 4.9). It was observed during a series of calibration tests that the roughness of this filter was causing uneven deformation of the porous filter making the pistons to tilt under compression. Therefore, the 1.0-inch porous filter’s top surface was ground with a lapping plate to a smooth finish to allow a more even vertical deformation and eliminate the tilting of the piston ends under compression. Figure 4.10 displays the 1.0-inch porous filter after being ground to a smooth surface finish. The bottom end, already smooth, was placed against the sample.

4.4.5 Permeability Tests

Permeability measurement was conducted under high-pressure conditions to simulate the in-situ condition of most reservoir shales. Steady-state permeability measurement and pulse decay permeability measurement were conducted on the same sample for comparison between the individual gas and liquid permeabilities. Laboratory grade 99.99% pure nitrogen was used to test for gas permeability at high pressures to eliminate Klinkenberg effects of gas slippage. The integral form of Darcy’s law is used to determine gas permeabilities for compressible fluid under steady-state conditions.

\[
k_a = \frac{2000 p_a \mu_a q_a L}{(p_1^2 - p_2^2) A}
\]

where \(k_a\) is the permeability, md; \(p_a\) is the atmospheric pressure, atm; \(p_1\) is the upstream pressure, atm; \(p_2\) is the outlet pressure, atm; \(L\) is the length, cm; \(\mu_a\) is the air viscosity, cp; \(q_a\) is the gas flow rate at atmospheric pressure, cm\(^3\)/sec; \(A\) is the cross-sectional area, cm\(^2\).
Flow rates are obtained to compute the air permeability by volumetric analysis of precise computer-controlled high-pressure pumps with 0.001 psi resolution. Brine permeabilities have been conducted by passing filtered, pre-vacuumed de-ionized fluid through the sample. Similarly, rates and steady-state pressure drop has been measured to obtain the liquid
permeabilities using Darcy’s equation.

\[ k_1 = \frac{1000\mu_1 q_1 L}{\Delta p A} \quad (4.11) \]

where \( k_1 \) is the liquid permeability, md; \( L \) is the length, cm; \( \mu_1 \) is the liquid viscosity, cp; \( q_1 \) is the gas flow rate at atmospheric pressure, \( \text{cm}^3/\text{sec} \); \( A \) is the cross-sectional area, \( \text{cm}^2 \); \( \Delta p \) is the pressure drop, atm.

Unsteady state permeability measurements were also conducted and compared to steady-state measurements with the same experimental setup. Pump levels associated with reservoir volumes have been carefully monitored and used to calculate the shale sample permeabilities. Recent studies from Cui et al. (2009) used the pulse decay method with some modification in the single-phase liquid, gas permeability adding two-phase relative permeability measurements in order to account for gas adsorption in shale samples during the permeability measurements.

4.4.6 Waveform Analysis

The dynamic measurements are measured acoustically from the longitudinal or compressional (P) and shear wave (S) velocities generated from transducers applied in ultrasonic Nondestructive Testing (NDT). The transducers convert the signal pulse in the form of electrical energy generated from the testing instrument into mechanical energy represented as sound waves traveling through the test sample. The testing equipment used for the experiment is an oscilloscope capable of generating, displaying and recording and displaying high-frequency sound waves. The oscillation of sound waves mostly has a sinusoidal pattern (Figure 4.11). The variation in magnitude of the peaks and amplitude following the arrival is a direct result of the material structure at the time of measurement. Natural fractures, fluid saturation, and stress conditions will affect the representation of the waveform. The arrival times displayed from the sound waves can then be determined from the polarity and excursion pattern of the waveform. In a typical phase, the polarity of the P wave arrival is negative or trends downward while the polarity of an S wave is positive and trends upwards.
For an inverted phase of $180^\circ$, the polarity for the P and S waves is reversed. In the experiments, an inverted phase angle setting was mostly used with the test instrument during the acoustic measurements. Thus the arrival time for the P waves mostly depicts a positive polarity while a negative polarity was depicted for the S waves. Contact transducers contain a piezoelectric element (aka crystal element) that generates the sound waves when excited by an electrical pulse. Piezoelectricity can be found naturally in quartz and tourmaline crystals. Industrially, piezoelectricity can be obtained artificially with certain ceramics such as lead zirconate titanate, barium titanate and lead titanate (Brignoli et al. 1996). This element is protected by a wear plate (shear plate material) that is backed with some damping material that lessens the generated sound pulse. The transducer components are housed within the cell piston which further dampens the signal frequency. Although the average frequency of the transducer is 1 MHz, the protecting damping material surrounding the crystal element and the surrounding piston lowers the transmission frequency to about 300 kHz.

![Oscillating Sine Wave](image)

Figure 4.11: Oscillating sinusoidal wave.

Two transducers are required for successful measurement of the sound wave through the tested sample. The housed transducers within the cell pistons are positioned on opposite sides of the sample to capture the travel time, one representing the transmitter end and
the other classified as the receiver end. A pulse is generated from the transmitter, which is recorded at the receiver transducer.

The wave velocity measurements were determined by picking the arrival times and calculation the travel time through the sample length. The sample length deforms in relation to the stress condition so the length has to be calculated based on the LVDT measurements before accurate calculating the velocity of the sound waves.

The intensity of the waveform depends on several factors; cell components, the flatness of components, piston and transducer plates. Applying coupling material to the piston ends can help to amplify the intensity of the waveform. For the most part, P-waves arrival time has clear distinctive polarity and can be determined easily. On the other hand, the arrival time for the S-wave is rather more complicated. Shear wave splitting, otherwise known as birefringence, can occur in anisotropic media such as shale (Liu and Martinez 2012). Following the split, the shear waves travel as two separate orthogonal modes having different velocities. Figure 4.12 is a diagrammatic representation of the shear wave splitting that occurs in anisotropic media. The two shear waves can be classified into two; one fast S-wave, S1 preserving its polarization as it transitions into the anisotropic medium and a slow S-wave, S2 which time delay is a representation of the anisotropic nature of the medium. In the anisotropic media, the fast shear wave can be used to predict the fracture orientation and the time delay between both S-waves can provide an indication of the fracture intensity or density of the media.

Based on observations in saturated soils, The S-wave arrival time can be represented in 6 different forms displayed in Figure 4.13 and these observations were used in picking appropriate S-wave arrival times. The first is the most simple to interpret but is the least usual where the initial signal polarity is positive. The arrival time at the receiver also corresponds to the first intense energy excursion. The second waveform arrival is preceded by relatively lower intensity waves in the form of a compressional wave which also corresponds to the arrival times of the compressional waves. The initial polarity of the S-wave is positive
while the initial lower intensity P-wave signal is negative. The third waveform’s first energy arrival is indicated at the point “X” with growing negative polarity intensity until the polarity suddenly changes to the positive at point “S” signifying the arrival of the S-wave. The fourth waveform is a combination of the characteristics of waveform two and three. The S-wave arrival is still clearly defined from the first intense positive polarity. For waveforms five and six, the first clear intensity pick of the S-wave is much less than the largest excursion or amplitude as seen on the waveform. Waveform five has the largest excursion in the same direction as the positive polarity of the S-wave while waveform six has the largest excursion in the opposite direction of the positive S-wave polarity. The region from point X to point S on the waveforms in Figure 4.13 is known as the “near-field effect” (Brignoli et al. 1996) were shear wave sources of finite dimensions convert energy into transverse motion. This creates the initial low-intensity longitudinal wave velocities with opposite polarities to the “far-field” arriving S-wave picked up at the receiver. The shear waves obtained and analyzed for the actual test samples are mostly representative of waveform 6 where there is a combination initial of low-intensity P-waves that trend into a negative polarity right before the S-wave.
arrival is picked up with positive polarity at the receiver transducer. The initial S-wave arrival point is usually also lower than the largest excursion usually observed in the opposite direction of the positive polarity. Additionally, the transducers used for the experiments are wear plate which is similar to the shear plates described in Figure 4.13 further justifying the type of waveforms observed in the experiments. Another important observation from the waveforms in the anisotropic shale samples is the distinct polarity spike further down the waveform. This is an indication of shear wave splitting where the slow S-wave arrives later at the receiver transducer after the initial fast S-wave arrival. Figure 4.14(a) shows an example of the picking of arrival time from the measured compressional waveform and Figure 4.14(b) shows the shear waveform where there are two distinct arrival times based on shear wave splitting.

4.5 Adsorption Considerations

Saidian et al. (2016) studied the effects of rock composition on the nitrogen adsorption Specific Surface Area (N₂-SSA) using spectrophotometric techniques. The N₂-SSA technique evaluates the external surface area of the clays and was observed to be linearly correlated with mixed layer illite-smectite content. The effect of organic matter on N₂-SSA was also determined to be more profound than CEC. Organic matter is seen to block the pores and throats by bituminous kerogen which restricts the access of nitrogen molecules to the clay surfaces. The relationship between N₂-SSA and mixed layer illite-smectite content in shale samples with low and high TOC is shown in Figure 4.15.

Cui et al. (2009) also reported valuable information on shale permeability measurements when accounting for adsorption. Permeability will be underestimated if adsorption is not considered when adsorption occurring is a likely scenario. The experimental setup and adsorption isotherms shown in Figure 4.16 indicates the permeability underestimation. If the upstream and downstream reservoirs are greater than the total pore volume in the sample,
Figure 4.13: Typical examples of shear wave arrivals recorded at the receiver in saturated soils (Brignoli et al. 1996).
Figure 4.14: Longitudinal and transverse waveforms.

(a) Compressional waves

(b) Shear waves
then the underestimation of permeability will be less than 10%. However, permeability underestimation becomes more significant when the ratio of the sample pore volume to reservoir volume is greater than 2. The permeability determined without correction for adsorption can be severely underestimated by more than 60% for cases with low experimental pressures and strong adsorption. Only for cases with small ratios (less than 0.04) of effective adsorption porosity to true porosity or sample pore volume to upstream/downstream reservoir volume that the permeability can be underestimated by less than 5% (See Figure 4.16). Therefore, adsorption effects cannot be neglected to accurately determine permeability using the pulse-decay technique. In considering adsorption effects, in this research, we utilize high fluid pressures and greater reservoir volumes as transfer piston cylinders in ratio to the pore volume of the Pierre shale sample during experiments.

Gas slippage effects occur in conventional tight gas sandstones when gas flows through the rocks at low pressures. Klinkenberg (1941) related the gas permeability to the equivalent
liquid permeability through the relationship he has developed (Eq. 4.12).

\[ k_g = k_\infty \left(1 + \frac{b}{P}\right) \]  \hspace{1cm} (4.12)

\[ b = \frac{4c\lambda}{r} \frac{1}{P} \]  \hspace{1cm} (4.13)

\[ \lambda = \frac{k_b T_0}{\sqrt{2\pi d_c^2 P}} \]  \hspace{1cm} (4.14)

where \( k_g \) is the gas permeability, md; \( k_\infty \) is the equivalent liquid permeability, md; \( P \) is the average pressure of core inlet and outlet, MPa; \( \lambda \) is the gas molecular mean free path; \( c \) is the scale factor; \( r \) is the radius of the pore spaces; \( k_b, T_0, d_c \) are the Boltzmann constant, absolute temperature, and gas molecular collision diameter respectively.

The Langmuir equation has been proposed as a means for calculating the adsorption curve and the desorption equation can be used to calculate the desorption curve.
where $V_s$ is the shale adsorption capacity, m$^3$/t; $V_L$ is the Langmuir volume or maximum adsorption capacity of shale, m$^3$/t; $p$ is the gas pressure (MPa); $p_L$ is the Langmuir pressure (pressure when adsorption volume reaches half $V_L$).

$$V_a = \frac{Vdp}{p + p_d} + C$$  \hspace{1cm} (4.16)

where $V_a$ is the adsorption volume when gas pressure decreases to $p$, m$^3$/t; $V_d$ is the maximum desorption capacity, m$^3$/t; $p_d$ is the constant related to desorption speed and the heat of adsorption, MPa; $C$ is the residue adsorption capacity, m$^3$/t.

Guo et al. (2017) reported that a linear relationship between the gas permeability and equivalent liquid permeability in shales at low pressures only occurs using helium gas where adsorption is assumed not to take place. A similar linear relationship occurs in tight gas sandstone using methane gas wherein adsorption is assumed to be absent. To observe the effects of gas slippage, methane gas was used on the shale where the gas to liquid permeability relationship becomes a curve pointing to the existence of gas slippage under low pressures. Greater TOC in the shale samples was also found to increase the maximum adsorption capacity. At higher gas pressures greater than 5 MPa, a direct and an inverse relationship with permeability occurs between pore pressure and confining pressures, respectively. The desorption gas increases rapidly with decreasing pressure for pressures less than 10 MPa. A similar experiment with helium shows an increase in the permeability at the same desorption conditions which indicates that desorption has an effect on the permeability. Permeability is shown to be constant at elevated average pore pressures exceeding 10 MPa (Figure 4.17).

Although the helium molecule size (140 pm) is approximately three times smaller than the methane molecule (0.414 nm) that should allow better flow and higher permeability because the gas molecule can access smaller pores, the increase of permeability is still associated with decline in desorption which indicates that adsorption or desorption has a strong effect on the shale permeability measured. Thus, gas desorption effects should be taken into account.
in shale gas development as the permeability noticeable increases along with gas desorption.

Figure 4.17: Shale permeability as a function of average pore pressure. (A) under high pressure with methane gas. (B) under high pressure with helium gas (Guo et al. 2017).

4.6 Anisotropic Nature of Pierre Shale Samples

The elastic properties in three principal directions were determined from acoustic data for sample PI-LC-WY-H-01 to have an understanding of the anisotropic nature of the sample. The acoustic measurements can be seen for the three principal directions in Table 4.6. The axial direction in the laboratory set up that is parallel to bedding depicted the highest poisons ratio of 0.2748 as the bedding planes in the perpendicular direction are the most
deformable. The Y plane in the radial direction has the highest Young’s modulus of 63.15 GPa. The Z-direction is the vertical direction of the sample and it the most deformable. This is consistent with the lowest Poisson’s ratio and Young’s modulus of 0.0535 and 36.5225 GPa respectively in this direction. In terms of elasticity, the stiffness ranked from highest to lowest is the Y-direction, X-direction and the Z-direction. The $E_h/E_v$ ratios are utilized in the model cases.

Table 4.6: PI-LC-WY-H-01 sample anisotropy at lab conditions

<table>
<thead>
<tr>
<th>Property</th>
<th>X: Axial direction - Parallel to bedding</th>
<th>Y: Radial direction - Parallel to bedding</th>
<th>Z: Radial direction - Perpendicular to bedding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Mass</td>
<td>25.211</td>
<td>25.211</td>
<td>25.211</td>
</tr>
<tr>
<td>Sample Diameter, in</td>
<td>0.986</td>
<td>0.986</td>
<td>0.986</td>
</tr>
<tr>
<td>Sample Length, in</td>
<td>0.672</td>
<td>0.672</td>
<td>0.672</td>
</tr>
<tr>
<td>$\rho$, g/cm$^3$</td>
<td>2.998</td>
<td>2.998</td>
<td>2.998</td>
</tr>
<tr>
<td>Property</td>
<td>P wave</td>
<td>S wave</td>
<td>Vp</td>
</tr>
<tr>
<td>unit</td>
<td>us</td>
<td>us</td>
<td>km/s</td>
</tr>
<tr>
<td>Arrival Time</td>
<td>0.324</td>
<td>0.460</td>
<td>4.713</td>
</tr>
<tr>
<td>Travel Time</td>
<td>3.946</td>
<td>6.960</td>
<td>4.713</td>
</tr>
<tr>
<td>Arrival Time</td>
<td>0.420</td>
<td>1.064</td>
<td>4.655</td>
</tr>
<tr>
<td>Travel Time</td>
<td>5.800</td>
<td>9.200</td>
<td>4.655</td>
</tr>
<tr>
<td>Arrival Time</td>
<td>7.574</td>
<td>11.480</td>
<td>3.501</td>
</tr>
<tr>
<td>Travel Time</td>
<td>7.154</td>
<td>10.416</td>
<td>3.501</td>
</tr>
</tbody>
</table>

4.7 Correlation between Static and Dynamic measurements

Sedimentary shales are considered to possess transverse isotropy that is characterized by five independent elastic constants. The static and dynamic measurements obtained from the tri-axial test (including acoustic logs) prove often time-inconsistent which makes the determination of these elastic constants to describe the anisotropic medium experimentally challenging (Wong et al. 2008). Calculation of the stiffness of geomaterials is affected by the strain rates applied during measurements. The static and dynamic measurement of the
laboratory results has been correlated to get an understanding of how the values differ but because of varying stress magnitudes and strain rates used experimentally, it is best practice to treat such static and dynamic properties separately. Tatsuoka et al. 2001 reported that the strain rate dependence on stiffness pertaining to geomaterials diminishes at strains less than about 0.001%. In this research, strain rates as low as 0.002% were applied during sample shearing to minimize the disparity between dynamic and static measurements as much as possible. The different phases of experimental testing conditions are highlighted in the result and discussion section.

4.8 Ancillary Laboratory Equipment

This section lists characteristics of the supporting experimental equipments.

4.8.1 Wave Transducer Description

Manufacturer: OLYMPUS
Part No: D7207
Serial No: 853844-S
Designation: Contact
Frequency: 1.00 MHz
Element Size: 0.5 in dia

Test Instrumentation:
Pulser/Receiver: Panametrics 5052UA 3EP023
Digital Oscilloscope: LwCroy LT342 / SN: LT34202249
Test Program: TP103-3 ver. 1113N7
CableE: RG 174/U length: 4ft
Measurement per ASTM E1065

Waveform duration:
-14db level --- 1.120 US
-20db level --- 1.792 US
Spectrum measurands:

Center Frequency ---- 1.01 MHz
Peak Frequency -------- 1.25 MHz
-6db bandwidth ------- 115.2%

4.8.2 MARTEL BetaGauge PIR-PRO Reference Class Digital Test Gauge

4.8.2.1 General Features (Model no: 1919692)

Temperature compensated accuracy over 0 to 50 °C

- 8 standard pressure ranges available
- Displays in 23 standard or 1 custom engineering unit
- Displays ambient temperature in °C or °F
- Large, back-lit, 5 digit display with 0.65” high digits and 20 segment bar graph
- Adjustable TARE zeros large system offsets
- User-configurable sample rate maximizes measurement performance and battery life
- User-configurable damping smooths readings
- Auto Shut-off for extended battery life
- Low battery indicator
- CSA Intrinsically Safe, Class 1, Div. 2 Groups A, B, C, & D;
- ATEX approved; CE approved
- Available with optional 24 V external power input
- Rubber boot standard on all stand-alone bottom mount gauges
4.8.2.2 Specifications

Accuracy

- ±0.04% of rdg ± 0.01% of FS

Temperature Compensation

- 0 °C to +50 °C (32 °F to +122 °F) to rated accuracy

Standard Engineering Units

- PSI, Bar, Kg/cm², inH₂O (4 °C, 20 °C or 60 °F),
- ft H₂O (4 °C, 20 °C or 60 °F), cmH₂O (4 °C and 20 °C),
- mH₂O (4 °C and 20 °C), KPa, mBAR, inHg, mmHg, TORR

Media Compatibility

- liquids and gases compatible with 316 stainless steel; except for ranges noted as non-isolated

Environmental

- Operating Temperature -10 °C to +55 °C
- Storage -20 °C to +70 °C (-4 °F to +158 °F)

Mechanical

- Dimensions 4.375 x 5.0 x 1.50
- Input Port 1/4 male NPT

Display

- 5 Digits, 0.65 (16.53 mm) height
• Bar Graph 0 to 100% in 20 segments

Power

• Battery three (3), size AA alkaline batteries

• Battery Life 1,500 hours without backlight; 4,000 hours at slow sample rate; battery life can be displayed on bar graph to indicate the amount of time left

• Low Battery Indicator displayed icon near the end of battery life
CHAPTER 5
EXPERIMENTAL PROCEDURES AND RESULTS

This chapter contains the results and discussion from the experiments

5.1 Summary

5.1.1 Experiment I (Pierre Shale Sample PI-H-01): Measurements conducted at 40°C

1. Measured permeability under varying confining stress conditions using nitrogen

2. Measured osmotic pressure under constant confining stress of 6,000 psi (Figure 5.1)

   (a) The core was saturated with 60,000 ppm NaCl

   (b) 1,000 ppm low-salinity brine was injected at the bottom of the core at 4,000 psi.

      i. Top of the core was initially at 0 psi and 60,000 ppm salinity. The fluid at
         the inlet was circulating while the fluid at the top was stationary; thus, the
         fluid pressure was increasing during the experiment

      ii. Changed circulating injection pressure to 5,000 psi, 3,000 psi and 2,000 psi to
          measure the osmosis pressure build up at these respective stress conditions

   (c) Changed fluid salinity to 257,000 ppm NaCl after the 1,000 ppm experiments were
       concluded:

      i. Started pore pressure injection at 2,000 psi

      ii. Changed net stress by varying the average pore pressures to 3,000 psi, 5,000
          psi and 4,000 psi to measure the osmosis pressure drop at these respective
          stress conditions

      iii. During flow measurements, also conducted dynamic rock property measure-
           ments
3. Measured permeability under confining stress using 257,000 ppm NaCl brine
   
   (a) Steady-state permeability measurements at 6,000 psi confining stress
   
   (b) Pulse decay permeability measurements at 6,000 psi confining stress

Figure 5.1: Type A osmosis pressure measurement tri-axial cell set up for experiment I.

5.1.2 Experiment II (Pierre Shale sample PI-H-02): Measurements conducted at 24°C

1. Brine saturation with 235,000 ppm NaCl under constant net stress
   
   (a) Measured axial swelling during saturation of 235,000 ppm NaCl solution at 100 psi effective stress
   
   (b) Measured dynamic elastic properties during saturation

2. B value test to determine the level of water saturation in the sample pore spaces

3. Permeability measurements using 235,000 ppm NaCl solution
   
   (a) Steady-state permeability measurements at net stress of 500 psi
(b) Pulse decay permeability measurements at net stress of 400 psi

4. Measured osmotic pressure under constant confining stress at 1,500 psi confining stress
(Figure 5.2(a))

(a) 60,000 ppm low salinity brine injected from the top of the sample at a differential pressure of 800 psi:
   i. Measured axial clay swelling in the horizontal direction
   ii. During flow measurements, also conducted dynamic rock property measurements

(b) Intermittent static Young’s modulus measurements in-between the 60,000 ppm brine injection:
   i. At pre-osmosis pressure activation conditions
   ii. During partially activated osmosis pressure
   iii. During full osmosis pressure activation

5. Sample Shear Failure Test - Unconsolidated undrained conditions

(a) Acquired dynamic measurements during shearing of the sample
(b) Static Young’s modulus determination during the shearing stages
(c) Determined cohesion and friction angle from M-C failure envelope

5.1.3 Experiment III: (Pierre Shale sample PI-LC-WY-H-01): Measurements conducted at 24°C

1. Static and dynamic elastic measurements on unsaturated dry sample
   (a) Determined static and dynamic Young’s modulus with increasing confining stress from 300 psi to 1,100 psi
   (b) Determined static bulk modulus with increasing confining stress from 300 psi to 1,100 psi
2. Brine saturation with 35,000 ppm NaCl
   (a) Measured axial clay swelling in the horizontal direction
   (b) Captured dynamic elastic properties during the brine imbibition and clay swelling with ultrasonic P and S wave measurements
3. Tested the water saturation level in the pore spaces with B value test
4. Static and dynamic measurements on 35,000 ppm NaCl solution saturated sample
   (a) Determined static Young’s modulus with increasing radial stress
   (b) Determined static bulk modulus determination with increasing confining stresses
5. Measured permeability with 35,000 ppm NaCl solution after full sample saturation
   (a) Measured steady-state permeability at 1,500 psi and 3,500 psi confining stresses
6. Osmosis pressure measurements at 3,500 psi confining stress (Figure 5.2(b))
   (a) Measured the horizontal clay swelling in the axial direction during the 10,000 ppm low salinity water injection:
      i. Determined the stress dependence on the membrane efficiency by reducing the injection pore pressures to 3,000 psi, 2,700 psi, 2,400 psi, 2,100 psi, 1,600 psi and 1,050 psi while measuring the osmosis pressure at these respective stress conditions
      ii. Dynamically measured the change in elastic properties during membrane efficiency tests with ultrasonic P and S wave velocity
   (b) Measured static bulk modulus and Young’s modulus after osmosis pressure tests
7. Sample shear failure test - Consolidated undrained conditions
   (a) Statically determined the bulk modulus in-between shearing stages
(b) Statically determined Young’s modulus during the shearing stages
(c) Acquired dynamic measurements during shearing of the sample

Figure 5.2: Type B osmosis pressure measurement tri-axial cell set up.

Figure 5.3: Axial loading parallel to bedding plane description.

5.1.4 Sample preparation for tri-axial measurements

All cores used in experiments were plugged prepared parallel to bedding (Figure 5.3). Prior to the initiation of tri-axial measurements, the end surfaces of samples were trimmed with fine high precision sandpapers up to grit sizes of 1000.
5.2 Experimental Setups

Two different tri-axial test setups are shown in Figure 5.4 and Figure 5.5 and were used to characterize the permeability, swelling, osmosis, ultrasonic wave velocity, static elastic moduli, and shear behavior under varying pore pressure and confining stress conditions. The test systems shown in Figure 5.4 and Figure 5.5 are referred to as Type A and B, respectively. Both systems are the same in the methodology of sample confinement. The cylindrical sample encased with rubber sleeve is confined with independent axial and radial stresses generated with axial metal piston and cell pressure oil, respectively. The pore pressure is regulated by using two independent syringe pumps connected to both sample ends through porous filters covering the sample ends. When the tested samples were saturated, pore fluid brine was injected from the bottom side of the sample through the porous filter along the flow paths indicated with the green arrows in the figures.

Figure 5.4: Experimental setup one – Osmotic displacement type pore pressure intrusion.
The syringe pumps controlling the pore pressure use deionized water to transmit fluid pressure. The pore fluid was switched from the deionized water to a given concentration of saline water by means of a transfer cylinder equipped with an internal piston. Salt precipitation in syringe internal wall can cause damage to the piston seal of the pump during fluid displacement operations. This can adversely alter the control of fluid flow and pressure essential to the success of these tests. Consequently, the fluid occupying the pressure pumps are kept solely as deionized water and separated from the cell by means of the transfer vessel. The main differences between the two systems are the flow path of new brine introduced to induce osmotic potential through the sample and the temperature exposure of the experimental system. Osmotic potential in the sample was created by displacing the pre-existing brine in the bottom porous filter with the new brine. The difference in water activity between two brines being in contact in the sample activates the osmosis.
In the type-A system, the new pore fluid is circulated through the bottom porous filter along the path shown with the red arrows in Figure 5.4 and encased in a temperature-controlled air bath set to 40°C. During the osmosis tests, the valve at the upper end of the sample is shut and the circulating fluid makes contact with the bottom of the sample where water is imbibed osmotically across the sample. A differential pressure transducer also measures the pressure at the upper end of the sample during the osmotic pressure generation. Flow path was switched between thru-flow along the green arrows and circulatory flow along the red arrows by controlling the valves connected in the pore fluid lines. Permeability test and saturation of the sample were performed after shutting off the outlet valve of the bottom circulating line, allowing continuous fluid injection to take place across the sample during these processes.

In the type-B system, the new triggering brine was injected into the shale sample from its top-end into the shale matrix and the system is exposed to the laboratory room temperature of approximately 24°C. The PPP tests in this system were carried out under one-dimensional displacement only. There is only a single path for pore fluid to be injected across the core from either end of the sample which is expected to be a more accurate way for measuring fluid injection volumes with a minimized volume of pore fluid lines. The advantage of this setup is that the fluid volume injected into the sample can be measured over time and used to determine the level of water saturation while measuring axial swelling and ultrasonic wave velocity simultaneously. The permeability measurements were also carried out under the one-dimensional displacement in this setup.

5.2.1 High Pressure Gauge

A high-pressure digital gauge called the BetaGauge PI-PRO digital test gauge is installed along the pore pressure line at the upper end of the sample to monitor generated osmotic pressures accurately to ± 0.01% Full Scale (Figure 5.6). The operating temperature of the high-pressure gauge is from -10°C to 55°C and its pressure is rated up to 5,000 psi (350 bar).
Its components are also compatible with both gas and liquid.

Lastly, there exists another minor difference in the axial loading control method between both systems. The axial stress in the type-A system is regulated by using a syringe pump regulating the driving force of the axial metal piston. In the type-B system, the MTS load frame of 250 kN capacity controls the axial force. The load frame is controlled by a feedback system working based on the PID algorithm. The MTS system enables us to load samples under displacement control conditions as well as force control conditions.

5.2.2 Digital Displacement Sensor

Linear variable displacement transducers with $1 \times 10^{-7}$ m resolution were fixated on the axial piston to point another end of the sample to monitor the change of the distance between two pistons as the axial displacement through the tri-axial tests. The axial displacement measured as piston displacement contains both the shale sample and 10-micron porous filter displacements which are relatively the most compressible components of the assembled cell. Following the tri-axial test with the sample, the porous filter deformation is calibrated along with an aluminum dummy sample for accurate measurement of static and dynamic tests.
The dummy sample is assumed to have 69 GPa of Young’s modulus. An axial stress increase by 10,000 psi causes approx. 0.1% of the axial strain in the aluminum dummy to cancel the dummy deformation. Importantly, the digital value read by the sensor increases with shrinkage or compression and decreases with elongation or swelling of the sample.

5.3 Sample Setup in the tri-axial Cell

The samples were encased with a neoprene rubber sleeve along with the porous filters. After this, the sample was vacuumed through the pore pressure lines and the vacuum pressure was shut off from the vacuum pump to check for leaks from vacuum pressure decline. This necessary step ensures that no flow avenue causing leaks are present and there is a good pressure seal between the sidewall of axial piston and rubber sleeve. After confirmation of no leaks, the cell was filled with hydraulic mineral oil using the high-pressure syringe pumps to confine the sample.

In the type-A system, the axial piston-driving pump was operated to compensate for the counteracting force generated by cell pressure pump pressure. In the type-B system in which Experiment III, the diameter of the axial piston body is larger than that of the shale sample. The hydraulic pressure acting on the shoulder surface of the piston body causes a counteracting force against the external compressive force controlled by the MTS load frame. Therefore, a force balance check between the axial piston and mineral oil was performed to ensure that the desired confining stress from the axial and radial applied stresses experienced by the sample was accurately set. The desired isotropic and anisotropic stress conditions are achieved throughout the experiment with this force calibration incorporated into the procedure. The axial stress acting on the sample end was determined as

$$\sigma_a = \frac{F_{ext}}{A_s} - \left(\frac{A_p}{A_s} - 1\right)P_c$$

(5.1)

where $A_s$ is the cross-sectional area of the sample, $\sigma_a$ is the axial stress, $F_{ext}$ is the external axial piston force, $A_p$ is the cross-sectional area of the axial piston, and $P_c$ is the confining pressure.
Nitrogen gas and NaCl solution brine were used as saturating fluids in this experiment. It is very important to saturate the core fully with either fluid when conducting the test to simulate in-situ conditions. The b-value test is conducted in experiments II and II to determine the level of fluid saturation. The permeabilities of the Pierre shale are in the nanodarcy ranges making the saturation process time-consuming. Initially, the nitrogen is injected into the pore pressure and takes about two days for the gas pressure to be fully transmitted through the core sample at injection pressures of 200 psi. Brine saturation takes from 3 to 5 days for full saturation to be achieved. The liquid saturation is injected at pressures from 1,000 psi to speed up the saturation process as quickly as possible.

5.4 Experiment One Steps: PI-H-01 (Osmotic Displacement Setup)

Sample Description:

From laboratory measurement, the sample dimensions and physical characteristics are as follows; 2.2 g/cm$^3$ bulk density, 0.9809 inch in length, 1.4697 inches in diameter.

5.4.1 Permeability test procedures

The permeability changing with stress were tested for nitrogen and 257,000 ppm NaCl brine by using the steady-state measurement method under constant pressure gradient condition. Nitrogen test was carried out first prior to any brine injection in dry conditions. It is important to note that the injection of brine having salinity different from the pore fluid causes chemical activates osmosis and hydration/dehydration that affects the permeability measurement. As osmosis pressure is generated within the sample, this acts as a driving force that may impede or accelerate the fluid flow rate. Therefore, the exiting pore fluid was displaced with testing fluid used for permeability measurement prior to the test to determine accurate fluid flow through the shale matrix.

After setting up the sample in the system, the sample was loaded up to 600 psi under isotropic confining stress states. Dry nitrogen was injected at 400 psi as the pore fluid from the bottom sample end by a high-pressure ISCO pump. The back pressure was initially set
at vacuum pressure during injection. Following this, the confining stress was increased to 2,200 psi while keeping the net stress at 200 psi. At this condition of 2,200 psi of confining stress and 2,000 psi of average pore pressure, the first nitrogen permeability test was started. Subsequently, the net stress was increased by increasing confining stress up to 7,500 psi to observe the stress-dependent change in nitrogen permeability. For the nitrogen steady-state permeability tests, the steady-state flow was observed after approximately 30 to 60 minutes from the beginning of the flow. The brine steady-state permeability was determined after at least 3 days to assure the establishment of steady-state flow. Permeability equations for gas and liquid permeabilities can be seen in the experimental system section of Chapter 4.5. The absolute flowrate (slope) values of the inlet and outlet pumps are typically different due to the differential pressure subjected across the core to measure the permeability. Particularly for the gas permeability tests, the lower pressure side will display a larger flow rate at equilibrium conditions due to the high compressibility of the gas.

5.4.2 Pulse decay permeability measurements

The pressure pulse decay permeability test is an unsteady state permeability test method that tests the decay rate of pore pressure pulse instantaneously applied to the inlet end of the sample. Both ends of the sample are connected to respective pressure reservoirs storing pressure fluid. The permeability is calculated by using the pressure decay rate and respective fluid compressibilities in both reservoirs. The pressure differential across the sample declining with time is recorded to determine the sample permeability by using the following equation:

\[ k = \frac{m\mu\beta L}{A} \times \left[ \frac{V_1V_2}{V_1 + V_2} \right] \]  

\[ \Delta P(t) = \Delta P_0 e^{-mt} \]  

where \( V_1 \) and \( V_2 \) are the upstream and downstream reservoir volumes; \( L \) is the length of the sample; \( A \) is the cross-sectional area of the sample; \( \mu \) is the fluid viscosity at temperature and mean pore pressure; \( \beta \) is the compressibility of fluid; \( t \) is elapsed time, \( m \) is the decay time.
constant (slope of $ln[\Delta P(t)]$ vs $t$) is the differential pressure; $\Delta P_0$ is the initial magnitude of pressure pulse. The syringes of pore pressure pumps were used as nitrogen storage. Nitrogen was injected into the sample from an upstream reservoir which was usually bottom-side pore pressure pump. Once the nitrogen pressure equilibrated throughout the entire system at the downstream reservoir pressure, the upstream pore pressure line was closed by shutting off the outlet valve of the upstream pore pressure pump. Next, the fluid pressure in the upstream reservoir was increased by 1,000 psi greater than the downstream reservoir (Experiment I). After the gas in the upstream reservoir was stabilized at a given constant volume, the outlet valve of the upstream reservoir was opened to transmit a pressure pulse to the sample inlet end. The decay rate of differential pressure pulse was monitored with the high-pressure ISCO pumps.

5.4.3 Nitrogen stress-dependent and brine permeability comparison

The stress dependence of steady-state nitrogen permeability of the dry Pierre sample is shown in Figure 5.7. The steady-state gas permeability is seen to decrease from 3,135 nd to 521 nd when the net stress is increased from 100 psi to 6,000 psi. Hysteresis in the permeability trend is observed, as the net stress level is reduced to 2,000 psi where the nitrogen permeability settles at 467 nD.

After the nitrogen test, the sample was saturated with a 60,000 ppm NaCl solution to test membrane efficiency and ultrasonic wave velocities under osmosis. The liquid brine permeability of this sample was measured using a high salinity 257,000 ppm NaCl solution after the conclusion of the osmosis test to minimize the effect of osmosis-driven fluid flow. The steady-state flows for nitrogen and brine beginning at 6,000 psi of confining stress are presented in Figure 5.8(a) and Figure 5.8(b) respectively. Figure 5.8(b) shows a steady-state test permeability confirmed after nearly 8 days of a straight-line slope indicative of equilibrium conditions following a 3 day period of unsteady-state flow. Equilibrium conditions for the nitrogen test were achieved at a much faster rate of about 2 to 4 hours. The flow rates for the brine permeability case can vary due to potential solute filtering taking place during
the permeability tests. Thus, the lower pressure outlet during the brine permeability test can have a lower flow rate also seen in Figure 5.8(b).

The respective steady-state permeabilities for outlet flow rates of 106.55 cm³/day in nitrogen and 0.354 cm³/day outlet flow in 257,000 ppm NaCl brine solution were 370 nd and 14.6 nd, respectively. The nitrogen and brine permeabilities of PI-H-01 in the pulse decay method were 355 nd and 20.0 nd (Figure 5.8(c) and Figure 5.8(d)), respectively. The nitrogen permeabilities given by both methods with 100 psi net stress difference are in a good agreement with 4% of the difference. Whereas, the brine permeabilities measured using the two methods differed by 37%. The higher unsteady brine permeability could be attributed to the 300 psi lower net stress as well as the structural changes taken place within the sample due to dehydration of clay minerals using the 257,000 ppm NaCl solution. The pulse decay measurement followed the steady-state measurement at which time further shrinkage of the sample had occurred due to the dehydration of swelling clay particles with the high salinity 257,000 ppm NaCl solution.
(a) Steady-state using nitrogen at 2,100 psi net stress

(b) Steady-state using 257,000 ppm NaCl at 2,500 psi net stress

(c) Pulse decay using nitrogen at 2,000 psi net stress

(d) Pulse decay using 257,000 ppm NaCl at 2,200 psi net stress

Figure 5.8: Permeability measurements on PI-H-01 at 6,000 psi confining stress.

It is also important to note that early time data provided a brine permeability value of 28.33 nd that suggests higher permeability at the initial stages of the pulse decay and reducing permeabilities during extended intervals of the decay in pressure pulse. For vertically cored shale samples, the permeability measurements will be performed in the actual axial direction. As in the case of Yang et al. (2016) study, we should expect lower permeabilities captured during the early time period indicative of transverse permeability which can be orders of magnitude lower than the permeability in the horizontal direction. Since the permeability test in this research is carried out in parallel to the bedding planes, the early time is capturing
more of the effective horizontal permeabilities before detecting the transverse and matrix permeability as the pulse decays with time. Similarly, significant time has to be allowed to reach equilibrium conditions during the steady state permeability measurements for this same reason. The initial unstable period of flow is representative of a mixture of the planar and transverse permeability across the tortuous pore path of the matrix, but as time passes more of the transverse and effective matrix permeabilities are revealed.

5.4.4 Shale membrane efficiency test

The membrane efficiency was tested by introducing 1,000 and 257,000 ppm NaCl solutions at the bottom end of the PI-H-01 sample under varying net stresses. Figure 5.9 shows the variations of pore pressure in the closed end and axial displacement of the sample. The sample initially stabilized at 6,000 psi of confining stress with 60,000 ppm NaCl as the saturating fluid. 1,000 ppm NaCl solution circulating at 4,000 psi pore pressure was injected to interact with the saturated sample. The pore pressure build-up from 0 psi to 4,085 psi can be seen to take place over a period of 5 days to reach an equilibrium osmosis pressure. Eventually, 85 psi higher pore pressure than the circulation fluid pressure was observed at the upper closed end of the sample. The osmosis-driven transportation of water molecules from the circulating solution through the shale sample resulted in the build-up of pore pressure in the closed end. The axial displacements also reciprocates the pressure response build-up where we observe a period of stable displacement during the first two days of injection. The axial displacement later begins to increase more rapidly, where it is assumed that the initial osmosis pressure is activated between the native saturated 60,000 ppm NaCl solution and the injected 1,000 ppm NaCl solution which later reaches zero displacement during the stabilization period of the osmosis pressure. Figure 5.10 shows the later stages of the 1,000 ppm NaCl solution injection where an osmosis pressure build-up of 72 psi is seen at 5,000 psi injection pressure. The injection pressure is later lowered to 3,000 psi and 2,000 psi to capture the generated osmosis pressure at these conditions.
Figure 5.9: Initial 1,000 ppm circulation in PI-H-01 sample of 60,000 ppm native fluid. Osmosis pressure build-up of 85 psi with circulating pressure of 4,000 psi.

Figure 5.11 displays the case for high salinity water circulation at 2,000 psi, 3,000 psi, 5,000 psi and 4,000 psi resulting in an eventual pressure drop of 855.7 psi, 750 psi, 511 psi, and 638 psi respectively due to chemical osmosis. This represents water molecules flowing out of the shale matrix causing the dehydration of the sample. The remaining calculated membrane efficiencies measured at the particular stress conditions have been recorded in Table 5.1.

The Pitzer equation from 4.4 to 4.9 is used to calculate the water activities of the brine solutions. The osmosis pressure build-up or drop is then used to calculate the membrane coefficient using 4.4 and 4.9 for the temperature of 40 °C at different effective stresses. Table 5.1 shows the membrane efficiency calculations for the native fluid of 60,000 ppm having a calculated water activity of 0.9659.
Figure 5.10: Later stages of 1,000 ppm injection in PI-H-01 sample of 60,000 ppm native fluid. Osmosis pressure build-up of 72 psi with circulating pressure of 5,000 psi.

Table 5.1: PI-H-01 Membrane efficiency determination. Native water has an Activity of 0.9659. Confining stress of 6,000 psi

<table>
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<th>Water Activity $aw_1$ fraction</th>
<th>Inlet Pore Pressure psi</th>
<th>Outlet Pore Pressure psi</th>
<th>Measured Osmosis Pressure psi</th>
<th>Osmotic Potential $\Delta\pi$ psi</th>
<th>Calculated Membrane $\omega$ %</th>
<th>Effective Stress psi</th>
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<td>0.9994</td>
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<td>-85.00</td>
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<td>1,957.50</td>
</tr>
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<td>0.8338</td>
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<td>638.00</td>
<td>3,084.59</td>
<td>20.683</td>
<td>2,319.00</td>
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<td>511.00</td>
<td>3,084.59</td>
<td>16.566</td>
<td>1,255.50</td>
</tr>
</tbody>
</table>
The experiments begin with the analysis of the Pierre shale PI-H-01 rich in smectite, swelling clay content of 65 wt.%. The clay make-up promotes the behavior of a semi-permeable membrane. A strong correlation between membrane efficiency and increasing effective stress is reported. A membrane efficiency of 16.6% is gotten with a low salinity water injection of 1,000 ppm onto a sample saturated with 60,000 ppm salinity native fluid (Figure 5.12). The linear relationship for the first stage of the first test presents an expected membrane efficiency of 7.8% in the absence of effective stress ($\sigma_{eff} = 0$) for the PI-H-01 sample with a slope of 0.0022. A higher slope of 0.0035 is obtained when the injection fluid is changed to a high salinity 257,000 ppm NaCl solution into the 60,000 ppm native fluid-saturated sample. The membrane efficiency of about 27.7% is calculated for this high salinity case. Understandably, the higher chemical potential created from the greater salinity difference along with the reduced swelling of clays is a factor for the improved membrane
efficiency in this case. Despite the presence of 65 wt.% smectite (swelling clays), the clays are in a more stable condition in the high salinity injection case to prevent the expansion of clays. Another linear relationship was established from the 257,000 ppm NaCl solution circulation on PI-H-01. It is evident from the 12.33% membrane efficiency obtained in the absence of effective stress that greater osmotic potential promotes a higher membrane efficiency. It can also be inferred that the swelling experienced from the lower salinity injection provides a membrane efficiency of 7.8% even in the absence of effective stress ($\sigma_{eff} = 0$) but ultimately, the higher chemical potential difference in the later stage test ensures that greater membrane efficiency is achieved with increasing net stress.
5.4.5 Modeling the stress-dependent membrane behavior

The membrane efficiency can be described as a measure of the degree of integrity of the sample as a permeable membrane. The membrane efficiency ranges from zero for non-selective membrane to one for perfect membrane. Shales are often classified as leaky membranes. The membrane efficiency of shale depends on its petrophysical properties such as permeability and porosity, clay surface area, cation exchange capacity, the ion size, and concentration or water activity (Van-Oort et al. 1995; Mese 1995; Zhang et al. 2008; Osuji et al. 2008). The membrane efficiency of shales is directly proportional to the ratio of the cation exchange capacity of the shale. The geometry of the pore structure also plays an important role in membrane efficiency. The ratio of the ion size to shale pore throat determines the ability of shale to restrict solutes from entering the pore space in the shale matrix. The pore size distribution across a shale matrix depends on stress. Therefore, the membrane efficiency of shale is dependent on the stress state (Figure 5.12). Although shales samples are anisotropic, the effect of the effective stress on the membrane efficiency was investigated assuming isotropic conditions in the tri-axial measurements. As the permeability and porosity decrease, the shale membrane efficiency is expected to increase. Hence, we employ the definition of the isothermal bulk compressibility provided in Eq. 5.4 to define a descriptive model for the effect of effective stress on the membrane efficiency in our experiments.

\[
c_b = -\frac{1}{V_b} \frac{\partial V_b}{\partial \sigma_{eff}}
\]  

(5.4)

where \(c_b\) is the bulk compressibility; \(\sigma_{eff}\) is the effective stress; \(V_b\) is bulk volume.

Eq. 5.4 can be rewritten as

\[
c_b \, d\sigma_{eff} = -\frac{1}{V_b} \, dV_b
\]

(5.5)

Integrating the Eq. 5.5 above we obtain:

\[
-c_b \int_{\sigma_{eff_i}}^{\sigma_{eff_f}} d\sigma_{eff} = \int_{V_{pi}}^{V_p} \frac{1}{V_b} \, dV_b
\]

(5.6)
\[ -c_b (\sigma_{eff} - \sigma_{eff,i}) = \ln \frac{V_b}{V_{b_i}} \]  \hspace{1cm} (5.7)

\[ V_b = V_{b_i} e^{-c_b \Delta \sigma_{eff}} \]  \hspace{1cm} (5.8)

where \( \Delta \sigma_{eff} = \sigma_{eff} - \sigma_{eff,i} \) is the change in effective stress. Since \( c_b \Delta \sigma_{eff} \) is small, \( e^{-c_b \Delta \sigma_{eff}} \) can be estimated using Taylor expansion as

\[ e^{-c_b \Delta \sigma_{eff}} = 1 - c_b \Delta \sigma_{eff} \]  \hspace{1cm} (5.9)

\[ V_b = V_{b_i} (1 - c_b \Delta \sigma_{eff}) \]  \hspace{1cm} (5.10)

or

\[ \frac{V_{b_i} - V_b}{V_{b_i}} = c_b \Delta \sigma_{eff} \]  \hspace{1cm} (5.11)

Since Young’s modulus of rock grains is typically much higher than that of the pore space, the change of the bulk volume is mainly contributed by the change of pore volume. In other words, \( (V_{b_i} - V_b) \) equals \( (V_{p_i} - V_p) \). Hence, we obtain Eq. 5.12:

\[ \frac{V_{b_i} - V_b}{V_{b_i}} = \frac{V_{p_i} - V_p}{V_{p_i}} = \phi_i - \phi = -\Delta \phi = c_b \Delta \sigma_{eff} \]  \hspace{1cm} (5.12)

The membrane efficiency of shale decreases with the increase of shale porosity and is often reported to be linearly proportional to the porosity (Osuji et al. 2008). We can assume the following correlation to relate membrane efficiency and porosity:

\[ \omega = \omega_{\phi_0} - A \Delta \phi \]  \hspace{1cm} (5.13)

Substituting \( \Delta \phi \) in Eq. 5.12 into Eq. 5.13, we can obtain:

\[ \omega = \omega_{\phi_0} + A c_b \Delta \sigma_{eff} \]  \hspace{1cm} (5.14)

where \( \omega \) is the membrane efficiency and \( A c_b \) coefficient represents the slope. Eq. 5.14 indicates that membrane efficiency is proportional to the effective stress as shown in Figure 5.12.
5.4.6 Dynamic elastic property response to fluid injection

The change of ultrasonic compressive and shear wave velocities were measured with nitrogen and 60,000 ppm NaCl solution at varying pore pressures and confining stresses. The main purpose of the test was to show the rock–fluid interaction that affects the mechanical properties and permeability of the Pierre shale sample. Figure 5.13(a) shows the dynamic Young’s modulus determined from the compression and shear wave velocities by assuming the linear isotropy for shale sample. As seen in Figure 5.13(a), the dynamic Young’s modulus increases gradually from about 6.4 to 8.6 GPa with increasing confinement pressures up to 7,500 psi. Hysteresis of Young’s modulus was observed after unloading the net stress from 6,000 psi to 2,000 psi. This hysteresis is consistent with the permeability hysteresis shown in Figure 5.7. The Young’s modulus settled at 8.3 GPa which was the final testing condition for brine injection and the later osmosis tests. Poisson’s ratio values decreased steadily from 0.366 to 0.318 (Figure 5.13(b)) with the increase in net stress of the sample and settled at 0.34 prior to the brine injection.

Upon saturation with 60,000 ppm NaCl brine, the dynamic Young’s modulus steadily increased to 14.9 GPa at 6,000 psi confining stress and 4,000 psi average pore pressure conditions. Following this period, the membrane efficiency was tested with 1,000 ppm NaCl solution circulating at decreasing net stress conditions starting from 3,500 psi. The inlet pore pressure was circulating at 4,000 psi while the top end was initially shut off at 1,000 psi and confining stress of 6,000 psi. The sample PI-H-01 was then re-injected with 60,000 ppm to displace the 1,000 ppm circulated NaCl solution saturated within 60,000 ppm NaCl brine after proceeding with varying net stresses for the osmotic pressure measurements. The membrane efficiency was later tested with high salinity 257,000 ppm NaCl solution initially circulated at 2,000 psi of pore pressure and 4,000 psi of effective stress followed with varied net stresses to measure osmotic pressures (Table 5.1). Changes in ultrasonic wave velocities of the shale sample were also observed during the osmosis tests.
(a) Dynamic Young's modulus trend with net stress

(b) Poisson's ratio trend with net stress

Figure 5.13: PI-H-01 dry sample dynamic elastic properties using nitrogen as the pore fluid.
Figure 5.14(a) shows the dynamic Young’s modulus changing with time in the process of osmosis test with 1,000 ppm NaCl solution. The circulation pressure of 1,000 ppm NaCl solution was increased from 4,000 to 5,000 psi under constant confining stress of 6,000 psi on the second data point at 4:28 pm on 7/1/2016. Due to the decrease of net stress, the dynamic Young’s modulus was observed to decrease to 14.7 GPa. Subsequently increasing the net stress caused a corresponding drop in the dynamic Young’s modulus to 13.99 GPa. It was expected that an increase in sample stiffness occurs with increased net stress but the weakening of the sample due to clay swelling during dilution of pore fluid with the 1,000 ppm solution should lower the sample elasticity. The Poisson’s ratio followed a similar trend during the 1,000 ppm NaCl circulation with a decline from 0.199 to 0.177 at the corresponding net stress conditions. This is an indication of the structural weakening of the sample due to the swelling. An overall increase in the dynamic Young’s modulus was observed upon the circulation of the high salinity 257,000 ppm NaCl solution at the base of the sample. As observed from the membrane behavior in Table 5.1, the maximum osmotic pressure drop of 855.70 psi at a net stress of 4,427.85 psi was experienced across the sample. This is as a result of dehydration as the water molecules within the native 60,000 ppm NaCl solution was transported outward of the shale matrix. The dynamic Young’s modulus was seen to rise with time following the continued circulation of the 257,000 ppm solution as seen in Figure 5.14(a) even after lowering the net stress conditions as depicted in Figure 5.14(b). Interestingly for the Poisson’s ratio, the trend began to reciprocate with that of Young’s modulus. After an initial rise to 0.206 during the 257,000 ppm circulation, the Poisson’s ratio declines as the circulation continues, which is further evidence of the increased stiffening of the sample.

Determination of the elastic properties using nitrogen as the pore pressures were performed under drained conditions in this experiment I series. Young’s modulus and Poisson’s ratio show similar trends during loading and unloading cycles prior to the stabilized testing conditions of 6,000 psi confining stress and 4,000 psi pore pressure for brine injection tests. During nitrogen injection, the maximum Poisson’s ratio in the axial direction was determined
Figure 5.14: PI-H-01 Elastic property changes during osmosis pressure generation from the circulation of NaCl solution brine.

from dynamic calculations to be 0.366 at a net stress of 500 psi. The maximum dynamic Young’s modulus calculated was 8.66 GPa at confining stress of 7,500 psi and pore pres-
sure of 1,500 psi. The Young’s modulus and Poisson’s ratio values can differ significantly for shales during drained versus undrained conditions. Similar Pierre shale samples tested under anisotropic stress conditions by Islam and Skalle (2013) showed that the drained Young’s modulus was approximately 48% of the undrained value. The drained Poisson’s ratio was 40% or lower on average than the undrained value.

5.5 Experiment Two Steps: PI-H-02 (Piston Displacement Setup)

5.5.1 Sample Description:

From laboratory measurement, the sample dimensions and physical characteristics are as follows; 2.018 g/cm$^3$ bulk density, 0.8305 inch in length, 1.46 inches in diameter. The main aim of this experiment was to capture permeability and structural changes during osmosis buildup in the 65 wt.% smectite sample. Another objective was to capture the swelling tendency of the Pierre shale sample PI-H-02 during brine injection under piston-like flow. Advantageously, the swelling response in relation to water imbibition or saturation can be determined from this experimental setup, unlike the previous experimental setup.

The swelling behavior of the 65 wt.% smectite Pierre shale sample during high salinity 235,000 ppm NaCl brine injection under effective stress condition of 100 psi (1,100 psi confining stress and 1,000 psi pore pressure) is shown in Figure 5.15. The high salinity fluid kept the swelling clays stabilized to an extent. It is expected that the swelling would be significantly greater if a lower concentration of NaCl brine is injected into this shale formation. Shale samples with less swelling clays will also swell differently depending on the salinity of the injected fluid. Bui and Tutuncu (2018) report a reduction in recovery factors from the rock matrix up to 55% when swelling is considered with a membrane efficiency of 10%. Young’s modulus is seen to decline by 28% during saturation of the sample PI-H-02 due to weakening of the sample (Figure 5.15(b)). A simultaneous axial swelling strain of 1% occurred during the sample weakening (Figure 5.15(a)) which has been previously reported in Adekunle and Tutuncu (2019) study. These axial swelling and Young’s modulus relationships are also considered in the modeling sections of Chapter 6.
Figure 5.15: Axial swelling and weakening of PI-H-02 during injection of 235,000 ppm NaCl solution at 100 psi net stress.
5.5.2 B value test:

Skempton’s coefficient (B value) is defined as the ratio of induced pore pressure to the change in applied stress for undrained conditions was used to determine the level of saturation of the sample prior to static measurements of the sample. The equation for determining the Skempton’s coefficient can be seen below;

\[
B \equiv - \left. \frac{\delta p}{\delta \sigma} \right|_{\zeta=0}
\] (5.15)

where \(\delta p\) is change in fluid pore pressure; \(\delta \sigma\) is the change in applied stress; \(\zeta\) is the increment of fluid content; \(\zeta = 0\) means undrained testing conditions.

At confining stress of 1,500 psi and pore pressure of 1,032 psi, the B value was determined by incremental confining stress of 200 psi was applied to the sample while measuring the change in pore pressure. The change in the pore pressure stabilized at 1,223 psi given a rise of 191 psi in the pore pressure. Thus, the measured Skempton’s coefficient gave a value of 0.955 indicative of a nearly fully saturated sample PI-H-02 at this stage of the experiments.

5.5.3 Osmosis and Mechanical Test on PI-H-02

The impact of the osmosis pressure in the failure properties of the sample and changes in stiffness of the sample was also observed. As such, an Unconsolidated Undrained (UU) test was conducted to determine the shear strength of the sample under short-term stability representative of drilling and hydraulic fracturing operations.

Tri-axial measurements were conducted using an MTS loading frame to determine the impact of generated osmotic pressure on a horizontally cored Pierre shale outcrop sample within a pressure cell setup capable of acoustic measurements, elevated confining and pore pressure control on the sample PI-H-02. The tri-axial cell has the capability of injecting fluids into the pore spaces of the sample under controlled pressures from ISCO syringe pumps. The sample is completely isolated from confining fluid by placing it in between 1.5-inch pistons surrounded by a rubber jacket. Porous filters are placed on each end of the sample to distribute the flow of fluid evenly across the top and bottom ends. The sample diameter
and length are approximately 1.5 inches and 1 inch respectively. A high-pressure gauge is installed in the pressure lines just after the top end of the sample to monitor pore pressures during the experiments. The porosity of the sample was originally determined to be 22.2% using CMS-300 equipment. The dry sample PI-H-02 was saturated with high salinity, 23.5% NaCl solution (235,000 ppm) under elevated pore pressures of 1,000 psi MPa and isotropic confining stress conditions of 1,100 psi (100 psi net stress). Figure 5.16 shows the pulse decay and steady-state permeabilities measured during the tri-axial tests. The steady-state brine permeability of the sample was determined to be 14.03 nd at 1,500 psi confining pressure and 500 psi net stress after a 2 day period of stable flow. Pulse decay permeability measurement resulted in 20.24 nd at 400 psi net stress after a 30 hour period. Saturated bulk density was calculated to be 2.02 g/cm³.

![Figure 5.16: PI-H-02 Brine pulse decay and steady state permeability.](image)

Subsequently, the reference Young’s modulus data were obtained by applying three cycles of axial loading to 2,000 psi and unloading to 1,500 psi. This procedure was repeated after creating an osmotic potential through the injection of a lower salinity 6 wt.% NaCl brine solution (60,000 ppm) into the top end of the shale sample under the same aforementioned stress loading and unloading conditions. The initial 60,000 ppm salinity NaCl solution was injected at 1,400 psi with a differential pressure of 800 psi across the core sample. Young’s
modulus was then measured after this initial injection period and later measured following another injection period of 60,000 ppm NaCl solution at 1,000 psi differential pressure to observe the distinct changes in the stiffness of the sample during injection. The axial deformations were recorded precisely using a linear variable differential transducer (LVDT) fixated to the body of the cell. The mechanical alteration was monitored continuously through the pumps and the installed high-pressure gauge sensor.

After 10% pore volume injection of 60,000 ppm NaCl solution into the top end of the sample PI-H-02 at a differential pressure of 800 psi (inlet pressure at 1,400 psi and outlet pressure at 600 psi), the outlet pore pressure valve was shut and the inlet pore pressure line was open to one of the pressure pumps where the pore pressure at the inlet was controlled at 730 psi. Figure 5.17 shows the osmotic pressure variation during this period where the inlet pump pressure is controlled at 730 psi. With minimal temperature fluctuations, the osmosis pressure at the top end of the same appears to be unstable but reaches a low pressure of 679.4 psi at stable temperature conditions. This undulating behavior in the osmosis pressure response was an indication of partially activated osmosis conditions and it was decided to resume injection of the 60,000 ppm NaCl solution to achieved fully activated osmosis conditions and measuring Young’s modulus of the sample.

Following 50% pore volume injection of 60,000 ppm NaCl solution into the top end of the sample PI-H-02 at a differential pressure of 1,000 psi (inlet pressure at 1,400 psi and outlet pressure at 400 psi), the outlet pore pressure valve was shut and the inlet pore pressure line was open to one of the pressure pumps where the pore pressure at the inlet was controlled at 900 psi. From the osmotic potential created across the sample, the overall flow of water began to move in the direction of the inlet pore pressure line at the bottom of the sample thereby causing the pump volume to increase. Progressively with time, the equilibrium pressure is achieved between the different salinity fluids with a noticeable pressure drop on the top end of the sample monitored using the high-pressure gage. The inlet pressure pump was then increased to 1,000 psi after about 14 hours of the osmosis pressure equilibration as
Figure 5.17: Partially activated osmosis pressure equilibration trend in PI-H-02 sample.

seen in Figure 5.18(a) and Figure 5.18(b). This caused a sudden rise of the osmotic pressure observed in the outlet pressure lines with an equilibrium pressure of 832.4 psi was reached in seven hours following the sudden rise.

The fluid injection pressures observed after the first and second Young’s modulus test was a partially activated osmosis pressure drop of 50.6 psi and a fully activated osmosis pressure drop of 168.6 psi. The pressure drop was measured with a high-pressure gage connected to the pore pressure lines at the top end of the sample. Table 5.2 shows the result of the fully activated osmosis pressure across the sample at the test stress conditions. The Young’s modulus of the sample PI-H-02 was also measured at this time to capture the final change in the stiffness of the sample following full chemical osmosis activation.

The deviatoric stress versus axial strain behavior during the process of loading and unloading is shown in Figure 5.19. Deviatoric stress is the difference between the axial stress and radial stress subjected to the sample during the axial loading of the sample. Using the
(a) Initial decline of fully activated osmosis equilibration trend

(b) Later period of fully activated osmosis pressure equilibration

Figure 5.18: PI-H-02 osmosis pressure equilibration measurement.

deviatoric stress essentially cancels out the changing pore pressures during undrained testing conditions.
Table 5.2: PI-H-02 Membrane coefficient determination. Native water has an Activity of 0.8506. Confining stress is 1,500 psi.

<table>
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<th>Water Activity aw fraction</th>
<th>Inlet Pore Pressure psi</th>
<th>Outlet Pore Pressure psi</th>
<th>Measured Osmotic Pressure (psi)</th>
<th>Osmotic Potential Δπ psi</th>
<th>Calculated Membrane Stress ω %</th>
<th>Effective Stress psi</th>
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<tr>
<td>0.9659</td>
<td>1,000</td>
<td>831.4</td>
<td>-168.6</td>
<td>-2,665.28</td>
<td><strong>6.326</strong></td>
<td>584.3</td>
</tr>
</tbody>
</table>

5.5.4 Significance of osmotic transport to the oil recovery from shale matrix

Bui and Tutuncu (2017) have investigated the effects of salinity on oil recovery by reducing the solute concentration surrounding the rock matrix to initiate osmotic transport. The membrane efficiency was kept constant at 10% but the efficiency of the membrane changes as a function of the changing salinity of the fluids and permeability variation during stress alterations of the rock matrix. Oil recovery is significantly higher depending on the membrane coefficient. A recovery factor of 42% was reported for a membrane efficiency of 40%. The results also indicate that lower salinity increases the amount of oil fluxing out of the matrix block. The effect of salinity on the stress-strain response during the loading cycles from 1,500 to 2,000 psi stress under undrained conditions indicated increased strain when compared to the reference test. This resulted in a reduced Young’s modulus of sample PI-H-02 under the same stress conditions. The sample becomes weaker with the generation of osmosis pressure, which drives water molecules into the shale matrix causing swelling and permeability reduction. For each level of generated osmotic pressure in Figure 5.19, the loading of the shale samples caused a gradual shift in the starting axial strain. Notwithstanding, the measured strains are almost fully recovered to the starting points during the unloading cycle representing a non-linear elastic behavior. The axial strain increases as the sample experiences chemical osmosis. However, the slopes of both loading and unloading curves are observed to be almost insensitive to the presence of the osmotic pressure created. We observed an increase in the non-linearity of the slopes during the presence of osmosis pressure. The secant Young’s modulus was estimated to vary by taking the slopes from the
start and endpoints of the loading and unloading cycles. The linear slopes appear to decrease slightly by approximately 5% from 1,935.5 MPa to 1,837.8 MPa and eventually by 9.5% to 1,750 MPa along each of the respective osmotic conditions as seen in Figure 5.19.

Figure 5.19: Pierre shale PI-H-02 stress-strain relationship during Young’s modulus test at undrained conditions of increasing levels of 60,000 ppm NaCl injection.

5.5.5 Failure test on PI-H-02

The stress-strain curve of a Pierre shale core sheared at three different confining stresses is shown in Figure 5.20. Strain rate of 0.03% was applied along with unconsolidated and undrained testing conditions for each radial stress increment stage to simulate the failure strength properties under rapid and fast loading. The first shearing stage commenced at 10.34 MPa of radial stress and began to plastically deform at approximately 20.68 MPa of axial stress. At this point, the radial stress was immediately increased to 13.8 MPa to restore the elastic deformation trend and continue shearing. Following this, another
initiation of shear failure was then observed at 24.5 MPa axial stress when the sample began to plastically deform again. Subsequently, the radial stress was increased to 20.68 MPa for the final radial stress condition. When 31.8 MPa axial stress was applied, the tangential slope of the stress-strain curve became nearly zero (Figure 5.20). The bulk sample behaves stiffer in the undrained conditions because both the pore fluid and skeletal frame resist the compression (Wang 2000). Figure 5.20 shows increasing pore pressure with applied axial stress as this increasing pore pressure due to confinement opposes the applied stress producing it.

The relationship between deviatoric stress, $\sigma_a - \sigma_r$ and net mean stress, $(\sigma_a + 2\sigma_r)/3 - P_p$, observed during the undrained shear is illustrated in Figure 5.21 as the stress path of the shearing. It is evident that the dilatancy behavior of this sample which was loaded parallel to its bedding plane, shifts to represent a more contractile one with increasing stress level. The deviatoric stress versus axial strain depicted in Figure 5.22 shows the peak deviatoric stress to be consistent with the stress path at about 10.5 MPa. The peak stress remains consistent
for the three levels of confining stresses representative of a typical UU test following the initial shearing stage. Young’s modulus of 1,086 MPa was also obtained from the linear slope of the deviatoric stress vs axial strain plot. Mohr-Coulomb failure criterion of the tested sample was determined as shown in Figure 5.23. As osmosis alters the net stress due to fluid pressure change, the sample failure was expected to take place differently. The friction coefficient is also a strong function of the saturation state and the type of fluid the sample is exposed to as discussed in detail by Tutuncu (2017).

Figure 5.21: Static stress path of Pierre shale PI-H-02 sample during shearing under undrained condition.

The failure criterion is given as

\[ \eta = C_0 + (\sigma_n - P)\tan\phi \]

where \( C_0 \) is cohesion given as the intercept of failure envelope on shear stress axis and \( \tan\phi \) is friction coefficient. When the Mohr-Coulomb failure criterion is utilized for failure, the shear rupture surface is the Mohr-Coulomb failure line with an intersection value of \( C_0 \) at the shear stress axis and a slope of \( \tan\phi \).
Figure 5.22: Deviatoric stress vs axial strain of Pierre shale PI-H-02 sample during shearing under undrained condition.

Failure test was conducted on sample PI-H-02 at three different stress states to obtain the nature of the failure envelope utilizing the Mohr-Coulomb criterion, presented in 5.16. Table 5.3 shows the failure results of the three shearing stages. In Figure 5.23, the first circle represents the failure condition for a consolidated matrix while the following two circles represent unconsolidated matrix conditions. Essentially, not enough time was allowed for consolidation when the confining stress was increased because of the fast strain rate of 0.03% implemented during the shearing stages. For an unconsolidated, undrained (UU test) and isotropic sample, we would expect an internal friction angle of zero which happens to be the case for the latter two shearing stages. The cohesion 5.5 MPa was determined from Figure 5.23. The third stage circle is about the same magnitude as the second stage circle. The slight difference can be attributed to the additional consolidating effect due to elevated radial stress before the pore pressure build-up cancels out or opposes the confining stress. Islam and Skalle (2013) showed that the shear strength of the Pierre shale sample changes depending on the loading orientation. The intrinsic anisotropy of our tested sample and activated chemical osmosis causes pressure imbalance across the sample which also contributes
to the partial consolidation of the sample observed in the third shearing stage. Chemical osmosis generates the pore pressure gradient in the axial direction providing additional axial stress during the shearing of the sample.

Figure 5.23: Mohr-Circle failure envelope of Pierre shale sample PI-H-02. CU loading in 1st stage and UU loading in the 2nd and 3rd stages. Loading is parallel to bedding. Data from experimental results.

Table 5.3: PI-H-02 Mohr-Coulomb failure criterion parameters. 1st stage is consolidated. 2nd and 3rd stages are Unconsolidated Undrained conditions.

<table>
<thead>
<tr>
<th>Maximum Axial stress, $\sigma_a$</th>
<th>Effective Max Axial stress, $\sigma'_a$</th>
<th>Radial Stress $\sigma_r$</th>
<th>Effective Radial Stress, $\sigma'_r$</th>
<th>Initial Pore Pressure</th>
<th>Pore Pressure at failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>MPa</td>
<td>MPa</td>
<td>MPa</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>20.240</td>
<td>11.450</td>
<td>10.34</td>
<td>1.550</td>
<td>6.89</td>
<td>8.790</td>
</tr>
<tr>
<td>31.840</td>
<td>16.150</td>
<td>20.68</td>
<td>4.990</td>
<td>6.89</td>
<td>15.690</td>
</tr>
</tbody>
</table>
Islam and Skalle (2013) also reported undrained failure conditions of the Pierre shale outcrop sample having similar characteristics of porosity (22.4%) and about half the concentration of smectite (31.5 wt.%) compared our tested sample. In their study, the sample was saturated with 3.5 wt.% NaCl brine solution prior to consolidation and loading was also performed parallel to bedding. Their representation of the Mohr-Circle failure criteria is illustrated in Figure 5.24 compared with the first shearing stage of sample PI-H-02. A friction angle of 26.57° and cohesion of 3.65 MPa is observed. The large difference in the value of friction angle between their sample and our sample can be attributed to the difference in sample consolidation in between shearing stages. In the literature experiments, the excess pore fluid pressure built up during the undrained test is allowed to drain from the sample during consolidation before continuing with the next undrained shearing stage. In the experiments on the sample PI-H-02, the pore fluid volume is maintained constant through the processes of confining stress elevation. Thus, the failure criterion of this sample has the nearly-zero friction angle as those of typical clayey sediments subjected to UU (unconsolidated and undrained) tri-axial tests.

Islam and Skalle (2013) also recognized the change in strength with varying orientation of the Pierre shale sample. The chemical osmosis induced alters the pore pressure gradient in the axial direction providing additional axial stress during the shearing of the sample. Similar changes in tensile strength have been observed in the Green River and Niobrara samples from Mokhtari and Tutuncu (2016). Overall, tensile strength increased with an increase in organic content. Laminations were activated within Green River shale samples when the Brazilian tests were conducted below 30° to the bedding plane. Induced fracturing occurred across the laminations when the bedding plane angle was above 30°. Failure occurred along natural fractures in Niobrara samples where the natural fractures were aligned parallel to the direction of the applied load. The natural fractures present a weaker plane having lower stress that induces failure.
Figure 5.24 also compares the failure stress state of our sample at 10.34 MPa confining stress (Pore pressure at failure is 8.79 MPa) with those of the literature data (Islam and Skalle, 2013). The testing stress and drainage condition during the consolidation stages of this study are quite different from the referenced literature study. Thus, just the failure stress state at the lowest stress level under consolidation is compared with the failure criterion of the literature data. It is observed that the PI-H-02 sample fails before reaching the failure criterion of the literature sample. The lower failure stress state is considered to be caused by osmotic pressure built up within the sample. We have found that osmotic pressure generated along the sample axis caused by two brine phases of 257,000 ppm and 60,000
ppm NaCl solution weakens the apparent shear strength. Figure 5.25 shows the comparison of Young’s modulus between the two studies. Sample PI-H-02 is saturated with relatively higher salinity fluids compared to the study from Islam and Skalle (2013), so it is expected that the sample will behave stiffer due to dehydration of the shale matrix. However, sample PI-H-02 was revealed to have a lower Young’s modulus compared to the literature sample. Water molecules imbibed into the matrix during the chemical osmosis process caused the apparent weakening of the sample.

![Figure 5.25: Comparison of Young’s modulus of sample PI-H-02 with literature data from Islam and Skalle (2013).](image)

In the latter two shearing cycles with confining radial stress, $\sigma_r$ of 13.79 MPa and 20.68 MPa, the shear resistance is believed to be attributed to internal friction because the intrinsic sample structure already experienced a certain degree of damage in the first stage of loading.
at $\sigma_r$ of 10.34 MPa. In the shear behavior of the first stage, we expected to observe some effects of intrinsic structure on shear behavior. Such intrinsic effect may be observed as sharp yielding in linear stress-strain shown in Figure 5.22. In the latter stages, yielding behavior becomes less sharp.

5.5.6 PI-H-02 Creep behavior

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. When subjected to a step constant stress, viscoelastic materials experience a time-dependent increase in strain. This phenomenon is known as viscoelastic creep. At a time $t_0$, a viscoelastic material is loaded with constant stress that is maintained for a sufficiently long time period. The material responds to the stress with a strain that increases until the material ultimately fails if it is a viscoelastic liquid. If, on the other hand, it is a viscoelastic solid, it may or may not fail depending on the applied stress versus the material’s ultimate resistance.

When the tangential slope of the stress-strain curve at $\sigma_r = 20.7$ MPa became nearly zero, we terminated the axial loading at a constant strain rate to test the creep behavior of the sample. The operation of the MTS loading system was switched to keep constant axial stress at 44 MPa. The sample was still in an undrained condition. The creep behavior observed is shown in Figure 5.26 with pore pressure change. The creep strain develops at a constant rate until 1.7 hours. Subsequently, the strain rate accelerates until reaching the failure point at 1.9 hours. The axial strain value at the failure point is 3.3%. The sample fails before reaching a significant strain level. In the entire creep stage, the pore pressure uninterruptedly increases. The creep failure of the sample should be triggered by the destabilization of shale structure when its stress state reaches the failure criterion because of excess pore pressure generation.
5.5.7 Young’s modulus and Poisson’s ratio trends during osmosis

A series of plots showing the evolution of dynamic mechanical properties during the membrane coefficient determination stage unto the shearing stages of the sample can be seen in the Figure 5.27. Acoustic measurements were used to calculate the dynamic Young’s modulus and Poisson’s ratios. From the osmosis test earlier described, 60,000 ppm NaCl representing a lower salinity is injected into the native fluid of the sample in this case. This initiates the flow of water molecules into the shale matrix causing simultaneous swelling and weakening of the shale matrix during water imbibition. Both stiffness and Poisson ratio is seen to decline during the initial stages of the osmosis pressure build-up. Young’s modulus and Poisson’s ratio during the osmosis test can be seen specifically in Figure 5.28. There is a decline in the elastic stiffness of the sample continued during the fully activated osmosis of 169 psi while the Poisson ratio began to increase. It is apparent at this point that there is a significant buildup of pressure to cause swelling of the sample making the sample weaker. This decline is in dynamic data is also consistent with the static data measured during the
Figure 5.27: PI-H-02 Dynamic properties during osmosis and shearing stages.
osmosis tests with the membrane efficiency results shown in Figure 5.12.

Figure 5.28: PI-H-02 Young’s modulus decline.
5.5.8 Dynamic data shear path

The shearing stages were performed under undrained and unconsolidated conditions where the strain rate was set to 0.03% to simulate rapid stress changes such as that experienced during drilling. The change in mechanical properties during the shearing stages is seen from the dynamic shear path. At the first confinement stage of 1,500 psi, the compressional velocity increased from about 2.38 km/s to 2.42 km/s before reaching the plastic deformation region. At this point, the confinement stress was increased to 2,000 psi while the shearing rate was maintained at 0.03%. The compressional velocity maintained about 2.43 km/s before reaching the plastic region and then having to increase the commitment to 3,000 psi. The highest recorded compressional velocity reached about 2.46 km/s after which the sample started yielding under plastic deformation. The velocity reduced to 2.44 km/s before the final failure was achieved. A general reduction in the shear wave was experienced during each confinement of the shearing stages starting from 1.56 km/s and ending up with 1.43 km/s. Understandably, the compressional velocities increased due to the compression and collapse of matrix grains upon themselves due to the increase in confinement. While the shear wave reduces simultaneously due to gradual slipping and sliding of rock grains as the shearing of the sample occurred. An overall increase of 5% in the longitudinal velocity was seen in the shearing stages from about 2.33 km/s to 2.46 km/s. Whereas a reduction of 8.33% in the shear wave was experienced across the shearing stages from 1.56 km/s to 1.43 km/s. Additionally, as there was not any time allowed for the consolidation of the sample, in between shearing stages, we observe this gradual increase and decline in the compressional and shear wave respectively across the stages.

More importantly, a steady decrease in the dynamic Young’s modulus is seen with a simultaneous increase in the Poisson’s ratio that was experienced during the shearing of the sample. This alludes to the fact that the sample is gradually losing its structural integrity as the shearing occurs until the eventual failure of the sample PI-H-02. Figure 5.28(a) shows the dynamic Young’s modulus depreciating from 10.95 – 10.3 GPa. The Poisson’s Ration ranges
from 0.12 – 0.18. Stiffer materials are expected to have lower Poisson’s ratio and thus, the stiffness of the material reduces which causes the Poisson’s ratio to increase. The Poisson’s ratio initially increases upon injection of the lower salinity 60,000 NaCl solution, gradually decreases with continued LSWI and increases with increasing net stress. The shearing stages following the osmosis test show that Young’s modulus of the sample increased while the Poisson’s ratio reduced steadily. The Young’s modulus statically and dynamically measured at the first confinement condition was 1.086 GPa and 10.728 GPa respectively. Thus the dynamic value represents a 9.87 factor of the static measurement in this instance. As seen in Figure 5.29, Young’s modulus dropped overall in between shearing stages while the Poisson’s ratio displayed a reverse trend where there was an overall increase due to net stress.

Figure 5.29: PI-H-02 Dynamic measurements during shearing stages.
5.6 Experiment Three Steps: PI-LC-WY-H-01 (Piston Displacement Setup)

Sample Description: From laboratory measurement, the sample dimensions and physical characteristics are as follows; 2.9983 g/cm$^3$ bulk density, 0.672 inches in length, 0.986 inches in diameter.

The main aim of this experiment is to capture similar changes in rock failure behavior, permeability and structural properties of the 3.5 wt.% TOC sample under osmotic conditions. The relationship between static and dynamic measurements was also correlated. This experiment also aims to determine the extent and limitations of the membrane efficiency by testing a shale formation possessing both clays and organic content. This part of the study also evaluates the mechanical behavior in a relatively high TOC Pierre shale sample, simulating the natural in-situ conditions of the shale formation at the time of deposition and evaluating the potential for EOR using low salinity water floods. Such interpretation based on lithology, mineralogy and permeability variations can be translated into other sedimentary basins to determine the impact of the chemical osmosis on the recovery process.

The swelling rate will depend largely on the stress conditions and salinity concentration of the injected brine. Under osmotic conditions, the swelling behavior also changes as we have water molecules flowing in and out of the matrix depending on the potential gradient created between the native formation water (simulated as the primary injected fluid or initial saturation fluid) and secondary injection fluid. It is important to capture these relationships to fully model the swelling behavior or rock formation under different conditions of stress and injected fluids. Mineralogy of the shale matrix will also impact the swelling behavior.

Steady-state permeability test was conducted on sample PI-LC-WY-H-01 using 35,000 ppm NaCl brine solution prior to the low salinity water injection during the osmosis tests to observe changes in permeability induced by chemical osmosis. A steady-state flow of 5.22 cm$^3$/day was achieved at 1,500 psi confining pressures at a differential pore pressure of 1,000 psi translating to the permeability of 284.55 nd and can be seen in Figure 5.30.
Shortly after determining the sample permeability, osmosis tests was initiated by injecting 10,000 ppm NaCl brine into the sample from the opposite end of the initial injection. This injection process was extensively carried out for about 48 hours to ensure that the low salinity brine was in full communication with the sample matrix and pre-existing 35,000 ppm sample saturated NaCl brine representing the in-situ native fluid of the Pierre shale sample. During this injection process, the permeability of the sample was also determined through steady-state measurements. A permeability of 9.39 nd (98.2% decrease) was realized under 3,500 psi confining pressure and net stress of 900 psi with a differential pressure of 2,600 psi. The reason for the 96.7% decline in permeability can be attributed to

- An increase in confinement pressure to 3,500 psi during measurement with most likely closed up any pre-existing natural or induced fractures that represented were favorable paths for fluid flow.

- Potential swelling of the shale matrix which narrows the pore spaces.

- Inherent Build-up of osmosis pressure within the shale matrix causing back pressure to the direction of fluid flow.

Figure 5.30: PI-LC-WY-H-01 Fracture dominated permeability.
The initial permeability if 284.55 nd measured was most likely as a result of fracture dominated flow. A noticeable induced fracture is seen to exist in the measured sample in Figure 5.30. Thus, with the increase in confinement stress, the permeability of 9.39 nd is more representative of the matrix permeability. Subsequently, the injection was paused to measure the pressure build-up induced from chemical osmosis at varying levels of net stress on the sample. Each membrane coefficient test was determined by observing the osmosis pressure buildup for at least 10 hours following the termination of LSWI to ensure that an equilibrium state was achieved before noting the chemical osmosis pressure induced within the sample. As such, a representation of the change in the shale membranes coefficient was determined from these observations discussed in the following section.

Static and dynamic measurements of the Young’s modulus and bulk modulus were also captured before water injection, during saturation of the simulated native fluid, during osmosis pressure build-up and the shearing stages. Summary of the static changes in Bulk modulus and Young’s modulus under drainage conditions can be seen in Figure 5.31. Figure 5.31(a) shows the bulk modulus of the dry sample PI-LC-WY-H-01 increasing with stress from 2.68 GPa to 4.85 GPa between 2.4 MPa to 5.2 MPa net stress. During saturation, the bulk modulus of the sample reduces to 1.13 GPa at 2.36 MPa confining stress due to fluid saturation and steadily arises to 7.18 GPa at 16.76 MPa net stress. Static Young’s modulus is also shown to increase in Figure 5.31(b) with net stress but with an overall increase in Young’s modulus for the saturated sample in comparison with the dry sample. The dry sample increase from 4.6 GPa to 10 GPa between 2.1 MPa and 4.1 MPa net stress. After saturation, Young’s modulus values can be seen to rise from 7.1 GPa at 2.1 MPa net confining stress up to 25.4 GPa at 17.2 MPa net confining stress.

5.6.1 PI-LC-WY-H-01 Mechanical properties during saturation

During saturation of the sample with 35,000 ppm NaCl, both the dynamic Young’s modulus and Poisson’s ratio calculated from the acoustic velocities is shown to continuously increase (Figure 5.32). The injecting pore pressure mainly causes this behavior where the
(a) Static bulk modulus variation with net stress

\[ y = 0.7583x + 0.7995 \]
\[ R^2 = 0.9697 \]

(b) Static Young’s modulus variation with net stress

\[ E_h = -0.0306x^2 + 1.6247x + 5.5414 \]
\[ R^2 = 0.9668 \]

\[ E_h = 2.5454x - 0.5045 \]
\[ R^2 = 0.9933 \]

Figure 5.31: PI-LC-WY-H-01 Static elastic properties trends.
sample exhibits a combination of an increased pore pressure filtering into the pore spaces while rendering additional structural support and an increase in the axial force from the injection end acting on the sample. As the net stress is periodically increased to speed up the rate of injection, the acoustic velocities also increase. Only when the sample is completely saturated with brine after 10 days of injection, does a noticeable drop in the P and S wave velocities begin to take place (Figure 5.32(a)). At this point, the weakening of the sample is clearly observable. The dynamic Young’s modulus increase from 40.22 GPa to 52.70 GPa during the saturation period, then drops to 44.04 GPa after the sample is fully saturated. The Poisson’s ratio values are also seen to rise from 0.29 to 0.32 during saturation and continues to rise further after the saturation period, reaching up to 0.35 which is another indication of sample weakening Figure 5.32(b).

The compressional velocity has a direct response to fluid imbibition and axial confinement increase due to pore pressure injection pressure. Transverse velocity is insensitive to fluid saturation but responds with an increase in confinement pressures. This increase in Young’s modulus during saturation has been noticed in other studies such as Zhang et al. (2017) where pore pressure buildup during injection in siltstone caused an increase in stiffness. An arch shape nature of the axial stiffness occurs for all saturation (Figure 5.33). For the dry sample, when injection is initiated, due to capillarity, the fluid fills the small pores before the larger ones making the majority of the deformation to occur in the large pore spaces. Due to the low permeability during the saturation of sample PI-LC-WY-H-01, the fluid is not given enough time to drain under compression, which results in a buildup of pore pressure making the sample stiffer. As shearing of the sample commences, cracks are initiated with lowers the pore pressure and axial stiffness of the sample. This arch shape is seen during saturation of sample PI-LC-WY-H-01 and initial loading during the shearing stages, with the dynamic Young’s modulus, as shown in Figure 5.32.
Figure 5.32: PI-LC-WY-H-01 changes in acoustic properties during saturation.
A gradual swelling relationship is also observed as shown in Figure 5.35 indicating a buildup of the salt solution into the pore spaces. The level of swelling from the existing clays (1% mica/illite, <5% smectite) in this case is inconsequential to the increase in stiffness caused by the pore fluid injection. Young’s modulus changes were observed throughout the process of injection. These changes may be seen in Figure 5.34 where the computed dynamic Young’s modulus trend is shown. After the sample was fully saturated, a correlation between the static and dynamic Young’s modulus was determined and shown in Figure 5.36. During the injection phase, the static Young’s modulus was computed from this correlation and compared with Poisson’s ratio during saturation of the sample with 35,000 ppm NaCl solution.
5.6.2 PI-LC-WY-H-01 Membrane efficiency determination

For reservoir shales with higher TOC and less swelling clays, membrane efficiencies are expected to increase with increased effective stress and greater chemical potential from different salinity fluid up to a reasonable limit. The membrane efficiency related to stress was
Figure 5.36: PI-LC-WY-H-01 saturated dynamic and static Young’s modulus correlation.

determined prior to the shearing of the sample PI-LC-WY-H-01. Injecting 10,000 ppm into a 35,000 ppm saturated native formation fluid of the sample improved the membrane efficiency and the results are listed in Table 5.4. Each data point was recorded after a minimum of 6 hour equilibration time for stabilized pressure and temperature conditions to be achieved. In Figure 5.37, the equilibrium osmosis pressure drop attained was 21 psi at a stable 24°C temperature and inlet pressure controlled at 3,000 psi. Figure 5.38 shows the pressure drop at 800 psi effective stress and outlet pressure regulated at 2,700 psi fluctuating with temperature. Only during stable temperature conditions was the equilibrium osmosis pressure drop noted to be 35 psi at the stress condition and used to calculate the membrane efficiency. The osmosis pressure equilibration at 1,100 psi effective stress is shown in Figure 5.39 where the outlet pressure was maintained at 2,400 psi and an osmosis pressure drop of 44 psi was witnessed. A strong correlation was also developed between effective stress and the membrane coefficient for this case with the efficiency reaching up to 18% at 1,425 psi effective stress (Figure 5.40). Increasing the effective stress beyond 1,600 psi at the optimal efficiency of 18.35%, brought about a decline in the shale membrane efficiency. A possibility is that there
is complete closure of micro-fractures that were previously open and allowing the selective filtering of water molecules into the matrix. Furthermore, the dynamic Young’s modulus measured during the osmosis pressure measurements increases continuously in Figure 5.41. As the net stress level increases, a simultaneous decrease in permeability is expected as the pore spaces and micro-fractures reduce in size. Therefore, the increasing sample stiffness can be attributed to the closure of the observable micro-fractures in Figure 5.30. In the later part of Figure 5.41 representing the declining membrane efficiency, the osmosis pressure decline during equilibration slowly drops and stabilizes after a long wait period. From Table 5.4, the osmosis pressure measured at 1,900 psi and 2,500 psi net stress stabilized after 6 hours and 14 hours respectively. Figure 5.42 and Figure 5.43 show these stabilization times for the declining data points in Figure 5.40 after the optimal efficiency point where a longer wait time to achieve equilibrium does not increase the osmosis pressure drop.

Figure 5.37: PI-LC-WY-H-01 Temperature fluctuation during chemical osmosis pore pressure stabilization. A 500 psi effective stress with a measured osmosis pressure of 21 psi.
Figure 5.38: PI-LC-WY-H-01 Temperature fluctuation during chemical osmosis pore pressure stabilization. Confining stress of 3,500 psi. Inlet pressure maintained at 2,700 psi.

Figure 5.39: PI-LC-WY-H-01 Temperature fluctuation during chemical osmosis pore pressure stabilization. Confining stress of 3,500 psi, Inlet pressure maintained at 2,400 psi.
Table 5.4: PI-LC-WY-H-01 Membrane coefficient Determination. Native water has an Activity of 0.9803. Confining stress at 3,500 psi.

<table>
<thead>
<tr>
<th>Water Activity $a_w$</th>
<th>Inlet Pressure psi</th>
<th>Outlet Pressure psi</th>
<th>Measured Osmotic Potential $\Delta \pi$ psi</th>
<th>Osmotic Potential $\omega$ %</th>
<th>Calculated Membrane Stress psi</th>
<th>Effective Stress psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9943</td>
<td>3,000</td>
<td>2979.0</td>
<td>-21.0</td>
<td>-282.72</td>
<td>7.428</td>
<td>510.5</td>
</tr>
<tr>
<td>0.9943</td>
<td>2,700</td>
<td>2665.0</td>
<td>-35.0</td>
<td>-282.72</td>
<td>12.384</td>
<td>817.5</td>
</tr>
<tr>
<td>0.9943</td>
<td>2,400</td>
<td>2356.0</td>
<td>-44.0</td>
<td>-282.72</td>
<td>15.584</td>
<td>1,122.0</td>
</tr>
<tr>
<td>0.9943</td>
<td>2,100</td>
<td>2048.8</td>
<td>-51.2</td>
<td>-282.72</td>
<td>18.080</td>
<td>1,425.6</td>
</tr>
<tr>
<td>0.9943</td>
<td>1,600</td>
<td>1552.3</td>
<td>-47.7</td>
<td>-282.72</td>
<td>16.872</td>
<td>1,923.9</td>
</tr>
<tr>
<td>0.9943</td>
<td>1,050</td>
<td>1024.9</td>
<td>-25.1</td>
<td>-282.72</td>
<td>8.878</td>
<td>2,462.6</td>
</tr>
</tbody>
</table>

Figure 5.40: Pierre shale sample PI-LC-WY-H-01 membrane efficiency dependence on effective stress. 0.9803 $a_w$ of native NaCl saturated sample injected with 0.9943 $a_w$ NaCl.
5.6.3 PI-LC-WY-H-01 Elastic properties during shearing

Static measurements of the elastic properties during shearing of sample PI-LC-WY-H-01 can be seen in Figure 5.44. The Young’s modulus is gotten for the straight-line slopes of the data after taking out the pore pressures and can be seen in Figure 5.47. The pore pressure can be seen to rise with axial stress uniformly until the plastic deformation begins to take place. When plastic deformation is observed, the stress level was increased to maintain the integrity of the sample for the 2,000 psi and 3,000 psi radial stress conditions. The sample is allowed to deform and reach the failure point for the last stress level at 3,000 psi. At the 3,000 psi radial stress, the pore pressure build-up and noticeably drops when the sample begins to enter plastic deformation. The pore pressure continuous dissipates beyond this point as the matrix structure reaches the failure point.
Acoustic compressional and shear wave velocities were also measured to calculate the dynamic elastic properties during the entire experiment III. Figure 5.45 shows the calculated P and S wave velocities from the beginning to the end of the experiment III. P and S waves rise steadily as stress conditions elevate. During the shearing stages of the experiment, the compressional velocities can be seen to increase from 5.3 km/s to 5.9 km/s for the radial stress of 3,000 psi. The shear wave velocity initially increases with stress but begins to drop upon further increase with stress. In the last shearing stage of 3,000 psi radial stress, shear wave rises from 2.95 km/s to 3.0 km/s before declining to 2.45 km/s. This reduction in the shear wave is an indication of the shearing of the sample as it loses its integrity during deformation. Figure 5.46(a) and Figure 5.46(b) shows the P and S wave times during shearing stages. Dynamic measurements of Young’s modulus and Poisson’s ratio during the shearing stages can be seen in Figures Figure 5.46(c) and Figure 5.46(d). The dynamic Young’s modulus is seen to initially rise and begin to drop as it reaches its maximum point.
in all three stress levels. It is assumed that Young’s modulus begins to drop at this point when the sample deformation enters the plastic region. The Poisson’s ratio increases steadily with stress for all three confining stress levels. The last confining stage of 3,000 psi begins at 0.27 and reaches up to 0.375.

5.6.4 PI-LC-WY-H-01 Failure measurements

The Mohr-Coulomb failure criterion was used to analyze the failure behavior of the sample. The three stages of confining pressure was simulated similar to the test on sample PI-H-02; 1,500 psi, 2,000 psi, and 3,000 psi. The result of the failure test are tabulated in Table 5.5 and can be seen in Figure 5.48. A Cohesion of 995 psi and an internal friction angle of 48.4 degrees was gotten. The Young’s modulus also increased from 20 GPa in the first stage to 74 GPa in the third stage of shearing (Figure 5.47). The relatively high value for these
parameters can be attributed to the low aspect ratio of the sample. The sample PI-LC-WY-H-01 cylindrical sample was 1-inch in diameter and 0.672 inches in length. The implication of the short length and diameter is that the shearing plane could have been bounded by
(a) Compressional wave velocities during shearing

(b) Transverse wave velocities during shearing velocities

(c) Young’s modulus trend during the shearing stages

(d) Poisson’s ratio trend during the shearing stages

Figure 5.46: PI-LC-WY-H-01 Dynamic property during shearing.

the piston ends during the shearing of the sample. This containment of the shearing plane could have caused the sample to behave much stiffer than expected. Additionally, the high density of the sample (2.998 g/cm³) due to the presence of 31 wt.% siderite, which is an Iron Carbonate (FeCO₃) material, is a possible reason for the high friction angle of the sample. Static and dynamic measurements showing the shear path of the sample PI-LC-WY-H-01 can be seen in Figure 5.44 and Figure 5.46 respectively. The sheared sample with visible failure planes at 25 degrees to the core samples vertical axis can be seen in Figure 5.49.
Figure 5.47: Average Young’s modulus during shearing stages.

\[ y = -0.5013x^2 + 14.02x - 22.387 \]
\[ R^2 = 1 \]

Figure 5.48: PI-LC-WY-H-01 Mohr-Coulomb failure envelope.
Table 5.5: PI-LC-WY-H-01 Mohr-Coulomb CU failure criterion parameters

<table>
<thead>
<tr>
<th>Maximum Axial Stress, $\sigma_a$ (psi)</th>
<th>Effective Max Axial Stress, $\sigma'_a$ (psi)</th>
<th>Radial Stress, $\sigma_r$ (psi)</th>
<th>Effective Radial Stress at $\sigma'_a$, $\sigma'_r$ (psi)</th>
<th>Initial Pore Pressure, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,155.7</td>
<td>4,011.8</td>
<td>1,500</td>
<td>143.9</td>
<td>1,000</td>
</tr>
<tr>
<td>8,380.6</td>
<td>8,021.0</td>
<td>2,000</td>
<td>359.6</td>
<td>1,000</td>
</tr>
<tr>
<td>15,198.6</td>
<td>13,971.0</td>
<td>3,000</td>
<td>1,227.6</td>
<td>1,000</td>
</tr>
</tbody>
</table>

Figure 5.49: PI-LC-WY-H-01 sample after shearing.
CHAPTER 6
IMPLICATION FOR ENHANCED OIL RECOVERY

Water can imbibe into the shale matrix by capillary pressure and osmosis. The osmotic imbibition is strongly governed by the membrane efficiency. In the previous chapter, I showed that the membrane efficiency is a strong function of stress. When water imbibes into the rock matrix, it causes matrix swelling. This reduces the pore size, blocking the transport of solute from moving out of the shale matrix, improving the membrane efficiency. This chapter is intended to show that the change of the membrane efficiency has some contribution to the oil recovery from the rock matrix. The chapter begins with the formulation of the transport model for a three-phases namely water, oil and solute phases, and a geomechanical model accounting for swelling. Predictive case studies are conducted to evaluate the potential of capillary and osmosis imbibition on oil recovery from a single matrix block. In this section, a model has been formulated and validated.

6.1 Model Formulation

Experimental results of solute transport in the Pierre shale have been modeled using an approach that incorporates the differential concentration as the driving mechanism for fluid and pressure transport in shale reservoirs. Diffusion is assumed to cause the chemical interaction and the diffusion coefficient is applied for each solute concentration (Tutuncu et al. 2016). Similar considerations for a flow model incorporating the effects of osmotic pressure to fluid flow in the rock matrix and fractures have been presented in this section. Heterogeneity and anisotropy in unconventional resources strongly influence fluid transportation through these formations which lead to permeability enhancement through hydraulic fracturing. Elastic wave measurements can be used to determine the level of anisotropy and estimation of the pore size and shape (Tutuncu and Mese 2011b). Similarly, wave velocity measurements can be used to estimate permeability anisotropy within the pore spaces as the
pore fluid will cause a reduction in the wave propagation and energy level that will impact both the velocities and attenuation of the waves. Several parameters can be attributed to velocity anisotropy most especially rock-fluid interactions, natural fractures, clay mineral orientation, and stress state.

### 6.2 Transport Model

Clay swelling can be related to the relative humidity or saturation of the pore spaces, therefore a fluid transport model is needed to compute the variation of water saturation and its concentration inside the rock matrix. The transport model by Bui and Tutuncu (2017) has been employed to simulate the contributory effects of osmotic pressure build-up as witnessed in the laboratory experiments. The model is a dual-porosity model that captures the effects of natural fractures present in the core sample. The following are the governing set of equations for different phases in the rock matrix.

For the water phase:

\[
\nabla \left[ \rho_w \frac{k_{wm}}{\mu_w} \nabla (p_{wm} - \gamma_w D_m) - \rho_w \frac{k_{wm}}{\mu_w} \frac{RT_m}{V_w} \nabla c_{sm} \right] + \rho_w \dot{q}_{wm} = \frac{\partial}{\partial t} (S_{wm} \rho_w \phi_m) \tag{6.1}
\]

For oil phase:

\[
\nabla \left[ \frac{k_{om}}{\mu_o} \nabla (p_{om} - \gamma_o D_m) \right] + \rho_o \dot{q}_{om} = \frac{\partial}{\partial t} (S_{om} \rho_o \phi_m) \tag{6.2}
\]

For solute phase:

\[
\nabla \left\{ c_{sm} \rho_s \frac{k_{wm}}{\mu_w} \left( \frac{\rho_w}{\rho_s} \frac{c_{sm}}{1 - c_{sm}} - \omega \right) \left[ \nabla (p_{wm} - \gamma_w D_m) - \omega \frac{RT_m}{V_w} \nabla c_{sm} \right] + \phi_m \rho_s D^{eff} \nabla c_{sm} \right\} + \rho_s \dot{q}_{sm} = \frac{\partial}{\partial t} (S_{wm} \rho_s \phi_m c_{sm}) \tag{6.3}
\]

The m, o, s, w subscripts are used to represent matrix, oil, solute, and water, respectively.

where \( k_{wm} \) is the permeability of water in the matrix; \( k_{om} \) is the permeability of oil in the matrix; \( c_{sm} \) is the solute concentration; \( \dot{q}_{im} \) is the specific flow rate of phase i (oil, solute, water); \( p_{im} \) is the pressure of phase i; \( S_{im} \) is the saturation of phase i; \( \rho_i \) is the density of
phase i; \( \gamma_i \) is the specific gravity of phase i; \( D_m \) is the elevation; \( V_m \) is the partial volume of water; \( D^{\text{eff}} \) is the effective diffusion coefficient of the porous medium; \( T_m \) is the matrix temperature; \( R \) is the universal gas content; \( \phi_m \) is the matrix porosity; \( t \) is the elapsed time; \( \omega \) is the membrane efficiency of the shale matrix.

The extremely tight pore spaces and tortuosity existent in shales slows the diffusivity of solutes in shales. Understanding that the diffusivity of the solute in a porous medium is a slow process, the effective diffusion coefficient is used to represent the diffusivity of solute in the shale matrix rather than the free diffusion coefficient which is more representative of diffusion in the bulk space of solution with larger boundary conditions. The effective diffusion coefficient of the porous medium is defined from free diffusion as:

\[
D^{\text{eff}} = \theta \tau^2 D_0 \tag{6.4}
\]

\[
\theta = 1 - \omega \tag{6.5}
\]

where \( \tau \) is the tortuosity; \( D_0 \) is the diffusivity in free solution; \( \theta \) is the effective solute porosity ratio of the connected porosity to the total porosity.

6.3 Geomechanical Model

For this osmosis study, the swelling behavior in shales is captured by solving the mass transport and geomechanical equations along with the conservation of momentum and conservation of energy equations for the rock matrix. Assuming isothermal conditions, the equation of motion is solved along with the transport equation. The equation of motion for the incremental effective stress and total strain is derived with the stress-strain relationship;

\[
\delta \sigma_{m, \text{eff}} = C_s : \delta \varepsilon \tag{6.6}
\]

where \( C_s \) is stiffness tensor; \( \sigma_{m, \text{eff}} \) is effective stress tensor; \( \varepsilon \) is the total strain tensor.

The total strain tensor is the summation of the volumetric elastic strain and swelling strain;

\[
\varepsilon = \varepsilon_e + \varepsilon_s \tag{6.7}
\]
where $\varepsilon_e$ is the elastic strain; $\varepsilon_s$ is the swelling strain.

The elastic strain as defined in terms of displacement $(u, v, w)$:

$$\varepsilon = \begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{bmatrix} = \begin{bmatrix}
\frac{\partial u}{\partial x} & \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) & \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \\
\frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) & \frac{\partial v}{\partial y} & \frac{1}{2} \left( \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) \\
\frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) & \frac{1}{2} \left( \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) & \frac{\partial w}{\partial z}
\end{bmatrix} \quad (6.8)
$$

The swelling strain tensor can be written as diagonal tensors:

$$\varepsilon_s = \begin{bmatrix}
\varepsilon_{sx} & 0 & 0 \\
0 & \varepsilon_{sy} & 0 \\
0 & 0 & \varepsilon_{sz}
\end{bmatrix} \quad (6.9)
$$

where $\beta$ is the thermal strain tensor; $\varepsilon_i$ is the swelling strain in the $i$ – direction.

Using Voigt notation, the constitutive equation can be written as:

$$\begin{bmatrix}
\sigma_{m,\text{eff}_{xx}} \\
\sigma_{m,\text{eff}_{yy}} \\
\sigma_{m,\text{eff}_{zz}} \\
\sigma_{m,\text{eff}_{xy}} \\
\sigma_{m,\text{eff}_{xz}} \\
\sigma_{m,\text{eff}_{yz}}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{bmatrix} \cdot \begin{bmatrix}
\frac{\partial u_x}{\partial x} + \varepsilon_{sx} \\
\frac{\partial u_y}{\partial y} + \varepsilon_{sy} \\
\frac{\partial u_z}{\partial z} + \varepsilon_{sz} \\
\frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) \\
\frac{1}{2} \left( \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right) \\
\frac{1}{2} \left( \frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z} \right)
\end{bmatrix} \quad (6.10)
$$

where $C_{ij}$ is the elastic coefficient of the rock matrix; $u$ is the displacement vector for rock particles.

$$C_s = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{21} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix} \quad (6.11)$$
For isotropic materials, the stiffness tensor can be written as:

\[
C_S = \frac{E}{(1 + \nu)(1 + 2\nu)} \begin{bmatrix}
1 - \nu & \nu & \nu & 0 & 0 & 0 \\
\nu & 1 - \nu & \nu & 0 & 0 & 0 \\
\nu & \nu & 1 - \nu & 0 & 0 & 0 \\
0 & 0 & 0 & 1 - 2\nu & 0 & 0 \\
0 & 0 & 0 & 0 & 1 - 2\nu & 0 \\
0 & 0 & 0 & 0 & 0 & 1 - 2\nu \\
\end{bmatrix}
\]  \tag{6.12}

where \( E \) is Young’s modulus; \( \nu \) is the Poisson’s ratio

As both oil and water phases exist in the rock matrix, the effective stress exposed to the rock is calculated from the total stresses surrounding the rock and within the pore spaces.

\[
\delta\sigma_{m,\text{eff}} = \delta\sigma_m - \alpha \delta(S_{wm}p_{wm} + S_{om}p_{om}) = \delta\sigma_m - \alpha \delta(p_{wm} + S_{om}p_{cwom}) \tag{6.13}
\]

where \( p_{cwom} \) is the water-oil capillary pressure of the matrix; \( \alpha \) is the Biot’s coefficient tensor.

The Biot’s coefficient tends to be directionally dependent which is a depiction of the anisotropic nature of shales. Thus, using the tensor form of the Biot’s coefficient helps to account for the heterogeneity of the rock formation. The effective stress can then be rewritten as:

\[
\sigma_{m,\text{eff}} = \begin{bmatrix}
\sigma_{mx} & \sigma_{my} & \sigma_{mz} \\
\sigma_{mx} & \sigma_{my} & \sigma_{mz} \\
\sigma_{mx} & \sigma_{my} & \sigma_{mz} \\
\end{bmatrix} - \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz} \\
\end{bmatrix} (p_{wm} + S_{om}p_{cwom}) \tag{6.14}
\]

Substituting Eq. 6.10 into Eq. 6.14 the components of the total stress tensor is obtained in terms of displacement \((u_i)\)

\[
\sigma_{m_{xx}} = C_{11} \frac{\partial u_x}{\partial x} + C_{12} \frac{\partial u_y}{\partial y} + C_{13} \frac{\partial u_z}{\partial z} + (C_{11} + C_{12} + C_{13}) \beta T_m \\
+ (C_{11} \varepsilon_{sx} + C_{12} \varepsilon_{sy} + C_{13} \varepsilon_{sz}) + \alpha_{xx} (p_{w,m} + S_{o,m}p_{cwom}) \tag{6.15}
\]

\[
\sigma_{m_{yy}} = C_{21} \frac{\partial u_x}{\partial x} + C_{22} \frac{\partial u_y}{\partial y} + C_{23} \frac{\partial u_z}{\partial z} + (C_{21} + C_{22} + C_{23}) \beta T_m \\
+ (C_{21} \varepsilon_{sx} + C_{22} \varepsilon_{sy} + C_{23} \varepsilon_{sz}) + \alpha_{yy} (p_{w,m} + S_{o,m}p_{cwom}) \tag{6.16}
\]
\[ \sigma_{mzz} = C_{31} \frac{\partial u_x}{\partial x} + C_{32} \frac{\partial u_y}{\partial y} + C_{33} \frac{\partial u_z}{\partial z} + (C_{31} + C_{32} + C_{33}) \beta T_m \]
\[ + (C_{31} \varepsilon_{sx} + C_{32} \varepsilon_{sy} + C_{33} \varepsilon_{sz}) + \alpha_{zz} (p_{w,m} + S_{o,m} p_{cwom}) \]  
(6.17)

\[ \sigma_{myy} = \frac{C_{44}}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) + \alpha_{xy} (p_{w,m} + S_{o,m} p_{cwom}) \]  
(6.18)

\[ \sigma_{mzz} = \frac{C_{55}}{2} \left( \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right) + \alpha_{yz} (p_{w,m} + S_{o,m} p_{cwom}) \]  
(6.19)

\[ \sigma_{mzx} = \frac{C_{66}}{2} \left( \frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z} \right) + \alpha_{zx} (p_{w,m} + S_{o,m} p_{cwom}) \]  
(6.20)

The equation of motion for the rock matrix or matrix deformation can be written as:

\[ \nabla \cdot \sigma_m + F = \rho_m \frac{dv_m}{dt} \]  
(6.21)

where \( F \) is the external force vector; \( v_m \) is the matrix velocity; \( \rho_m \) is the matrix density.

During the slow deformation process of small particles, the acceleration term can be ignored. The equilibrium equation can then be written in terms of incremental stress as:

\[ \nabla \cdot \sigma_m = 0 \equiv \begin{cases} \frac{\partial \delta \sigma_{mxx}}{\partial x} + \frac{\partial \delta \sigma_{myx}}{\partial y} + \frac{\partial \delta \sigma_{mzx}}{\partial z} = 0 \\ \frac{\partial \delta \sigma_{myy}}{\partial x} + \frac{\partial \delta \sigma_{mxy}}{\partial y} + \frac{\partial \delta \sigma_{myz}}{\partial z} = 0 \\ \frac{\partial \delta \sigma_{mzx}}{\partial x} + \frac{\partial \delta \sigma_{mzy}}{\partial y} + \frac{\partial \delta \sigma_{mzz}}{\partial z} = 0 \end{cases} \]  
(6.22)

In 3-D Cartesian coordinates, the substituted set of equations 6.14 and 6.22 above becomes:

\[ \frac{\partial}{\partial x} \left[ C_{11} \frac{\partial \delta u_x}{\partial x} + C_{12} \frac{\partial \delta u_y}{\partial y} + C_{13} \frac{\partial \delta u_z}{\partial z} \right] + \frac{\partial}{\partial y} \left[ \frac{C_{44}}{2} \left( \frac{\partial \delta u_x}{\partial y} + \frac{\partial \delta u_y}{\partial x} \right) \right] 
\[ + \frac{\partial}{\partial z} \left[ \frac{C_{66}}{2} \left( \frac{\partial \delta u_z}{\partial x} + \frac{\partial \delta u_x}{\partial z} \right) \right] \]
\[ = -\beta (C_{11} + C_{12} + C_{13}) \frac{\partial \delta T_m}{\partial x} - \frac{\partial}{\partial x} \left( C_{11} \delta \varepsilon_{sx} + C_{12} \delta \varepsilon_{sy} + C_{13} \delta \varepsilon_{sz} \right) \]
\[ - \alpha_{xx} \frac{\partial}{\partial x} [\delta p_{w,m} + \delta (S_{o,m} p_{cwom})] \]
\[ - \alpha_{yz} \frac{\partial}{\partial y} [\delta p_{w,m} + \delta (S_{o,m} p_{cwom})] - \alpha_{zx} \frac{\partial}{\partial z} [\delta p_{w,m} + \delta (S_{o,m} p_{cwom})] \]  
(6.23)
\[
\frac{\partial}{\partial x} \left[ \frac{C_{44}}{2} \left( \frac{\partial \delta u_x}{\partial y} + \frac{\partial \delta u_y}{\partial x} \right) \right] + \frac{\partial}{\partial y} \left[ C_{21} \frac{\partial \delta u_x}{\partial x} + C_{22} \frac{\partial \delta u_y}{\partial y} + C_{23} \frac{\partial \delta u_z}{\partial z} \right] \\
+ \frac{\partial}{\partial z} \left[ C_{55} \frac{1}{2} \left( \frac{\partial \delta u_y}{\partial z} + \frac{\partial \delta u_z}{\partial y} \right) \right] \\
= -\beta \left( C_{21} + C_{22} + C_{23} \right) \frac{\partial \delta T_m}{\partial y} - \frac{\partial}{\partial y} \left( \frac{C_{21} \delta \varepsilon_{sx} + C_{22} \delta \varepsilon_{sy} + C_{23} \delta \varepsilon_{sz}}{\partial T_m} \right) \\
- \alpha_{xy} \frac{\partial}{\partial x} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] \\
- \alpha_{yz} \frac{\partial}{\partial y} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] - \alpha_{zz} \frac{\partial}{\partial z} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] \quad (6.24)
\]

\[
\frac{\partial}{\partial x} \left[ \frac{C_{66}}{2} \left( \frac{\partial \delta u_x}{\partial y} + \frac{\partial \delta u_y}{\partial x} \right) \right] + \frac{\partial}{\partial y} \left[ \frac{C_{55}}{2} \left( \frac{\partial \delta u_y}{\partial z} + \frac{\partial \delta u_z}{\partial y} \right) \right] \\
+ \frac{\partial}{\partial z} \left[ \frac{C_{31}}{2} \frac{\partial \delta u_x}{\partial x} + \frac{C_{32}}{2} \frac{\partial \delta u_y}{\partial y} + \frac{C_{33}}{2} \frac{\partial \delta u_z}{\partial z} \right] \\
= -\beta \left( C_{31} + C_{32} + C_{33} \right) \frac{\partial \delta T_m}{\partial z} - \frac{\partial}{\partial z} \left( \frac{C_{31} \delta \varepsilon_{sx} + C_{32} \delta \varepsilon_{sy} + C_{33} \delta \varepsilon_{sz}}{\partial T_m} \right) \\
- \alpha_{xz} \frac{\partial}{\partial x} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] \\
- \alpha_{yz} \frac{\partial}{\partial y} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] - \alpha_{zz} \frac{\partial}{\partial z} \left[ \delta p_{w,m} + \delta \left( S_{o,m} \rho_{cwom} \right) \right] \quad (6.25)
\]

6.3.1 Matrix geomechanical changes - Swelling constitutive model

- Strain related to water content

In modeling reservoir flow, the shale swelling behavior has to be taken into account under different salinity fluids and stress conditions. Bui and Tutuncu (2018) presented a step by step approach to modeling the mass transport physics and mechanical interaction in unconventional reservoirs by modeling the mass exchange and mechanical interaction between rock matrix and surrounding natural fractures. The validation of the model can also be found in the paper. Most importantly, the swelling constitutive model is incorporated into the transport and rock deformation equation to fully represent rock fluid interactions experienced. Likewise, Young’s modulus is also related to moisture content is obtained from experiments and used with strain relationship.
Similar to Bui and Tutuncu (2018) approach, we obtain a swelling correlation in the form below

Sample PI-H-02:

\[ \varepsilon_{sh} = K_1 \Delta S_w + K_2 \Delta S_w^2 = [0.00375 S_w + 0.004339 S_w^2] \] (6.26)

Sample PI-LC-WY-H-01:

\[ \varepsilon_{sh} = K_1 \Delta S_w + K_2 \Delta S_w^2 = [0.004678 S_w + 0.007309 S_w^2] \] (6.27)

where \( K_1 \) and \( K_2 \) are expansion coefficients determined from the moisture injection and swelling relationship from the experiment; \( \varepsilon_{sh} \) is the swelling vertical strain captured from the experimental system, and \( \Delta S_w \) is the change in water content in terms of the percentage weight of the pore volume. The vertical swelling strain may be obtained from the horizontal strain as

\[ \varepsilon_{sv} = f \varepsilon_{sh} \] (6.28)

where \( f \) is a constant \( (0 \leq f^{-1} \leq 1) \).

Young’s modulus related to effective stress; laboratory test results capturing the modification of the samples stiffness under saturated and under saturated conditions are discussed in Chapter 5. These effects are used to compute Young’s modulus based on effective stress. The Young’s moduli in the equations below are in GPa.

Sample PI-H-02:

\[ E_{dyn} = E_0 + K_3 \Delta S_w = (12.52 - 2.395 \Delta S_w) \] (6.29)

Sample PI-LC-WY-H-01:

\[ E_{stat} = E_0 + K_3 \Delta S_w = (20.198 - 2.160 \Delta S_w) \] (6.30)
6.3.2 Permeability and porosity changes due to swelling

Understandably, the permeability and porosity of a shale matrix will change depending on the clay content and type of clay present. As the cation exchange capacity lowers, the influence on porosity and permeability will decrease. Therefore, swelling clays will have the biggest influence on permeability and porosity change followed by illite and kaolinite. As seen in the experimental section, both air and liquid permeabilities were calculated from results obtained from stress-dependent permeability measurements during tri-axial measurement. Nitrogen was used for the air permeability measurements while sodium chloride brine at different salinities, depending on the osmosis test conducted, was used to measure the liquid permeability at different stress conditions. Calculating liquid permeabilities from either steady-state or unsteady state (pulse-decay) measurements takes a large amount of time to compute. The steady-state is reached after a significantly long period based on the tortuosity of the pore spaces and anisotropic stress conditions of the shale matrix. Similarly, monitoring the decay in pulse for the unsteady state measuring can also take several days for each measurement. As observed in the experimental section, the condition for steady-state and adequate pulse decay can take up to 3 days to be achieved for permeability measurements in shales. The brine salinity also contributes to the permeability calculation. As swelling increases with lower brine concentration, pore spaces are narrowed which causes further permeability reduction. This situation adds to the time needed to achieve the condition of steady-state or adequate pulse decay depending on which permeability measurement is used.

Air permeability measurements are much faster relatively where conditions for steady-state conditions can be achieved within an hour. For unsteady state air permeability calculations, the pulse decline is relatively rapid compared to the liquid permeability test. Due to this reason, the porosity and permeability changes for the model computation is based on the laboratory results of nitrogen permeability. It is important to note that the effective permeabilities used for the shale matrix are still based on liquid permeabilities but the changes in permeability due to effective stress changes are base on the nitrogen permeability
6.3.3 Permeability and porosity changes due to effective stress changes

Based on permeability results, permeability and porosity changes for the Pierre shale matrix portrays a linear relationship between permeability and effective stress after undergoing stress loading cycles. In relation to an actual reservoir constantly exposed to surrounding stress conditions, this correlation can effectively be used to depict the behavior of the formation under effective stress changes. Raghavan and Chin (2004) primarily investigated the effect of stress-dependent permeability relationships on productivity based on three different rock types exhibiting exponential, linear and a power-law relationship with effective stress and porosity changes. Changes in mechanical properties of the rock, such as the Poisson ratio and bulk modulus contribute to the loss in the level of reservoir productivity. The Pierre shale samples tested in this study were determined to depict exponential and linear relationships with effective stress and their permeability changes have therefore been model according to this observation. The following correlation corresponding from laboratory observation has been incorporated into the geomechanical model.

Exponential relationship:

\[
\begin{align*}
  k_f &= k_{fi} e^{-c_{fk} \Delta \sigma'_{eff}} \\
  \phi_f &= \phi_{fi} e^{-c_{fk} \Delta \sigma'_{eff}}
\end{align*}
\]

(6.31)

where \( k_{fi} \) is the initial fracture permeability at mean effective stress; \( \Delta \sigma'_{eff} \) is the variation in effective stress; \( \phi_{fi} \) is the initial porosity at mean effective stress of \( \Delta \sigma'_{eff} = 0 \); \( c_{fk} \) is the fracture permeability coefficient, \( psi^{-1} \); \( \Delta \sigma'_{eff} = 0 \) is determined from experimental data; \( c_{fk} \) is the fracture porosity coefficient, \( psi^{-1} \).

Linear relationship:

\[
\begin{align*}
  k_f &= k_{fi} (1.0 - m.\Delta \sigma'_{eff}) \\
  \phi_f &= \phi_{fi} (1.0 - m.\Delta \sigma'_{eff})
\end{align*}
\]

(6.32)

where \( m \) is a parameter determined from experimental data.
The results of both correlations have been investigated and reported in the result section.

6.4 Transport Model Validation

This section describes the development of the transport model, fully discretized and validated.

6.4.1 Phase Pressure in the Matrix

The solution of the mass transport equation is obtained by refining the grid size on each matrix block. The solution of this equation gives us the saturation of fluid, oil and water, and phase pressures in the rock matrix. The total pressure equation for the matrix block is solved for oil phase pressure or water phase pressure depending on the wettability of the matrix block. For simplicity, the numerical solution of the matrix total pressure equation for water-wetted rock is presented here. The solution to this equation for oil-wetted rock is similar. From the matrix total pressure equation, we obtain the algebraic equation as:

\[
M_{xb}P_{wm_i,j,k}^{n+1} + M_{yb}P_{wm_i,j-1,k}^{n+1} + M_{zb}P_{wm_{i,j,k-1}}^{n+1} + M_{m}P_{wm_{i,j,k}}^{n+1} + M_{xf}P_{wm_{i+1,j,k}}^{n+1} + M_{yf}P_{wm_{i,j+1,k}}^{n+1} + M_{zf}P_{wm_{i,j,k+1}}^{n+1} = M_{xR} \tag{6.33}
\]

where

\[
M_{xb} = \frac{1}{\Delta x_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta x} + \frac{k_m \lambda_{wm}}{\Delta x} \right)_{i-\frac{1}{2}, j, k} \tag{6.34}
\]

\[
M_{xf} = \frac{1}{\Delta x_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta x} + \frac{k_m \lambda_{wm}}{\Delta x} \right)_{i+\frac{1}{2}, j, k} \tag{6.35}
\]

\[
M_{yb} = \frac{1}{\Delta y_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta y} + \frac{k_m \lambda_{wm}}{\Delta y} \right)_{i, j-\frac{1}{2}, k} \tag{6.36}
\]

\[
M_{yf} = \frac{1}{\Delta y_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta y} + \frac{k_m \lambda_{wm}}{\Delta y} \right)_{i, j+\frac{1}{2}, k} \tag{6.37}
\]

\[
M_{zb} = \frac{1}{\Delta z_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta z} + \frac{k_m \lambda_{wm}}{\Delta z} \right)_{i, j, k-\frac{1}{2}} \tag{6.38}
\]
\[ M_{zf} = \frac{1}{\Delta z_{i,j,k}} \left( \frac{k_m \lambda_{om}}{\Delta x} + \frac{k_m \lambda_{wm}}{\Delta z} \right)^n_{i,j,k+\frac{1}{2}} \]  

\[ M_m = -\left\{ M_{xb} + M_{xf} + M_{yb} + M_{yf} + M_{zb} + M_{zf} + \frac{(1 - \epsilon_{vm})}{\Delta t_m} \left[ \phi_m c_{tm} \right]_{i,j,k}^n \right\} \]  

\[ M_{xR} = \frac{1}{\Delta x_{i,j,k}} \left\{ \left( \frac{k_m \lambda_{om}}{\Delta x} \right)_{i+\frac{1}{2},j,k}^n \left[ p_{cwom_{i,j,k}}^{n+1} - p_{cwom_{i+1,j,k}}^{n+1} + \gamma_{o_{i,j,k}} \left( D_{i+1,j,k} - D_{i,j,k} \right) \right] \right\} + \frac{1}{\Delta y_{i,j,k}} \left\{ \left( \frac{k_m \lambda_{om}}{\Delta y} \right)_{i,j+\frac{1}{2},k}^n \left[ p_{cwom_{i,j,k}}^{n+1} - p_{cwom_{i,j+1,k}}^{n+1} + \gamma_{o_{i,j,k}} \left( D_{i,j+1,k} - D_{i,j,k} \right) \right] \right\} + \frac{1}{\Delta z_{i,j,k}} \left\{ \left( \frac{k_m \lambda_{om}}{\Delta z} \right)_{i,j,k+\frac{1}{2}}^n \left[ p_{cwom_{i,j,k}}^{n+1} - p_{cwom_{i,j,k+1}}^{n+1} + \gamma_{o_{i,j,k}} \left( D_{i,j,k+1} - D_{i,j,k} \right) \right] \right\} \]

\[ \frac{\omega R T_m}{V_w \Delta x_{i,j,k}} \left[ \left( \frac{k_m \lambda_{wm}}{\Delta x} \right)_{i+\frac{1}{2},j,k}^n \left( c_{sm_{i+1,j,k}}^n - c_{sm_{i,j,k}}^n \right) \right] - \left[ q_{wm} + \hat{q}_{om} \right]_{i,j,k}^n - \left[ (1 - \epsilon_{vm}) \phi_m c_{tm} \right]_{i,j,k}^n \frac{p_{cwom_{i,j,k}}^{n+1} - \phi_m c_{tm}^n}{\Delta t_m} \]  

\[ \frac{\omega R T_m}{V_w \Delta y_{i,j,k}} \left[ \left( \frac{k_m \lambda_{wm}}{\Delta y} \right)_{i,j+\frac{1}{2},k}^n \left( c_{sm_{i,j+1,k}}^n - c_{sm_{i,j,k}}^n \right) \right] \]  

\[ \frac{\omega R T_m}{V_w \Delta z_{i,j,k}} \left[ \left( \frac{k_m \lambda_{wm}}{\Delta z} \right)_{i,j,k+\frac{1}{2}}^n \left( c_{sm_{i,j,k+1}}^n - c_{sm_{i,j,k}}^n \right) \right] \]

\[ \frac{\omega R T_m}{V_w \Delta z_{i,j,k}} \left[ \left( \frac{k_m \lambda_{wm}}{\Delta z} \right)_{i,j,k+\frac{1}{2}}^n \left( c_{sm_{i,j,k+1}}^n - c_{sm_{i,j,k}}^n \right) \right] \]

6.4.2 Phase saturation in matrix

The derivations of the phase saturation equations are described in the following sections.
6.4.2.1 Water saturation

Matrix water saturation is calculated from the continuity equation for the water phase in the matrix (Eq. 6.1) as;

\[
\nabla \cdot \left[ \frac{k_{wm}}{\mu_w} \nabla (p_{wm} - \gamma_w D_m) \right] - \nabla \cdot \left( \frac{k_{wm}}{V_w \mu_w} \omega RT_m \nabla c_{sm} \right) + \dot{q}_{wm} = \frac{\partial}{\partial t} \left[ (1 - \epsilon_{vm}) S_{wm} \phi_m \right] \quad \text{(6.42)}
\]

\[
S_{wm,i,j,k}^{n+1} = (S_{wm})_{i,j,k}^n + \frac{\Delta t_m}{\left[(1 - \epsilon_{vm}) \phi_m\right]_{i,j,k}^n} \left\{ \begin{array}{l}
\frac{1}{\Delta x_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{p_{wm,i,j,k+1}^{n+1} - p_{wm,i,j,k}^{n+1} - \gamma_{w,i,j,k} (D_{i+1,j,k} - D_{i,j,k})}{\Delta x_{i+\frac{1}{2},j,k}} \right] \\
- \frac{1}{\Delta y_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{p_{wm,i-1,j,k}^{n+1} - p_{wm,i,j,k}^{n+1} - \gamma_{w,i,j,k} (D_{i,j,k} - D_{i-1,j,k})}{\Delta y_{i,j+\frac{1}{2},k}} \right] \\
\frac{1}{\Delta z_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{p_{wm,i,j,k-1}^{n+1} - p_{wm,i,j,k}^{n+1} - \gamma_{w,i,j,k} (D_{i,j,k} - D_{i,j,k-1})}{\Delta z_{i,j,k+\frac{1}{2}}} \right] \\
- \frac{\Delta t_m}{\left[(1 - \epsilon_{vm}) \phi_m\right]_{i,j,k}^n} \left\{ \begin{array}{l}
\frac{1}{\Delta x_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{c_{wsm,i,j,k}^{n} - c_{wsm,i+1,j,k}^{n}}{\Delta x_{i+\frac{1}{2},j,k}} \right] \\
- \frac{1}{\Delta y_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{c_{wsm,i,j,k+1}^{n} - c_{wsm,i,j,k}^{n}}{\Delta y_{i,j+\frac{1}{2},k}} \right] \\
\frac{1}{\Delta z_{i,j,k}} \left[ k_{wm} \lambda_{wm} \frac{c_{wsm,i,j,k+1}^{n} - c_{wsm,i,j,k}^{n}}{\Delta z_{i,j,k+\frac{1}{2}}} \right] \\
\end{array} \right\} \quad \text{(6.43)}
\]

6.4.2.2 Oil saturation

The oil saturation in the rock matrix is calculated from water saturation in rock matrix as;

\[\text{as;}\]
Solute Concentration in the Rock Matrix

Solute concentration in rock matrix is calculated from continuity equation for solute in matrix (Eq. 6.3) as:

\[
c_{sm_{i,j,k}}^{n+1} = \frac{\hat{q}_{sm_{i,j,k}} \Delta t}{(1 - \epsilon_v m) \phi_{m_{i,j,k}} S_{wm_{i,j,k}} \rho_s} + \frac{[S_{w,m} c_{sm}]^{n}_{i,j,k}}{S_{w,m_{i,j,k}}} [S_{wm_{i,j,k}}^{n+1} - S_{wm_{i,j,k}}^{n} - \gamma_w (D_{i,j,k} - D_{i,j,k-1})]
\]

\[
+ T_{x_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta x} \right]^{n}_{i+\frac{1}{2},j+\frac{1}{2}} \left[ c_{sm_{i+1,j,k}}^{n} - c_{sm_{i,j,k}}^{n} \right] + T_{x_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta x} \right]^{n}_{i-\frac{1}{2},j+\frac{1}{2}} \left[ c_{sm_{i,j,k}}^{n} - c_{sm_{i-1,j,k}}^{n} \right]
\]

\[
- T_{y_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta y} \right]^{n}_{i+j+\frac{1}{2}} \left[ c_{sm_{i,j+1,k}}^{n} - c_{sm_{i,j,k}}^{n} \right] + T_{y_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta y} \right]^{n}_{i-j+\frac{1}{2}} \left[ c_{sm_{i,j,k}}^{n} - c_{sm_{i+1,j,k}}^{n} \right]
\]

\[
- T_{z_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta z} \right]^{n}_{i,j+k+\frac{1}{2}} \left[ c_{sm_{i,j,k+1}}^{n} - c_{sm_{i,j,k}}^{n} \right] + T_{z_{i,j,k}} \left[ \frac{\omega R T_m}{V_w \Delta z} \right]^{n}_{i,j+k-\frac{1}{2}} \left[ c_{sm_{i,j,k}}^{n} - c_{sm_{i,j,k-1}}^{n} \right]
\]

\[
- C_x \left[ \frac{\phi_m D_{eff}}{\Delta x} \right]^{n}_{i+\frac{1}{2},j+\frac{1}{2}} \left[ c_{s_{i+1,j,k}}^{n} - c_{s_{i,j,k}}^{n} \right] - \left( \frac{\phi_m D_{eff}}{\Delta x} \right) \left[ \left[ c_{s_{i,j,k}}^{n} - c_{s_{i-1,j,k}}^{n} \right] \right]
\]

\[
- C_y \left[ \frac{\phi_m D_{eff}}{\Delta y} \right]^{n}_{i+j+\frac{1}{2}} \left[ c_{s_{i,j+1,k}}^{n} - c_{s_{i,j,k}}^{n} \right] - \left( \frac{\phi_m D_{eff}}{\Delta y} \right) \left[ \left[ c_{s_{i,j,k}}^{n} - c_{s_{i+1,j,k}}^{n} \right] \right]
\]

\[
- C_z \left[ \frac{\phi_m D_{eff}}{\Delta z} \right]^{n}_{i,j+k+\frac{1}{2}} \left[ c_{s_{i,j,k+1}}^{n} - c_{s_{i,j,k}}^{n} \right] - \left( \frac{\phi_m D_{eff}}{\Delta z} \right) \left[ \left[ c_{s_{i,j,k}}^{n} - c_{s_{i,j,k-1}}^{n} \right] \right]
\]

where
\[ C_x = \frac{\Delta t}{[(1 - \epsilon_{vm}) \phi_{m1,i,j,k}] \Delta x_{i,j,k} S_{w,m_{i,j,k}}^{n+1} \rho_s} \rho_w \]  
\[ (6.46) \]

\[ C_y = \frac{\Delta t}{[(1 - \epsilon_{vm}) \phi_{m1,i,j,k}] \Delta y_{i,j,k} S_{w,m_{i,j,k}}^{n+1} \rho_s} \rho_w \]  
\[ (6.47) \]

\[ C_z = \frac{\Delta t}{[(1 - \epsilon_{vm}) \phi_{m1,i,j,k}] \Delta z_{i,j,k} S_{w,m_{i,j,k}}^{n+1} \rho_s} \rho_w \]  
\[ (6.48) \]

\[ T_{x,i,j,k} = C_x \left[ c_{sm} \frac{k_m \lambda_{wm}}{\Delta x} \left( \omega + \frac{\rho_w}{\rho_s} c_{sm} \right) \right]^{n}_{i+\frac{1}{2},j,k} \]  
\[ (6.49) \]

\[ T_{y,i,j,k} = C_y \left[ c_{sm} \frac{k_m \lambda_{wm}}{\Delta y} \left( \omega + \frac{\rho_w}{\rho_s} c_{sm} \right) \right]^{n}_{i,j+\frac{1}{2},k} \]  
\[ (6.50) \]

\[ T_{z,i,j,k} = C_z \left[ c_{sm} \frac{k_m \lambda_{wm}}{\Delta z} \left( \omega + \frac{\rho_w}{\rho_s} c_{sm} \right) \right]^{n}_{i,j,k+\frac{1}{2}} \]  
\[ (6.51) \]

### 6.4.4 Volume Flux Rate

The volumetric exchange rate is computed at every time step by calculating the flow rate through the node on the boundary as:

\[
\begin{align*}
q_{w,m_{1,j,k}}^{n+1} &= A_{1,j,k} \left[ (k_{wm} \lambda_{wm}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta x_{i,j,k}} \right] - \left( \frac{k_{wm} \omega}{V_{wm} \mu_w} RT_m \right) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta x_{i,j,k}} \\
q_{o,m_{1,j,k}}^{n+1} &= A_{1,j,k} \left[ (k_{om} \lambda_{om}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta x_{i,j,k}} \right] \\
q_{w,m_{i,1,k}}^{n+1} &= A_{i,1,k} \left[ (k_{wm} \lambda_{wm}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta y_{i,j,k}} \right] - \left( \frac{k_{wm} \omega}{V_{wm} \mu_w} RT_m \right) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta x_{i,j,k}} \\
q_{o,m_{i,1,k}}^{n+1} &= A_{i,1,k} \left[ (k_{om} \lambda_{om}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta y_{i,j,k}} \right] \\
q_{w,m_{i,j,1}}^{n+1} &= A_{i,j,1} \left[ (k_{wm} \lambda_{wm}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta z_{i,j,k}} \right] - \left( \frac{k_{wm} \omega}{V_{wm} \mu_w} RT_m \right) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta x_{i,j,k}} \\
q_{o,m_{i,j,1}}^{n+1} &= A_{i,j,1} \left[ (k_{om} \lambda_{om}) \frac{n_{i,j,k}^{n+1} - n_{i,j,k}^n}{\Delta z_{i,j,k}} \right]
\end{align*}
\]  
\[ (6.52) \]

where \( A \) is area; \( q \) is mass flux rate; \( n' \) is the step \( n' \) of the reservoir scale simulation.
6.4.5 Solution of Geomechanical Equations

The finite difference equation for equation of motion in x-direction is:

\[
X_{bmm}\delta u_{x,i,j-1,k} + X_{mbm}\delta u_{x,i,j-1,k} + X_{mmn}\delta u_{x,i,j,k} + X_{fmm}\delta u_{x,i+1,j,k} + X_{mmf}\delta u_{x,i,j+1,k} \\
+ X_{mmf}\delta u_{x,i,j+1,k+1} + Y_{bmm}\delta u_{y,i-1,j,k} + Y_{fmm}\delta u_{y,i+1,j,k+1} \\
+ Y_{fmm}\delta u_{y,i+1,j,k+1} + Y_{fmm}\delta u_{y,i+1,j,k+1} + Y_{fmm}\delta u_{y,i+1,j,k+1} = RX_{i,j,k} \tag{6.53}
\]

where:

\[
X_{bmm} = \frac{1}{2\Delta x_{i,j,k}} \left( \frac{C_{11}}{\Delta x} \right)_{i-\frac{1}{2},j,k} ;
X_{mbm} = \frac{1}{2\Delta y_{i,j,k}} \left( \frac{C_{44}}{\Delta y} \right)_{i,j-\frac{1}{2},k} \\
X_{mmn} = -\frac{1}{2\Delta x_{i,j,k}} \left[ \left( \frac{C_{11}}{\Delta x} \right)_{i+\frac{1}{2},j,k} - \left( \frac{C_{11}}{\Delta x} \right)_{i-\frac{1}{2},j,k} \right] \\
- \frac{1}{2\Delta z_{i,j,k}} \left[ \frac{C_{66}}{\Delta z} \right]_{i,j,k+\frac{1}{2}} - \frac{1}{2\Delta z_{i,j,k+\frac{1}{2}}} \left[ \frac{C_{66}}{\Delta z} \right]_{i,j,k-\frac{1}{2}} \\
X_{fmm} = \frac{1}{2\Delta x_{i,j,k}} \left( \frac{C_{11}}{\Delta x} \right)_{i+\frac{1}{2},j,k} ;
X_{mf} = \frac{1}{2\Delta y_{i,j,k}} \left( \frac{C_{44}}{\Delta y} \right)_{i,j+\frac{1}{2},k} \\
X_{mmf} = \frac{1}{2\Delta z_{i,j,k}} \left( \frac{C_{66}}{\Delta z} \right)_{i,j,k+\frac{1}{2}} \tag{6.54}
\]

\[
Y_{bmm} = \frac{2 (C_{12})_{i-1,j,k} + (C_{44})_{i,j-1,k}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right)} \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right) \tag{6.55}
\]

\[
Y_{fmm} = \frac{-2 (C_{12})_{i-1,j,k} - (C_{44})_{i,j+1,k}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right)} \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right) \tag{6.56}
\]

\[
Y_{fmm} = \frac{-2 (C_{12})_{i+1,j,k} + (C_{44})_{i,j+1,k}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right)} \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right) \tag{6.57}
\]

\[
Y_{fmm} = \frac{-2 (C_{13})_{i-1,j,k} - (C_{66})_{i,j,k+1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right)} \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right) \tag{6.58}
\]

\[
Z_{bmm} = \frac{-2 (C_{13})_{i-1,j,k} - (C_{66})_{i,j,k+1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right)} \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right) \tag{6.59}
\]

\[\]
The finite difference equation for equation of motion in y-direction is:

\[
Z_{bmb} = \frac{2 (C_{13})_{i-1,j,k} + (C_{66})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right) \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta z_{i,j-\frac{1}{2},k} \right)} \tag{6.60}
\]

\[
Z_{fmb} = \frac{-2 (C_{13})_{i+1,j,k} - (C_{66})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right) \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta z_{i,j-\frac{1}{2},k} \right)} \tag{6.61}
\]

\[
Z_{fmb} = \frac{2 (C_{13})_{i,j,k+1} + (C_{66})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right) \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta z_{i,j-\frac{1}{2},k} \right)} \tag{6.62}
\]

\[
RX_{i,j,k} = \frac{-(C_{11} \delta \epsilon_{sx})_{i+1,j,k} - (C_{11} \delta \epsilon_{sx})_{i,j,k}}{\Delta x_{i,j,k}} - \frac{(C_{12} \delta \epsilon_{sy})_{i+1,j,k} - (C_{12} \delta \epsilon_{sy})_{i-1,j,k}}{\Delta x_{i,j,k}} - \frac{(C_{13} \delta \epsilon_{sz})_{i+1,j,k} - (C_{13} \delta \epsilon_{sz})_{i,j,k}}{\Delta x_{i,j,k}}
\]

\[
\frac{\alpha_{xx}}{\Delta x} \left[ \delta p_{w,m_{i+\frac{1}{2},j,k}} - \delta p_{w,m_{i-\frac{1}{2},j,k}} + \delta (S_{o,m} P_{cwom})_{i+1,j,k} - \delta (S_{o,m} P_{cwom})_{i-\frac{1}{2},j,k} \right] - \frac{\alpha_{yy}}{\Delta y} \left[ \delta p_{w,m_{i+\frac{1}{2},j,k}} - \delta p_{w,m_{i-\frac{1}{2},j,k}} + \delta (S_{o,m} P_{cwom})_{i,j+\frac{1}{2},k} - \delta (S_{o,m} P_{cwom})_{i,j-\frac{1}{2},k} \right]
\]

\[
- \frac{\alpha_{zz}}{\Delta z} \left[ \delta p_{w,m_{i+\frac{1}{2},j,k}} - \delta p_{w,m_{i-\frac{1}{2},j,k}} + \delta (S_{o,m} P_{cwom})_{i,j+\frac{1}{2},k} - \delta (S_{o,m} P_{cwom})_{i,j-\frac{1}{2},k} \right] \tag{6.63}
\]

The finite difference equation for equation of motion in y-direction is:

\[
X_{bblm} \delta u_{x_{i-1,j-1,k}} + X_{fbm} \delta u_{x_{i+1,j+1,k}} + X_{fmb} \delta u_{x_{i+1,j-1,k}} + X_{bfm} \delta u_{x_{i-1,j+1,k}} + Y_{mbm} \delta u_{y_{i-1,j,k}} + Y_{ffm} \delta u_{y_{i+1,j+1,k}} + Y_{fmb} \delta u_{y_{i+1,j-1,k}} + Y_{bmf} \delta u_{y_{i-1,j+1,k}} + Y_{mmf} \delta u_{y_{i,j+1,k+1}} + Y_{mmn} \delta u_{y_{i,j-1,k+1}} + Z_{mff} \delta u_{z_{i,j+1,k+1}} + Z_{mmb} \delta u_{z_{i,j-1,k+1}} + Z_{bbm} \delta u_{z_{i,j+1,k-1}} + Z_{mbf} \delta u_{z_{i,j+1,k-1}} + Z_{mmf} \delta u_{z_{i,j+1,k+1}} + Z_{mmn} \delta u_{z_{i,j+1,k+1}} + Z_{mmm} \delta u_{z_{i,j+1,k+1}} = RY_{i,j,k} \tag{6.64}
\]

where:

\[
X_{bblm} = \frac{(C_{44})_{i-1,j,k} + 2 (C_{21})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right) \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right)} \tag{6.65}
\]

\[
X_{bbm} = \frac{(C_{44})_{i-1,j,k} + 2 (C_{21})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k} \right) \left( \Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k} \right)} \tag{6.66}
\]
\[ X_{f_m} = \frac{(C_{44})_{i+1,j,k} + 2(C_{21})_{i,j+1,k}}{2\left(\Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k}\right)} \left(\Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k}\right) \] (6.67)

\[ X_{f_m} = -\frac{(C_{44})_{i+1,j,k} - 2(C_{21})_{i,j-1,k}}{2\left(\Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k}\right)} \left(\Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k}\right) \] (6.68)

\[ X_{b_m} = \frac{(C_{21})_{i,j+1,k} - 2(C_{44})_{i-1,j,k}}{2\left(\Delta x_{i+\frac{1}{2},j,k} + \Delta x_{i-\frac{1}{2},j,k}\right)} \left(\Delta y_{i,j+\frac{1}{2},k} + \Delta y_{i,j-\frac{1}{2},k}\right) \] (6.69)

\[ Y_{b_m} = \frac{1}{2\Delta x_{i,j,k}} \left(\frac{C_{44}}{\Delta x}\right)_{i-\frac{1}{2},j,k} ; \quad Y_{m_f} = \frac{1}{2\Delta x_{i,j,k}} \left(\frac{C_{44}}{\Delta x}\right)_{i+\frac{1}{2},j,k} ; \quad Y_{m_m} = \frac{1}{2\Delta z_{i,j,k}} \left(\frac{C_{22}}{\Delta y}\right)_{i-\frac{1}{2},j,k} \] (6.70)

\[ Y_{m_m} = \frac{-1}{2\Delta x_{i,j,k}} \left[ \left(\frac{C_{44}}{\Delta x}\right)_{i+\frac{1}{2},j,k} - \left(\frac{C_{44}}{\Delta x}\right)_{i-\frac{1}{2},j,k} \right] - \frac{1}{\Delta y_{i,j,k}} \left[ \left(\frac{C_{22}}{\Delta y}\right)_{i,j+\frac{1}{2},k} - \left(\frac{C_{22}}{\Delta y}\right)_{i-\frac{1}{2},j,k} \right] \] (6.71)

\[ Y_{m_f} = \frac{1}{2\Delta y_{i,j,k}} \left(\frac{C_{22}}{\Delta y}\right)_{i,j+\frac{1}{2},k} ; \quad Y_{m_m} = \frac{1}{2\Delta z_{i,j,k}} \left(\frac{C_{55}}{\Delta z}\right)_{i,j+\frac{1}{2},k} ; \quad Y_{m_m} = \frac{1}{2\Delta z_{i,j,k}} \left(\frac{C_{55}}{\Delta z}\right)_{i,j-\frac{1}{2},k} \] (6.72)

\[ Z_{m_b} = \frac{(C_{23})_{i,j-1,k} - (C_{55})_{i,j,k-1}}{2\left(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k}\right)} \left(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}}\right) \] (6.73)

\[ Z_{m_f} = \frac{(C_{23})_{i,j+1,k} - (C_{55})_{i,j,k-1}}{2\left(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k}\right)} \left(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}}\right) \] (6.74)

\[ Z_{m_f} = \frac{-2(C_{23})_{i,j-1,k} - (C_{55})_{i,j,k+1}}{2\left(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k}\right)} \left(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}}\right) \] (6.75)

\[ Z_{m_f} = \frac{(C_{23})_{i,j+1,k} + (C_{55})_{i,j,k+1}}{2\left(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k}\right)} \left(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}}\right) \] (6.76)
The finite difference equation for equation of motion in z-direction is:

\[
RY_{i,j,k} = - \left( \frac{C_{21} \delta \varepsilon_{xx}}{\Delta y_{i,j,k}} \right)_{i,j+\frac{1}{2},k} - \left( \frac{C_{21} \delta \varepsilon_{xx}}{\Delta y_{i,j,k}} \right)_{i,j-\frac{1}{2},k} - \left( \frac{C_{22} \delta \varepsilon_{xy}}{\Delta y_{i,j,k}} \right)_{i,j+\frac{1}{2},k} - \left( \frac{C_{22} \delta \varepsilon_{xy}}{\Delta y_{i,j,k}} \right)_{i,j-\frac{1}{2},k} - \left( \frac{C_{23} \delta \varepsilon_{sz}}{\Delta y_{i,j,k}} \right)_{i,j+\frac{1}{2},k} - \left( \frac{C_{23} \delta \varepsilon_{sz}}{\Delta y_{i,j,k}} \right)_{i,j-\frac{1}{2},k}
\]

\[
- \frac{\alpha_{xy}}{\Delta x} \left[ \delta p_{w, m, i, j+\frac{1}{2}, k} - \delta p_{w, m, i, j-\frac{1}{2}, k} + \delta (S_{o, m Pcwom})_{i, j+\frac{1}{2}, k} - \delta (S_{o, m Pcwom})_{i, j-\frac{1}{2}, k} \right] 
\]

\[
- \frac{\alpha_{yy}}{\Delta y} \left[ \delta p_{w, m, i+\frac{1}{2}, j, k} - \delta p_{w, m, i-\frac{1}{2}, j, k} + \delta (S_{o, m Pcwom})_{i+\frac{1}{2}, j, k} - \delta (S_{o, m Pcwom})_{i-\frac{1}{2}, j, k} \right] 
\]

\[
\frac{\alpha_{zz}}{\Delta z} \left[ \delta p_{w, m, i, j, k+\frac{1}{2}} - \delta p_{w, m, i, j, k-\frac{1}{2}} + \delta (S_{o, m Pcwom})_{i, j, k+\frac{1}{2}} - \delta (S_{o, m Pcwom})_{i, j, k-\frac{1}{2}} \right]
\]

(6.77)

The finite difference equation for equation of motion in z-direction is:

\[
X_{bmb} \delta u_{x_{i-1, j, k-1}} + X_{bfm} \delta u_{x_{i-1, j+1, k-1}} + X_{fmb} \delta u_{x_{i+1, j, k-1}} + X_{fmm} \delta u_{x_{i+1, j+1, k-1}} + Y_{mbb} \delta u_{y_{i, j-1, k-1}} 
\]

\[
+ Y_{mbf} \delta u_{y_{i, j-1, k+1}} + Y_{mfb} \delta u_{y_{i, j+1, k-1}} + Y_{mff} \delta u_{y_{i, j+1, k+1}} + Z_{bbm} \delta u_{z_{i-1, j, k-1}} + Z_{bmm} \delta u_{z_{i-1, j+1, k-1}} + Z_{fmm} \delta u_{z_{i+1, j, k-1}} + Z_{mmm} \delta u_{z_{i+1, j+1, k-1}} = RZ_{i,j,k}
\]

(6.78)

where:

\[
X_{bmb} = \frac{(C_{66})_{i+1, j,k} + 2 (C_{31})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2}, j,k} + \Delta x_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.79)

\[
X_{bfm} = \frac{(C_{66})_{i-1, j,k} + (C_{31})_{i,j,k+1}}{2 \left( \Delta x_{i+\frac{1}{2}, j,k} + \Delta x_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.80)

\[
X_{fmb} = \frac{-(C_{66})_{i+1, j,k} - (C_{31})_{i,j,k-1}}{2 \left( \Delta x_{i+\frac{1}{2}, j,k} + \Delta x_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.81)

\[
X_{fmm} = \frac{(C_{66})_{i+1, j,k} + 2 (C_{31})_{i,j,k+1}}{2 \left( \Delta x_{i+\frac{1}{2}, j,k} + \Delta x_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.82)

\[
Y_{mbb} = \frac{-(C_{55})_{i,j,k-1} - 2 (C_{32})_{i,j,k-1}}{2 \left( \Delta y_{i+\frac{1}{2}, j,k} + \Delta y_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.83)

\[
Y_{mbf} = \frac{(C_{55})_{i,j,k+1} + 2 (C_{32})_{i,j,k+1}}{2 \left( \Delta y_{i+\frac{1}{2}, j,k} + \Delta y_{i-\frac{1}{2}, j,k} \right) \left( \Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}} \right)}
\]

(6.84)
such as phase pressure

\[ Y_{mf_1} = -\frac{(C_{55})_{i,j,k+1} + 2(C_{32})_{i,j,k-1}}{2(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k})(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}})} \]  

(6.85)

\[ Y_{mff} = \frac{(C_{55})_{i,j,k+1} + 2(C_{32})_{i,j,k+1}}{2(\Delta y_{i+\frac{1}{2},j,k} + \Delta y_{i-\frac{1}{2},j,k})(\Delta z_{i,j,k+\frac{1}{2}} + \Delta z_{i,j,k-\frac{1}{2}})} \]  

(6.86)

\[ Z_{bmm} = \frac{1}{2\Delta x_{i,j,k}} \left( \frac{C_{55}}{\Delta y} \right)_{i-\frac{1}{2},j,k} ; \]

\[ Z_{fmm} = \frac{1}{2\Delta x_{i,j,k}} \left( \frac{C_{66}}{\Delta x} \right)_{i+\frac{1}{2},j,k} ; \]

\[ Z_{mbm} = \frac{1}{2\Delta y_{i,j,k}} \left( \frac{C_{55}}{\Delta z} \right)_{i,j-\frac{1}{2},k} \]  

(6.87)

\[ Z_{mfm} = \frac{1}{2\Delta y_{i,j,k}} \left( \frac{C_{55}}{\Delta y} \right)_{i,j+\frac{1}{2},k} ; \]

\[ Z_{mmb} = \frac{1}{2\Delta z_{i,j,k}} \left( \frac{C_{33}}{\Delta z} \right)_{i,j}\frac{1}{2},k} ; \]

\[ Z_{mmf} = \frac{1}{2\Delta z_{i,j,k}} \left( \frac{C_{33}}{\Delta z} \right)_{i,j,k+\frac{1}{2}} \]  

(6.88)

\[ RZ_{i,j,k} = -\frac{(C_{21}\delta s_{x})_{i,j,k+\frac{1}{2}} - (C_{21}\delta s_{x})_{i,j,k-\frac{1}{2}}}{\Delta z_{i,j,k}} \]

\[ -\frac{(C_{22}\delta s_{y})_{i,j,k+\frac{1}{2}} - (C_{22}\delta s_{y})_{i,j,k-\frac{1}{2}}}{\Delta z_{i,j,k}} \]

\[ -\frac{(C_{23}\delta s_{z})_{i,j,k+\frac{1}{2}} - (C_{23}\delta s_{z})_{i,j,k-\frac{1}{2}}}{\Delta z_{i,j,k}} \]

\[ -\frac{(\frac{\alpha_{zz}}{\Delta x})_{i,j,k}}{\Delta z_{i,j,k}} \left[ \delta p_{w,m_{i+\frac{1}{2},j,k}} - \delta p_{w,m_{i-\frac{1}{2},j,k}} + \delta (S_{o,m_{cwom}})_{i+\frac{1}{2},j,k} - \delta (S_{o,m_{cwom}})_{i-\frac{1}{2},j,k} \right] \]

\[ -\frac{(\frac{\alpha_{yy}}{\Delta y})_{i,j,k}}{\Delta z_{i,j,k}} \left[ \delta p_{w,m_{i+\frac{1}{2},j,k}} - \delta p_{w,m_{i-\frac{1}{2},j,k}} + \delta (S_{o,m_{cwom}})_{i+\frac{1}{2},j,k} - \delta (S_{o,m_{cwom}})_{i-\frac{1}{2},j,k} \right] \]

\[ -\frac{(\frac{\alpha_{zz}}{\Delta z})_{i,j,k}}{\Delta z_{i,j,k}} \left[ \delta p_{w,m_{i,j,k+\frac{1}{2}}} - \delta p_{w,m_{i,j,k-\frac{1}{2}}} + \delta (S_{o,m_{cwom}})_{i,j,k+\frac{1}{2}} - \delta (S_{o,m_{cwom}})_{i,j,k-\frac{1}{2}} \right] \]  

(6.89)

The staggered grid system is used in the numerical solution. The flow related variables such as phase pressure \((p_{1,j,k}^{n+1})\) and phase saturation \((S_{1,j,k}^{n+1})\) are obtained at the center of the
grid cells. While the geomechanical related variables \( \delta u^{n+1}_{x_{1,j,k}}, \delta u^{n+1}_{y_{1,j,k}}, \delta u^{n+1}_{z_{1,j,k}}\) are obtained at the edge of the node. No displacement is considered for the grid block at the center of the matrix block. The pressure at the boundary of the matrix block is considered to be constant at every time step of the reservoir scale simulation. The effective stress acting on the outer boundary node of the matrix block is constant and equal to the fracture pressure. Since two phases, water and oil, co-exist in the fracture, an average fracture pressure equation is used. Hence, the outer condition is written in the incremental form as:

\[
\begin{align*}
\delta \sigma_{m,eff_{xx}} &= C_{11'} \frac{\partial \delta u}{\partial x} + C_{12'} \frac{\partial \delta u}{\partial y} + C_{13'} \frac{\partial \delta u}{\partial z} + (C_{11'} \delta \varepsilon_{sx} + C_{12'} \delta \varepsilon_{sy} + C_{13'} \delta \varepsilon_{sz}) = \delta \bar{p}_f = \delta (S_{of} p_{of} + S_{wf} p_{wf}) \\
\delta \sigma_{m,eff_{yy}} &= C_{21'} \frac{\partial \delta u}{\partial x} + C_{22'} \frac{\partial \delta u}{\partial y} + C_{23'} \frac{\partial \delta u}{\partial z} + (C_{21'} \delta \varepsilon_{sx} + C_{22'} \delta \varepsilon_{sy} + C_{23'} \delta \varepsilon_{sz}) = \delta \bar{p}_f = \delta (S_{of} p_{of} + S_{wf} p_{wf}) \\
\delta \sigma_{m,eff_{zz}} &= C_{31'} \frac{\partial \delta u}{\partial x} + C_{32'} \frac{\partial \delta u}{\partial y} + C_{33'} \frac{\partial \delta u}{\partial z} + (C_{31'} \delta \varepsilon_{sx} + C_{32'} \delta \varepsilon_{sy} + C_{33'} \delta \varepsilon_{sz}) = \delta \bar{p}_f = \delta (S_{of} p_{of} + S_{wf} p_{wf})
\end{align*}
\]

This boundary conditions can be written in the discretized equation as:

x-direction:

\[
\begin{align*}
(C_{11}) \frac{\Delta x}{2} \left( \delta u^{n+1}_{x_{2,j,k}} - \delta u^{n+1}_{x_{1,j,k}} \right) + (C_{12}) \frac{\Delta y}{2} \left( \delta u^{n+1}_{y_{1,j+1,k}} - \delta u^{n+1}_{y_{1,j,k}} \right) + (C_{13}) \frac{\Delta z}{2} \left( \delta u^{n+1}_{z_{1,j,k+1}} - \delta u^{n+1}_{z_{1,j,k}} \right)
\end{align*}
\]

y-direction:

\[
\begin{align*}
(C_{21}) \frac{\Delta x}{2} \left( \delta u^{n+1}_{x_{i+1,j,k}} - \delta u^{n+1}_{x_{i,j,k}} \right) + (C_{22}) \frac{\Delta y}{2} \left( \delta u^{n+1}_{y_{i+1,j,k}} - \delta u^{n+1}_{y_{i,j,k}} \right)
\end{align*}
\]

z-direction:

\[
\begin{align*}
(C_{21}) \frac{\Delta x}{2} \left( \delta u^{n+1}_{x_{i,j+1,k}} - \delta u^{n+1}_{x_{i,j,k}} \right) + (C_{22}) \frac{\Delta y}{2} \left( \delta u^{n+1}_{y_{i,j+1,k}} - \delta u^{n+1}_{y_{i,j,k}} \right) + (C_{23}) \frac{\Delta z}{2} \left( \delta u^{n+1}_{z_{i,j,k+1}} - \delta u^{n+1}_{z_{i,j,k}} \right)
\end{align*}
\]
\[
\left( \frac{C_{31}}{\Delta x} \right)_{i+\frac{1}{2},j,1} (\delta u_{x,i+1,j,1}^{n+1} - \delta u_{x,i,j,1}^{n+1}) + \left( \frac{C_{32}}{\Delta y} \right)_{i,j+\frac{1}{2},k} (\delta u_{y,i,j+1,k}^{n+1} - \delta u_{y,i,j,k}^{n+1}) + \\
\left( \frac{C_{33}}{\Delta z} \right)_{i,j+\frac{1}{2}} (\delta u_{z,i,j,2} - \delta u_{z,i,j,1}) + (C_{31}\delta \epsilon_{x} + C_{32}\delta \epsilon_{y} + C_{33}\delta \epsilon_{z})_{i,j,1} = \delta p_{f,i,j,1} \quad (6.93)
\]

After the displacement is calculated, the stress can be obtained from the constitutive equation (Eq. 6.10). The fracture permeability can be obtained when the stress on the external node on each matrix block is computed.

\[
k_{f,eff,i,j,k}^{n+1} = k_{f,eff,i,j,k}^{n} \exp \left[ \left( \sigma_{xm_{1,j',k'}}^{n+1} - \sigma_{xm_{1,j',k'}}^{n} \right) c_{f,t} \right] \quad (6.94)
\]

6.5 Predictive Model Results and Discussion

The relative permeability and capillary pressure parameters used in the predictive model simulation can be seen in Table 6.1. In this predictive cases, a single porosity model is utilized to show the impact on oil recovery with a fixed membrane efficiency versus a changing membrane efficiency dependent on incremental stress conditions. A 40% residual water saturation along with 20% oil saturation in the matrix block is assumed.

Table 6.1: Input parameters for relative permeability and capillary pressure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{*_{wm}}$</td>
<td>0.025</td>
<td>$n_{om}$</td>
<td>1.5</td>
<td>$S_{wmx}$</td>
<td>0.6</td>
</tr>
<tr>
<td>$k_{*_{rom}}$</td>
<td>0.12</td>
<td>$S_{om}$</td>
<td>0.2</td>
<td>$a_{m1}$</td>
<td>-85</td>
</tr>
<tr>
<td>$n_{wm}$</td>
<td>2.0</td>
<td>$S_{wm}$</td>
<td>0.4</td>
<td>$a_{m2}$</td>
<td>127.5</td>
</tr>
</tbody>
</table>

The geomechanical model formulation previously described in this chapter is used to capture the geomechanical changes during simulation. The axial swelling and stiffness parameters captured during increasing water saturation obtained from the laboratory results...
are incorporated into the models. Table 6.2 and Table 6.3 shows the parameters used in the simulation.

Table 6.2: Input parameters for 1-D consolidation: 4,000 days of injection

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{initial}$</td>
<td>1,200</td>
<td>psi</td>
<td>$c_o$</td>
<td>$3.44 \times 10^{-6}$</td>
<td>psi$^{-1}$</td>
</tr>
<tr>
<td>$P_{inlet}$</td>
<td>1,200</td>
<td>psi</td>
<td>$c_w$</td>
<td>$2.975 \times 10^{-6}$</td>
<td>psi$^{-1}$</td>
</tr>
<tr>
<td>$T_m$</td>
<td>296.85</td>
<td>deg.K</td>
<td>$c_\varphi$</td>
<td>$3.482 \times 10^{-7}$</td>
<td>psi$^{-1}$</td>
</tr>
<tr>
<td>$c_{initial}$</td>
<td>35,000</td>
<td>ppm</td>
<td>$\varphi_m$</td>
<td>3.89</td>
<td>%</td>
</tr>
<tr>
<td>$c_{inj}$</td>
<td>1,000</td>
<td>ppm</td>
<td>$D_{eff}$</td>
<td>$3.88 \times 10^{-9}$</td>
<td>ft$^2$/sec</td>
</tr>
<tr>
<td>$k_m$</td>
<td>27.58</td>
<td>nD</td>
<td>$\omega$</td>
<td>2.196</td>
<td>%</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>186.04</td>
<td>lb/ft$^3$</td>
<td>$V_w$</td>
<td>$6.362 \times 10^{-4}$</td>
<td>ft$^3$/mole</td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>50.88</td>
<td>lb/ft$^3$</td>
<td>$g$</td>
<td>32.152</td>
<td>ft/s$^2$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>63.55</td>
<td>lb/ft$^3$</td>
<td>Matrix block size</td>
<td>5 x 5 x 5</td>
<td>ft$^3$</td>
</tr>
<tr>
<td>$\mu_w$</td>
<td>0.996</td>
<td>cp</td>
<td>$R$</td>
<td>8.314</td>
<td>JK$^{-1}$mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_o$</td>
<td>0.4</td>
<td>cp</td>
<td>Number of Grid</td>
<td>100 x 1 x 1</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: Laboratory Geomechanical parameters used in matric block simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>20.198</td>
<td>GPa</td>
<td>K1</td>
<td>$4.68 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.33</td>
<td>-</td>
<td>K2</td>
<td>$-7.31 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$f$</td>
<td>1.7</td>
<td>-</td>
<td>K3</td>
<td>2.1601</td>
<td>GPa</td>
</tr>
</tbody>
</table>

6.6 Assumptions for the Model Formulation

The entire matrix block is assumed to be under in-situ conditions with surrounding stresses acting on the matrix block. The fluid saturating and surrounding the sample has
an initial pressure of 1,200 psi. The native in-situ brine concentration is at 35,000 ppm while the surrounding brine is at 1,000 ppm. Salt does not exist in the solid phase of the matrix and only dissolves in the water phase making up the solute concentration. When the lower salinity brine imbibes into the rock matrix, the pore pressure increases which lowers the net stress acting on the matrix block. As water imbibes into the rock due to chemical osmosis, oil simultaneously flows out of the rock matrix causing depletion and lowering of the pore pressure until equilibrium conditions are achieved. During the osmotically driven imbibition process, brine imbibes into the rock matrix and causing oil to flow out of the matrix block. During this process, the net stress on the matrix block increases as more of the oil is produced. The net stress causes the pore spaces to reduce in size which lowers permeability and enhances membrane efficiency. For the fixed membrane efficiency simulation case, an increase in the net stress has no effect on the selectivity of the pore spaces whereas, for the changing membrane efficiency with net stress, the ion-selectivity capability of the shale membrane increases over time with increasing net stress. Essentially for the changing membrane efficiency with effective stress, the net stress on the matrix block increases over time causing the pore spaces to reduce in size. This pore space reduction enhances the membrane efficiencies as recovery of the oil takes place over time. Reduction of the pore size increases the selectivity of the solute ions promoting imbibition of the water molecules into the higher salinity rock matrix that increases the oil recovery. The simulation time for both cases are 4,000 days. Figure 6.1 shows the relative permeability and capillary pressure curve parameters used in the model simulation. The water and oil saturations change with time as the imbibition process continues.

6.6.1 Case 1: Fixed membrane efficiency

Figure 6.2 shows the change in the water and oil saturation along the length of the matrix block over the 4,000-day simulation period for the fixed membrane case. The oil saturation reduces from 58 to 35% at the matrix block boundary. Imbibed water can be observed to physically penetrate up to 1 ft of the rock matrix increasing the water saturation to from 42 to
Figure 6.1: Simulated relative permeability and capillary pressure curves.
65% at the boundary. As water imbibes into the rock matrix, oil is simultaneously mobilized of the matrix. Figure 6.3 shows the process of water influx into the matrix block. Initially, the flow rate increases rapidly initially at the matrix boundary before declining steadily with time. The water flux reaches 3.45 m$^3$/sec at the end of the 4,000 day simulation period. The solute concentration is seen (Figure 6.4(a)) to penetrate even further up to 4.5 ft into the 5’ X 5’ matrix block assisted by the additional support from the induced chemical osmosis pressure built up. The decline of Young’s modulus at the matrix boundary can be observed in Figure 6.4(b). The majority of the influx penetrated up to 1 ft of the matrix block making the outer boundary weaker that the core of the matrix block. The core of the matrix is still intact at this point in the simulation. The weakening process will continue with longer simulation as the water imbibes further into the matrix block. A recovery factor of 7.2% is achieved at the end of the 4,000-day simulation as seen in Figure 6.5.

![Figure 6.2: Fluid saturation changes during the chemical osmosis process in the fixed membrane case.](image)
6.6.2 Case 2: Varying membrane efficiency with stress

Water and oil saturation changes along the length of the matrix block for the 4,000 day simulation period can be seen in Figure 6.6 in the varying membrane case. The oil saturation drops from 58 to 33% while the water saturation increase from 42 to 66%. Figure 6.7 shows the brine solution being mobilized into the matrix block. The simulation shows that the water influx at the boundary translates into the swelling stress that largely felt at the boundaries of the matrix block. This stress disseminates into the matrix at a slow pace controlled by capillarity of the pore spaces. The rate of the water influx, in this case, decreases faster than the fixed membrane case. The water flux rate is highest at 8.85 m$^3$/sec at 300 days and drops to 2.88 m$^3$/sec at the end of the simulation. The net stress increase improves membrane efficiency and as the pore spaces reduce, the rate of the water influx further slows down.
Figure 6.4: Rock-Fluid Interaction.

(a) Solute concentration along the matrix block

(b) Stiffness changes across the matrix block after simulation
Figure 6.5: Recovery factor for 4,000 days of simulation with fixed membrane efficiency.

Figure 6.6: Fluid saturation changes during the chemical osmosis process in varying membrane case.

The solute concentration change along the matrix block can be observed in Figure 6.8. The 1,000 ppm brine is seen to be the concentration of the water phase at the end of the 4,000-day simulation. The in-situ native salinity of 35,000 ppm still exists at 4.5 ft along the matrix block which is an indication of the dilution of the higher concentration salinity brine.
in the matrix due to osmotically induced imbibition. The Young’s modulus understandably decreases but this is localized at the matrix boundary where most of the swelling is taking place. The core of the matrix is also still very much intact as shown in Figure 6.9. The recovery factor gets up to 9% at the end of the 4,000-day simulation period in Figure 6.10.
Figure 6.9: Stiffness change across the matrix block after simulation.

Figure 6.10: Recovery factor for 4,000 days of simulation with varying membrane efficiency with stress.
CHAPTER 7
CONCLUDING REMARKS AND RECOMMENDATIONS

This chapter summarizes the findings of this research with concluding remarks and recommendations for further investigation and field operation.

7.1 Concluding Remarks

I modified our experimental facility to measure osmosis pressure and clay swelling in the Pierre shale samples. I experimentally characterized the mechanical properties of the Pierre shale in both 65 wt.% smectite outcrop and 3.5 wt.% TOC samples when saturated with different salinity brines. Shales with lower clay content undergo volumetric expansion during low salinity water injection. The weakening of the shale formation affects its elastic properties such as Young’s modulus, Poisson’s ratio, and bulk modulus. Dynamic Young’s modulus decreases by 28% in the PI-H-02 Pierre shale sample having 65 wt.% smectite when saturated with 235,000 ppm NaCl solution. The same PI-H-02 Pierre shale sample displayed a noticeable 9.5% drop in its static Young’s modulus when 60,000 ppm NaCl solution was injected to activate the osmosis pressure across the core.

The presence of natural fractures greatly affects the permeability and the mechanism for osmosis membrane efficiency as seen in the case of sample PI-LC-WY-H-01. The effective permeability of the sample PI-LC-WY-H-01 exponentially changes from 284.55 nd to 9.39 nd when the effective confining stress is increased from 1,500 psi to 3,500 psi. Fracture dominated effective permeability is assumed to be the mechanism in place at lower net stresses.

Since the samples are cored in the horizontal direction, the membrane efficiency is controlled by the most permeable bedding layer of the sample. The experimental results show that the membrane efficiency is a strong function of stress. A model was derived to obtain the change of the membrane efficiency with effective stress and the model parameters were
obtained from the experimental data. A linear correlation was also derived to show how the membrane efficiency changes with stress based on the isothermal bulk compressibility of the rock.

The imbibition of LSW into the rock matrix by osmosis is one mechanism for IOR/EOR. Low salinity water IOR/EOR could potentially be used in the Pierre shale formation because the reservoir shales of the Sharon Springs member experience less swelling due to their low percentage of smectite. A membrane coefficient of 0.0035 (slope) was observed during the injection of 257,000 ppm NaCl solution into 60,000 ppm NaCl saturated PI-H-01 Pierre shale outcrop sample. Whereas, a lower membrane coefficient of 0.0022 (slope) was observed during the injection of 1,000 ppm NaCl solution into the sample. The difference in the membrane coefficient between these two cases is largely due to the chemical osmotic potential gradient between the different salinity fluid. A higher potential gradient will lead to greater membrane efficiency. In sample PI-LC-WY-H-01, a higher membrane coefficient of 0.01153 (slope) was observed mainly due to the lower permeability of the sample.

A significant 1% axial swelling in the horizontal plane was experienced for the 65 wt.% smectite sample (PI-H-02) injecting 235,000 ppm NaCl solution at 100 psi net stress. 0.075% axial swelling was experienced in the case of the low smectite 3.5 wt.% TOC sample PI-LC-WY-H-01 injecting 35,000 ppm NaCl solution at 500 psi net stress. The swelling that occurred in the PI-LC-WY-H-01 sample was largely attributed to pore pressure penetration of the matrix due to the injection of 35,000 ppm brine.

Using experimental data, a coupled model was developed to predict the imbibition of water into the shale matrix accounting for swelling, osmosis imbibition, and the variation of membrane efficiency. The result suggested that osmosis is one important transport mechanism for improving the oil recovery from the rock matrix. Also, the membrane coefficient is a determining factor for osmosis imbibition, where the change of membrane efficiency with stress, swelling, as well as the variation of mechanical property of shales are considerably important for IOR/EOR.
7.2 Recommendations

It is recommended to investigate the swelling tendencies of shale formations before any water injection operations, especially for low salinity water injection. It is important to incorporate the changes of the membrane efficiency and clay swelling into reservoir models by accounting for varying mineralogy, clay content and total organic content in the simulation studies. Controlling net stress through pore pressure regulation can assist in maintaining optimal membrane efficiency. Hence, the behavior of the membrane with stress has to be determined as in this study.

Clay swelling does not appear to be prominent for the Sharon Springs member of the Pierre shale and thus, IOR/EOR processes such as LWSI can be adopted to further improve the recovery in this shale reservoir.

Further research is required on other shale reservoirs to fully understand the changes in the flow mechanism caused by induced osmosis pressure. It is recommended to investigate how the membrane efficiency changes with stress using different ions such as those found in seawater.

Studies should also be conducted to determine the influence of osmosis pressure generation on permeability measurements within the sample. When fluid imbibes into the rock, it weakens the rock. The work in this research presents a clear picture of this occurrence when incorporated it into a numerical model to observe how it affects porosity and permeability of the matrix.

Due to clay swelling, the matrix permeability decreases, creating a thin layer at the boundary of the matrix block. With significant swelling, LSWI will not be recommended for use.
REFERENCES CITED


