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Three-Phase Relative Permeability of Hydrate-Bearing Sediments

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Three-Phase Relative Permeability of Hydrate-Bearing Sediments

by

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Thesis
Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in Engineering

The University of Texas at Austin
August 2018
Acknowledgements

I would like to thank my advisors, Hugh Daigle and David DiCarlo, for their support and guidance throughout my experiments. As experimental work can often be frustrating and slow, I greatly appreciate their patience and willingness to work through these experimental issues with me. I have grown tremendously as a researcher and experimentalist as a result of their guidance.

This work would not have been possible without the help of David Fukuyama, who is my partner in this work. He has been a tremendous resource and great addition to the project. Thank you for your work and willingness to always run to the lab to check on the experiments.

The entire methane hydrate group at the Jackson School of Geosciences has been always welcoming and are critical to the success of this project. I am very appreciative to Peter Flemings for his guidance and comments throughout this project. I would like to especially thank Josh O’Connell for his assistance and willingness to help in constructing my experimental setup. Additionally, Peter Polito, Dylan Meyer, Kehua You, Steve Phillips, Lauren Churchwell, and John DiCarlo have been tremendous resources throughout my experiments. I would also like to thank Leilani Swafford for her assistance.

Lastly, I would like to thank the Department of Energy and the Hildebrand Department of Petroleum & Geosystems Engineering at the University of Texas at Austin for their financial support.
Three-Phase Relative Permeability of Hydrate-Bearing Sediments

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The University of Texas at Austin, 2018

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Abstract: During production of methane gas from hydrate-bearing sediments, gas, brine, and hydrate may all be present in the sediment. In such a situation, the relative permeability of each phase is the key parameter affecting flow. Thus far, the majority of relative permeability measurements made for hydrate bearing sediment are for gas in the presence of hydrate (no water) or water in the presence of hydrate (no gas). This thesis presents methodology and preliminary results from conducting three-phase relative permeability measurements on hydrate bearing sediment.

The experiments took place in a cold lab kept at a hydrate-forming temperature (6°C). A sandstone core that was representative of Gulf of Mexico sediment and was 22” in length and 1.5” in diameter was used. The core holder had pressure taps along its length that are connected to differential pressure transducers to measure pressure drops and minimize sensitivity to capillary end effects. The core or sandpack was partially saturated with DI water to a water saturation of approximately 40% by injecting a specified volume of water into the core or mixing the sand with DI water before packing. The sample was then brought to hydrate forming pressure (1250 psi) by injecting methane. To determine the hydrate saturation, a pump monitored the volume of methane injected into the core in order to maintain 1250 psi.

Once hydrate formed, hydrate stability was controlled by pressure, temperature, and salinity. At constant pressure and constant temperature, changes in salinity moved the stability
conditions and at certain salinity, the system reached three-phase equilibrium. Three-phase brine was injected to allow flow through the core without destroying or forming any additional hydrate while continuously monitoring the pressure drops. After steady state was reached, as indicated by the pressure drop and saturation remaining constant with time, varying rates of gas were injected to change the gas saturation, and again obtain steady-state pressure drops. This process was completed for representative saturations of gas and water to create a full relative permeability curve. A procedure has been developed for forming hydrates in a pressure vessel and relative permeability values have been measured for samples with hydrate saturations of 24% and 35%. The methodology developed in this thesis will be used to conduct numerous three-phase relative permeability measurements on hydrate bearing sediment.
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Chapter 1: Overview and Background

1.1 Thesis Overview

This master’s thesis has four chapters and focuses on the methodology and progress made thus far on measuring three-phase relative permeability of hydrate bearing sediment. The first chapter will present an overview of the project, definitions and overview of key concepts, and a literature review of previous work. The second chapter will discuss the method used for forming hydrate in sandpacks and cores and present results from hydrate forming experiments. The third chapter will discuss and present the relative permeability experiments run thus far as well as the process improvements made. Lastly, the fourth chapter will be a conclusion and discussion of lessons learned with plans for future work.

1.2 Background

1.2.1 Methane Hydrates

Methane hydrates or clathrates are solid, ice-like compounds that form when water and methane gas interact at high pressures and low temperatures. It is estimated that there are \( \sim 3 \times 10^{14} \) m\(^3\) of technically-recoverable methane from worldwide hydrate reservoirs but may be higher if clay-dominated reservoirs become feasible targets (Boswell and Collett, 2011). Therefore these deposits are of great interest from an energy and environmental perspective. Tremendous amounts of research are conducted to better understand these deposits: how they form, where the methane comes from, and eventually how to produce gas from these reservoirs.

1.2.2 Hydrate Stability Conditions

Due to the unique stability conditions, hydrates are mainly found in the shallow subsea sediment along deepwater continental margins (Kvenvolden, 1993) or beneath arctic permafrost
(Collett and Dalimore, 2000). As seen in Figure 1-1 below, in marine environments there is a clear pressure and temperature zone in which methane hydrates are stable and if they are removed from that stability zone, they will dissociate into water and gas. This stability region is constrained by the hydrostatic pressure of the ocean and the geothermal gradient (Trehu et al., 2006). Below the base of the hydrate stability (BHSZ), methane will exist as a free gas phase due to the increasing temperature. Because of the temperature profile in the water column, methane can also exist as a free gas phase in shallow water depths due to low pressure and higher temperatures.

![Figure 1-1 Hydrate stability in a marine environment. Hydrate stability zone is purple region. Three-phase region occurs at base of hydrate stability. Figure from Tréhu et al 2006.](image)

### 1.2.3 Three-Phase Stability Conditions

As seen in Figure 1-1, the BHSZ is estimated from hydrostatic pressure and geothermal gradient and is where hydrate stability begins to change. Above the BHSZ, hydrate and water or hydrate and gas can coexist. Below the BHSZ, hydrate will not be present and free gas and water
will coexist. However, as hydrate approaches this phase boundary, it is possible for three-phases of methane to be at equilibrium: hydrate, methane gas, and dissolved methane. The three-phase region has been studied in depth because this transition zone could result in inaccurate estimates of hydrate reserves and the location of the BHSZ (Ruppel, 1997; Liu and Flemings, 2011). In addition to P-T conditions, three-phase stability can be controlled by pore-size distribution, capillary effects, and salinity (Henry et al., 1999; Liu and Flemings, 2006; Liu and Flemings, 2011). For the purposes of this thesis, capillary effects are ignored, and three-phase equilibrium will occur for a given temperature at a specific pressure and salinity conditions. Three-phase conditions are controlled by pressure, temperature, and salinity as seen in Figure 1-2 (You, 2015). As hydrate forms and salt is excluded, the salinity of the remaining brine increases until the system reaches three-phase equilibrium (Liu and Flemings, 2006; You, 2015). At a constant pressure and temperature, hydrate formation will be buffered by the salinity of the system as pore water salinity increases and eventually reaches three-phase equilibrium, as seen in Figure 1-2.

![Figure 1-2 Pressure, temperature, and salinity diagram for hydrate three-phase equilibrium. Three-phase surface shown in red. Red dashed lines represent increasing salinity. Figure from You 2015.](image)

Besides estimating the BHSZ, three-phase situations are also particularly likely during production or dissociation scenarios where there is gas and water flowing through a hydrate-bearing interval (Yousif et al. 1991). While there have been experiments conducted at two-phase
conditions, hydrate and gas or hydrate and water, there have been very limited experiments run at three-phase conditions (Jaiswal, 2004). Models have been built to simulate formation processes or methane flow in the three-phase region, but these models all make assumptions about the relative permeability (Malinverno, 2010; You, 2015; Nole, 2016; Nole, 2017). By running experiments at three-phase conditions, I will achieve a better understanding of gas and water flow through hydrate reservoirs and of production scenarios where all water, gas, and hydrate will coexist.

1.2.2 Overview of Relative Permeability

In order to model and predict production profiles, two-phase and three-phase relative permeability must be properly measured and understood. While there have been limited measurements of two-phase relative permeability by flowing gas or water in the presence of hydrate, there has never been a measurement of three-phase relative permeability involving the simultaneous flow of gas and water in the presence of hydrate. Therefore, the focus of this project is to directly measure the three-phase relative permeability of hydrate bearing sediment in a laboratory setting.

When multiple immiscible fluids are present in the pore space, the flow rate of a particular phase at a particular pressure gradient is lower than what you would predict from Darcy’s law because the presence of other fluid(s) interferes with the flow of the phase in question. Relative permeability is the measure of a change in permeability in a porous medium due to fluid interaction during multi-phase flow and is the key parameter in understanding and modeling flow in such instances. Measured in the field or in the laboratory, relative permeability is a dimensionless ratio of the effective permeability of a single phase to the absolute permeability of the media. Traditionally, this ratio has been measured for petroleum reservoir
rocks with gas, water, and oil as the fluid phases. In the petroleum engineering literature, there are countless examples of experiments of two- and three-phase relative permeability measurements for reservoir rocks (Leverett and Lewis, 1941; Corey et al. 1956; Oak et al., 1990). In order to properly model hydrocarbon production especially during water flooding, the relative permeability of the specific porous medium must be experimentally determined. For this thesis, I am interested in understanding how the presence of hydrate in a porous medium will impact the flow of gas and water. My experiments, therefore, measure three-phase relative permeability of hydrate, gas, and water.

1.2.3 Laboratory measurement of relative permeability

There are two standard methods for measuring relative permeability in a laboratory setting, the unsteady-state and the steady-state method (Peters, 2012). Both methods are based on Darcy’s Law. To solve for relative permeability, the Darcy-Buckingham Equation is used:

\[
Q_i = \frac{k_{ri} K A}{\mu_i} \cdot \frac{\Delta P^i}{L}
\]

where, for phase i, \( Q_i \) is the flow rate, \( K \) is absolute permeability of the porous medium, \( A \) is the cross-sectional area of the medium normal to the direction of flow, \( \Delta P^i \) is pressure drop, \( L \) is length, and \( k_{ri} \) is relative permeability. This equation is simply Darcy’s Law with a \( k_{ri} \) value that can be less than 1.

1.2.3.1 Steady State Method

During the steady state method, one or more phases are co-injected at a fixed ratio until steady state is achieved meaning the pressure drop and phase saturation remain constant over time (Peters, 2012). The measurements made during this experiments are the injection rate of
each phase and the pressure drop. The saturation, pressure drop, and flow rate will all remain constant with time and can be used to solve for the relative permeability. These local measurements of relative permeability will represent the relative permeability of the entire reservoir rock. Due to the ease and accuracy of the measurements, the steady state method is the most frequently used method for measuring relative permeability.

While the steady state method is the most common method for measuring relative permeability, capillary effects can cause issues especially at the inlet and outlet of the core (Leverett, 1939). Capillary end effects are caused by the difference in capillary pressure between the core and the outlet. When injection occurs, the wetting phase will accumulate at the outlet to until the wetting phase saturation equals the wetting phase saturation at zero capillary pressure on the imbibition curve (Peters, 2012). In coreflooding experiments, the end effects can create saturation discrepancies, displacement errors, and incorrect relative permeability values. When measuring the pressure drop across the core, the capillary end effects will alter the pressure readings at the outlet. These effects can be corrected for or can be avoided experimentally. To avoid the issue, pressure drops are measured in the center of the core where end effects are not an issue (Chen, 2016). Our pressure vessel therefore has 5 pressure taps evenly spaced along the length of the core.

To create a complete relative permeability curve, measurements must be taken at different injection ratios of gas and water. By measuring the effluent to keep track of the mass balance or by scanning the pressure vessel, the phase saturations can be determined for each injection ratio. However, since the sample is water wet, there will always be some water present, Swi or irreducible water saturation, so the core will never reach Sw=0. This water must be accounted for in the mass balance calculations, so Swi is calculated for the sample before
experiments begin (Peters, 2012). Steady state must be reached for each injection ratio or saturation to achieve a full relative permeability curve. For very low permeability media, this process can be quite time intensive. However, since the Gulf of Mexico equivalent sand being used is quite permeable, steady state is achieved quickly (~1 pore volume injected), but at the endpoints for low viscosity fluids, like methane, this process can still be very time consuming (Jaiswal, 2004).

1.2.3.2 Unsteady State Method

The unsteady state method for measuring relative permeability is faster compared to the steady state method but requires great care and some assumptions to be made (Welge, 1952). The main difference in the unsteady state method is that saturation equilibrium is not achieved, thus making it a faster process. Additionally, phases are not co-injected but rather fluids are displaced at a constant rate. Since steady state is not reached, Darcy’s Law is not used but rather the Buckley-Leverett equation is used to inversely solve for relative permeability and phase saturation (Peters, 2012). While the unsteady-state method can provide an entire relative permeability curve in one displacement, the results are greatly affected by phase distribution and have repeatability concerns since properties may be changing throughout the experiment. There are many unsteady-state methods, but all make some assumptions and may not represent the entire reservoir.

While both methods have useful applications, I choose the steady state method due to the ease, accuracy, and ability to achieve steady state with a high permeability sample. Additionally, since hydrate bearing sands are heterogeneous in nature, the steady-state method is superior for measuring relative permeability of hydrate bearing sediments (Jaiswal, 2004; Johnson et al., 2009).
1.2.3.3 Limitations of Relative Permeability Measurements

There are many factors that could affect laboratory relative permeability measurements but most importantly for these experiments, temperature and heterogeneity. Temperature (and pressure) do not affect the relative permeability of porous media but can create an experimental artifact. This artifact is caused by the changes to the fluids due to pressure and temperature effects. Since our experiments must be run at hydrate stability conditions, there are pressure and temperature effects on the viscosity of the phases and the interfacial tension (Krevor et al, 2012). For relative permeability measurements, the capillary pressure effects are usually ignored. However, as the viscosity of the fluids changes, the capillary effects can become more noticeable. Therefore, the pressure drop across the entire core will be impacted by the capillary effects at the inlet and outlet of the core. To mitigate this issue, there are incremental pressure taps along the core which measure the center section of the core where the capillary effects are negligible.

1.3 Definitions

There are many key concepts that must be clearly defined and understood in order to fully comprehend this paper. While most of these terms or concepts are common to multi-phase flow and relative permeability research, there can be some confusion due to the presence of hydrate. In this section, I will provide definitions for key terms and explain the significance or difference in the presence of hydrates.

*Porosity* is the volume percentage of a porous medium that is void space or can hold fluid. Hydrate saturation does not affect porosity, but is considered as an immobile, pore-occupying phase. Therefore, I assume that the porosity of our samples does not change, regardless of the presence of hydrate.
Saturation is the fraction of the pore volume occupied by a particular fluid phase. For our experiments, \( Sh + S_g + S_w = 1 \).

Hydrate Saturation (\( Sh \)) is the fraction of the pore space of our sample that is occupied by hydrate. This value is estimated by using mass balance and the stoichiometry of methane hydrate.

Water Saturation (\( Sw \)) is the fraction of the pore space of our sample that is occupied by water. Before and after hydrate is formed, this value is the percentage of the overall pore space occupied by water/brine.

Gas Saturation (\( S_g \)) is the fraction of the pore space of our sample that is occupied by methane. Before and after hydrate is formed, this value is the percentage of the overall pore space occupied by the free gas.

Reduced Gas/Water Saturation. In the presence of hydrate, the reduced gas/water saturation is the fraction of the pore volume not occupied by hydrate that is occupied by gas/water.

Absolute (intrinsic) Permeability is a measure of the ability to flow fluid through a porous medium. This measurement is taken when there is a single fluid phase fully saturation the medium. Generally, when permeability is discussed, this refers to the absolute permeability of the porous medium which is measured in units of \( L^2 \) (m² or darcies). In our experiments, the absolute permeability of the sample is measured before there is hydrate present in the sample.

Effective Permeability is a measure of the ability to flow a fluid when there are multiple fluids present in the sample. This value is affected by the saturation of each fluid. For our experiments, effective permeability is measured for a fluid in the presence of hydrate. For example, the
effective permeability of gas in the presence of hydrate or the effective permeability of water in the presence of hydrate. Effective permeability has units of $L^2$, like intrinsic permeability.

*Relative permeability* is used in multiphase flow and is a dimensionless ratio of the effective permeability of a phase to the absolute permeability. Relative permeability is a measure of the ability of fluids to flow in the presence of each other.

### 1.4 Literature review and previous work

This section provides a summary of applicable previous work on methane hydrates and (relative) permeability measurements. This sections is not exhaustive but rather provides a highlight of the resources that were most valuable in developing and conducting our experimental procedure.

*Methane hydrate formation*

There have been numerous studies on the best method for forming methane hydrate in a laboratory setting. These studies have formed hydrate with a variety of methods with the goal of resembling natural hydrate deposits. Since our experiments were meant to resemble Gulf of Mexico hydrate bearing sediment, I decided that the best formation method was the excess gas method (Handa and Stupin, 1992). The excess gas method is conducted by distributing water through a medium and then entering hydrate stability conditions by cooling and pressurizing with gas, which allows hydrate to form. This method is thought to produces a grain-cementing hydrate that preferentially forms at gas-water interfaces (Waite et al., 2004). As determined by Kneafsey (2011), the excess gas method creates samples that have a higher saturation of and more homogenous distribution of hydrate. However, samples can also be quite heterogeneous since hydrate alters the capillary strength of the medium and draws water towards it (Gupta et al.,
The hydrate then continues to form outwardly resulting in potentially nonuniform hydrate.

Kneafsey et al. (2011) tested eight different formation methods and reported on the resulting quality of the sample. While Kneafsey did not determine a superior method, based on their observations, the excess gas method was selected for these experiments due to the speed, ease, and quantity of hydrate formed. The excess gas method, however, may not form hydrates that perfectly resemble the pore habit of natural samples (Dallimore and Collett, 2004). While there are some deficiencies in the excess gas method, it has become the method of choice for hydrate formation due to the speed of formation, high saturation, and relatively even distribution.

Another important factor in hydrate formation is the creation of a homogenous distribution of hydrate in the sample. Following Kneafsey et al. (2011), others have attempted to make a more homogenous sandpack by using other methods. Choi et al. (2014) developed a method for temperature and pressure cycling the sample to create a better distribution. They developed this method to form noncementing methane hydrates in sandy sediments since most natural hydrate bearing sediment displays a noncementing habit. The saline water injection and temperature and pressure cycling will allow the cementing hydrate to dissociate and reform as noncementing hydrate which best represents natural samples. The principles of Choi et al. (2014) were utilized in the experiments conducted in this thesis.

Since hydrate formation is buffered by salinity, salt is excluded during hydrate formation and will drive the system to three-phase stability conditions (You, 2015). You completed hydrate formation experiments in partially brine-saturated sand samples in a controlled laboratory setting. The salinity limited hydrate formation and dissociation once three-phase salinity conditions were reached. Additionally, You et al. (2015) created a model to predict these three-
phase conditions. The formation methods and equilibrium model were used extensively in these experiments.

*Relative permeability of hydrate bearing sediment*

As discussed, there have been limited measurements made of relative permeability of hydrate bearing sediments, especially at three-phase conditions. Jaiswal (2004) successfully created an apparatus to conduct gas-water relative permeability experiments. They were able to form hydrates and run unsteady-state permeability experiments. Many assumptions were made in these experiments, but relative permeability curves for gas and water were created at various hydrate saturations. Many experimental challenges were experienced, such as hydrate blockage, dissociation, and sand flow. Additionally, hydrate distribution was extremely heterogeneous and unknown. While understanding of hydrate pore habit has improved and there have been many advances in hydrate forming techniques, there is very limited other relative permeability data collected.

Johnson et al. (2009) conducted unsteady-state relative permeability measurements on hydrate bearing samples from the Mount Elbert hydrate system, Alaska North Slope. Natural samples were used and it was determined that the presence of hydrate significantly influenced (lowered) permeability. Many of the experimental problems experienced in this study were applicable this project, especially hydrate formation and blockage. Johnson et al. (2009) suggested that steady-state may be a superior method for measuring relative permeability of hydrate bearing sediments. However, these experiments were not conducted at three-phase stability and are only for two-phase relative permeabilities.

Seol et al. (2006) estimated relative permeability of hydrate bearing sediments by inverse modeling by matching predictions with a controlled waterflood experiment. The sandpack
creation, hydrate formation, and coreflooding procedure as well as the setup provided the foundation for the experimental methods used in this thesis. Kneafsey et al. (2011) conducted experiments on the permeability of hydrate bearing sands using x-ray computed tomography. They determined that hydrate significantly influences water flow through the sample which will impact gas permeability. Additionally, hydrate formed not only in pore throats, but also in pore bodies which decreases their size. Therefore, relative permeability should be modeled with hydrate occupying pore throats and smaller pore bodies (Kneafsey et al., 2011; Liang et al., 2011). As discussed, there have been permeability experiments and unsteady-state relative permeability measurements made on hydrate bearing samples. Additionally, permeability in hydrate reservoirs has been measured and estimated from many well tests (Winters et al., 2011; Daigle et al., 2015). However, steady-state experiments have not been run at three-phase conditions. Previous work on hydrate formation and permeability was extremely valuable but much of the experimental procedure had to be created and required significant trial and error.
Chapter 2: Phase 1 – Sandpack Creation and Excess Gas Method

2.1 Overview

The objective of the first phase of this project was to understand and improve the procedure of creating hydrate bearing sediment in a laboratory environment. Multiple methods have been established for forming hydrates in a laboratory setting (Kneafsey 2010). My experimental requirements were a hydrate saturation up to 50% that was quantifiable and evenly distributed throughout the pore space. Therefore, based on Kneafsey (2010), I determined the excess gas method to be the best method for my experiment since it is simple and provides uniform samples. Simply, to form hydrates using the excess gas method, I fully saturated a core (or sandpack) with deionized water and then injected with methane to reach a desired water saturation (30-40%) at room temperature. I then increased the pore pressure to experimental conditions, then the entire system was then cooled into the hydrate stability zone. I achieved this cooling by using the cold storage room in the Jackson School of Geosciences, where the temperature was maintained at approximately 6°C. As the core cooled and entered the hydrate stability zone, hydrate formation occurred. By monitoring the amount of methane injected into the core, I determined the final hydrate saturation to a reasonable accuracy. In this chapter, I discuss the excess gas method, results of my tests, and the challenges faced as I tested and developed my hydrate formation methodology.

2.2 Background/Motivation

The hydrate bearing sandpacks and methodology developed during Phase 1 of the project have been designed to be used in subsequent flow experiments (Phase 2) as well as other experiments within the UT Hydrate Group. As hydrate research continues at UT, there are various research projects that will use synthetic hydrate cores and samples. I tested different
formation methods and provided guidance on future projects to the hydrate group. To create the most realistic and reproducible samples, multiple hydrate formation methods were tested with the goal of creating a homogenous sandpack with a high hydrate saturation. In agreement with my literature review, I confirmed that the excess gas method was the best and most repeatable method for creating a well distributed sample with a high hydrate saturation.

2.3 Methodology

Before all of the ordered equipment for this project had arrived, I aimed to test the excess gas method with basic equipment. The first step of this phase was to design a simple setup that could run the excess gas method, Figure 2-1.

![Initial excess gas setup](image)

*Figure 2-1 Initial excess gas setup*

The core holder used in these initial experiments was a Phoenix Instruments vessel that had an inner diameter of 2” and held a sample ranging from 2-6” in length. The vessel was rated to hold pressures up to 10,000 psi, well beyond the experimental conditions for this project. I only formed hydrates in this vessel and did not perform any core flood experiments during this phase. The simple Phoenix vessel is shown below in Figure 2-2.
To create the sandpack, a known mass of dry sand was measured and then mixed with a known mass of water to create the desired initial water saturation (40%). Based on the volume of the core holder, the amount of sand needed to reach the desired porosity of 35% was determined. In these experiments, I used 50-70 mesh pure silica sand that had a median grain size of 250 microns. Using the volume of the core holder and desired porosity, the mass of sand needed was calculated and weighed in a large plastic bag. Depending on the desired final hydrate saturation, deionized water was added to the sand to reach the desired weight percent up to 40%. The water and sand were then thoroughly mixed together until homogenously distributed. In order to create a sand pack with uniform porosity and water saturation, approximately 3 tablespoons (~1”) were added to the sample at a time. After each addition, the sand was tamped using a tamping rod (1” diameter) to pack the sand. Each addition was tamped 25 times in both the clockwise and counterclockwise direction in order to create as homogenous a pack as possible. By lifting the
tamping rod the same height above the sample, equal amounts of force were applied on each tamp. Additionally, the sample was rotated after each addition to ensure that one side was not over/under tamped. This process was continued until the desired mass of sand and water was added to the core to achieve the intended porosity. By weighing the remaining sand compared to the initial weight of the sand and water mixture, I determined how much sand was added to the core. Since I was assuming the sand and water were evenly distributed throughout the sample, I calculated the porosity (~35%) and the water saturation (40%) and assumed them to be homogenous.

Based on my packing experience and the literature on packing a sand sample (Germaine 2009), I believed that the porosity and water distribution in my sample was homogenous. While the old, temporary Phoenix pressure vessel cannot be CT scanned due to steel parts, I have scanned samples packed with my method in an x-ray transparent vessel (Figure 2-8). The initial sandpacks had a very poor porosity range (±10%) but after improvements in tamping methods, the porosity was more homogenous (±4%). The lower porosity was at the bottom of the core since it was tamped more than the top which has a higher porosity. For the water saturation, I selected a lower water saturation that will coat the grains and not drain to the bottom of the core. While there was likely some water transport due to gravity, the saturation was believed to be homogenous throughout the core. It should be noted that regardless of how good one’s packing methodology is, there will always be heterogeneities in a sandpack. I have used the best method within my abilities and believe I have created a sandpack that will successfully form a homogenous hydrate sample.

Once the sandpack had been created with a known water saturation and porosity, the sample was sealed in the core holder. The confining pressure of the core was increased to
approximately 500 psi with the pore pressure at 0 psi. This effective stress of ~500 psi must be maintained throughout the experiment to maintain the seal as well as keep the sample under constant stress while measuring permeability. The methane tank was then connected to an ISCO syringe pump. To pressurize the pump, the pump was emptied and opened all the way at atmospheric pressure. The pump was then opened to the sample and to the methane tank so the pump and the sample were filled with pressurized methane gas. The pressure was increased on the methane regulator and monitored on the pump and the regulator. While still at room temperature, the pore pressure was increased using a pressurized methane supply as the confining pressure was increased simultaneously. Once the desired pore pressure (1250 psi) was reached and the desired confining pressure (1500 psi) was reached, the pumps were set to constant pressure mode to maintain these conditions. The P-T path of the excess gas method used is illustrated below in Figure 2-3

![Experimental Conditions for Excess Gas Method](image)

*Figure 2-3 PT path of excess gas experiments*
The entire cart (Figure 2-4) was then wheeled into the cold storage room and allowed to cool to ~6°C. As the temperature decreased, the gas compressed so the pump supplied more methane to maintain the pore pressure of 1250 psi. From literature review and past experiments, it was determined that hydrate formation occurs slightly faster if pressurized then cooled compared to cooling then pressurizing.

Once the system entered the hydrate stability zone, hydrates formed after 2-20 hours. Since methane in the hydrate structure occupied less space than free gas, the pump injected more methane to maintain the pore pressure. The conversion of methane and water to hydrate resulted in a rapid injection of methane into the sample that was detectable by the pump. After the initial hydrate formation, secondary formation would continue for days or weeks. The formation of hydrate was limited by the amount of fresh water in the pore space to form hydrate. Approximately 85% of this water was converted into hydrate, but if left for long enough (months-years) greater than 85% conversion of water would occur. The final hydrate saturation was determined by measuring the total amount of methane that was injected into the core as hydrates were forming.
2.4 Results

2.4.1 Excess Gas: Experiment 1

Multiple formation experiments were conducted in order to determine the best method for consistent, homogenous formation. I tested different packing methods, different PT conditions, and pressurization/cooling techniques. By examining the final hydrate saturation and conversion rate, I developed a procedure that worked best for forming hydrates with my setup and conditions. The results from select formation experiments are presented below.

For my first experiment (Figure 2-5), I pressurized the sample to 1250 psi and had the room set to 6.5°C. Based on the P-T diagram (Figure 2-3), this provided ~6°C of subcooling below the hydrate stability curve. At a given pressure, subcooling is how far the temperature is below the stability conditions. In experiment #1, hydrate formation began at 17.5 hours when a large drop in the pump volume occurred. I must first discuss the cyclical behavior of the temperature (and therefore the volume of gas in the pump). This fluctuation was caused by the cooling system in
the cold room, which had two cooling units that cycle on/off in 12 hour cycles. This cycle caused a ±1.2°C fluctuation in the temperature in the cold room. While temperature control was important, the extremely predictable and cyclical nature allowed us to filter out the temperature cycles by adjusting the volumes using the ideal gas law, as seen in Figure 2-6. In addition to filtering out temperature cycles, I changed the y-axis from volume of methane remaining in pump to the total volume of methane injected into core.

![Figure 2-6](image)

*Figure 2-6 Experiment #1 with temperature cycles filtered out and volume of methane injected*

As seen above, approximately 40 mL of methane was converted (injected) in this reaction, which means about 74% of available water in the core was converted to hydrate. This results in a hydrate saturation of 36%. Over the next 30+ hours, methane was still converting, meaning more hydrate was forming. Hydrate formation would continue for a very long time and the formation rate would eventually level off. However, due to time constraints, I stopped the experiments after 5 days or when I achieved a conversion rate of at least 75%.
2.4.2 Excess Gas: Experiment 2

In a subsequent formation test (experiment #2) using the same sandpack, the hydrate formed faster and had a higher conversion rate due to the memory effects that have been documented by other studies (Zhao, 2015, Wu, 2010). To achieve this, I depressurized and warmed up the sample to dissociate the hydrate. Once the core returns to ambient conditions, I re-pressurized and re-cooled the sample following the original procedure. The highest conversion rate achieved was 86% which equals a 43% hydrate saturation. These values were consistent with previously documented maximum values for the excess gas formation (Kneafsey et al., 2011). The results from this highest conversion test are shown below in Figure 2-7.

![Hydrate Formation Experiment #2: Volume of Methane Injected](Figure 2-7 Hydrate formation experiment #2)
As seen above, hydrate formation occurred much faster in this second test and more methane was converted resulting in a higher hydrate saturation, 43%. Hydrate formation began after only 5 hours in the second test, and the rate of formation leveled off much faster. The faster formation time may be due to the memory fact and/or improvements in my experimental procedure.

2.5 Discussion

2.5.1 Sandpack Quality

Multiple additional sandpacks were created and approximately 10 hydrate formation tests were run. After scanning my initial sandpacks, the porosity and water distribution of the sandpacks was determined to be extremely heterogeneous, as seen in Figure 2-8 (Meyer, 2018).

![Figure 2-8 CT image showing porosity of initial sandpack](image)
The porosity ranged from 27-36% due to issues with my tamping method. Therefore, I explored methods to improve my method to produce a uniform and homogenous sandpack. Sandpack creation is a topic that has been explored in great depth, especially in the geotechnical engineering literature. Germaine (2009) provided a thorough discussion of different packing and tamping methods, so I tested and modified my procedure accordingly. Although unable to scan additional sandpacks, the porosity likely improved with the new techniques. However, there are inherent issues with all sandpack methods that will result in heterogeneities.

2.5.2 Determination of Hydrate Saturation

To calculate the hydrate saturation when using the excess gas method, the simple stoichiometry of hydrates was used. The molar ratio for hydrate for one mole of structure I hydrate contains 1 mole of methane and 5.75 moles of water. Since methane in the hydrate phase is denser than free gas, as hydrate forms, more methane gas will be injected by the pump to maintain the pore pressure. The pump kept track of the total volume of methane injected into the core. Using this volume, the number of moles of methane that were injected was determined. Using the molar ratio of hydrate (5.75:1), the number of moles of hydrate present was determined and therefore the volume and saturation of hydrate.

Using the excess gas method resulted in a core where the hydrate saturation was known and was therefore used in my subsequent tests. The excess gas method allowed us to have a good understanding of the mass balance in my system which means I could calculate the hydrate saturation to a reasonable extent. While this initial saturation was an estimate, I run a degassing experiment at the end of each my experiments to confirm the hydrate saturation. In my experience thus far, the final hydrate saturation was within ±2.0% of the initial estimated hydrate saturation.
2.5.3 Hydrate Sample Quality

Not all hydrate formation tests are presented in this thesis. The hydrate tests not presented either took much longer to begin formation or had a significantly lower conversion rate and hydrate saturation. These initial tests helped us determine the best method for sandpack formation and hydrate formation. It appears that in the second reported test (Figure 2-7), hydrate formation began almost immediately once the sample entered the hydrate stability zone. Test 2 had the highest conversion rate and final saturation, likely due to memory effect. Once hydrate has formed in a porous medium and is then dissociated, hydrate reforms in that sample much faster. This phenomenon is referred to as the memory effect. The reason for the memory effect is not specifically understood but is likely caused by remaining structures and methane saturation in the pore fluid. After the initial formation, subsequent formation occurs faster and potentially with a more homogenous distribution. Therefore, after initial formation, I increased conversion and saturation by cycling in and out of the hydrate stability zone (Choi et al., 2014). Hydrate either formed or dissociated almost immediately after entering or leaving stability conditions, respectively. I used this to my advantage by quickly bringing the sample in and out of stability to increase hydrate saturation.

One problem with any of the documented methods of forming methane hydrate, including the excess gas method, was creating a homogenous distribution of hydrate. While there was no perfect solution to this problem, I took many steps to ensure as even of a distribution as possible. By creating a sandpack with homogenous grain size, porosity, and water distribution, I achieved a more even hydrate distribution. Additionally, if the hydrate is left to form over a longer period, this would result in a more homogenous hydrate distribution. Lastly, as seen in Choi et al. (2014), I pressure- and temperature-cycled my samples in order to achieve as
homogenous a distribution as possible. By bringing the sample in and out of the hydrate stability zone, the hydrate was able to form and reform throughout the pore structure and achieved a better distribution. As seen in Phase 2 (Chapter 3), after pressure cycling the hydrate distribution was significantly improved based on the pressure drops between the each section.

For the second phase of my experiments, I needed to be able to create samples that have varying levels of hydrate saturation. Therefore I needed to develop a method where I could control the amount of hydrate created. This control was easily achieved by altering the amount of water initially added to the sample. Since hydrate formation is limited by the initial Sw, I controlled the amount of hydrate formed by increasing or decreasing the amount of water initially in the sandpack. The maximum hydrate saturation for the excess gas method was approximately 45%, and I was able to control and produce hydrate saturations between 20-45%.

2.6 Challenges

Many challenges arose during Phase 1 of this project. The majority of the issues were caused by the sand clogging flowlines or interfering with sealing surfaces. While filters and intensive cleaning helped mitigate some of these issues, they seemed to be unavoidable to some degree due to the size and sheer quantity of sand. To eliminate sand clogs, I placed mesh filter and porous discs at all inlet and outlet points in the core. These filters must be cleaned and replaced regularly to eliminate sediment buildup but when maintained work well at preventing sand clogs. The sealing surfaces in the core holder must be cleaned to create a leak-free seal. Sand, however, inevitably entered these surfaces and prevented the sample from properly sealing. I solved this problem by vigorously cleaning the sealing surface before and after the sample is placed in the vessel. In addition to the cleaning required between each test, I thoroughly leak tested the setup. The initial leak tests lasted for weeks as small leaks were
systematically eliminated. In order to have a good estimate of the hydrate saturation, there must be no gas leaks in the system. The small gas leaks were isolated and removed by tightening or replacing fittings. During my construction phase, I attempted to use as few valves and fittings as possible as to reduce the amount of leak points. After my leak testing, I was able to reduce the leak rate to less than 1.0 mL/week. This miniscule leak rate allowed us to accurately measure the volume of methane that was injected into the core. Most of these challenges were ongoing and had to be monitored to keep experiments operational and safe. The many challenges that arose during the Phase 1 of the project were critical to solve for the success of the overall experiment.

2.7 Conclusions

Through my research and testing, I have decided that the excess gas method was the best method for forming hydrates. I came to this conclusion based on the control I have over hydrate saturation and the potential for good distribution of hydrate (Kneafsey et al., 2011). In order to improve the hydrate distribution, I have developed a method of cycling the core in and out of stability conditions (Choi et al., 2014). This process allowed the hydrate to dissociate and reform with a more homogenous distribution. In addition to hydrate formation procedure improvements, I have developed a packing method to create a sandpack with evenly distributed water saturation and consistent porosity (Germaine, 2009). By creating a high quality sandpack, I was more likely to create well distributed hydrate with a high hydrate saturation. The repeatability and consistency of my packing method was very important in creating a homogenous sandpack so each experiment was run under similar conditions. The results of my flow experiments were dependent on the homogeneity of the sandpack and of the hydrate distribution and therefore, tremendous time and effort was devoted to Phase 1.
Chapter 3: Phase II – Steady State Relative Permeability

3.1 Overview

After my sandpack and hydrate formation procedure was developed, the objective of Phase 2 was to construct a system to perform steady-state relative permeability measurements and develop a procedure for conducting these experiments on hydrate bearing sediments or cores. This phase began once all of the new equipment for my experiment arrived. The most important items were a continuous injection Quizix Pump, a Bronkhorst Instruments mass flow controller, 6 Rosemount differential pressure transducers, and a Phoenix Instruments 24” core holder with 5 incremental pressure taps. The new equipment allowed me to run continuous injection core floods in the presence of hydrates.

3.2 Background

3.2.1 Overview

As discussed in Chapter 1, the process for conducting steady state relative permeability measurements relies on Darcy’s law to solve for relative permeability (Peters, 2012). I will solve for relative permeability given the Darcy-Buckingham equation:

$$Q_i = \frac{k_i KA}{\mu_i} \cdot \frac{\Delta P^i}{L}$$

*Equation 3-1 Darcy-Buckingham Equation*

With this system, I was able to control $Q$, the flow rate, and measured $\Delta P$. $K$, $A$, $\mu$, and $L$ were all known constants. I then solved for relative permeability, $k_{ri}$. Using a mass flow controller (MFC) for the gas and a continuous injection pump for the brine/water, I was able to control the flow rates of the two fluids. I used the pressure taps and differential pressure transducers to measure the $\Delta P$ in psi. The basic setup and flow design is shown in Figure 3-1.
Once steady state was reached and the ΔP does not change with time, I was able to solve for \( k_r \) for each phase, gas and brine. By solving for \( k_{ri} \) at multiple saturations of gas and brine, I was able to create complete relative permeability curves for the two phases.

### 3.2.2 System Construction

With the addition of the new equipment, the first step of this phase was to design and construct the new system to run steady state relative permeability measurements. The complete setup for phase II, with the additional equipment, can be seen below in Figure 3-1.
Once all of the equipment was acquired, the six differential pressure transducers were assembled and placed on the cart in order to be able to move the entire set up into the cold storage room for hydrate formation. Additionally, the Rosemount differential pressure transducers must be wired, calibrated, leak tested, and pressure tested. The transducers are set up to each measure a section of the core and connected to a data acquisition system. The sections and transducers setup can be seen in Figure 3-1 and 3-2.

3.2.3 Three-Phase Conditions

In addition to construction and calibration, I also had to establish a method for keeping the entire core and cart at three-phase stability once hydrate formed. The equipment was on a cart that can be wheeled into the cold storage room at UT, Figure 3-3, however the temperature inside of the cold room was ~6.0°C±1.0°C.
Figure 3-3 Equipment and set up on cart to be wheeled into cold storage room

Given the experimental conditions, this temperature was sufficient for producing hydrates (~6°C subcooling) as it lies within the stability zone, Figure 3-4. However, in order to conduct more accurate relative permeability measurements, I would like the temperature to be more constant than ±1.0°C to stay at three-phase stability conditions. Therefore, I set up a temperature monitoring system in the cold room and measured the temperature at the inlet to the core. Since there is minor insulation from the aluminum core holder, the confining fluid, and the Viton sleeve, the temperature fluctuations in the core were less than in the fluctuations in the room. Additionally, I wrapped the core holder in foam insulation. The temperature fluctuations in the core were approximately less than ±0.1°C, which was constant enough to stay at three-phase conditions.
As seen in Figure 3-4 above, three-phase stability is controlled by pressure or temperature (Liu and Flemings, 2006). However, the pore water salinity also controls the stability conditions and will shift the stability curve towards experimental conditions. Having accurate control of pressure and temperature could be challenging with DI water since any deviation from three-phase stability would result in hydrate formation or dissociation. Therefore, I altered the pore water salinity to shift the stability conditions to the experiment conditions. As seen in You (2015), salinity changes the stability conditions of hydrates. Using code from You, I was able to estimate the three-phase stability salinity for 6°C and 1250 psi to be 10.8% NaCl. After hydrate formation, I added multiple pore volumes of 10.8% brine to reach three-phase conditions, where hydrate should not form or dissociate. The stability curve changes and experiment conditions for phase II can be seen below in Figure 3-5.
3.3 Methodology

Some of the challenges from sandpacks were discussed in Chapter 2, but the main issues with sandpacks were sample pressurization and sand clogs, especially in the pressure taps/transducer lines. The sample would not seal on the sandpack and sand would flow and get into the pressure taps and clog the transducer. I added filters and porous discs but still had significant blockage. After dealing with these complications from the sandpack, I decided to use a sandstone core that had similar properties to a Gulf of Mexico sediment. I used a Boise Sandstone core since it has a high absolute permeability (4-6 Darcy), high porosity (~20%), and comparable grain size. While I will eventually run these experiments on a sandpack, the use of a rock core allowed us proceed with my experiments instead of only troubleshooting the sand
problems. Once I decided to use rock cores, I was able to begin my experiments and successfully run three-phase core floods.

As discussed in Chapter 1, the first step in my experiment was to pack the sample into the core holder with a known water saturation (~35%). Once the sample was packed, the confining pressure was increased to ~500 psi and a constant effective stress of 500 psi was maintained throughout the experiment. I then increased the pore pressure of the sample with methane as I simultaneously increased the confining pressure. Once the sample reached 1250 psi and the confining was 1750 psi, I allowed the sample to reach equilibrium. The pressure transducer lines, which were previously pressurized to ~1500 psi and vented to remove any air from the transducer lines, were then opened to the core and pressure drops across the core were monitored. At this point, since there was no flow, all pressure transducers should read 0 psi. After I ensured there are no leaks in the system, the entire setup/cart was transported in the cold room and allowed to reach experimental conditions ~6°C. The pore pressure was controlled by an additional ISCO pump which was set to constant pressure mode at 1250 psi. As the system cools, gas was injected to maintain the pressure. After 6-15 hours, hydrate formation will begin and can be seen by the amount of gas injected by the pump. In order to allow maximum conversion, I allowed the system to continue to form hydrate for 2-3 days.

Once hydrate formation was complete and pressure cycling has improved hydrate distribution, the hydrate saturation was ~30% with a water conversion rate of ~75%. The next step was reach three-phase stability in the core. Since brine will buffer the formation of hydrates, I have estimated the salinity for three-phase brine at the experimental P-T conditions (1250 psi and 6°C) using code from You (2015). At experimental conditions, the three-phase brine was 10.8 wt% NaCl. I injected brine and bleed off any excess gas in the system until the sample is
fully brine saturated. Once fully saturated, multiple flow rates were injected to determine the pressure drops and measure the effective permeability of the sample when Sh+Sw = 1 (no gas in system).

After determining the endpoint effective permeability for water, I injected gas using the MFC. Gas and brine were injected at multiple flow rates and ratios to alter the gas and water saturation. Using the pressure differential from the different injection ratios, I was able to solve for the relative permeability for each phase and construct a relative permeability curve. A simplified illustration of each step of the flow experiments is presented below in Figure 3-6.

Figure 3-6 (A) Absolute permeability conditions (B) Hydrate formation and brine injection conditions (C) Co-injection of gas and brine conditions
3.4 Step-by-Step Procedure

A step-by-step procedure for forming hydrates and running a steady state relative permeability measurement is given below.

1. Create Sand Pack
   1. Determine desired sample size (volume of sample minus desired porosity (35%))
   2. Weigh desired mass of sand in plastic bag
   3. Zero scale and add deionized water
   4. If using 2.65 g/cc sand, sand to water wt. ratio is 12.13:1 for ~40% Sw
   5. Thoroughly mix in plastic bag
   6. Weigh initial mass of bag+sand+water
   7. After mixture is well incorporated, add to sleeve ~3 tablespoon scoops at a time
   8. Tamp 25x with 1 inch tamping rod – both clockwise and counterclockwise
   9. Rotate sample after every addition as to not over tamp on side of the sample
   10. Continue additions until sample reaches desired height and/or all sand is in core
   11. Weigh final mass of Bag+Sand+Water to determine exact amount of sand added to core (should be zero sand left which would mean bulk porosity is what initially was calculated)
   12. Insert top flange and end cap to seal core

2. Transducer preparation
   1. Close transducer valves to core
   2. Open all transducer valves so transducer system is open
   3. Connect ISCO pump to transducer line
   4. Inject 14% NaCl brine into transducer lines until pressurized to 1400 psi
   5. Open vent fitting on each transducer to purge all air from system
      a. Must be completed for each side on each transducer
   6. Allow system to return to 1400 psi
   7. Zero all transducers on Labview VI
   8. Close of pump valve
   9. Shut valve (green) on each transducer
      a. dP should remain 0 psi for each transducer
   10. Disconnect pump from transducer line

3. Pressurization
   1. With cart at room temperature, close outlet valve and open gas inlet valve (attached to ISCO pump)
   2. Begin ALL data collection
   3. Completely purge ISCO pump, then refill with air so pump reads completely full but is empty
   4. Connect ISCO methane pump to methane source
      a. Pump will be connected to methane tank on one side and core on other side
      b. Pump will not be running
   5. Attach Quizix pump to bottom confining inlet
6. Add confining fluid until confining volume is completely purged of air
   a. Seal confining fluid
7. Increase confining pressure to ~400 psi
8. Open methane source and increase pressure with regulator slowly to ~75 psi
   a. Monitor pump psi (not regulator) to confirm pressure
9. Increase confining and pore pressure in alternating steps of 100 psi until desired
   pressure is reached
   a. Always make sure pore pressure is always below confining, this core holder
      WILL leak if pore pressure>confining pressure
   b. Go as slowly as possible to insure that sand is not disturbed
10. Once desired pressure is reached (1250 psi) close off valve to methane supply
11. Detach system from methane supply
12. Set ISCO pump to constant pressure mode and maintain pore pressure of 1250 psi
13. Perform leak test on set up and make sure the pump holds 1250 psi with very little/no
    leaks
14. Open pressure transducer lines and allow system to reach equilibrium
15. Once pressure transducer are reading dP of zero and system is leak free, prepare to
    move cart into cold room
16. Unplug power supply and wheel cart (minimum 2 ppl) into cold room
17. Immediately plug in power supply (can only run for ~10 min on battery)
18. Make sure pump is still operating and maintaining pressure of 1250 psi and data
    collection is enabled
19. Leave cart in cold room for minimum 2 days to allow for hydrate formation
   a. Ideally 5+ days to allow more conversion

4. Pressure cycling and reaching three-phase stability
1. Using code from You (2015), estimate three-phase salinity
2. Make brine of that salinity
3. Set BPR to three-phase pressure
4. Using Quizix pump, inject brine for 2-3 pore volumes
5. To ensure three-phase stability, lower pressure very slowly and watch for pressure
   rebounds
6. Hydrate should just begin to dissociate and then pressure rebound will be at three-
   phase stability
   a. I have noticed that three-phase stability pressure is slightly below (25-50 psi)
      what is estimated from code
7. Gas should be purged from the sample and should be only hydrate and water
8. Change pump to constant pressure at three-phase pressure
9. Shut in valve before BPR so no flow will occur
10. Allow sample to sit at three-phase conditions
11. Decrease pressure to 50-100 psi below stability
12. Allow sample to sit for ~8 hours
13. Increase pressure to three-phase conditions
14. Allow sample to sit for ~8 hours
15. Increase pressure to 50-100 psi above stability
16. Allow sample to sit for ~8 hours
17. Return sample to three-phase conditions
18. Allow sample to equilibrate for 8 hours
19. This cycling can be completed multiple times to improve distribution
20. After cycling, the transducers should still be reading 0 psi
   a. If not, transducers must be re-zeroed

5. **Injection of gas and brine**
   1. Connect Quizix pump to brine inlet
   2. Have supply of three-phase brine
   3. Connect MFC to gas inlet
   4. Connect MFC to gas supply
   5. Pressurize MFC line to above pore pressure before opening valve to core
   6. Zero scale at effluent collection point to begin mass balance tracking
   7. Begin brine flow and open BPR to maintain pressure in core
   8. Open gas valve and allow gas to flow
   9. Run at multiple injection ratios to change gas and brine ratio
   10. Start with low gas saturation (high brine flow/low gas flow) and move to high gas saturation (high gas flow/low brine flow)
   11. Allow each injection ratio to reach steady state (1-2 pore volumes of fluid injected)

6. **Data Collection**
   1. Data collection must be run through entire experiment
   2. During hydrate formation, must collect data for ISCO pump volume
   3. During injection, for MFC and Quizix pump flow rates and injection volumes must be logged
   4. During flow, there should be a scale to measure the effluent from the core to determine the saturation using mass balance

7. **Degassing**
   1. Once all flow experiments have been conducted sample must be degassed to determine hydrate saturation
   2. Shut in all valves to core (inlet, outlet, pressure taps)
   3. Make sure outlet pressure transducer is collecting data
   4. Connect degassing vessel to outlet and to vent
   5. Using degassing method from Phillips 2018, slowly drop pressure in core and measure amount of methane released
   6. There will be small amounts of free gas before hydrate dissociation
   7. Pressure will not rebound
   8. Once hydrate is dissociating, pressure will rebound
   9. Once pressure rebounds, continue slowly degassing until the pressure is zero
   10. Record all pressures and volumes of methane released
   11. After initial free gas, all remaining methane is from hydrate
   12. Using volume of methane, hydrate saturation can be determined
   13. Compare with estimates from initial saturation from excess gas method
3.5 Results

In this section, I will present results from one two-phase relative permeability measurement in a Berea Sandstone and the two most successful multiphase flow experiments in a Boise Sandstone with hydrates. There were many experiments and tests that did not provide usable data but rather helped to develop or improve my procedure. The lessons learned and process improvements will be discussed in section 3.7. The results from these experiments are not complete but provide a current summary of what I have accomplished to date. My experiments are ongoing and will continue as I pursue my PhD in the Jackson School of Geosciences.

3.5.1 Two-Phase Experiment 1

Due to the complications of sand packs and hydrate, I tested the system with a Berea Sandstone core to confirm that the setup worked with only nitrogen and DI water. By using nitrogen and DI water, I was able to practice taking relative permeability measurements using the new setup before I introduced the complications of hydrates into the system. I conducted absolute permeability and two-phase relative permeability measurements on the Berea core. The results from the two-phase relative permeability experiments can be seen in Table 3-1.

<table>
<thead>
<tr>
<th>Sw</th>
<th>1.0</th>
<th>0.99</th>
<th>0.85</th>
<th>0.68</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>krw (DI water)</td>
<td>0.99</td>
<td>0.92</td>
<td>0.39</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>krg (nitrogen)</td>
<td>0.00</td>
<td>0.03</td>
<td>0.09</td>
<td>0.27</td>
<td>0.68</td>
</tr>
</tbody>
</table>
The saturations were estimated by monitoring the mass balance of the system with a scale and were viewed as rough estimates. The purpose of this experiment was to only verify the equipment worked and familiarize myself with a steady-state experiment. After comparing these results with published results (Chen 2016), I was comfortable with the setup and design and moved forward with the hydrate experiments (Figure 3-7).

3.5.2 Hydrate Experiment 1

The first hydrate experiment, Table 3-2, was run with a Boise Sandstone and only brine was successfully injected since gas caused hydrate blockage at the outlet.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Porosity (%)</th>
<th>Absolute Permeability (Darcy)</th>
<th>Hydrate Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boise Sandstone</td>
<td>~21</td>
<td>3.9-5.5</td>
<td>24</td>
</tr>
</tbody>
</table>

Figure 3-7 Comparison of two-phase relative permeability for Berea sandstone with published results (Chen, 2016).
However, using my process improvements, I was able to successfully determine the relative permeability of brine in the presence of hydrate. To find the relative permeability, I first determined the absolute permeability of the Boise sandstone with a single brine phase. Once the sample was fully saturated with a single phase (DI water), I ran multiple flow rates and measure the dP for each flow rate. I saw a linear correlation between flow rate and pressure drop, Figure 3-8, which was expected based on Darcy’s Law. Since the sample had a high permeability, steady state was reached almost instantaneously.

Experiment 1: Absolute permeability measurement

![Graph showing pressure drop versus flow rate in the Boise sandstone core](image)

*Figure 3-3 Pressure drop versus flow rate in the Boise sandstone core*

From these values, I calculated absolute permeability. The absolute permeability from the Boise sandstone ranged from 3.9 to 5.5 Darcy, which was consistent with established values (Table 3-3). The variation in pressure drop and permeability seen in the sample was due to the natural variance in the permeability of the sandstone.
Table 3-3 Absolute permeability values for different sections of the Boise sandstone

<table>
<thead>
<tr>
<th>Section</th>
<th>Permeability, Darcy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>5.5</td>
</tr>
<tr>
<td>4</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Following the absolute permeability measurements, I formed hydrate in the core and performed my pressure cycling procedure. The hydrate saturation in this sample was 24%. I flowed 10.5% salinity brine through the core at flow rates ranging from 5 to 15 ml/min to measure two phase effective permeability and to ensure linear behavior, Figure 3-9.

Experiment 1: Effective permeability measurement

![Figure 3-4 Pressure drop versus flow rate in the Boise sandstone core with 24% hydrate saturation](image)

After confirming the linear relationship discussed above between pressure drop and flow rate, I calculated effective permeabilities of each section as well as relative permeability (Table 3-4). Section 5 had a much lower permeability, which was likely due to end effects, and not a true representation of the permeability in that section.
After I successfully determined the $k_{rw}$ endpoint, I began gas injection. Once gas was injected, I immediately had a blockage at the outlet and was unable to flow through the core. After testing, I determined this blockage was most likely caused by hydrate formation at the BPR/outlet. I tested multiple methods to solve this blockage and compromised the core in the process. The best method for fixing this blockage was to submerge the BPR in a warm water bath to prevent hydrate formation in the BPR. I used this strategy moving forward. Lastly, the sample was quantitatively degassed, and the final hydrate saturation was determined to be 22.4%. This final hydrate saturation was very close to the initial estimated saturation, and I therefore assumed the hydrate saturation did not change during the experiments.

### 3.5.2 Hydrate Experiment 2

The second experiment that provided usable data was run in the same Boise Sandstone core so the absolute permeability was the same as measured in experiment 1, Table 3-5.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Porosity (%)</th>
<th>Absolute Permeability (Darcy)</th>
<th>Hydrate Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boise Sandstone</td>
<td>~21</td>
<td>3.9-5.5</td>
<td>35</td>
</tr>
</tbody>
</table>

The difference in this experiment was that I was able to successfully inject gas and brine at the same time. However, the MFC that I was using during this experiment did not have a high
enough flow rate to collect data at high gas saturations. Here I will present the data I have for co-injection and present a relative permeability curve for multiple injection ratios. In this experiment, the hydrate saturation was 35% as determined from the methane injected in Figure 3-10.

![Experiment 2: Hydrate formation](image)

*Figure 3-5 Volume of methane remaining in pump for hydrate formation experiment 2*

Once I reached 35% hydrate saturation, I stopped injecting additional methane and began pressure cycling to create a homogenous hydrate saturation. Once I was satisfied by the hydrate distribution, I reached three-phase stability by saturating the remaining pore space with three-phase brine. At this point, there was only brine and hydrate in the pore space. I then injected brine at different flow rates to determine the effective permeability when Sh+ Sw= 1. These multiple flow rates and resulting pressure drops are presented below in Figure 3-11.
Due to the higher hydrate saturation (compared to experiment 1), the permeabilities for these sections ranged from 0.3-0.6 Darcy. The variation in experiment was due to potentially higher hydrate saturation in Section 3 and/or natural variation in permeability of the sample. After collecting this endpoint permeability, I injected gas using the MFC. I was able to inject multiple pore volumes of gas at varying flow rates before hydrate blockage occurred. While I was unable to measure or determine the phase saturations at these different flow rates (see 3.7.1), I was able to measure relative permeabilities for different injection ratios. I started with the higher brine injection ratio and gradually increased the gas injection rate, until I was injecting 85% gas. I was not able to go higher than 85% for this experiment due to flow limitations of the MFC and the high permeability of the sample. With the low flow rate from the MFC and very low viscosity of gas, there was no readable pressure drops at higher gas injection ratios. The results from these different injection ratios are presented below in Figure 3-12.
The figure above was the most successful I have been to date in creating a full relative permeability curve. The low relative permeabilities for middle three data points were probably still at a very low gas saturation. The endpoint (far left) gas relative permeability was collected after injecting gas continuously for over 3 days.

Traditionally, relative permeability is plotted against water saturation, but I do not have an accurate method for measuring phase saturations. This limitation is part of my current and future work as discussed in Chapter 4. With the success of the co-injection, I will continue to run experiments on the core until I can repeatedly run these core floods. With each experiment, my method has drastically improved and the quality of data collected has improved.
3.6 Discussion

3.6.1 Challenges and Troubleshooting

Throughout the formation and flow experiments, I have had issues with sand and sediment causing leaks on sealing surfaces and clogging lines. I temporarily improved this by using a sandstone core instead of unconsolidated sediment.

The most persistent and difficult issue to solve was that hydrate can form anywhere in the core and cause blockages during flow. Since the entire setup was in the hydrate stability zone, hydrate would form if the methane and water of the appropriate salinity come into contact. Having precise control over three variables, salinity, temperature, and pressure, was extremely challenging. I initially wanted hydrate to form in the core, but after initial formation, I wanted to inhibit any further formation. I noticed that hydrate was forming/dissociating near/in the pressure taps which was blocking the pressure transducer lines. This blockage prevented us from being able to accurately measure the pressure drop. Additionally, since each tap was shared by two transducers, if one tap was blocked, two transducers were therefore ineffective. In order to solve this problem, I have filled the transducer lines with brine that is more saline than three-phase stability (~13-15wt% NaCl). This has prevented hydrate from forming in the lines but I still have noticed blockage of at least one pressure tap in each experiment. I have tried increasing the salinity of the brine in the transducer lines to limited success. Additionally, I have injected brine from the transducer lines into the core to dissociate any hydrate that has formed at the pressure taps. Hopefully, this brine will remain in place and prevent any further formation at the pressure taps. However, since this is a dynamic system, the only solution was to ensure I was operating at exactly three-phase stability conditions.
As discussed in section 3.6.1, I have also noticed hydrate formation and blockage with gas injection. Although the system should be fully saturated with three-phase brine, there was hydrate forming in the gas outlet/BPR which prevents flow. As the pressure builds in the core, it reached the supply pressure of the MFC and once those pressures are equal, the MFC no longer flowed. To solve this, I placed the BPR in a warm water bath (~12°C) so that hydrate dissociated and stopped forming in the outlet/BPR. Warming the BPR solved the blockages caused by gas flow, and I was able to flow gas at all flow rates with no blockage.

3.7 Conclusions

I have successfully developed and tested a method for running three-phase core floods in hydrate bearing samples. Having the system and procedure to conduct these experiments was a major breakthrough, and I will now be able to conduct countless experiments using this procedure. While there have been tremendous challenges in reaching this point, the methodology and the experiments have progressed from each failed test. I am now able to form hydrates ranging from 15-35% saturation in a 24” x 1.5” core holder with 5 pressure taps and successfully measure pressure drops as gas and brine are simultaneously injected through the core. With this setup, methodology, and technique, I will be able to collect relative permeability curves for various hydrate saturations and for various samples.
Chapter 4: Conclusion and Future Work

4.1 Summary and Achievements

The goal of this master’s thesis was develop and test a method for determining the three-phase relative permeability of hydrate bearing sediments in order to improve fluid modeling of hydrate reservoirs. I accomplished this by successfully building and testing a system that can form hydrates and run multi-phase flow experiments. Additionally, I was able to collect data to begin to construct three-phase relative permeability curves. While there is still significant work to be done, there has been tremendous progress made and there is a system in place to make these measurements.

1. I developed a method for forming hydrates to a predetermined saturation between 0-45% in a sandpack or a sandstone core. The hydrate that is produced by the excess gas method forms quickly, 5-15 hours, and is more homogenously distributed than other methods.

2. I have increased homogeneity of a hydrate sample by cycling the sample into and out of the hydrate stability zone. This cycling (Choi 2014) allows hydrate to quickly form and reform throughout the core and improves distribution.

3. I have built a system to conduct steady-state relative permeability measurements and have successfully conducted a two-phase relative permeability measurement on Berea Sandstone.

4. I have measured the absolute permeability and two-phase permeability of hydrate-bearing sediments using the steady-state method.

5. I have found the true three-phase stability to be slightly lower (0-100 psi) lower than the estimated three-phase stability.
6. I have successfully degassed my sample to precisely determine the hydrate saturation. The final hydrate saturations that we have determined have been within 5% of the estimated initial hydrate saturation. The low change in hydrate saturation means that there was not significant formation or dissociation after initial hydrate formation meaning three-phase conditions were achieved.

There have been many challenges in this project that have required experiments to be started over, rethought, or abandoned. Each challenge has provided an important lesson and improved our methodology and technique. Sand blockages and hydrate formation/blockages have been the most prevalent problem and will continue to be a problem for all hydrate flow experiments. However, I am confident that I have solutions in place to solve each of these problems moving forward.

4.2 Future Work

As I continue on with this research, there is a lot of work still to be completed on this project. Now that there is a method and system in place to make these measurements, I must run many more experiments at different hydrate saturations. As discussed earlier, three-phase relative permeability measurements have never been made before and present a significant opportunity in the field of methane hydrate research. These measurements will be made to improve our understanding of fluid flow in the presence of hydrates and better predict production profiles.

I will be able to create complete relative permeability curves for a wide range of hydrate saturations. I am currently running the experiments on sandstone cores but will eventually transition back to sandpacks. The sandpacks will be more representative of Gulf of Mexico sediment but present many challenges as discussed throughout this thesis.
Additionally, in order to measure phase saturations, I am currently building a cooling jacket for the core holder so the experiments can be run in a CT scanner. By scanning the core, I will be able to determine the water and hydrate saturation at each injection ratio. This method for determining phase saturation is far superior to using a scale to measure the mass balance and will vastly improve our relative permeability curves.

The relative permeability data collected could then be applied to different models for flow in hydrate systems. Since there is very little data available for the relative permeability of hydrate bearing sediment, these curves would be a major breakthrough for many hydrate models. Most hydrate models currently use an over simplified model of relative permeability so the ability to use laboratory derived relative permeability curves would drastically improve these models of multi-phase flow and production profiles.

Once extensive relative permeability experiments have been run on synthetic hydrate samples, there are opportunities to run these relative permeability measurements on natural samples collected in the Gulf of Mexico. The Jackson School of Geosciences has collected hydrate bearing pressure core samples that are currently stored in the cold lab at UT-Austin. Eventually, I hope to run multi-phase flow experiments on these cores. Due to the extremely high value of each sample, the methodology and technique for co-injection must be perfected before any experiments are run on the natural samples.
References


Chen, X. (2016), Experimental Studies on CO2-Brine-Decane Relative Permeabilities in Berea Sandstone with New Steady-State and Unsteady-State Methods, PhD Dissertation, Univ. of Texas, Austin.


