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New Experimental Approach to Measure Petrophysical Properties of Organic-Rich Shales

Mehrdad Zamirian

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New Experimental Approach to Measure Petrophysical Properties of Organic-Rich Shales

Mehrdad Zamirian

**Dissertation submitted
to the Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements for the degree of**

**Doctor of Philosophy in
Petroleum and Natural Gas Engineering**

Kashy Aminian, Ph.D., Chair

Samuel Ameri, M.S., P.E.

Ebrahim Fathi, Ph.D.

Timothy Carr, Ph.D.

Pramod Thakur, Ph.D.

Department of Petroleum and Natural Gas Engineering

Morgantown, West Virginia

2015

**Keywords: Shales, Steady-State Permeability Measurements, Adsorption,
Desorption, Pore Size Characterization, Matrix-Fracture Characterization**

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ABSTRACT

New Experimental Approach to Measure Petrophysical Properties of Organic-Rich Shales

Mehrdad Zamirian

Production from hydrocarbon reservoirs is strongly dependent on the permeability of the formation. For decades, the permeability of conventional reservoirs, which are typically in milli-Darcy range, has been measured by the steady-state laboratory technique which provides accurate and fast results. In contrast, unsteady state techniques such as GRI or pulse decay have been used to measure the permeability of unconventional formations such as shales due to their ultra-low permeability. GRI technique is carried on crushed samples and is considered a fast technique for matrix permeability measurement. However, recent studies have found that reported GRI measurements results by different commercial laboratories are often inconsistent. This may be related to the sample crushing method. Moreover, GRI technique cannot measure the permeability of the sample under reservoir stress conditions. Pulse decay is a different technique for measuring permeability of the core plugs. Pulse decay measurement results are also found often to be inconsistent.

This study introduces a new, fast and robust technique for measurement of the shale core plug sample permeability under steady-state condition. A laboratory set-up has been designed and assembled which has a resolution of one millionth standard cubic centimeters per second for gas flow rate and one hundredth cubic centimeters for pore volume measurement. This resolution allows permeability measurements in nano-Darcy range. Extremely accurate differential transducers are used to measure the pressure drop as gas flows through the core plugs under confining pressure. The application of confining pressure and maintaining isothermal conditions allows replication of the in-situ conditions. The laboratory set-up is fully automated to eliminate any human error and more importantly to maintain the temperature stable within the enclosed unit. The permeability can be measured under wide range of pore and confining pressures. Gas slippage corrections can be applied to the results to evaluate the absolute permeability. When adsorbate gases such as CO_2 and CH_4 are used in this laboratory setup, the measurements can provide the permeability hysteresis due to adsorption or desorption. Moreover, the ability to test the sample under different stress conditions can be used for the matrix-fracture characterization of the shale sample. Finally, the experimental results can be interpreted for sorption and pore size characterization.

Dedicated to

My mother, the sun of my day

&

My father, the moon of my night

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CHAPTER 1.

INTRODUCTION

1.1 Importance of Unconventional Shale Reservoirs

Unconventional natural gas resources include tight gas formations, coal seams, organic-rich shales and natural gas hydrates. The term unconventional has been introduced to reflect that the conventional drilling, completion, and stimulation practices cannot be applied to these types of reservoirs. Unconventional shale reservoirs, such as Marcellus shale, are sedimentary rocks that are rich sources of natural gas and oil. The application of multi-stage hydraulic fracturing treatments in horizontal wells has allowed enormous amounts of gas to be released from the shale. Currently, shale formations play an important role in hydrocarbon production in the United States. According to the U.S. Energy Information Administration, a 56% increase in total natural gas production from 2012 to 2040 results from the increased development of shale gas, tight gas, and offshore natural gas resources. Shale gas production is the largest contributor, growing by more than 10 TCF, from 9.7 TCF in 2012 to 19.8 TCF in 2040. The shale gas share of total U.S. natural gas production increases from 40% in 2012 to 53% in 2040 (Figure 1-1). This growth results in the United States transitioning from being a net importer of 1.5 TCF of natural gas in 2012 to a net exporter of 5.8 TCF in 2040 (EIA, 2012).

Figure 1-1: Natural Gas Production in U.S. (TCF), *Natural Gas Annual 2012* (DOE/EIA)

1.2 Problem Statement and Motivation

Even though the advances in hydraulic fracturing and horizontal well technology have unlocked considerable reserves of hydrocarbons contained in shale formations, quantification of the key petrophysical properties in shale reservoirs still remain challenging. The permeability of conventional reservoirs, which are in milli-Darcy range, can be accurately and quickly measured by the steady-state laboratory techniques. By contrast, the unconventional formations such as shales typically have permeability values in nano-Darcy range. It is not practical to measure the permeability of the shale samples by steady state techniques because of very low flow rates and length of time required to reach the steady state condition. Therefore, unsteady state methods such as GRI and pressure pulse decay have been extensively used to estimate permeability of the shale samples because they are faster and can measure permeability in nano-Darcy range. However, the permeability values measured by these techniques often exhibit variations by as much as three orders of magnitude. This large margin of uncertainty and non-uniqueness can be attributed to the experimental conditions, interpretations techniques and reproducibility issues. Furthermore, the gas sorption phenomena associated with organic-rich shale results in complexity in the measurement of shale petrophysical properties. These difficulties and limitations were the motivations for the design, construction and the development of the new experimental protocols for a fast, repeatable, and reliable measurement of shale petrophysical properties.

1.3 Research Objectives

The objective of this research is to develop and evaluate a new technique for measurement of the shale petrophysical properties including porosity, permeability, formation compressibility, and sorption parameters more accurately and faster than the commonly used techniques in oil and gas industry.

The other goal of this study is to investigate the effect of different gases on measurement of the shale properties. The results of this study can provide a better understating of the

changes in shale petrophysical properties during production or injection and more accurate prediction for future development.

Throughout the entire life of a reservoir, from drilling to hydraulic fracturing, and throughout the production, the in-situ stress is continuously changing due to the dynamic conditions and inherent behavior of the formation. It is therefore, important to study the effect of these alterations on porosity and permeability. For this reason, the impact of the stress field alterations is investigated as another goal of this study which can provide matrix-fracture characterization.

1.4 Dissertation Outline

This dissertation includes 5 Chapters:

Chapter 1 presents the problem statement, motivations and objectives of this research.

Chapter 2 reviews the background and current methods used in organic-rich shales characterization including adsorption, permeability and pore size measurements techniques.

Chapter 3 introduces the experimental setup (PPAL) and its capabilities for measuring petrophysical properties. The experimental procedure for pore size distribution tests with ASAP 2020 is also discussed. Finally, an optimum experimental protocol to measure the petrophysical properties is presented in this chapter.

Chapter 4 presents the experiments, in chronological order, and their results followed by and the discussion of the results. The determination of the gas permeability, absolute permeability, porosity, adsorption parameters, and pore size distribution are presented and discussed in this chapter. Furthermore, the effect of stress and type of gas on shale properties are evaluated and discussed.

Chapter 5 presents the concluding remarks and recommendations for possible future studies

CHAPTER 2.

LITERATURE REVIEW

Overview

In order to estimate the original gas-in-place, predict the production rates, and optimize the hydraulic fracturing treatments, reliable values of the shale key petrophysical properties including permeability and porosity, which are often characterized by the pore size distribution, along with adsorption characteristics are necessary. The quantification of the shale petrophysical properties, however, is challenging due to the complex nature of the shale. Shale is an organic-rich, naturally-fractured formation with ultra-low matrix permeability. The gas is stored as free gas in the limited pore space of the shale matrix and as an adsorbed gas on the surface of shale organic materials. There is also some gas amount stored as an absorbed gas in the bulk phase and dissolved in water or trapped by clay minerals. To have a better understanding of petrophysical properties of shale different techniques that have been used to measure sorption parameters, permeability, and to investigate the pore size characterization will be discussed here.

2.1 Sorption Phenomena

Gas can be stored by three different mechanisms including absorption, adsorption and as free gas in the organic-rich shales. Absorption and adsorption occur in the rock matrix, while gas can be stored in larger pores and fractures in free state. Gregg and Sing proposed sorption term for absorption and adsorption processes (Gregg, 1967).

Absorption, physical or chemical, takes place at a molecular level where the gas molecules fill the macro-molecular openings. In absorption, since gas is dissolved in the rock or the liquid within the rock, gas molecules are under strong influence of the other phase. Absorbed gas can be released only by heating or chemical treatments.

Adsorption is a physical phenomenon where the gas molecules adhere to a solid surface. On contrast to absorption, intermolecular force between gas and solid is relatively weak. The amount of adsorbed gas depends on the solid surface area in the porous material.

Organic rich shales are suitable for gas adsorption due to presence of the micro and meso-pores leading to large surface areas.

Gas sorption capacity is defined by a nonlinear relationship between the volume of adsorbed gas on the surface of adsorbent and the gas pressure at a constant temperature. Adsorption isotherms have been classified into six types (Sing, 1985) as illustrated in Figure 2-1.

Figure 2-1 : Different Types of adsorption isotherm, (Sing, 1985)

The isotherms for micro-porous materials are normally of the reversible Type I. Coals and organic-rich shales, where natural gas adsorbs to the kerogen, are considered as Type I. Type I isotherm is associated with the monolayer adsorption. Type II and IV isotherms are typically observed in non-porous or macro-porous materials. This type represents unrestricted monolayer-multilayer adsorption. Point B, the beginning of linear section, is where monolayer adsorption concludes and multilayer adsorption initiates. Type IV isotherm exhibiting a hysteresis loop is related to capillary condensation in meso-pores.

The uncommon Type III and V isotherms occur when adsorbent-adsorbate interactions are weak and the gas intermolecular (adsorbate-adsorbate) interactions play the most important role. Type VI isotherm represents stepwise multilayer adsorption on a uniform non-porous surface.

Hysteresis occurs when desorption and adsorption isotherms do not follow the same trend. Hysteresis could be the result of capillary condensation in meso-pores associated with the multilayer adsorption. According to the International Union of Pure and Applied Chemistry, IUPAC, there are four types (loops) of hysteresis as shown in Figure 2-2. Type H1 occurs in regular uniform pores without interconnecting channels. Type H2 occurs in pores with interconnecting channels. Type H3 and H4 are contributed to the slit-like pores. At high pressures, H3 does not exhibit a limiting value while H4 exhibits a limiting value similar to type I isotherm (Sing, 1985).

Figure 2-2: Hysteresis loops

In unconventional reservoirs, sorption isotherms are used for gas-in-place calculations and reserves estimation. Besides, during production of natural gas, the adsorbed gas can be related to the reservoir pressure. The sorption isotherms can be used to predict the

amount of gas released as result of the reservoir pressure drop and to evaluate the potential of reservoir for CO_2 sequestration.

The most common monolayer adsorption model used in coals and shales industry is Langmuir isotherm (Langmuir, 1918) which expresses the gas storage capacity as function of the gas pressure (P) and Langmuir pressure (P_L) and volume (V_L):

$$G_s = \frac{V_L P}{P_L + P} \quad \text{Eq. 2-1}$$

The term G_s is the gas adsorbed (in SCF/ton) at pore pressure P . At higher pressures, all the sites available on the pore wall are occupied by the gas molecules; hence, the rock cannot adsorb any more gas molecules. This point is known as the saturation point and the volume of gas adsorbed at saturation pressure is the Langmuir volume (V_L). The Langmuir pressure, on the other hand, is the pressure at which the half of the maximum adsorption capacity of the shale is taken. Langmuir equation can be linearized by plotting $1/G_s$ against $1/P$ with the slope of P_L/V_L and intercept of $1/V_L$ (Mavor, 1990).

2.2 Gas Sorption Measurement Techniques

There are two common techniques including Gravimetric and Volumetric method for adsorption measurement which will be discussed briefly here.

2.2.1 Gravimetric Method

Di Giovanni (2001) introduced the gravimetric method to measure the mass of adsorbed gas. He used a magnetic suspension balance to measure the adsorption of CO_2 on silica. In this method as shown in Figure 2-3, first, a small amount of sample is placed in a basket where the whole apparatus, except micro balance, is located in a vacuum. The initial mass (MP_0) is measured with the micro balance. Then, the system is filled with helium to a desired pressure. The new mass (MP_1) is measured with the micro balance. The system volume can be calculated based on the helium density. Finally, the system is evacuated and filled with the desired gas and weighted again (MP_2). The mass and

volume of adsorbed gas can be then determined from these measurements (Di Giovanni, 2001).

Figure 2-3: Gravimetric CO₂ adsorption test, (Di Giovanni, 2001)

Gravimetric method was later used by Bea et al. (2006) and Ottiger (2008) on Australian coals. The gravimetric system allowed them to measure adsorption volume up to 40 Mpa pressure and 532 K temperature. Also, series of low pressure adsorption tests such as BET and DFT tests (these methods are discussed in the pore size distribution section of this chapter) were applied to characterize the adsorption and the pore size distribution. Results showed the amount of adsorbed gas has an inverse relation with temperature while it has a direct relation to the pore size and surface area of the coal. Figure 2-4 shows the effects of temperature and the surface area on gas adsorption. Table 2-1 provides the samples surface area obtained by different methods (Bae, 2006).

Table 2-1: Surface areas of different methods, (Bae, 2006)

Method	Coal A	Coal B
BET (m ² /g)	99.223	86.139
DFT (m ² /g)	126.293	114.368

In Figure 2-4, n_{abs} stands for absolute adsorption which refers to actual number of molecules present in the pores, while the scattered smooth line shows the excess adsorbed amount referring to the difference between absolute adsorbed amount and the amount of moles displaced by the volume of the adsorbed phase at bulk density.

Figure 2-4: Effect of temperature on adsorption, (Bae, 2006)

Later, gravimetric adsorption was applied on Sulcis Coal Province (Italy). There, the adsorption of binary and tertiary mixtures of N_2 , CO_2 , and CH_4 were investigated on coals. Their results showed that CO_2 has preferential adsorption over CH_4 and N_2 which indicates the viability of CO_2 storage for enhanced coalbed methane recovery (ECBM) processes (Ottiger, 2008). Similarly, other studies have shown that CO_2 can be adsorbed up to 4 and 10 times higher than CH_4 and N_2 to the surface of minerals, respectively (Melnitchenko, 2000) (Volzone, 2002).

Hence this method measures mass directly; no equation of state is needed to calculate the volume. It is useful when only a small amount of sample is available. This method however cannot be performed under stress conditions since applied on crushed samples.

2.2.2 Volumetric Method

Volumetric sorption measurement technique uses equation of states to calculate the amount of gas adsorbed. This method, which is applied on crushed or plug samples, is performed using a reference and a test cell. In a routine test, a crushed sample is put in a cell (test cell) with known volume and charged to a desired pressure. Then, second cell (reference cell) is charged to a different pressure (usually higher than the test cell). Finally, both cells are connected together and allowed to reach to the equilibrium condition. The test is performed in several stages at successively higher pressures. The amount of the adsorbed gas for each stage is determined using material balance and an Equation of State (EOS). This experiment can be performed at constant temperature by submerging the system in a temperature control bath. Figure 2-5 shows the schematic used to perform volumetric adsorption on coals (Mavor, 1990). Lu improved this method for Devonian shales and suggested that the smaller the reference cell volume is, the more accurate results will be (Lu, 1995).

Figure 2-5: Volumetric adsorption measurement on crushed samples, (Mavor, 1990)

Using EOS to calculate the amount of adsorbed gas, one needs to consider the behavior of a real gas and the gas compressibility effect by imposing gas deviation factor or z-factor in calculations. The inaccuracy in calculation of the gas deviation factor complicates the analysis, especially when a gas mixture is used or test is performed at pressure or temperature close to the gas critical points (Romanov, 2006).

Recently, Kang et al. (2011) introduced a five-stage laboratory technique to measure sorption parameters of Barnett Shale samples to different gas types under different stress conditions. He stated that by performing the adsorption test in only five stages, not only Langmuir volume, V_L , and Langmuir pressure, P_L , can be determined, but also pore volume compressibility, C_p , pore volume at ambient pressure, V_{p0} , and adsorbed phase density, ρ_{ads} can be determined (Kang, 2011). For that, he developed a system of five nonlinear equations as follow:

According to Equation 2-2, the total molar gas stored (n_s) in the pores is the combination of the amount of gas stored as free gas (n_{free}) and the amount of gas absorbed/adsorbed to the pores (n_{ads}).

$$n_s = n_{free} + n_{ads} \quad \text{Eq. 2-2}$$

The adsorbed amount of gas can be defined in a molar form of Langmuir model as shown in Equation 2-3.

$$n_{ads} = n_{max} \frac{P}{P_L + P} \quad \text{Eq. 2-3}$$

Also n_{max} can be related to the Langmuir volume as defined in Equation 2-4 where M is the molecular weight of the gas and w is the weight of the sample:

$$V_L = \frac{M n_{max}}{\rho_{ads} w} \quad \text{Eq. 2-4}$$

The amount of free gas can be determined using compressibility equation of state as shown in Equation 2-5.

$$n_{free} = n_{max} \frac{PV_{eff}}{zRT} \quad \text{Eq. 2-5}$$

V_{eff} is the pore volume with the free gas at pressure P considering the pore compressibility and the adsorption layer thickness. Thus, V_{eff} can be written as Equation 2-5:

$$V_{eff} = V_{P0} - \Delta V_{CP} - \Delta V_{ads} \quad \text{Eq. 2-6}$$

Where V_{P0} is the pore volume at the standard condition associated with the effect of confining stress, ΔV_{CP} , and the adsorption thickness effect, ΔV_{ads} , on the pore volume.

The change in the pore volume due to the compressibility effect can be presented as Equation 2-7:

$$\Delta V_{CP} = C_p V_{P0} P \quad \text{Eq. 2-7}$$

Performing the adsorption experiment at five different pressure steps and using the above equations would yield to calculate the parameters of interest in sorption measurements. This method, however, has some limitations. First, a unique solution for parameters does not exist. Additionally, solving these simultaneous nonlinear equations to obtain unknown parameters is dependent on the initial assumed values for them. Santos modified the five-stage to a faster four-stage method. This method employs a non-adsorbate gas like Helium (*He*) in two equilibrium stages to evaluate pore volume at ambient pressure and pore volume compressibility. The next two stages are conducted with an adsorbate gas such as Carbon Dioxide or Methane in order to determine sorption parameters (Santos, 2012).

2.3 Permeability Measurement Techniques

2.3.1 GRI Technique

A common method used in commercial laboratories for measuring permeability of the crushed shale samples is the GRI technique. This technique, similar to Boyle's law double cell porosity measurement (API 1998), uses Helium as an inert gas, which is expanded from a reference cell into a second cell containing the crushed rock sample and a pressure decay curve is used to obtain the shale matrix permeability. Figure 2-6 shows the set-up for GRI.

Many researchers have compared the results obtained by GRI technique against other transient and steady state ones. A comparison between pulse decay and GRI techniques on Devonian shales reported 3 to 10 times higher permeability values measured by GRI (Luffel, 1993). However, Egermann (2005) compared GRI measurements on cuttings and conventional core permeability measurements and found consistent results. Profice (2011) applied GRI technique to measure the permeability of shale samples using diffusivity equation, assuming all crushed grains are uniformly spherical and they are packed as beds of monodisperse. His technique requires a precise selection of grains for the experiment. He reported not only the size of the grains plays a significant role in permeability calculations, but also a small error in porosity measurement results in a large margin of error in permeability calculations (Profice, 2011).

Figure 2-6: Schematic of GRI technique (Tinni, 2012)

GRI technique is popular because it is fast and inexpensive. However, it has some drawbacks and limitations. Since crushed samples are used in this method, the measurements cannot be performed under confining stress. An adsorption correction must be applied on pore volume measurements when GRI test is performed with Methane or other adsorbate gases. Also, GRI lacks a standard analytical expression and several studies have found significant inconsistencies. Moreover, since the GRI is applied at low pressures, the flow of gas through shale's matrix nano-pores may be governed by free-molecular or transition flow regimes where Darcy's law fails to describe the fluid flow and transport (Wilson, 2012). Finally, recent studies have shown that GRI results are controversial due to the inconsistent measurements results from different laboratories (Sondergeld C. N., 2010). This inconsistency has been related to different sample particle sizes, equilibrium pressures, ratio of the sample to the cell volumes and interpretation techniques (Tinni, 2012). Moreover, it carries the major fundamental problem with the assumption that crushing of the sample will remove the micro-fractures in the shale which could be open under the test condition but most likely are closed under reservoir stress conditions. The presence of micro-fracture has been postulated as the reason for the differences in measured permeability between crushed samples and core samples (Bustin, 2008). Micro-CT images have however shown that micro-fractures can exist, even in finely crushed samples (Tinni, 2012).

2.3.2 Pulse Decay Technique

Pulse decay technique was introduced to measure granite permeability (Brace, 1968). It can be used for permeability measurement in tight rocks with permeability as low as a few nano-Darcy. In this method, a core plug under confining pressure is brought to an equilibrium pressure. Then a pressure pulse is imposed on the upstream side of the plug and the pressure decay and the build-up is recorded over time on the upstream and downstream sides of the plug, respectively. The change in the pressure pulse with time is then interpreted to estimate the sample permeability. To estimate the sample permeability, the slope of a plot of natural logarithm of the pressure vs. time is

considered as a known function of permeability. This interpretation, assumes plug pore volume and rock compressibility are negligible, is based on transient Laplace equation. Figure 2-7 shows the schematic of pulse decay technique.

Figure 2-7: Schematic of pulse decay technique (Jones S. , 1997)

Over decades, researchers have tried to develop analytical solutions for the pressure decay, and to optimize the necessary time to complete the test. A review on the solution suggested by Brace stated that his assumption is valid when the upstream volume is at least 10 times larger than pore volume; otherwise, the ratio of upstream volume to pore volume has to be considered in the experimental set-up or calculations (Yamada, 1980).

Hsieh suggested a general analytical solution which accounted for the rock compressibility and was valid for all combinations of vessel size (Hsieh, 1981). Then, his solution was utilized to calculate specific storage and hydraulic conductivity of shales (Neuzil, 1981).

Lin applied both numerical and analytical methods to solve the diffusivity equation of 1-D flow for rocks with permeability range of 1 to 10,000 nD. He observed that the results of the numerical methods differ from Brace's (1968) analytical method results due to the relative fluid storage. Relative fluid storage is defined as the ratio of the storage volume of the sample to the total upstream and downstream storage volume. His results implied

when relative fluid storage is greater than 0.03, then the analytical results differ significantly from numerical solution of diffusivity equation (Lin, 1982).

Walls introduced a pulse decay method similar to Brace (1968). He used a large upstream and a small downstream volume. A large upstream volume keeps the upstream pressure constant, while allowing pressure to buildup downstream. This specific design of upstream and downstream volumes allows one to analyze the pressure pulse only after 20% decay. He developed an error function for early time solution with upstream constant pressure boundary condition. The permeability results were found in a margin of $\pm 5\%$ for a wide range of steady-state permeability measurements (Walls, 1982). Later, an alternative solution similar to Walls experimental arrangement was introduced by Chen (1984). He concluded that the error function solution is valid when dimensionless time ($t_D = \frac{kt}{\phi \mu c L^2}$: where c is a constant and L is the length of the core plug) is less than one and downstream volume is less than 0.6. For dimensionless times less than 0.3, the solution reduces to Brice's exponential decay solution. Also, He showed that Brace's solution underestimated permeability which is dependent on the downstream to pore volume ratio and only if this ratio is much less than one, exponential decay is valid (Chen, 1984).

Another experimental set-up, which allowed fast and accurate measurement, utilized upstream and downstream vessels with volumes almost equal to the pore volume of the sample. A simple approximate solution with 0.3% accuracy was introduced (Dicker, 1988).

A study on pulse decay demonstrated that the permeability measured by this technique can be interpreted in terms of core scale heterogeneities. It concluded that simplified late time analysis could lead to erroneous results if the core is heterogeneous (Kamath J. B., 1990).

The most common technique used by commercial labs is the one proposed by Jones (1997). This technique can measure permeability as low as 10 nD. In this set up, both upstream and downstream vessels have equal volumes to maintain a constant mean pore pressure during the exponential portion of decay. To eliminate the time consuming

process of pressure equilibrium, the set-up is modified by including two large additional vessels to upstream and downstream in a way that each upstream and downstream volume should be 2 to 20 times the pore volume of the sample (Jones S. , 1997). Figure 2-8 shows the modified pulse decay schematics.

Figure 2-8: Modified pulse decay schematics (Jones S. , 1997)

Recently, pulse decay has been extended to shale formations by incorporating the effect of gas adsorption. These studies state that micro-pores have a unique adsorption behavior which affects the porosity and permeability (Cui, 2009). Another approach to consider the adsorption effect was defined by Akkutlu and Fathi (2012). They assumed that Organic matter, inorganic media and fracture networks are connected in a series arrangement, where the net stress of the system in the pulse decay test is high enough to have the fractures closed. Then a nonlinear history matching algorithm (RML) was applied on the governing transport equation of these series system to find matrix permeability, kerogen to total pore volume, free gas diffusivity in kerogen, adsorbed-phase diffusivity in kerogen, and adsorption kinematics parameters (Akkutlu, 2012).

Pulse decay technique, in contrast to GRI method, can be performed under confining stress conditions. Similar to GRI, it requires accurate pore volume and pore compressibility measurements as well as the correction for adsorption. Pulse decay method can be time consuming and complicated to interpret which are other drawbacks. A single step test for a plug sample with few nano-Darcy permeability might take a week

to complete. In addition, the gas slippage correction (Klinkenberg, 1941) and the recent gas double-slippage correction (Fathi, 2012) cannot be applied to the results. Several researchers have reported that the permeability values estimated by the plus decay method are 2 (Carles, 2007) to 8 times (Rushing, 2004) higher than the values measured by steady-state techniques. These researchers did not provide any explanation for these differences.

2.3.3 Mercury Injection

A number of authors have proposed a relationship between mercury injection curves to capillary pressure and permeability (Thomeer, 1960; Swanson, 1981; Kamath J. , 1992). This technique is not preferable due to contamination of the sample, alteration of the pore structure during high pressure injection, the inability of mercury to access smaller pores, and the inability to apply confining stress.

2.3.4 Steady-State Methods

Beside aforementioned common techniques, there have been some attempts to apply steady-state method to measure the permeability of ultra-tight samples. However, these applications were either limited to micro-Darcy permeability range or lacked validation (Rushing, 2004; Carles, 2007; Sinha, 2012; Wilson, 2012). Therefore, it is essential to develop a robust technique for accurate measurement of the organic-rich shales characteristics under reservoir conditions.

2.4 Pore Size Characterization

According to IUPAC, pores are classified into four categories based on their width shown in Table 2-2. In heterogeneous mediums like rocks, pores ranging in size from micro-pores to macro-pores could be found. Thus, pore size distribution curves are used. Typically, pore size distribution curves are displayed as cumulative, incremental or differential curves. The cumulative curve is a plot of pore volume versus pore width. Derivation of the pore volume with respect to the pore width as a function of pore width is the differential curve, and incremental in pore volume as the function of pore width is

referred to incremental curve. To find the pore size distribution and effective pore size, different methods are used.

Table 2-2: Pore size Classification

Class	Pore Width
Ultra-micropore	≤ 0.7 nm
Micropore	> 0.7 nm and < 2 nm
Mesopore	≥ 2 nm and < 50 nm
Macropore	≥ 50 nm

2.4.1 MICP and NMR Methods

Mercury injection capillary pressure (MICP) and nuclear magnetic resonance (NMR) methods are two of the more common methods to determine the pore size distribution in shales. In mercury injection method, mercury is intruded into the sample at high pressures up to 60,000 psi and the amount of mercury intruded is measured and pore width is calculated as a function of applied pressure. However, in shales, MICP has a limitation (60,000 psi) to measure the pores smaller than 1.8 nm (Curtis, 2011). NMR relaxation spectroscopy which senses the hydrogen atoms inside the pores is another method for pore size investigation. In this method the T_2 relaxation time (change of signals by time) is related to the pore radius. MICP and NMR studies on Barnett shale samples suggested the pore throat radii ranges between 1.8-36 nm and 5-150nm, respectively (Sondergeld C. A., 2010).

2.4.2 SEM and STEM Methods

These techniques image the microstructure of the pores directly. The use of scanning electron microscopy (SEM) can show small pores, however some of the pores are smaller than the maximum resolution of the equipment. Therefore, scanning transmission

electron microscopy (STEM) is used to image pores as small as 2-3nm in diameter (Curtis, 2011).

2.4.3 Low Temperature Adsorption

Difficulties to image or measure pores in the micropore category (<2 nm), necessitates another approach for pore size distribution. Using low temperature (77 K) N_2 adsorption experiments allows access to these smaller micropores. Typically Brunauer, Emmett and Teller (BET) combined with t-plot method (Lippens, 1965) yields the micro-pore surface area and Horvath-Kawazoe (H-K) method is used for micro pore size distribution. For mesopore size distribution and pore volumes Barret, Joyner, and Halenda (BJH) method is used. Also, density function theory (DFT) method is used for micropore-mesopore distribution determination.

For micropore size analysis, the BET method (Brunauer, 1938) is the extension of Langmuir's monolayer adsorption theory to the multilayer. BET theory determines the surface area of adsorbent, assuming the uppermost adsorbed molecules are in equilibrium. The t-plot method which is valid for multilayer adsorption, measures the multilayer thickness of the adsorbed phase under equilibrium conditions. The H-K method (Horvath, 1983), assumes that the adsorbate-adsorbent interaction energy is directly related to relative pressure required to fill a concrete size and shape micropore (Roque-Malherbe, 2007).

For mesopore size analysis, The BJH method (Barrett, 1951) relies on desorption process. At initial stages of desorption where relative pressure (test pressure to the vapor pressure) is close to unity, it involves the removal of capillary condensates (in mesopores) and then desorption involves thinning of the multilayer in larger pores. The DFT method is a statistical technique which uses the isotherm points in the experiment and associates a pore size to the adsorbed amount at that point considering the density profile (Adesida, 2011).

CHAPTER 3.

METHODOLOGY

Overview

This chapter provides the detailed description of the apparatus, the theoretical basis for evaluating different petrophysical properties, and the step by step procedure for performing a complete set of experiments.

3.1 Apparatus Design

The multitasking machine has been designed and constructed in a manner to measure different petrophysical properties by applying different techniques. However, its main purpose is to measure permeability using modified steady-state technique. The apparatus, referred to as Precision Petrophysical Analysis Laboratory (PPAL), is inspired from CORAL (Computer Operated Rock Analysis Laboratory), designed at the Institute of Gas Technology where it was used to measure porosity and permeability of tight sandstones of Mesaverde (Randolph, 1983). PPAL is designed for shale samples with lower permeability and sorption characteristics that can perform tests in a shorter time compared to CORAL taking advantage of recent hardware developments in high precision pressure measurement and data acquisition technology.

PPAL consists of a high pressure biaxial core holder, two one-gallon gas tanks, pneumatic and electric valves, and pressure and pressure-differential transducers. The apparatus is contained in a closed box to maintain the temperature constant during the experiments. The core holder is solid stainless steel and is positioned in the center of the unit allowing it to warm evenly and maintain a constant temperature. Figure 3-1 illustrates the details of the core holder including the fixed and floating ends as well as the rubber sleeve (Dalton, 2012). The core holder can hold core plugs with diameter of one inch and length from one to three inches. The core sample is placed in the sleeve which is made of Viton Synthetic Elastomer. The sleeve isolates the sample from the water that is used to apply confining pressure. An air driven liquid pump is used to

pressure the water up to a maximum of 10,000 psia. The confining pressure is connected to a pressure transducer which can record the pressure with an accuracy of one psia. A calibrated positive displacement pump is used to displace gas into the system for volume measurements. The tanks are used to store gas at upstream and downstream pressure. The tanks are connected to upstream and downstream ends of the core holder. The tank volumes are sufficient to keep the pressure constant during the experiments at both ends of the core holder. The upstream tank is connected to a pressure transducer which records pressure up to 1,500 psia with accuracy of 0.75 psia. A differential-pressure transducer (MDP) with accuracy of 0.2 psia records the pressure difference between the upstream and downstream tanks. Two ultra-precise differential-pressure transducers (UDPT) are connected to the upstream and downstream valves. These UDPTs are capable of measuring the pressure difference of up to 0.5 psia within an accuracy of 5×10^{-4} psia. A manual pressure generator with $4.395 \times 10^{-3} \text{ cm}^3$ volume displacement accuracy is connected to upstream valve at end of UDPT. The compact electric heaters, programmable temperature controller, and circulation fans are mounted on the system to maintain the temperature stable within the PPAL enclosure. The control valves, electric actuators, and sensitive pressure and pressure-differential transducers are utilized to automatically control the flow and monitor the pressures. The data acquisition system, solenoid valves, relays, and a computer with the necessary software (LabView) are used to operate the system and collect the data. Figure 3-2 shows the layout of the PPAL components. For a detailed specification about the components of PPAL, one can refer to Dalton's dissertation (Dalton, 2012).

Figure 3-1: Core holder assembly and a two inch long core plug sample (Dalton, 2012)

Figure 3-2: Schematic of PPAL

3.2 Technical Considerations

Being able to measure flow rate through nano pores and measure pore volumes of shale samples, transducers especially UPDTs must be calibrated regularly. Our experience shows that not only is the factory calibration is not reliable, but also using different gases and different pressures necessitates extra calibration stage in the laboratory. All transducers are designed to record the electrical current as the output. These currents have minimum and maximum values which correspond linearly to a minimum and maximum allowable reading pressure. For calibrating transducers, regularly and with every type of gas, a zero gauge or zero differential pressure is applied to the transducers to record minimum allowable current. Then, a pressure higher than full scale pressure of the transducers is applied to measure maximum allowable current. With these minimum and maximum current values, a calibrated conversion between current to pressure will be obtained.

After calibrating the transducers a moving average should be defined for recording pressure throughout time. These transducers record current as an output every 0.5 seconds and since current is recorded with eight decimals; a small change of current shows a significant change on pressure. Thus, even with the system in a static situation, a fluctuation will be seen in the pressure recordings. To avoid these fluctuations, a floating average of current is defined for PPAL averaging current over a certain amount of readings. This averaging moves with time which impedes current fluctuations in dynamic and static conditions like permeability and porosity measurements, respectively.

The next technical concern is the leakage rate of the system. Since PPAL is designed to measure flow rates as low as $10^{-6} \text{ cm}^3/\text{sec}$, and a complete set of experiments might take a couple of days, we have to ensure that the leakage rate is acceptable over that time. To perform the leakage test, each section must be tested separately. This helps one to find the leaking section(s) which are generally at joints and valves easier. Those sections which are always connected to the up-stream and down-stream tanks (V_4 to V_5 and PV to V_4) are the least important concerned sections. The most vulnerable section to leakage is from V_6 to PV through V_2 where gas builds up in the down-stream and flow rate is measured. The next important section is from V_1 to V_6 which is considered for porosity

measurement (Figure 3-2). Since porosity measurement can be done in less than 10 minutes, a small leakage rate is acceptable and would not make a significant error in results. Generally, for each section the acceptable leakage rate is related to the accuracy of the transducer connected to that section. A leakage test must be run each time the core holder is opened and/or the sample has changed, because these actions put some stress on joints and valves connected to the core holder which might cause leakage. For the sections which are not in direct contact with the core holder, just one leakage test is needed. Leakage tests must be monitored over time (more than 12 hours) in order to eliminate the possible effects of temperature fluctuation in the system and to detect significantly small leakages which may not be detected in a short time period.

3.3 Line Volume and Porosity Measurement

Line volume and porosity of samples are calculated based on the Boyle's law. A modern Boyle's law states that the absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system. Applying this law to PPAL needs some modifications because the gas in the system is not ideal and also since two different sections are connected together, mass of gas is not constant. For porosity measurement, volume of section V_1 to V_2 through V_6 , Called V_D , is needed. For this purpose, first, a blank is put inside the core holder and some confining pressure is inserted on it. Since the blank is not compressible the confining pressure value is not important. Second, section V_1 to V_2 is charged with a down-stream pressure, P_D . Third, by closing valves V_1 and V_2 , this section is isolated. All the sections from upstream tank to pressure generator cylinder (V_3 to V_5) are charged with up-stream pressure P_U bigger than P_D . Fourth, by closing V_5 and V_3 , this section, called V_U , is isolated and pressure is trapped at one end of UPTD₁. When all isolated sections have reached to equilibrium, V_1 is opened and both upstream and downstream sections get connected. When the system reaches to equilibrium, its pressure is a value between P_D and P_U . Therefore, UPTD₁ reads a value greater than zero. Finally, the volume of pressure generator is changed manually (ΔV) till UPTD₁ reads zero. This means that pressure in the whole system has reached to the initial upstream pressure, P_U . Now, the following equations can give the volume of section V_1 to V_2 . In

these equations, in order to reduce the non-ideality of gases their compressibility factors are considered. This procedure can be done for measuring volume of other sections. For porosity measurement, the same procedure can be done except the sample is replaced with the blank, and the difference between the volume (V_D) calculated by the sample and the blank yields the pore volume. For a better understanding, all these stages have been shown in a simpler diagram, Figure 3-3.

Figure 3-3: Volume measurement

At stage one, upstream and downstream sections have been pressurized and isolated. The equation of state for each upstream and downstream chamber can be written as follows, where Equations 2-1 and 2-2 show it respectively.

$$\frac{P_U V_U}{n_U Z_U} = RT \quad \text{Eq. 3-1}$$

$$\frac{P_D V_D}{n_D Z_D} = RT \quad \text{Eq. 3-2}$$

Since the left hand side of Equations 3-1 and 3-2 are equal, the right hand side of both equations will be equal too, as displayed in Equation 3-3:

$$\frac{P_U V_U}{n_U Z_U} = \frac{P_D V_D}{n_D Z_D} \quad \text{Eq. 3-3}$$

Rearranging Equation 3-3 in order to find the relation between upstream moles (n_U) and downstream (n_D) moles:

$$n_D = n_U \frac{P_D V_D Z_U}{P_U V_U Z_D} \quad \text{Eq. 3-4}$$

At stage two, upstream and downstream chambers have been connected to each other to stabilize. Then, by reducing the volume in the upstream chamber, the pressure in connected chambers was brought back to the upstream pressure. The EOS for this situation is:

$$\frac{P_U (V_U + V_D - \Delta V)}{(n_U + n_D) Z_U} = RT \quad \text{Eq. 3-5}$$

The left hand side of Equations 3-1 and 3-5 are equal; the right hand side of both equations will be equal too, as shown in Equation 3-6:

$$\frac{P_U(V_U + V_D - \Delta V)}{(n_U + n_D)Z_U} = \frac{P_U V_U}{n_U Z_U} \quad \text{Eq. 3-6}$$

Replacing Equation 3-4 on the left side of Equation 3-6 to omit n_D from the equation and simplifying it, would yield the downstream volume (V_D):

$$V_D = \Delta V \frac{P_U Z_D}{P_U Z_D - P_D Z_U} \quad \text{Eq. 3-7}$$

This procedure can be repeated for different sections to find the volume of each section, separately. To validate the volume measurements, for each section, the line volume test has been repeated for different upstream and downstream pressures. Final results of line volume measurement for each section are shown in Table 3-1. The detailed results of line volume measurement are discussed in Chapter 4.

Table 3-1: Line volume of each section

Section	Volume , cm ³	Application
V ₁ to V ₆	3.65	Por. / Perm.
V ₁ to V ₂ (V _D)	5.53	Porosity
V ₁ to PV	20.21	Permeability

For porosity calculation, it is sufficient to consider the pore volume of the sample which is added to the line volumes which is measured before ($V_D=5.53$ cc). Thus the pore volume can be calculated as:

$$V_D + V_P = \Delta V \frac{P_U Z_D}{P_U Z_D - P_D Z_U} \quad \text{Eq. 3-8}$$

$$V_P = \Delta V \frac{P_U Z_D}{P_U Z_D - P_D Z_U} - V_D \quad \text{Eq. 3-9}$$

Here is the step by step procedure to perform the porosity measurement:

- ✓ Close valves V_1 and V_4 to separate upstream from downstream.
- ✓ Open all other Valves (V_2 , V_3 , V_5 , V_6 , and PV).
- ✓ Set the upstream pressure by using P_1 transducer.
- ✓ Set the downstream pressure by using MDP partial differential transducer and inserting a pressure difference between two upstream and downstream tanks.
- ✓ Record upstream and downstream pressures (P_U and P_D) and find their compressibility factor.
- ✓ Make sure both UDPT's read a zero value.
- ✓ Close Valves V_2 , V_3 , and V_5 to isolate the streams from the tanks.
- ✓ Open V_1 to connect upstream and downstream and wait for at least one minute till the system reaches to an equilibrium. Meanwhile, keep an eye on UDPT₁ to make sure passes its maximum reading value (0.5 psi).
- ✓ Turn the handle on the manual displacement pump till UDPT₁ reads zero.
- ✓ Read the change of volume on the displacement pump (ΔV).
- ✓ Use Equation 3-9 to find the pore volume and porosity of the sample.

3.4 Adsorption Measurement

Adsorption measurement is based on porosity measurement. First, porosity of the sample is measured with a non-adsorbate gas like helium. Then, the gas in the whole system is replaced with an adsorbate gas like CO_2 or CH_4 , and a porosity test will be applied. Due to the existence of organic materials in the sample, the gas tends to adsorb on the surface area of the sample which decreases the pressure in the system till it reaches to equilibrium where no more gas would be adsorbed. This adsorption, which reduces the pressure in the system, induces an apparent pore volume which makes the manual pump to displace more volume to compensate this reduction in pressure due to the adsorption. When the sample is fully adsorbed and pressure is stabilized at the upstream pressure by using the manual pump, the test is over and the apparent pore volume can be calculated from Equation 3-9. Since the actual pore volume is measured with a neutral gas (helium) before, the difference between apparent and actual pore volumes would be equal to the

amount of gas that has adsorbed. To fulfill a complete adsorption test and calculate Langmuir parameters, the adsorption test has to be repeated at successively higher pressures. The adsorption test is a time taking process which can be optimized by minimizing the number of times the sample has to reach to the equilibrium. For that, it is suggested that during these sequential tests, the downstream pressure of the next stage should be equal to the upstream pressure (equilibrium state) of the last stage. This way the sample will not go through excessive adsorption or desorption due to the change in its pressure.

For adsorption measurement, the porosity with helium is measured only once and all the adsorption measurements are based on the assumption that pore volume of the sample does not change due to the adsorption and compressibility effect. However, recent studies show that pore volume changes due to the adsorption (Santos, 2012). An answer to this issue is that, if the adsorption test is done under a condition that the net stress on the sample is constant, or in other words there is no pore compressibility effect, then the effect of pore volume change due to the adsorption can be ignored because the change in pore volume due to the adsorption is much smaller than the volume of the gas that has adsorbed on the sample. This will be discussed further in the results chapter.

3.5 Permeability Measurement

The permeability of the core sample is measured by introducing a pressure difference across the core sample to allow the gas to flow. Gas flows from the upstream tank through the core sample and then accumulates in the small line on the downstream side of the core holder. This line is connected to an automated bellows valve (PV in Figure 3-2) which is actuated automatically when the pressure difference across the valve reaches a desired value. The pressure difference across the valve is measured with an ultra-precise differential pressure transducer (UDPT₂ in Figure 3-2) with a maximum limit of 0.5 psi pressure-differential. Over time, as the gas accumulates in the downstream line, the pressure difference across the valve increases. Once the pressure difference reaches 90% of transducer's limit, or 0.45 psi, the automated bellows valve is actuated by a computer signal. This valve stays open until the pressure in the line equalizes the downstream tank

pressure (5 to 10 seconds). The valve is then closed and the pressure buildup starts over. Since the upstream pressure is constant during the test and downstream pressure builds up no more than 0.45 psi, the flow rate can be considered under a steady-state condition. The flow rate is then determined based on the difference in the initial and final moles of the gas in the core holder and the downstream line using the measured pressure-differential. This allows flow rates as low as 10^{-6} cm³/s to be determined accurately. The data acquisition system records the pressure buildup in the line over time and the software uses the results to determine the flow rate on real time basis. This would allow the flow to be monitored continuously throughout the experiment. The permeability of the sample under the set conditions (temperature, confining pressure, pore pressure) is then determined by Darcy's equation.

Step by step procedure to perform the permeability test is:

- ✓ Close valves V_1 and V_4 to separate upstream from downstream.
- ✓ Open all other Valves (V_2 , V_3 , V_5 , V_6 , and PV).
- ✓ Set the upstream pressure by using P_1 transducer.
- ✓ Set the downstream pressure by using MDP partial differential transducer and inserting a pressure difference between two upstream and downstream tanks.
- ✓ Make sure both UDPTs read zero.
- ✓ Close valve V_6 to separate the upstream and the downstream of the core holder.
- ✓ Close valve PV for gas build up at downstream during test.
- ✓ Set the software for pressure and time recording.
- ✓ Record the number of the times that PV has been opened from the software panel.
This value shows the number of times the test has been completed.
- ✓ Open valve V_1 to let the gas flow through the sample and begin the test.
- ✓ Stop the test when the measurement has repeated sufficiently.

To find the flow rate, the material balance equation has to be written for the system. For better understanding, only the sections of PPAL which are needed for permeability measurement and calculation have been shown in Figure 3-4.

Figure 3-4: Permeability measurement

Before starting the test, when upstream and downstream are isolated, the pressure after V_6 through downstream tank is P_D . The volume of this section from V_6 to PV known as V_L is measured previously (16.5 cc). The initial number of moles accumulated in the downstream before gas flow can be obtained using Equation 3-10.

$$n_1 = \frac{P_D V_L}{Z_D R T} \quad \text{Eq. 3-10}$$

When the test begins and V_1 is opened, gas flows thorough the sample and accumulates on the downstream which increases the pressure and UDPT₂ increases, too. UDPT₂ shows the increment in P_D . Since the PV valve opens when UDPT₂ reads its maximum value, 0.45 psi, the final pressure at downstream will not exceed 0.45 psi of the initial downstream pressure. So, it can be assumed that due to this very small change in pressure, their compressibility factor (Z) is the same. Similar to the condition before the test, the final mole number accumulated in downstream can be written as Equation 3-11.

$$n_2 = \frac{(P_D + UDPT_2) V_L}{Z_D R T} = \frac{P_D + UDPT_2}{P_D} n_1 \quad \text{Eq. 3-11}$$

Subtracting Equation 3-10 from Equation 3-11, gives the amount of gas that has passed through the sample during the test time (Δt). Equation 3-12 shows the amount of gas that has flowed through the sample during the test.

$$\Delta n = n_2 - n_1 = \frac{UDPT_2 V_L}{Z_D RT} = \frac{UDPT_2}{P_D} n_1 \quad \text{Eq. 3-12}$$

Calculating gas permeability using Darcy's law, volume of flow rate has to be considered at the mean pressure. The mean pressure of the test at the end of the test would be:

$$P_m = \frac{P_U + P_D + UDPT_2}{2} \quad \text{Eq. 3-13}$$

Writing the EOS for the amount of gas passed through the sample (Δn) at mean pressure would give the volume of gas passed through the sample:

$$\Delta V_m = \frac{\Delta n Z_m RT}{P_m} \quad \text{Eq. 3-14}$$

Substituting Equations 3-12 and 3-13 in Equation 3-14, simplifies it as:

$$\Delta V_m = \frac{2V_L Z_m UDPT_2}{Z_D (P_U + P_D + UDPT_2)} \quad \text{Eq. 3-15}$$

The maximum pressure difference (MDP) which can be applied between upstream and downstream of PPAL is 200 psia. Thus, the pressure difference between downstream pressure and mean pressure would never exceed 100 psia. Therefore, is it a safe assumption that compressibility factors at mean pressure and downstream pressure can considered to be equal which cancel each other in Equation 3-15.

$$\Delta V_m = \frac{2V_L UDPT_2}{(P_U + P_D + UDPT_2)} \quad \text{Eq. 3-16}$$

Darcy's law for gases to calculate permeability is:

$$k = \frac{q_m \mu L}{A(P_U - (P_D + UDPT_2))} \quad \text{Eq. 3-17}$$

Replacing Equation 3-16 into Equation 3-17 yields:

$$k = \frac{2\mu L V_L UDPT_2}{A \Delta t (P_U^2 - (P_D + UDPT_2)^2)} \quad \text{Eq. 3-18}$$

Where:

k : Permeability, Darcy

$UDPT$: Pressure build up, atm

μ : Viscosity, cp

P_D : Down-stream absolute pressure, atm

L : Length of the plug, cm

P_U : Up-stream absolute pressure, atm

V_L : Line Volume = 16.56 cm³

A : Cross section area of the plug, cm²

It should be noticed that in Equation 3-18, line volume is considered from V_6 to PV valve, where gas accumulates in the downstream. However, the core sample has its own porosity which adds its pore volume to the downstream volume where gas accumulates. To correct for this, the pore volume of the sample has to be added to the line volume. Thus, Equation 3-18 would be modified to Equation 3-19 where V_{L+P} is the total volume of the downstream section plus pore volume.

$$k = \frac{2\mu L V_{L+p} UDPT_2}{A \Delta t (P_U^2 - (P_D + UDPT_2)^2)} \quad \text{Eq. 3-19}$$

In case the pore volume is ignored in the permeability calculations, it can be claimed that the measurements are still reliable. The reason is that the ratio of pore volume to the line volume is small enough which it would not significantly affect the results. For example a 30 cm³ sample with 3% porosity (typical porosity for Marcellus shales) adds 0.9 cm³ to

the system line volume which is 16.56 cm^3 originally. The ratio of adding pore volume to ignoring pore volume would be 1.05, which means if the pore volume is ignored, the permeability is 5.4% underestimated. In reality, even if 5.4% error is acceptable, still we know that the whole pore volume of the sample is not actually added to the line volume, because one side of the sample is always connected to the upstream which has a different from downstream pressure. So, ideally half of the pores are connected to upstream and the other half has a downstream pressure. This way, 0.45 cm^3 should be considered as the added pore volume to the line volume rather than 0.9 cm^3 meaning 2.6% underestimation of permeability which is an acceptable range of error in the lab. Thus, a higher porous sample results in more underestimating of the permeability if the pore volume is ignored. Ignoring or including the pore volume in the calculations can be determined by defining a tolerance for the error.

3.6 Pore Size Distribution

Pore size distribution was measured using Micromeritics ASAP 2020 which utilizes Nitrogen adsorption at low temperature (77K). Micromeritics ASAP 2020 consists of two Nitrogen dewar flasks, a sample tube, a temperature controller, and an analysis port. Figure 3-5 shows the ASAP 2020 setup.

Before beginning the adsorption test on the sample, it has to be prepared. For that, first the sample has to be crushed and sieved and mixed thoroughly. Then a small amount of sample (typically around two grams) is put into the pre washed and dried sample tube and weight of the sample mass is recorded. This tube is put in the degassing system under the vacuum for couple of hours to make sure no gas is left in the tube. The degassing system is coupled with a heating system that provides one to degas the sample at any desired temperature up to 350°C . The recommended degassing temperature is at the temperature that sample was acquired under the ground or a temperature which does not change the characteristics of the sample (Adesida, 2011). After degassing, the sample tube is connected to the analysis port and dewar flasks are filled with liquid Nitrogen. Weight of the degassed sample and characteristics of the adsorbate (gas Nitrogen) are inserted to the software. Finally, the measurement test and analysis is started from the computer

automatically. After a complete set of adsorption and desorption tests on sample, the software (Micromeritics Datamaster) reports the detailed pore size characterization based on different analysis methods like Langmuir, BET, BJH, H-K, t-plot and DFT in a text file.

Figure 3-5: ASAP 2020 setup

3.7 Test preparation for Permeability Measurement

Shale plug samples obtained from cores are kept in a relative-humidity oven at 60 °C and 45% humidity and their weight is recorded over time until it stabilizes. This temperature and humidity removes all the free water except one or two layers of water on the clays. This condition prevents the minerals deformation due to drying (Bush, 1970; Soeder, 1988).

To place the plug in the core holder, first the fixed end of the core holder is removed. Then, the fixed end and the large rubber O-ring are lubricated with a thick, clean, petroleum jelly. The rubber sleeve is fitted over the greased end. The plug sample is then removed from the sealed container and placed in the sleeve. Then, the floating end of the core holder is inserted into the sleeve such that it comes in contact with the core plug sample. This assembly is then fitted into the core holder body. Both ends of the core holder can be screwed in completely. The confining pressure system is pressurized first. The water line is opened to allow water to pass through the confining pump and into the bottom of the core holders. The valves on top of the core holders are opened until all the air is bled out. The top valves are then closed and the confining pressure is increased until the desired confining pressure is achieved. The valve connecting the pump to the system is closed in order to lock the confining pressure in the core and transducers. Meanwhile the confining pressure is set on the sample, the core holder is completely isolated from the gas line, to prevent water entering the gas line in case the plug is not appropriately inserted in the core holder. The gas is then introduced in to the tanks and the rest of the system. The entire system is brought up to the desired downstream pressure. Then the valve between the two tanks is closed and the upstream tank is pressured up to the desired value (a maximum of 200 psi pressure difference). The access door to the unit is then closed. The heaters are turned on and the desired operating temperature is set. The unit is left uninterrupted until the temperature stabilizes. Once the desired temperature is reached, the gas pressures can be adjusted to the desired set points. Since the PPAL is designed to measure extremely small flow rates, it is imperative to avoid even minute leaks. Thus, the pressure in the system is continuously monitored over an extended period of time. If a leak detected, each section of the plumbing is isolated with ball valves until the exact section that is leaking could be identified and repaired or replaced (If any tube, joint, or valve was replaced in the system, it is crucial to have a new line volume measurement for that replaced section). Once the system is confirmed to have no leakage, temperature is stabilized, and gas pressures are set, the tests can be started.

3.8 Protocol for Complete Set of Tests:

Preparing a complete report on petrophysical properties of a sample requires different tests, with different gases, and at different pressure or temperature conditions. Thus, it is imperative to have a detailed stepwise procedure to optimize the time need to perform the tests and to minimize the damages to the plug sample during the experiments. A stepwise procedure has been prepared here to run a full set of tests on a sample as following:

1. Cutting the core plug sample and dry it in humidity oven at 60 °C and 45% humidity till its weight stabilized.
2. Load the sample in the core holder and insert the confining pressure around 500 psia. This pressure preserves the sample from Geomechanical changes due to net stress effect on it and reveals any possible problem during loading the sample which may lead water thorough the gas lines. If no water leaks from the gas lines, then connect the core holder to the gas system.
3. Pressurize the system with the gas pressure around 200 psia. (If this is the first time, the gas has to be helium as a non-adsorbate gas).
4. Close the box to isolate PPAL from room, and set the temperature and leave it for at least 24 hours till temperature in the whole system reaches to the set temperature. During winter, it might take up to 72 hours for the system stabilizes, since the confining liquid is provided from the water tap.
5. Isolate all the sections in the PPAL by closing all the valves, and monitor the pressure over time to detect leakage in the system.
6. Repair or replace sections showing leakage and monitor the pressure again over time. Repeat this part till no leakage is seen in the system.
7. Set the upstream (150 psia) and downstream (50 psia) pressures, and begin the porosity test and then the permeability test. It is recommended that the permeability should be repeated at least 30 times to be able to determine tests are reliable and the sample is completely saturated (adsorbed/desorbed). The porosity test usually takes 10 to 15 minutes, while the permeability test depending on the permeability and TOC of the sample and the type of using gas might take few minutes to 10 hours.

8. Increase the upstream and downstream pressures for the next pressure test when the test is done at that pressure. At this part, when gas pressure is increased, the confining pressure should be increased in a way that net stress remains constant during the test. In this part, the main interest is measuring the effect of gas type and its pressure on permeability not geomechanical effects on it. Since the net stress does not change during these tests and helium has no adsorption to the shales, it is expected that pore volume and porosity would not change. So, there is no need to perform porosity test every time that permeability has been measured. However, it is recommended to measure the porosity randomly once in higher pressures to validate the initial measurement. For adsorbate gases like CO_2 or CH_4 , the pore volume might change due to the adsorbed layer thickness at high pressures above 3000 psi (Santos, 2012). Since these tests are done at low pressures it is not recommended to measure porosity at every pressure.
9. Repeat the permeability test at more than four different mean pressures between 100 to 400 psia to have a good curve fitting for the gas slippage correction.
10. Repeat the permeability test more than four times, decreasing the mean pressure from 400 to 100 psia. This allows capturing any hysteresis occurrence during adsorption and desorption. This part should be performed when the test gas is an adsorbate and it is not necessary when the test gas is helium.
11. If the next purpose is evaluating the effect of different gases on measurements, go to the next step (step 12), otherwise if the next purpose is evaluating geomechanical effects, skip to step 13.
12. To perform the test with other gases, if the previous gas was an inert gas or had not adsorption effect on the sample, just replace the non-adsorbate gas in the system with the next desired gas. Otherwise, if the sample showed adsorption on the previous gas, take the sample out of core holder, vacuum it for 12 hours and put it in the humidity oven till its weight stabilizes. Then, repeat steps two through ten.
13. To evaluate the geomechanical effects, only confining pressure would be changed. First, measure permeability with a desired gas and pressure at a low net stress and repeat permeability and porosity tests at 500 psia incremental confining

pressures till the confining pressure reaches 9,000 psia or till permeability reaches to a value beyond PPAL's tolerance (1 nD).

14. Decrease confining pressure in 500 psia steps and perform porosity and permeability test to evaluate the geomechanical hysteresis effect on these properties.
15. Finally, crush the sample, sieve it, and perform the low temperature adsorption test and the pore size distribution test using ASAP 2020 when all experiments are done with PPAL. This step can be completed simultaneously at any other steps, if extra sample is available and there is no need to crush the plug core sample.

CHAPTER 4.

RESULTS AND DISCUSSION

Overview

This chapter presents the results of the experiments performed and the evaluation of the porosity, permeability, gas slippage effect, gas type effect, adsorption, stress effect, and pore characterization. A detailed discussion of the results is also presented.

4.1 Line Volume Measurement Results

To validate the results of line volume measurement, a series of sensitivity analysis experiments were performed for every section which its volume was needed for the porosity and permeability measurements. These experiments were designed to evaluate the fluctuation of line volume calculations at different upstream and downstream pressures. Since the volume of each section is property independent from the gas type or the gas pressure, they all should result in the same value. However, due to the gauges reading tolerance, non-ideality of the used gases, inevitable leakage (even though very small), minute temperature fluctuations, and human errors, it is imperative to repeat the measurements enough times to be able to find a reliable result and rule out the erroneous one. This helps to minimize the future errors due to line volume measurements in petrophysical properties measurements.

Volume of three sections of V_1 to V_2 , V_1 to V_6 , and V_1 to PV (See Figure 3-2) were calculated by applying Boyle's law. For each section the experiment was repeated more than 10 times changing the upstream pressure with a pressure difference (MDP) on the other side of the core holder ranging from 70 psia to 170 psia and 10 to 30 psia, respectively. The range of test pressure was based on the API recommended (API, 1998) test pressure for routine porosity core analysis. For the pressure difference on both side of the core holder, this pressure was dictated while the differential pressure transducer (MDP) had a 30 psia limit. However, this transducer was replaced with another one with

200 psia limit to accelerate tests and for CO_2 permeability measurement a year later. Table 4-1 shows the result of the line volume measurement on the section V_1 to PV.

Table 4-1: Line volume measurement for section V_1 to PV

Series Name	P_U Psia	MDP (ΔP) Psia	P_D Psia	Volume Cm^3
68	68.4	11.3	57.1	18.798
	68.05	17.35	50.7	18.913
	68.04	23.65	44.39	18.634
	67.25	28.81	38.44	18.725
171	171.03	12.12	158.91	20.655
	171.1	20.02	151.08	20.699
	168.6	28.01	140.59	20.259
147	147.6	12.05	135.55	20.729
	147.67	17.48	130.19	20.795
	147.77	23.83	123.94	20.307
	147.4	28.31	119.09	20.083
126	126.55	11.62	114.93	20.441
	126.03	18.11	107.92	20.403
	126.05	24.58	101.47	19.927
	123.7	29.33	94.37	19.762
108	108.15	9.986	98.164	19.970
	108	17.04	90.96	20.156
	107.35	20.63	86.72	19.796
	107.7	24.84	82.86	19.782
	107.5	28.16	79.34	19.666

To have a better understanding, these results were plotted based on their upstream pressure and pressure difference in Figure 4-1. Regarding to this Figure, the results from test $P_U=68$ are completely off comparing to the rest of results. Thus, they have to be omitted. For the other four series of tests which were consistent with each other, a statistic analysis was done on them to find a value for the final line volume. The results

can be seen in Table 4-2. Regarding to this table, the volume of that section would be 20.21 cm^3 with 0.20 cm^3 of 95% confidence.

Figure 4-1: Line Volume measurement for V₁ to PV section

Table 4-2: Statistical analysis for Section V₁ to PV

Value	cm^3
Mean	20.21442
Standard Error	0.094838
Median	20.20774
Standard Deviation	0.379352
Sample Variance	0.143908
Skewness	0.137280
Range	1.129051
Minimum	19.66587
Maximum	20.79492
Confidence Level (95.0%)	0.202142

A similar experiment and analysis was done for sections V₁ to V₂, and V₁ to V₆ to find their volumes. The results for section V₁ to V₂ are shown in Table 4-3 and Figure 4-2. The statistical analysis shown in Table 4-4 suggests 5.53 cm³ for the volume with 0.069 cm³ with 95% confidence.

Table 4-3: Line volume measurement for section V1 to V2

Series	P_U	MDP (ΔP)	P_D	Volume
Name	Psia	Psia	Psia	Cm³
170	169.319	16.15	153.169	5.206
	169.73	20	149.73	5.000
	168.91	24.21	144.7	5.535
	169.3	28.28	141.02	5.342
151	151.23	11.86	139.37	4.736
	151.3	20.52	130.78	5.509
	151.3	25.11	126.19	5.509
	151	29.53	121.47	5.518
111	112.1	10.24	101.86	5.173
	111.66	17.28	94.38	5.439
	111.77	25.23	86.54	5.530
	107.58	29.66	77.92	5.636
67	67.3	11.83	55.47	5.201
	67.3	18.53	48.77	5.500
	64.7	25.19	39.51	5.636
	60.73	28.653	32.077	5.723

Figure 4-2: Line Volume for Section V₁ to V₂

Table 4-4: Statistical analysis for Section V₁ to PV

Value	cm ³
Mean	5.534264
Standard Error	0.0309
Median	5.51799
Standard Deviation	0.102485
Sample Variance	0.010503
Skewness	0.082419
Range	0.380785
Minimum	5.341861
Maximum	5.722647
Confidence Level (95.0%)	0.06885

The results for section V₁ to V₆ are shown in Table 4-5 and Figure 4-3. The statistical analysis shown in Table 4-6 suggests 3.65 cm³ for the volume with 0.075 cm³ with 95% confidence.

Table 4-5: Line volume measurement for section V₁ to V₆

Series Name	P _U Psia	MDP (ΔP) Psia	P _D Psia	Volume Cm ³
68	68.4	11.2	57.2	3.624
	68.07	17.35	50.72	4.130
	67.95	24.21	23.44	44.51
	67.26	28.28	28.91	38.35
171	171.38	12.04	159.34	3.003
	170.82	19.8	151.02	3.118
	168.5	28.11	140.39	3.452
147	147.65	29.53	12.07	135.58
	147.67	10.24	17.39	130.28
	147.47	23.88	123.59	3.746
	147.43	28.15	119.28	3.695
126	126.55	11.6	114.95	3.357
	126.2	17.92	108.28	3.359
	126.5	24.43	102.07	3.692

Figure 4-3: Line Volume for Section V₁ to V₆

Table 4-6: Statistical analysis for Section V₁ to V₆

Value	cm ³
Mean	3.646951
Standard Error	0.031671
Median	3.678705
Standard Deviation	0.089578
Sample Variance	0.008024
Skewness	-1.6628
Range	0.294322
Minimum	3.45166
Maximum	3.745981
Confidence Level (95.0%)	0.074889

Subtracting the volume of V₁ to V₆ from the volume of V₁ to PV, would yield the volume from V₆ to PV gives 16.56 cm³ which is used for permeability calculations.

4.2 Steady-State Flow Rate Validation

One of the important and prior objectives of this study was to perform the permeability tests under a steady-state condition. Applying routine and conventional permeability measurement techniques on shales having permeability in the range of nano-darcy is not practical. This was our drive and motivation to design and build PPAL to measure shale permeability. Thus, before any further permeability experiment, validating the steady-state flow rate across the sample is crucial as a proof of concept.

One-dimensional steady-state condition based on Darcy's law is when the pressure drop across the sample stays constant over time (Tarek, 2010). To satisfy this condition, two one gallon upstream and downstream tanks were installed in PPAL to make sure no change in upstream and downstream pressures. To measure the flow rate of the gas through the core plug, the UDPT₂ was improvised at downstream which allows the

pressure to build up only 0.5 psia in the downstream and then releases the gas to maintain the constant downstream pressure and the steady-state condition.

Darcy's law (Darcy, 1856) is valid when the flow is linear. In our studies, the pressure build up on UDPT₂ over time is checked for every cycle in every single experiment to make sure the linear flow is not violated. A cycle of experiment in this study refers to the time when the pressure builds up in the downstream, then it is released by opening UDPT₂ and the permeability measurement is completed. This cycle can be repeated as many times as is desired. Therefore, when 40 cycles have been counted for a test, it means the permeability test was repeated 40 times for the same pressure and temperature condition. Linear pressure build up at UDPT₂ indicates a linear flow of gas through the sample.

Figure 4-4 shows the example of an experiment with N_2 (as a non-adsorbate gas) for 42 cycles during four hours. This means that during this time, permeability has been measured at the same pressures and temperature condition 42 times. Also, the enlarged portion of the figure confirms the linearity of the flow rate over time for one of the cycles. This linear flow allows applying Darcy's law to calculate permeability. To avoid the human error and to minimize the calculation and analysis time, all the calculations were coded in MATLAB. The code receives the recorded pressures over time, gas viscosity, and temperature as an input data, and calculates flow rate, permeability and checks the linearity of the flow for every cycle and reports them in graphs and tables as an output.

Figure 4-4: Repeated cycles in an experiment and linear flow check

4.3 Stress Effect on Permeability and Porosity

This sample was acquired from the Marcellus Shale formation located in Burlington, WV. This shaly limestone sample consisted 17% quartz, 74% calcite, and 6% illite/muscovite and the rest of the weight percent was barite, regarding to X-Ray diffraction tests provided by DOE (URS Corporation, 2012). Moreover, carbon analysis tests showed the sample has 0.8 % total organic carbon (TOC).

4.3.1 Stress Effect on Permeability

The first set of experiments was designed to measure porosity and permeability of shales under different stress conditions. For this purpose, the sample was loaded in the core holder and an upstream and downstream gas pressure was inserted on each side of the sample. Then, porosity and permeability of the sample was measured at different confining stresses increasingly from 1,000 psia to 5,000 psia. To investigate the existence of any hysteresis during the stress change, the test was repeated by decreasing the confining pressure from high to low pressures. To avoid any gas type and pressure effect

on permeability measurements, all the experiments were performed at the same gas pressure with N_2 .

The whole experiment performed at six different confining pressure runs sequentially increasing and five more different confining pressure runs decreasing sequentially (total 11 runs), counted 400 cycles meaning permeability was measured 400 times. In other words, for every confining pressure run, the permeability measurement was repeated 36 times averagely. Figure 4-5 shows results of the permeability measurement at the 3rd run, 65 cycles counted, where the confining pressure was 3,542 psia and the average gas pressure was 470 psia. This run took 2,900 minutes implying each permeability test (cycle) took averagely 44 minutes to fulfill.

Figure 4-5: Permeability measurement of each cycle for Run 4

Figure 4-5 shows that permeability values for those 65 cycles varied between 46.3 to 58.5 nD. Statistical analysis is performed on 65 cycles and single representative value for permeability is reported for specified experimental conditions. R square test is performed to remove the outliers first and then arithmetic averaging is used to obtain the representative value.

In Figure 4-6, the cycles which had R-squared value more than 99.5% were selected and the rest were eliminated.

Figure 4-6: Linear flow check for cycles of Run 3

After the linearity check, 16 cycles were eliminated. Figure 4-7 shows the cycles passed and failed the linearity test together with their distribution.

Figure 4-7: Distribution of cycles which were eliminated and passed in Run 3

Then, a descriptive statistical analysis was applied on the 49 remaining cycles. Statistical analysis results for Run 3 are shown in Table 4-7.

Table 4-7: Statistical analysis for Run 3

Permeability	nD
Mean	51.20143
Standard Error	0.271596
Median	51.21084
Standard Deviation	1.901172
Sample Variance	3.614453
Skewness	-0.17705
Range	8.447212
Minimum	46.27682
Maximum	54.72404
Count	49
Confidence Level (95.0%)	0.54608
Confidence Level (99.0%)	0.728476

In Table 4-7, the mean value, 51.20 nD, is acceptable due to low standard error and standard deviation. Moreover, with 0.728 nD tolerance in 51.2 nD, 99% of cycle tests fall in this range which confirms the repeatability and reliability of the tests.

The R square test and statistical analysis were repeated for all other 10 runs. Finally, a single permeability value was reported for each run. Figure 4-8 shows the summary of 11 runs performed to evaluate the effect of stress on Permeability. Figure 4-8 indicates that as the confining pressure is increased from 1,100 psia to 5,000 psia in six steps (run 1 through 6) permeability has decreased dramatically due to the stress. It can also be observed that the decline in the permeability is linear with respect to the stress. On the other hand, as the confining pressure was decreased (runs 7 through 11), permeability increased linearly with the stress. However, the permeability did not regain its initial value.

Two aspects of these experimental results require further discussion. First, is the alteration in permeability due to the stress change permanent or would it change as a function of time? Furthermore, if alteration in permeability diminishes over time, does the sample regain its initial value, suggesting elastic behavior, or it may show a higher value due to inducing fractures in this unstressed outcrop sample?

To answer these questions, if the permeability alteration is permanent, it means that the structure of the sample was changed leading to permeability reduction. Thus, for future samples, the stress tests should be performed at later stage of the experiments to keep the sample intact. However, the elastic behavior of this specific sample does not mean the same elasticity for other samples. Also, if stress changes have been induced fractures in the sample, its structure has already been changed. Therefore, it is necessary to perform a new set of experiments to determine how permeability will change after an extended period of time. Thus, it was decided to let the sample relax over time in oven (for 2 weeks) and measure its permeability again.

In conclusion the experimental protocol, which was proposed in chapter 3, considered all these issues by scheduling the stress tests at the latest stages of experiments to minimize the damage to the samples.

The second issue is the total time of the experiment. It took 16,550 minutes (11.5 days) to complete these 11 sets of tests consisting of over 400 permeability measurements. Although these measurements proved reliability and repeatability of the experiments, 11 days to complete them is still longer than desirable time of experiment. To optimize the duration of the experiment, it was decided to perform each run with 30 measurements. For example for Run 3, the test could have been stopped after 43 cycles (with 30 acceptable results) which would take 1,880 minutes instead of 2,900 minutes. In summary, the entire experiment (11 runs) could be completed in 8 days instead of 11 days. Table 4-8 shows the statistical analysis for the results of first 30 cycles which had linear correlation coefficient of 99.5% or higher. A comparison between Table 4-8 and Table 4-7 proves that decreasing the number of cycles to minimize the time of the test does not affect the final result for permeability.

Table 4-8: Statistical analysis for Run 3 with 30 cycles

Permeability	nD
Mean	51.45
Standard Error	0.361474
Median	51.2015
Standard Deviation	1.979874
Sample Variance	3.9199
Skewness	-0.19488
Range	8.447212
Minimum	46.27682
Maximum	54.72404
Count	30
Confidence Level (95.0%)	0.73929
Confidence Level (99.0%)	0.99636

4.3.2 Stress Effect on Porosity

The porosity of the sample was simultaneously measured during the 11 aforementioned permeability measurement runs to evaluate the stress effect on porosity. The results are illustrated in Figure 4-9. Increasing stress on the sample resulted in the linear reduction of the porosity similar to permeability. However, the reduction in porosity is less severe than the permeability. As the Figure 4-9 illustrates, porosity lost 20% of its initial value when confining pressure was increased from 1,100 psia to 5,000 psia. In the same of confining pressure range, permeability lost 47% of its initial value. Moreover, after decreasing the confining pressure from 5,000 psia to its initial value of 1,100 psia, the porosity regained its initial value and did not exhibit any hysteresis.

Figure 4-9: Stress effect on porosity

The reason for these different behaviors can be related to the nature of the shales. Shales are known as naturally fractured formations. Beside the fractures, shales contain organic material known as kerogen in their matrix media. Thus, each media has its own porosity and permeability. Generally speaking, permeability of fracture is higher than permeability

of matrix due to the higher conductivity in fractures, while porosity of matrix is higher than the porosity of fracture due to its higher storage capacity. In other words, when a sample, which is a combination of these two media, undergoes porosity and permeability tests, matrix plays the dominant role in porosity measurement, while fracture plays the dominant role in permeability measurement. Knowing this, it can be explained that porosity did not show hysteresis because pores in the matrix media have not lost their volume and grains are not damaged or crushed. On the other hand, the fractures which play the dominant role in permeability did not completely open after the stress was released which caused permeability hysteresis.

The other interesting behavior observed in evaluating the effect of stress was the linear behavior of both porosity and permeability with the stress. Normally, for rocks, by increasing the stress fractures start to close and pores become smaller and finally after a point even grains begin to crush. Since fractures are the dominant player in permeability, it is expected that permeability to decrease much faster when fractures are open as opposed to when fractures are closed and only the matrix provides the flow paths.. In other words, the rate of permeability reduction by increasing stress is higher when the fractures are open (or exist) rather than the time when fractures are closed (do not exist). This type of behavior predicts to have a power or exponential relation between permeability and stress which are reported by many investigators (Athy, 1930; Hoholick, 1984; Shi, 1986; Debschutz, 1989; David, 1994; Evans, 1997; Dong, 2010). For this sample, since the CT-scan photos had confirmed the existence of the fracture, the only explanation for this linear behavior was that over this range of stress, the fractures were fully open and the observed permeability reduction was related only to the fractures.

4.4 Gas Pressure (Slippage) Effect on Permeability

4.4.1 Klinkenberg Correction

When the permeability of a rock sample is measured by the flow of a gas, the measured permeability values increase as the gas pressure decrease because of the gas slippage effect. To investigate this effect, an experiment was designed to measure the permeability

of gas at different gas pressures. To eliminate the effect of stress on the measurements, tests were performed by maintain the difference between the confining pressure and gas pressure constant. Net (effective) stress can be determined from Equation 4-1.

$$P_{net} = P_c - \alpha P_p \quad \text{Eq. 4-1}$$

Where P_{net} is the net stress, P_c is the confining stress, and α is the Biot's poroelastic factors. Biot's factor can be measured by acoustic experiments. For different formations, Biot's factor varies around unity. In this research, it was considered equal to unity.

This set of experiments was performed at 6 different average gas pressures ranging from 465 psia to 1,190 psia while the net stress was constant 3,500 psia. The results are shown in Figure 4-10. It is clearly evident from this figure that at lower pressures (more gas slippage) results in higher measured permeability values. However, the absolute permeability is an intrinsic property reflecting the internal structure of the rock. This means permeability of the rock is a constant value no matter what non-reactive fluid type (with different viscosity) or condition (pressure) is used. Thus, the slippage effect has to be corrected to be able to find the absolute permeability.

Figure 4-10: Gas pressure (slippage) effect on permeability

Klinkenberg demonstrated that the permeability of porous media to gases is a linear function of the reciprocal mean pressure as shown in Equation 4-2 (Klinkenberg, 1941):

$$k_g = k_\infty \left(1 + \frac{b_k}{\bar{p}} \right)$$

$$\frac{b_k}{\bar{p}} = \frac{4c\lambda}{r}$$

Eq. 4-2

Where k_∞ is the intercept and is equivalent to liquid (absolute) permeability, b_k is the slippage factor, λ is mean free path, and, r is pore-throat radius. Thus, the commonly used slippage (Klinkenberg) correction in core laboratories was applied on the results as illustrated in Figure 4-11. According to this figure, the estimated absolute (liquid) permeability from the linear trend analysis is -1.76 nD. This value is obviously not possible since the absolute permeability cannot be a negative value. The reason of this inconsistency is the governing flow regime in the sample and its pore structure requiring further discussion and investigation.

Figure 4-11: Klinkenberg correction on gas permeability measurements using N_2

4.4.2 Discussion on Klinkenberg Correction Failure

Recently, using the focused ion beam scanning electron microscopy (FIB/SEM), have shown that two distinct porous media exist in organic-rich shale, i.e., Organic and Inorganic (Ambrose, 2010). A significant portion of the pores associated with gas storage is found within organic materials “kerogen pockets” that are 200-500 nanometers (nm) in size. The pores in these “kerogen pockets” are in the range of micro-pore (less than 2.0 nm) and meso-pore (2-50 nm) sizes with the average pore size typically being below 10 nm (Adesida, 2011). The pore size range indicates that in general the organic-rich shale can be considered as a naturally occurring nano-porous material. At this scale the classical approach of modeling gas flow based on continuum equations may not be valid.

Knudsen number (K_n), defined as the ratio of molecular mean free path to a characteristic length of pores (H), is used to determine the validity of continuum equations. Different flow regimes based on Knudsen number are categorized to (Roy, 2003):

1. Continuum (viscous) flow ($K_n < 0.001$): In this regime, all conventional fluid dynamic equations such as Euler and Navier-Stokes equations are valid.
2. Slip flow ($0.001 < K_n < 0.1$): In this regime, gas molecules slippage at the surface of porous media dominates the flow. Gas slippage near solid walls was first introduced by Maxwell (Maxwell, 1879). In this case, Navier-Stokes equations with slip conditions can be used to describe the fluid flow in porous media.
3. Transition flow ($0.1 < K_n < 10$): In this regime, a combination of slip and diffusion flow occurs. The diffusion can be the bulk diffusion in large pores due to natural collision of gas molecules with each other and/or Knudsen diffusion where pore diameters are comparable with molecular mean free path leading to promotion of fluid-solid interactions. In some cases adsorbed phase transport or surface diffusion can also be dominating if significant organic nano-pores are available. In transition flow regime, conventional fluid dynamic equations fail and more general equations such as Burnett or Boltzmann equations are required to describe the fluid flow and transport. However, attempts have been made to correct Navier-Stokes equations in

this flow regime (Sampath, 1982; Mitsuya, 1993; Beskok, 1999; Tang, 2005; Zhu, 2007; Ziarani, 2012).

4. Free molecular flow ($K_n > 10$): In this regime, the molecular model which considers the fluid as a swarm of discrete particles colliding and streaming in capillaries is required.

It is important to know that Klinkenberg validated his equation using samples with permeability in the order of milli-darcy. However, this relationship fails in formations with permeability in the nano-darcy range. Klinkenberg's theory considers the momentum carried by the gas molecules hitting the pore walls, gas slippage, which results in higher gas rates. However, it ignores the momentum that gas molecules can carry to the bulk fluid. Recently, by using a Lattice Boltzmann simulator, the momentum carried by bouncing back molecules was incorporated in slip flow leading to a linear relation between permeability and reciprocal of pressure-squared "Double Slippage Correction" as follow (Fathi, 2012):

$$k_g = k_\infty \left[1 + \left(\frac{b_k}{p} \right)^2 \frac{L_{Ke}}{\lambda} \right] \quad \text{Eq. 4-3}$$

Where L_{Ke} is a length scale associated with the kinetic energy of the bouncing-back molecules. The double-slippage effect can lead to measured permeability values that are higher than those predicted by Klinkenberg theory at low pressures. Others have observed this phenomenon where the higher gas flow was inadvertently attributed to turbulent flow in nano-pores at low pressures (Rushing, 2004) while the impact of the turbulent flow in shale due to very low Reynolds number (Wu, 1998) is negligible as compared to gas slippage effects at low pressures.

4.4.3 Double Slippage Correction

The double slippage correction was applied to the gas permeability results because Klinkenberg correction failed to provide a feasible value for the absolute permeability.

The double slippage correction as illustrated in Figure 4-12, resulted in a value of 12.15 nD for absolute permeability which is a feasible value.

Figure 4-12: Double slippage correction on gas permeability using N_2

To confirm the validity of this analysis technique, more experiments were needed. Furthermore, the experiments should be repeated for different gases to assure the consistency of double slippage analysis technique. Finally, it is necessary to determine the flow regime during the experiments to theoretically justify the application of the double slippage correction. Estimation of the flow regime requires pore size distribution of the sample which could be obtained by using ASAP 2020.

4.5 Relaxation Effect on Permeability

As mentioned earlier, one of the questions needed to be answered was to check whether the hysteresis observed in permeability as the result of the stress changed is permanent, or it will diminish over time. Thus, the sample was stored in the oven for two weeks to

relax, and the stress tests were repeated. To eliminate the gas slippage factor, the experiment was performed at the same gas pressure used during the previous stress tests. Figure 4-13 shows the results of permeability under stress conditions after relaxation and compares them against the original results (before relaxation).

Figure 4-13: Permeability comparison under stress effect before and after relaxation

Figure 4-13 indicates that the permeability value increased to values higher than its initial value after relaxation. The permeability values are significantly higher at low stress (confining pressures of 1,100 psia) and merges into the measured values prior to relaxation at high stress (confining pressures 4,000 psia). Therefore, it can be concluded for this originally unstressed sample (outcrop sample), fractures have been induced due to stress changes.

Ruling out the possible mistakes during permeability measurement, the slippage effect was evaluated on the sample and compared with results gained prior. Being able to compare permeability before and after relaxation, the stress condition (3,500 psia) on the sample was kept the same. Figure 4-14 and Figure 4-15 show the comparison by Klinkenberg and double slippage corrections, respectively.

Figure 4-14: Klinkenberg correction: Comparison between before and after relaxation

Figure 4-14 shows that Klinkenberg correction fails by providing a negative 8.8 nD for the absolute permeability, while Figure 4-15 illustrate a feasible 45.98 nD for the absolute permeability after relaxation which is almost four times higher than before. Therefore, extra fractures have been induced in the sample under stress changes escalating in permeability.

Figure 4-15: Double slippage correction: Comparison between before and after stress relaxation

4.6 Effect of CO₂ on Petrophysical Properties

Organic materials known as kerogen packets play an in important role in production in coal bed methane and shale formations. It is crucial to evaluate the behavior of these formations when they are in contact with adsorbate gases like CH_4 and CO_2 during production or injection. Therefore, it was decided to continue the experiments and measure porosity, adsorption and permeability with stress effect on it with CO_2 . The reasons why CO_2 was chosen rather than CH_4 were safety issues, lower price and higher adsorption of CO_2 as compared to CH_4 .

4.6.1 CO₂ Permeability Measurement

First, a set of experiments were performed on the sample to evaluate the effect of CO_2 pressure and slippage on the permeability. To eliminate the stress effect on measurements, net stress was maintained at 2,600 psia. Moreover, these experiments were performed at gas mean pressure between 130 to 300 psia. Results of this experiment

after Klinkenberg and double slippage correction are shown in Figures 4-16 and 4-17, respectively.

Figure 4-16: Klinkenberg correction on CO₂ measurements

Figure 4- 17: Double slippage correction on CO₂ measurements

Similar to N_2 measurements, the Klinkenberg correction failed, while double slippage correction resulted in a 28.89 nD value for the absolute permeability.

Since these measurements were done before with N_2 , the absolute permeability results from N_2 and CO_2 are compared with each other. The experiment with N_2 was done at 3,500 psi net stress (Figure 4-15) while it was done at 2,600 psia for CO_2 . Therefore, we expected to have higher absolute permeability with CO_2 than N_2 . On the contrary, the measurements with CO_2 after relaxation provided a lower absolute permeability value (28.89 vs. 45.98 nD). This means that due to the adsorption of CO_2 on the surface area of the pores, the open pore radii became smaller, resulting in a lower permeability.

Changing the permeability due to the gas adsorption necessitates checking the adsorption effect on the porosity, too. Thus, after the permeability tests, at different gas pressure step, the porosity of the sample was also measured. Results summarized in Table 4-9 states that the adsorption of CO_2 on the sample did not affect the porosity.

Table 4-9: Porosity Results at 2,500 psia net stress

Gas	Temp., ° F	Press., psia	Porosity, %
N_2	80	465	4.32
CO_2	79	139	4.39
CO_2	79	162	4.29
CO_2	79	187	4.22
CO_2	79	211	4.36
CO_2	79	238	4.35
CO_2	79	296	4.37

After the slip effect on the sample with CO_2 , the effect of stress change of on the permeability using CO_2 was evaluated on the sample. For that, the sample was charged at 275 psia average pressure and the permeability was measured by increasing the confining pressure from 1,000 to 5,300 psia and then decreasing it to the initial stress, similar to experiments with N_2 . Figure 4-18 illustrates the results.

Figure 4-18: Stress effect on permeability measurement using CO_2

The results are similar to those obtained with N_2 . Hysteresis in permeability was also observed as the stress was decreased. Permeability lost 37% its initial value at 2,300 psia stress (the highest permeability value on the blue line). However, the permeability value only increased by 6% when the stress was decreased by 4,300 psia. The permeability value varied linearly with the stress. This linear behavior which is consistent with results with N_2 strengthens this hypothesis that in this stress range, fractures are still open. This hypothesis will be verified later.

Conducting experiments with CO_2 had two significant outcomes:

1. Prior to CO_2 experiments, it was intended to complete the tests as high as 500 psia CO_2 pressure, the limit CO_2 remains in gas phase. However, during the experiments, it was noticed that above 280 psia pressure, CO_2 becomes so dense

that 30 psia pressure difference along the core is not sufficient to allow the gas flow in reasonable time. Thus, it was decided to change the MDP differential transducer with a new one allowing up to 200 psia pressure difference along the core. This modification allowed the experiments at higher pressures to be performed while maintain the measurement time reasonable. However, a sensitivity analysis is required to check the accuracy of the results and the steady state flow assumption.

2. It was noticed that nano pores shrink when they adsorb CO_2 which decreases the permeability. Similar to stress, it was crucial to determine whether hysteresis is present during desorption. Moreover, to find whether desorption is a reversible process, a low temperature adsorption/desorption test with ASAP 2020 is required. Therefore, it was planned to check both desorption and adsorption effects on permeability later and perform a low temperature adsorption test on the samples.

4.6.2 CO_2 Adsorption Isotherm Parameters

One of the capabilities of PPAL is measurement of the adsorption parameters i.e. Langmuir volume and pressure. To measure these parameters, first any remaining gas from previous experiments must be extracted from the sample by putting the sample under vacuum and drying it using temperature controlled oven. For this reason, the sample was removed from core holder to extract the remaining CO_2 from previous experiments. It was noticed that the sample had highly swelled which could be seen by naked eyes. This known deformation caused by adsorption has been reported and studied by several authors on coal and shales (Ross, 2007; Cui, 2009; Yang, 2011). Figure 4-19 shows the sample after deformation. This deformation, which might have significant effect on the structure of the sample in micropore size scale, might change properties like permeability and porosity. Thus, it was decided to perform the adsorption test to capture the utmost possible deformation, and repeat the permeability and porosity tests after that.

Figure 4-19: Deformation after CO₂ adsorption

When the sample weight stabilized and did not change over time and making sure no gas is remained in the sample, it was returned in the core holder. Under constant net stress of 2,500 psia and temperature of 79 °F, the adsorption test was performed at nine successive pressures from 100 to 380 psia. At each pressure step, the volume of gas adsorbed on the sample was measured and after finishing all the steps, in a plot shown in Figure 4-20, reciprocal of adsorbed volume was plotted against reciprocal of the pressure to find the Langmuir volume and pressure by a linear curve fit. Results show that this sample has a 54.35 SCF/ton Langmuir volume and its Langmuir pressure is 240 psia.

This experiment took three months to successfully complete. The reason for such a long time is related to the design of UPDT₁ in PPAL (see Figure 3-2). The adsorption test is based on porosity measurements using UPDT₁ with the maximum limit of 0.5 psia. For porosity or adsorption tests, the sample is at equilibrium with downstream pressure and after connecting the upstream chamber to it and by using the manual pump, pressure of the sample (a pressure between downstream and upstream) will be brought up to the upstream pressure, where UPDT₁ reads zero. When a non-adsorbate gas is used in the system, it does not take much time (couple of minutes) for the system to reach to

equilibrium at upstream pressure since there is no adsorption, while using CO_2 as an adsorbate gas, it takes much longer time. Because every time the manual pump is turned, it was only possible to increase the equilibrium pressure by 0.5 psia. This limitation of PPAL, which involves manual increases in pressure by 0.5 psi, required three months to reach equilibrium at upstream pressure to measure the adsorbed gas volume. Thus, the adsorption isotherm measurements were limited to this single set of measurements. However, it is proposed by adding two valves after the one gallon tanks and a new transducer to PPAL, the problem can be solved and routine adsorption tests can be performed.

Figure 4-20: Adsorption isotherm parameters

Earlier to this experiment, a crushed portion of this sample was sent to a commercial lab for adsorption isotherm measurements to compare the results obtained by PPAL. However, it is useful to understand the differences in experimental procedures between the commercial lab and PPAL which may affect the results.

The first difference is the temperature of the experiments. The commercial lab performed the experiment at 169 °F while it was performed at 79 °F with PPAL. Adsorption has a reverse correlation with temperature.

Second is the alteration of the surface area of the sample. In the commercial lab, the experiment was performed on a crushed sample without stress application, while in PPAL it is performed on a core plug under confining stress. Crushing the sample provides more surface area for the gas to adsorb.

The commercial lab had completed the experiment in six successive steps from 107 psia to 1,490 psia. They resulted in 84.23 SCF/ton and 2749 psia for Langmuir parameters while with PPAL these parameters were 54.35 SCF/ton and 240 psia. This means more than 50% difference in Langmuir volume and 1,000% difference in Langmuir pressure. Even though the experiments were performed at different conditions, this level of inconsistency cannot be attributed all to the test conditions. Thus, either the results from the commercial lab or PPAL are not reliable. To find the answer, a search in literature was conducted to find a reported adsorption results on Marcellus shale samples which had similar TOC to our sample (0.8 %) and the test was performed at a temperature condition close to one of the two sets of tests. A reported CO_2 adsorption measurements on crushed Marcellus sample with 1.2% TOC at 104 °F at nine successive pressures approximately from 50 to 600 psia, indicated 63.7 SCF/ton and 263.2 psia for Langmuir volume and pressure, respectively (Heller, 2014). This crushed sample had higher TOC and the test was performed at higher temperature than our sample. The higher TOC compensated for the higher temperature and resulted in a slightly higher Langmuir volume and pressure. Based on this comparison, it was concluded that the commercial lab results were incorrect and the measurements with PPAL are reliable. Table 4-10 and Figure 4-21 show the comparison between PPAL, commercial lab and Heller results.

Table 4-10: Adsorption isotherm: comparison between different labs

Lab	Sample	TOC, %	Temp., ° F	P _L , psia	V _L , SCF/ton
PPAL	Plug	0.8	79	240	54.35
Heller	Crushed	1.2	104	263	63.7
Commercial	Crushed	0.8	169	2,748	84.23

Figure 4-21: Successive adsorption study: comparison among different labs

4.7 Pore Size Distribution

A low pressure/temperature N_2 adsorption/desorption test was needed to find the pore size distribution of the sample, average pore size, shape of the pores, and find possible hysteresis during adsorption and desorption. Having the pore size distribution and its average size would support the reason to apply double slippage correction. Also, knowing the possible hysteresis during adsorption and desorption phenomena would clear new

horizons for better understanding of the pores and their petrophysical properties like permeability behavior during these processes.

A sequential adsorption and desorption tests were applied on the 60 °C degassed chunk sample. Recent studies show crushing the samples significantly increases the pore volume and the surface area; however, it does not affect the pore size (Adesida, 2011). Thus, this sample was not crushed and the test was performed on a small chunk of it. Regarding to Figure 4-22, desorption shows hysteresis consistent with H3 hysteresis loop type suggesting slit-like pores (Sing, 1985).

Figure 4-22: Low temperature adsorption/desorption

BET and t-Plot methods were used for surface area determination. BET provides the total surface area and t-Plot provides the external surface area. The difference between these two surface areas, results in micropore surface area. Also, t-Plot method results provide the micropore volume. Knowing the pore shapes (slit-like), the effective pore size in micropore category can be calculated as Equation 4-3:

$$d_{eff} = \frac{2V_{t-plot}}{A_{t-plot}} \quad \text{Eq. 4-4}$$

HK method for micropore size distribution and BJH method for micropore-mesopore size distribution were used. Result of each method is shown in Table 4-11. Also, Figure 4-23 shows the pore size distribution.

Table 4-11: Pore size distribution results

BET		t-Plot			
Surface Area m ² /g	Average Pore Width nm	External Surface Area m ² /g	Micropore Area m ² /g	Micropore Volume cm ³ /g	Average Micropore Width nm
1.3931	7.58	0.8666	0.5265	0.000226	0.858
HK		BJH (2-50 nm)			
Micropore Volume cm ³ /g	Median Pore Width nm	Surface Area m ² /g	Volume cm ³ /g	Average Pore Width nm	Micropore %
0.000569	1.57	1.661	0.002137	6.48	21.02

Figure 4-23: BJH pore size Distribution

Pore size distribution section can be concluded as:

1. The adsorption/desorption test is done at 77 K where N_2 liquefies, the adsorption reaches to its maximum value, and liquid condensation in the pores causing hysteresis can be captured. According to CO_2 results, permeability of the sample was altered and since N_2 has adsorption, even very small, it might affect permeability especially for samples with much higher TOC and more adsorption. Since this sample had low 0.8% TOC, probably the adsorption effect of N_2 was not significant on the permeability. To evaluate this theory, it was decided to perform permeability test with He as well as N_2 and CO_2 because He has less adsorption tendency and its smaller molecular size might provide accessibility to the smaller pore N_2 could not penetrate into.

2. Capturing hysteresis during N_2 desorption, brought up the possibility that permeability might show hysteresis during desorption. To evaluate this possibility for permeability, the experiment should be started at low gas pressures and be increased successively to complete adsorption, and then the gas pressure should be decreased successively to the initial low pressure to complete desorption. Therefore, the adsorption/desorption permeability experiment was planned for the next step using He , N_2 , and CO_2 .

4.8 PPAL Modification and Optimization

Regarding the difficulties encountered during permeability measurement using CO_2 , as mentioned earlier, the current MDP transducer was replaced with a new one allowing up to 200 psi pressure difference along the core holder. To validate the accuracy of measurements at higher differential pressures, four set of experiments were designed. These experiments were performed at four different sets of upstream and downstream pressures in a manner that average pore pressure remains constant. Since gas permeability is related to the average pore pressure, these sets of experiments allow to check the accuracy of measurements at higher differential pressures and to validate the dependency of gas permeability on average pore pressure, not the pressure difference along the core. In other words, gas permeability is not dependent on upstream or downstream alone, but it is only dependent on mean pressure.

According to Figure 4-24, when the pressure difference along the core holder increases from 52 to 181 psi, the average time needed to complete a cycle reduces 4 times and the fluctuation in each cycle's measurement reduces, too. In other words, with higher differential pressures, not only more cycles are completed in a shorter time, but also a smaller number of cycles are needed for the measurement to reach to a steady state condition where all the flow paths in the sample are developed. Moreover, all the measurement results are consistent with the same gas permeability, stating the measurements are only dependent on average pore pressure, not other individual pressures. A detailed comparison between different experiments is shown in Table 4-12.

Figure 4-24: Sensitivity analysis on pressure difference at constant mean pore pressure

Table 4-12: Detailed setting and results of experiments

Set No	P_m psia	P_U psig	ΔP (MDP) psia	P_D psig	Time min	Cycles No.	R-squared	Permeability, nD
1	221.7	297.7	181.3	116.3	4.7	18	0.9993	175.1
2	220.6	270.9	130.0	140.9	6.9	19	0.9965	171.1
3	221.1	252.9	92.9	159.9	9.6	27	0.9970	171.2
4	220.2	231.4	52.0	179.5	17.4	64	0.9634	171.1

4.9 Adsorption/Desorption Effect on Permeability

Three gases of He , N_2 , and CO_2 were used separately to measure the permeability at adsorption and desorption stages. Before switching the experiment gas with the other one, the sample was completely degassed to extract any remaining gas from the previous experiment. Also, to eliminate the stress effect on measurements, all tests were done at constant net stress. For this sample, experiments were started with He , and after a sequence of adsorption and desorption steps, it was repeated by N_2 . For both gases, no hysteresis was observed after the desorption test shown in Figure 4-25.

Figure 4-25: Adsorption/Desorption effect on permeability using He and N_2

Regarding to Figure 4-25, He (Helium) shows higher permeability than N_2 . Smaller molecular size of He compared to N_2 , causes higher Knudsen number and more gas slippage and therefore, higher gas permeability at the same condition.

Since no hysteresis existed during sorption processes, for gas slippage correction both adsorption and desorption measurements of each gas could be considered as a single sorption phenomenon. As a routine, first Klinkenberg and then double slippage correction was applied on the results. After Klinkenberg correction, shown in Figure 4-26, *He* (Helium) measurements resulted a negative value of -66 nD while *N*₂ measurements resulted a positive 11 nD. Permeability is an intrinsic property, and since both gases had no adsorption effect to change the characteristics of the rock and performed at the same stress condition, it is expected that absolute permeability should be independent of the gas type. However *N*₂ suggest a feasible absolute value, its value is not only inconsistent with *He* measurements, but also is much lower than previous measurements.

Figure 4-26: Klinkenberg correction on *He* and *N*₂ measurements

On the contrary, after double slippage correction, shown in Figure 4-27, both gases suggested the same absolute permeability (155 nD) which validates the measurements

and confirms that the absolute permeability, as the rock characteristic, is independent of the gas type as long as the experiment is performed at the same stress condition and gases has no adsorption effect due to its low 0.8 TOC.

Figure 4-27: Double slippage correction on He and N₂ measurements

Later, the permeability experiments were repeated with CO₂ during adsorption and desorption to evaluate the hysteresis existence. It was noticed during desorption process, shown in Figure 4-28, gas permeability shows higher values than adsorption process causing hysteresis. During desorption, some of the gas molecules will not detach from the surface area of the sample. In micropore scale, these remaining molecules reduce the pore width size causing more gas slippage and consequently higher gas permeability values.

Figure 4-28: Hysteresis in permeability during desorption using CO_2

Klinkenberg correction on permeability resulted in negative values for absolute permeability for both sorption processes (Figure 4-29). Double slippage correction, however, suggested plausible equal values for the absolute permeability shown in Figure 4-30. The absolute permeability value measured by CO_2 is smaller than values measured by He or N_2 .

Figure 4-29: Klinkenberg correction for permeability measurements using CO_2

Figure 4-30: Double slippage correction for permeability measurements using CO_2

The absolute permeability value measured by CO_2 is smaller than values measured by He and N_2 . When CO_2 adsorbs on the surface area of the sample, it tightens the micropore throats changing the characteristics of the rock reducing its permeability. This reduction in absolute permeability value during adsorption and desorption processes is not affected by hysteresis since the rock characteristics are not changed significantly during desorption compared to adsorption. Table 4-13 shows a comparison between absolute permeability values measured using He , N_2 , and CO_2 .

Table 4-13: Absolute permeability measurement using different gases

He	N_2	CO_2	
		Adsorption	Desorption
154.3	155.5	124	122.8

During the permeability measurement using an absorbent gas like CO_2 , when a test is going to be performed at a new pore pressure, the sample would begin to adsorb gas if the new pore pressure is higher than previous step, or the sample would begin to desorb gas if the new pore pressure is lower than previous step. In other words, by changing the equilibrium pressure of the sample, sorption phenomena happens in the sample till it reaches to a new equilibrium where sample is fully saturated (no adsorption/desorption occurs) or desorb any gas. Reaching to the new equilibrium stage which takes time affects the mass flow rate of gas through the sample. Since the gas permeability is calculated based on the flow rate, it is crucial to consider the flow rate that sample is fully saturated and flow rate is stabilized. For a better understanding, the flow rate discussion is more elaborated in three sections of non-adsorbate gas, adsorption process, and desorption process.

1. Non adsorbate gas: when an inert gas like He is used for permeability measurements, no gas would adsorb or desorb since the rock has no affinity to that gas. Thus, the same amount of gas that passed the sample from upstream would exit from downstream. Therefore, the sample stabilizes very fast and the same flow rate would be repeated over time. Figure 4-31 shows an example of He flow rate over 250 minutes (122 cycles) for the sample. Statistical analysis shows that the standard deviation and the standard error for these measurements are $2.04E-6$ and $1.8E-7$, respectively confirming the flow is constant over time.
2. During the test using adsorptive gas, at early times, some amount of gas would adsorb to the sample causing a lower outlet flow rate. The difference between inlet and outlet flow rates diminishes over time until the sample reaches equilibrium where inlet and outlet flow rates become equal and flow rate stabilizes. In other words, during adsorption two concurrent phenomena control the flow rate. The pressure difference between two sides of the sample forces the gas through the sample, convection flow, while rock affinity for the gas impedes it. Since the experiment is at steady state (constant convection flow) and over time adsorption completes, flow rate increases over time until sample is fully saturated with the gas and the flow rate becomes constant (Figure 4-32).

Figure 4-31: Non-adsorbate gas flow rate over time

Figure 4-32: Flow rate over time during adsorption

3. During the desorption process, on contrast to the adsorption, rock tends to release the gas at early times which is added to the convection flow rate. Thus, causing a higher outlet flow rate at early time which diminishes over time until sample is fully desorbed (Figure 4-33).

Figure 4-33: Flow rate over time during desorption

According to the aforementioned discussion, the cycles acquired after the full saturation of gas are only to be considered for the permeability measurement cause, after that time flow rate measurements and permeability calculations do not need any correction for sorption. In Figures 4-32 and 4-33 the red points are the cycles that should be considered for permeability calculation.

The experiments shown in Figures 4-32 and 4-33 were completed at close upstream and downstream pressures (less than 10 psi difference), while one in Figure 4-32 was performed during adsorption and the one in Figure 4-33 during desorption. Regarding to Figure 4-32 it took more than 500 minutes till the sample is completely adsorbed while

according to Figure 4-33 the sample was fully desorbed in 300 minutes. This difference in time concludes that desorption process is much faster than adsorption.

4.10 Extra Shale Samples: Petrophysical Study

Two additional Marcellus shale samples were provided for petrophysical studies. Based on the protocol explained in chapter 3 to minimize the alteration of the structure and changing its properties, a set of porosity and permeability measurements were performed on these samples at low net stress condition by *He* to eliminate stress and sorption effects on the measurements. Then, the permeability measurements were repeated with N_2 and CO_2 during adsorption and desorption processes since no TOC data was available. Both samples showed hysteresis using N_2 and CO_2 suggesting high TOC in those samples. Finally, Klinkenberg and double slippage corrections were applied on the permeability measurements to find the absolute permeability. Figures 4-34 and 4-35 shows the Klinkenberg correction for samples 1 and 2, and Figures 4-36 and 4-37 shows the double slippage correction. Before CO_2 measurements on sample 2, it broke down to pieces and the experiments were discontinued at that point.

As expected, Klinkenberg correction fails for both samples. For sample 2, however, for N_2 measurement the absolute permeability is not negative, the absolute permeability value obtained from adsorption (5.43 nD) is not consistent with value obtained from desorption (2.5 nD) conflicting with the definition of absolute permeability an intrinsic rock property and its independency from desorption/ adsorption processes with the same gas (Figure 4-35).

On the contrary, the double slippage correction succeeds in estimating the absolute permeability value. *He* and N_2 measurements are consistent with each other. Also, Adsorption and Desorption results for N_2 and CO_2 are consistent. In addition, the presence of hysteresis in N_2 measurements and the significant reduction in permeability with CO_2 measurements implies the high TOC for both samples (Figures 4-36 and 4-37).

Figure 4-34: Klinkenberg correction for sample 1

Figure 4-35: Klinkenberg correction for sample 2

Figure 4-36: Double slippage correction for sample 1

Figure 4-37: Double slippage correction for sample 2

Permeability measurements for both samples showing absolute permeability values less than 10 nD were done under low stress conditions. Thus, evaluating stress effect on permeability was not applicable.

After the permeability measurements, samples were crushed and low pressure-temperature adsorption/desorption experiment was performed on them. Both Figures 4-38 and 4-39 suggest shows H4 type hysteresis implying slit-like pores which is associated to type I isotherm happening in micro-porous materials and having a small external surface area. Applying different methods like BET, BJH, HK, and t-plot confirms both samples have small surface area, pores and pore volumes. Figures 4-40 and 4-41, the BJH pore size distribution shows that majority of pores have sizes less than 2 nm width. Results of pore characterization for both samples using different methods are summarized in Table 4-14.

Figure 4-38: Low temperature adsorption/desorption for sample 1

Figure 4-39: Low temperature adsorption/desorption for sample 1

Figure 4- 40: BJH pore size distribution for sample 1

Figure 4-41: BJH pore size distribution for sample 2

Table 4-14: Pore size distribution results for samples 1 & 2

Sample	BET		t-Plot			
	Surface Area m^2/g	Average Pore Width nm	External Surface Area m^2/g	Micropore Area m^2/g	Micropore Volume cm^3/g	Average Micropore Width nm
1	1.0397	5.46	0.7474	0.2924	0.000119	0.814
2	2.007	3.1	1.294	0.713	0.000302	0.847
Sample	HK		BJH (2-50 nm)			
	Micropore Volume cm^3/g	Median Pore Width nm	Surface Area m^2/g	Volume cm^3/g	Average Pore Width nm	Micropore %
1	0.000418	1.21	1.661	0.001037	2.48	28.7
2	0.000831	1.17	3.117	0.000766	2.06	52%

High affinity of samples respect to N_2 and CO_2 during permeability measurements along the high percentage of micro-pores gathered from low temperature adsorption suggests a higher TOC value for both samples. Sample 1 was sent for TOC measurements which came with 5.48%. Table 4-15 shows a comparison between petrophysical properties measured for all three samples.

Table 4-15: Comparison between the petrophysical properties of samples

Sample	TOC %	BET Avg. Pore Width nm	Porosity <600 psia Net Stress %	Permeability, nD < 600 psia Net Stress				
				<i>He</i>	N_2		CO_2	
					Ads.	Des.	Ads.	Des.
Outcrop	0.8	7.58	4.83	154.3	155.5		122.83	124.06
1	5.48	5.46	2.70	9.07	11.77	10.5	1.75	1.53
2	NA	3.1	2.23	8.69	8.32	7.22	NA	

Regarding to Table 4-15, there is a meaningful relation between TOC, average pore size and permeability. By increasing the TOC, the higher amount of kerogen packets which are in micro-pore range, cause the average pore size to reduce. Also at higher TOC values, samples show more affinity to N_2 and CO_2 resulting in hysteresis during adsorption and desorption. The higher affinity of shales to CO_2 than N_2 causes a reduction in permeability value and the percentage of reduction in permeability is directly related to the TOC value.

4.11 Matrix-Fracture Characterization

Previously, during the stress tests on porosity and permeability shown in Figures 4-8, 4-9, and 4-18 a linear behavior between both porosity and permeability versus stress was noticed. However, with regard to many researches this relationship, especially in fractured formations should be power law, exponential, logarithmic or even polynomial (Jones F. , 1975; Gangi, 1978; Walsh J. , 1981; McKee, 1988; Reyes, 2002; Dong, 2010; Chalmers, 2012; Cho, 2012). The only explanation for this conflict was the fractures which play the dominant role in total permeability of the rock did not close at high confining pressures and permeability behaved linearly. A routine procedure to check the status of fractures as being close or open is plotting $\left(\frac{k}{k_0}\right)^{1/3}$ vs. $\ln\left(\frac{P}{P_0}\right)$ where k is the measured permeability at P confining pressure (net stress) and k_0 is the permeability at lowest confining pressure P_0 . On this plot, the first straight line represents the pressures where the fractures are open and by changing the slope of the line (second straight line) the fractures are closed after that pressure (Walsh J. B., 1984). This method was applied on the permeability measurements up to 5,000 psia net stress using N_2 and CO_2 for the sample shown in Figure 4-42.

Figure 4-42: Walsh effect on permeability measurements

According to Figure 4-42, it was confirmed that in those ranges of net stress pressures (500 to 5,000 psia), fractures were still open and as the dominant player in permeability its behavior was linear.

These results brought up the following questions needed to be answered:

1. What is the fracture closure pressure in this particular sample?
2. If permeability is measured in a wide range of net stress, what is the correlation between permeability and net stress?
3. What is the effect of sequential forth and back change of net stress on porosity, permeability and fracture closure pressure.
4. Since the gas permeability decreases drastically by net stress, is this extensive decrease would be the same for the absolute permeability?

To answer the first three questions, a set of experiments with constant gas pressure and varying confining pressures from 700 to 7,900 psia were applied on the sample. To capture the hysteresis effect the experiment was performed at in a forth and backward series. Regarding to the results shown in Figure 4-43, permeability decreases logarithmically as stress increases, while it increases with a power law behavior during decreasing stress accompanied with hysteresis.

Figure 4-43: Permeability behavior under stress conditions

Walsh's theorem was applied on the measurements to find the fracture closure pressure. The results demonstrated in Figure 4-44 suggest 4,700 psia for the fracture closure pressure.

The first set of stress experiments with N_2 and CO_2 both had suggested that in 5,000 psia net stress, fractures were still open; however, this time the fracture closure pressure was reduced to 4,700 psia. During the hydraulic fracturing process, the formation goes under sequential series of injecting and retrieving fracturing fluid in the formation which impose a significant change in the pore pressure and the net stress of the formation. Thus, it became necessary to evaluate the effect of sequential series of inserting and releasing the stress on the formation properties. For this purpose, 4 sequential series of stress change experiments were performed on the sample. During the first and second, both porosity and permeability were measured. During the third series only porosity was measured and in the fourth only permeability was measured.

Similar results were obtained in permeability measurements. Increasing the net stress reduces the permeability value logarithmically and decreasing the net stress retains permeability with a power law behavior. During all series permeability shows hysteresis, although the hysteresis diminishes as number of sequences increases. Figure 4-44 shows how permeability decreases logarithmically when stress decreases for different series.

Then, Walsh's theorem was applied on these series of permeability measurements. The results shown in Figure 4-45 implies the fracture closure pressure decreases as the sequential series of the stress that sample has gone under increases. In other words, the fracture closure in the fourth series has reduced to 2,490 psia from 4,700 psia in the first series which is consistent with the time when fracture closure was higher than 5,000 psia (Figure 4-42).

Figure 4-44: Permeability behavior by sequential net stress increasing

Figure 4-45: Fracture Closure pressure for different sequences

By decreasing the stress over the sample, permeability retains some of its value with a power law behavior; however, it never comes back to its initial value (Figure 4-46). This hysteresis which was seen in all the series diminishes as the number of sequential series increases. A comparison between the first series and the fourth series during increasing and decreasing stress in Figure 4-47 shows how hysteresis diminishes.

Figure 4-46: Permeability behavior by sequential net stress decreasing

Figure 4- 47: Comparison between series 1 and series 4 hysteresis

Along these sequential permeability measurements, porosity was measured sequentially at the same time. On contrary of permeability that shows significant hysteresis sequentially, porosity did not show a significant hysteresis. Figure 4-48 shows the porosity behavior during these series. Regarding to after the third sequence at 8,000 psia, porosity has reduced from 2.7% to 2.6% which is insignificant with respect to permeability. Also, at low stress pressures, porosity retains its initial value.

Figure 4- 48: Porosity behavior by sequential net stress change

With a closer look on the porosity results obtained from second and third series, it can be seen that porosity behavior can be divided into two distinctive linear curves intersecting at a pressure consistent to the fracture closure pressure.

In general, porosity is more contributed to the larger pores which are less sensitive to stress while permeability is more contributed with fractures rather than matrix. Compressibility of a formation is related to the formation porosity and rate of porosity change by stress and the shape of the pores. Formation compressibility can be calculated by the following Equation 4-5:

$$C_f = \frac{1}{\phi} \left(\frac{d\phi}{dp} \right) \quad \text{Eq. 4-5}$$

Formation compressibility for each series and for different net stress pressure is shown in Figure 4-49.

Figure 4-49: Formation compressibility in sequential stress series

Formation compressibility ranges between 1E-5 to 8E-5 psia⁻¹. By increasing the stress, the pores which are already compressed lose their compressibility. Thus, by increasing the stress, the rate of compressibility change decreases. This range of compressibility is 5 to 10 times higher than typical compressibility of other formations. This high compressibility value is contributed to the foliated structure of the shales and slit-like pores.

To find the relation between the absolute permeability and the net stress, 50 sets of experiments consisting five different average gas pressures ranging from 150 to 350 psia at ten different net stress pressures ranging from 500 to 8,000 psia where done on the sample. By changing the gas pressure at 5 steps and keeping the net stress constant, absolute permeability can be calculated at that net stress condition by using double

slippage correction. By repeating these 5 average pore pressure measurements at 10 different net stress conditions, a complete profile of absolute permeability at a wide range of stresses can be obtained. Results of absolute permeability measurement after double slippage correction are shown in Figure 4-50.

Figure 4-50: Absolute permeability by double slippage correction under stress condition

Obtained absolute permeability measurements from double slippage correction at different stress conditions were plotted in Figure 4-51. Regarding to this figure, absolute permeability has lost 45% of its initial value in 7,000 psia stress change. Similar to the previous series which displayed a logarithmic relation in the reduction of permeability versus increasing stress; this same logarithmic behavior was observed for the absolute permeability.

Figure 4-51: Effect of stress on absolute permeability

CHAPTER 5.

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following Conclusions were drawn from this research study:

- Permeability of shales can be measured under steady-state condition. This method is fast, repeatable, and does not require a complicated interpretation or adsorption correction like pulse-decay or GRI methods.
- In tight formations where Knudsen number is high and transition flow regime exists, Klinkenberg fails while double slippage correction results in consistent plausible absolute permeability.
- Adsorption and desorption have significant impact on permeability measurements causing a hysteresis in permeability during adsorption and desorption. The amount of adsorption depends on the gas type and TOC of the formation. CO_2 showed the highest adsorption while He did not show any adsorption effect. High adsorption of CO_2 causing pore size reduction which reduces the absolute permeability. The reduction in the permeability becomes more significant when samples have smaller pores and higher TOC values. For N_2 , the samples with higher TOC showed affinity to N_2 , however, it did not affect the absolute permeability.
- Low temperature adsorption experiments suggest a type H3 or H4 hysteresis exists for Marcellus shale samples both implying a dominant of slit-like pores. Also, samples with higher TOC have smaller average pore size which is consistent with other studies implying nano-pores are associated with the organic materials in shales.

- Change of stress has a significant impact on permeability measurements. By increasing the stress, permeability can lose 50% of its initial value. Also, the stress effect is irreversible and by decreasing the stress, permeability will not retain its initial value. However, over sequential series of stress, this hysteresis and the reduction in permeability diminishes.
- Non-linear behavior of permeability respect to stress is contributed to the response of the fracture and matrix to the stress which can be successfully verified with Walsh theory. This theory shows the pressure above which the fractures are closed and the flow is dominated that by matrix.
- Sequential series of stress changes, similar to those during hydraulic fracturing, reduces the closure pressure for fractures and this reduction diminishes when the number of stress sequences increases.
- Porosity, contrary to permeability, does not decline significantly by increasing the stress. It also does not exhibit hysteresis with stress. Also, porosity is not sensitive to adsorption at pressures lower than 500 psi.

5.2 Recommendations

For future research the followings are recommended:

- PPAL modification: The only reason measuring the Langmuir parameters were stopped was the time consuming of the process. To be able to do adsorption measurements, it is recommended to modify PPAL in order to apply routine volumetric adsorption measurements. The modification can be done by adding two valves before large upstream and downstream tanks and a pressure transducer after V_2 .

- Low temperature adsorption: For future research, CO_2 or CH_4 can be used for pore size distribution. These two gases get adsorbed at higher temperatures than N_2 . Also, CO_2 has access to the pores smaller than 1 nm while N_2 does not.
- Stress-dependent study: It is recommended to investigate more Marcellus shale sample under stress to be able to find a general (if possible) mathematical relation between permeability, porosity, and net stress.
- However all the experiments were performed under constant temperature, this temperature was lower than the reservoir one. It is recommended to add a heat jacket over the core holder to simulate the reservoir temperature and measure permeability at that condition with adsorbate gases because adsorption process is also dependent on temperature.

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