EFFECT OF ROCK COMPOSITION AND TEXTURE ON PORE SIZE DISTRIBUTIONS IN SHALES: APPLICATIONS IN LOW FIELD NUCLEAR MAGNETIC RESONANCE

by

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

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ABSTRACT

There are various methods to assess the pore size distribution (PSD) of porous materials; amongst all, NMR is the only technique that can be utilized for subsurface applications. The key parameter to transform NMR time domain response to PSD size domain data is surface relaxivity. The common practice is to consider a constant surface relaxivity throughout a well, formation or rock type regardless of the variations in rock compositions; this results in inaccurate PSD estimation using NMR log data.

In this thesis I established a methodology to calculate the surface relaxivity in shales considering the rock composition and texture. I present the steps to achieve this goal in three steps: (a) Understanding the challenges of NMR acquisition, analysis and interpretation in shales, (b) Measuring the porosity, PSD and surface area and providing a practice to check the reliability of these measurements in shales, (c) Developing a methodology to calculate the surface relaxivity honoring the variations paramagnetic mineral content, susceptibility, distribution and texture.

Application of NMR in unconventional rocks requires adjustment of NMR data acquisition and analysis to the unique properties of these rocks such as high level of heterogeneity, complex pore structure, fine grains, and presence of nano-scale pores. Identifying these challenges improves our understanding of NMR response in shales and increases the quality of the acquired and analyzed data.

Calculation of surface relaxivity, as a measure of how fluids and rock surfaces react, requires reliable measurement of different petrophysical properties of the rock such as porosity, total specific surface area, and PSD using other techniques. I studied the reliability of different techniques to measure these petrophysical properties for
shales by performing a thorough comparative study of porosity and PSD for different shale formations. The result of my study showed that clay type and content, total organic carbon (TOC), and thermal maturity are the main factors that affect the reliability of a measurement technique in organic rich shales.

The final step for surface relaxivity measurement is to combine the mentioned petrophysical measurement with NMR data and investigating the effect of rock composition and texture on surface relaxivity. The surface relaxivities were calculated for organic rich samples with different thermal maturity and also shales with no organic content. My results show that identification of paramagnetic minerals that affect the surface relaxivity, their content and distribution are the key factors that affect the surface relaxivity of the rock. In absence of ferromagnetic minerals, paramagnetic clays such as chlorite, illite and illite-smectite mixed layer are the main mineral groups that affect the surface relaxivity. Since clays are one of the controlling factors of rock quality and gamma ray logs respond to clays occurring in oil and gas producing formations, these logs can be used to help perform a more accurate NMR log interpretation.
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ACKNOWLEDGEMENTS

First and foremost, I would like to acknowledge my advisor Dr. Manika Prasad for her continuous support and inspiration. I will remain indebted to her throughout my life for the things she has taught me in my professional and personal life. Thanks for your patience, kindness and trust in me.

I would also like to thank my thesis committee members: Dr. Andre Revil, Dr. Erdal Ozkan, Dr. Yuan Yang, Dr. Jennifer Miskimmins, Dr. Dick Merkel, Dr. Todd Hoffman, and Dr. Mike Mooney for their significant contribution to my education in Mines. I also pay my sincere respect to Dr. Mike Batzle whose memory will always remain with me as a great mentor, colleague and person.

This long and joyful journey would not reach to an end without the help and support from many other people whom I would like to acknowledge here: Evan McCarney from Magritek for his continuous support and fruitful discussions about the NMR instrument and experiments. Leo Alcanter-Lopez and Don Harville from Chesapeake Energy for their hospitality at Chesapeake laboratory and collaboration for FESEM experiments. Douglas McCartey from Chevron ETC, Tomasz Topór and Arek Derkowski from Polish Academy of Science for help with XRD experiments. Ben Harrell, from Micromeretics, for his help with mercury intrusion experiments and also being an amazing friend. Gerhard W. Heij and Dr. Richard D. Elmore from University of Oklahoma for performing bulk magnetic susceptibility measurements. Kurt Livo, Cesar Mapeli, Ashley Burk, Rana ElGhonimi, Bilel Attia and Everton Val for their help with other experiments such as NMR, nitrogen adsorption, water immersion porosity and FESEM imaging. My mentors at Maersk Oil Houston, Mosab Nasser and Torben
Rasmussen, Andres Mantilla, and at BP America, Julianna Toms and Joanne T. Fredrich for all I learned from them during my summer internships and their continuous support and patience. Dr. Carolyn Koh from hydrates research group and her student Ahmad Afif Abdul Majid for such a fruitful and joyful collaboration in hydrate and emulsion characterization.

I am grateful to all my friends and colleagues in Colorado School of Mines especially at OCLASSH group and Center of Rock Abuse for sharing time during my stay and for making it such a memorable and joyful part of my life: Saeed, Kuila, Ravi, Elshan, Saul, Andre, Kurt, Lemuel, Azar, Asm, Sanyog, Liwei, Patricia, Rana, Jesse, Alejandra, Fernando, Farnoush, Weiping, Naser, Mohsen, Stuti, Wendy.

Special thanks to Terri Synder, Denise Winn-Bower, Patti Hassen and Alyda Morosco for making my stay smoother by helping in administrative hassles.

Any amount of acknowledgement would be insufficient for my family: My loving mother Azimeh Askari and amazing father Safar Ali Saidian, my dear brothers Mohsen, Amin, Hooman and my beautiful little sister Mahsa. You have always stood by me and dealt with all of my absence from many family occasions with a smile. Also my gratitude to the new additions to my wonderful family whom, unfortunately being so far from home, I did not have the privilege to spend more time with; Parastoo, Samira, Niloufar and my little nephew Nima. The last, but not the least, my deepest thanks and appreciation to Ghazal and Poochi Bales for being such amazing companions in the last three years and sharing your life with me. I love you all.
CHAPTER 1
INTRODUCTION

“Questions of personal priority, however interesting they may be to the persons concerned, sink into significance in the prospect of any gain of deeper insight into the secrets of nature.”

- Baron William Thomson Kelvin

Shales are fine-grained rocks with more than 50% of particles less than 62.5 µm (Folk, 1974, Friedman 2003, and Javadpour, 2005). Like other sedimentary rocks, they are composed of a wide range of minerals such as clay, quartz, feldspar, carbonates, and heavy minerals such as pyrite (Passey et al., 2010). Besides mineral components, mudrocks may contain organic matter as a significant component of the rock (Bohacs et al., 2013). In today’s terminology, shale reservoirs are either siliciclastic or carbonate mudrocks and need not necessarily contain clay minerals. Although alternate terms have been used for shale reservoirs such as unconventional, self-resourcing rocks, organic-rich rocks and mudstones, the term shale has endured. In this work we use the term shale, mudrock and unconventional rocks interchangeably to refer to these reservoirs.

Porosity and pore size distribution (PSD) data are crucial for reservoir quality and volume evaluation (Ambrose et al., 2010). These properties can be measured using different methods. Among them, the Nuclear Magnetic Resonance (NMR) log is the only tool to assess PSD in the subsurface. Application of wireline NMR logs is a long
established method to measure porosity and assess pore size distributions in high porosity formations (Timur, 1969). The complexity of NMR measurements in shales due to low porosity and fast relaxation creates new challenges in subsurface NMR acquisition and analysis.

In this thesis, I established a methodology to calculate the surface relaxivity in shales considering the rock composition and texture. I present the steps to achieve this goal in three steps: (a) Understanding the challenges of NMR acquisition, analysis and interpretation in shales, (b) Measuring the porosity, PSD and surface area and providing a practice to check the reliability of these measurements in shales, (c) Developing a methodology to calculate the surface relaxivity honoring the variations in paramagnetic mineral content, susceptibility, distribution and texture.

The need for shale rock characterization and the unique properties of these rocks has brought NMR acquisition, analysis and interpretation to a new and more challenging level. These challenges, if not taken into account, can cause over or under interpretation of the NMR signal and result in significant errors in porosity and PSD evaluation. I identified the challenges associated with NMR measurements in shales and emphasized on the factors that increase accuracy and reliability of NMR measurements in these samples. I focused on two most common NMR downhole measurements, namely, the transverse relaxation time ($T_2$), mainly used for pore size distribution measurement, and 2d diffusion-$T_2$ ($D$-$T_2$) maps, used for fluid identification based on diffusion coefficient of the fluids. My results and observations are submitted to the Journal of Magnetic Resonance.
Calculation of surface relaxivity, as a measure of how fluids and rock surfaces react, requires reliable measurement of different petrophysical properties of the rock such as porosity, total specific surface area, and PSD using other techniques. I used different porosity measurement techniques such as water immersion, helium expansion to study the reliability of different measurement techniques that presumably measure the same property. I also used techniques that measure both porosity and PSD such as NMR, mercury intrusion, and nitrogen adsorption. Mineralogical and geochemical measurement, scanning electron microscope and magnetic susceptibility data were used to understand the texture, pore topology and physical properties of the samples. Our work in this subject is accepted for publication in American Association of Petroleum Geologists (AAPG) Memoir Series 110: Imaging Unconventional Reservoir Pore Systems.

The final step for surface relaxivity measurement is to combine the mentioned petrophysical measurement with NMR data and investigate the effect of rock composition and texture on surface relaxivity. I studied the effect of mineral magnetic susceptibility, texture, content and distribution, as well as thermal maturity, and the total organic carbon on the rock surface relaxivity which is the key parameter for application of NMR log and laboratory measurement. The findings for organic rich and organic lean samples are submitted to Geophysics Journal and Journal of Fuel, respectively, for publication. We also filed part of this work as a patent which is in the provisional stage.

As part of my PhD, I have studied different aspects of NMR apart from shales. At my summer internship at Maersk Oil Houston I studied the effect of presence of solid hydrocarbons on NMR response in a carbonate reservoir and provided a work flow for
identification and quantification of the solid hydrocarbon. My project is published in Interpretation Journal and also is presented here as Appendix A.

I also did a joint project with Center for Hydrate Research at Colorado School of Mines focusing on bubble size distribution measurement in oil-water emulsions using advanced NMR techniques such as 2d diffusion-$T_2$ measurement. This joint project is published in Canadian Journal of Chemistry (Appendix B), and it also resulted in a joint patent which is in the provisional stage.

1.1 Organization of the Thesis

This thesis consists of six chapters. Chapters 2 through 5 are four articles that are already published in or submitted to peer-reviewed journals. The main results and discussions of my research are presented in these chapters. Chapters 1 and 6 are general introduction and conclusions for these chapters, respectively. In the following, I will briefly explain the subject of each chapter and highlight the main problems that are addressed:

**Chapter 1** addresses the general problem statement for this thesis and also provides a general introduction to the objectives.

**Chapter 2** focuses on technical and mathematical challenges that we face acquiring, analyzing and interpreting NMR responses in unconventional rocks. Learning points from this chapter helped us to improve the quality of acquired data for shale samples and understand the problems that we might encounter while analyzing and interpreting the NMR response. This is the first step for pore size distribution assessment of shales. In this chapter a systematic comparison between a sandstone and a shale sample is provided. This comparison highlights the challenges that we face
due to unique properties of shale pore structure and composition. This chapter is submitted to Geophysics Journal. My co-author Dr. Manika Prasad, who is my adviser as well, guided me during the project.

**Chapter 3** presents the result of a thorough comparison of porosity and pore size distribution measurement using different techniques for four different oil and gas producing organic rich shales. NMR interpretation and surface relaxivity calculation, which are the final goals of this thesis, require a reliable measurement of porosity, total specific surface area and PSD. This chapter discusses the main rock compositional and geochemical properties that affect the reliability of the measurements. Understanding these properties sets the stage for an accurate measurement of the surface relaxivity and eventually pore size distribution using NMR data. This chapter will be published in American Association of Petroleum Geologists (AAPG) Memoir 110. Utpalendu Kuila, Saul Rivera, and Lemuel Godinez performed as major portion of the measurements as part of their thesis. Dr. Manika Prasad is my thesis adviser and Leo Alcantar Lopez performed the imaging experiments.

**Chapter 4** presents how we used the learning points from Chapters 2 and 3 to acquire, analyze and interpret the NMR data and also to find reliable techniques for porosity, pore size distribution and surface area measurement in Middle Bakken and Three Forks samples. We calculated the surface relaxivity using various techniques and investigated the effect of rock mineralogy and texture on surface relaxivity values. This chapter is accepted for publication by Journal of Fuel. My co-author is Dr. Manika Prasad who is my thesis adviser.
Chapter 5, similar to Chapter 4, shows data on calculation of the surface relaxivity using different techniques and correlates rock composition and texture to the variations in surface relaxivity. The main difference between Chapters 4 and 5 is that, in Chapter 4 we tested our methodology for surface relaxivity calculation and studies on shale samples that are not organic rich and do not contain swelling clays, but in Chapter 5 we increased the complexity by using organic rich shales at different levels of maturity and clay types. This chapter is accepted for publication by Geophysics Journal. My co-author is Kurt Livo who performed some of the NMR measurements. Dr. Manika Prasad is also my thesis adviser.

Chapter 6 summarizes the main conclusions of this thesis and provides future works and recommendations.

Appendix A presents a case study that shows how NMR logging improves the petrophysical characterization of a carbonate reservoir that has a dispersed reservoir bitumen issue. We used NMR log with other log and core data to introduce a work flow for quick identification of the reservoir bitumen and also to provide a volumetric model to calculate reservoir bitumen saturation. This chapter is published by Interpretation Journal. Dr. Torben Rasmussen was my petrophysics supervisor and did the volumetric modeling, Dr. Mosab Nasser was my mentor along with Dr. Andres Mantilla, my project manager, provided guidance, data and measurements. Dr. Rick Tobin was the principal geologist who analyzed the thin section images.

Appendix B shows a detailed study of bubble size distribution of water in oil emulsions using advanced NMR techniques such as 2d Diffusion-$T_2$ measurements. We used a mathematical model to convert the restricted diffusion data to bubble size. This
paper is published by the Canadian Journal of Chemistry. Ahmad A. A. Majid is the first author who prepared the samples and owned the idea. I designed and ran the NMR measurements and data analysis. Dr.s Koh and Prasad are our thesis advisers who guided us throughout the project.

1.2 List of Publications

We published different parts of the thesis in multiple books, journal papers and conferences. In this section I introduce the publications and where they are (or will be) published.

1.2.1 Published at, or Submitted to Peer Reviewed Journals


### 1.2.2 Conference Proceedings and Abstracts


28-30 September, SPE 175069-MS.


Monterey, and Eastern European Silurian Formations, Unconventional Resources Technology Conference, 25-27 August, Denver, CO, URTeC 1922745.


1.2.3 Patents filed


1.3 References


CHAPTER 2

Nuclear Magnetic Resonance (NMR) Measurements for Mudrock (Shale) Characterizations: Challenges in Data Acquisition and Signal Processing

A paper submitted to the Geophysics

Milad Saidian, Manika Prasad

“Our very survival depends on our ability to stay awake, to adjust to new ideas, to remain vigilant and to face the challenge of change.”

-Martin Luther King Jr.

2.1 Abstract

Nuclear magnetic resonance (NMR) is widely used to measure porosity and pore size distributions of high porosity rocks in the laboratory and at downhole conditions. Tight, low-porosity, multi-mineralic, organic-rich rocks (known as shales or mudrocks) are characterized by fast relaxing NMR signals with low amplitude. Considering these requirements, we discuss quality assurance of NMR data acquisition parameters and critical parameters for NMR data processing as applicable to mudrocks (shales). To address the significance of NMR data acquisition parameters, we compare experimental NMR data for a sandstone and a mudrock. We also use simulations to assess the differences between mathematical inversions and restricted diffusion in simulated sandstone and mudrock responses.
NMR data quality is affected by echo spacing (TE), acquisition delays, number of echoes, and background signals. To capture the fast relaxation in the micropores of mudrocks, a balance must be reached between NMR data acquisition with the smallest TE that is still large enough to minimize contributions from acoustic ringing and background signal. The background signal is created by sample holders, plastic warps and air moisture. Uncorrected background signals can be interpreted as micropores.

After acquisition, the NMR data must be processed to get relaxation times. All inversions need to be optimized for three major control factors: smoothing, signal to noise ratio (SNR) and relaxation rate. Our simulations show that (a) the mathematically calculated smoothing parameter over-smoothes the $T_2$ distribution in mud rocks and (b) even at a very high signal to noise ratio (> 100), the fast relaxing hydrogen nuclei prevent the inversions to capture multi-modal pore size distributions.

Models of attenuation due to diffusion with a Gaussian phase distribution (GPD) and short gradient pulse (SGP) reveal that in nanometer sized pores, large gradients must be applied for the spins to diffuse. Low frequency (2 MHz) logging and laboratory devices with a maximum gradient amplitude of 0.5 T or less are not able to measure diffusion in pores smaller than 5 µm because the fast relaxing spins relax before the acquisition starts. Our work can help design optimal conditions for NMR data acquisition and assess its limitations to measure the complex pore structure of mudrocks.

2.2 Introduction

Wireline NMR logs are used to measure porosity and assess pore size distributions in high porosity sandstone and carbonate formations (Kleinberg, 2001). Technological advances in hydraulic fracturing and horizontal drilling have made
economic production of oil and gas from tight mudrocks (unconventionals or shales) viable. The term “unconventional reservoir” encompasses a wide range of lithologies or hydrocarbon bearing rocks. In this paper, we refer to tight oil, or gas-producing reservoirs which may or may not be organic rich and are often called “shales”. Shales can be either siliciclastic or carbonate mudrocks and are not necessarily clay-rich. In this study we use the terms shale and mudrock interchangeably to denote low-porosity, low-permeability materials with complex mineralogy and possibly organic-rich. With increasing application in mudrocks, the procedures and assumptions required interpreting NMR data for porosity and pore size distributions need to be examined critically for specific requirements to characterize mudrocks.

Porosity and pore size distribution data are crucial for reservoir quality and volume evaluation (Ambrose et al., 2010). Pore size distribution can be used to evaluate permeability (Nelson, 2009), and to calculate elastic properties (Kuila and Prasad, 2011). There are numerous ways to assess the pore size distribution of mudrocks, for example, scanning electron microscopy (Alcantar-Lopez and Chipera, 2013; Zargari et al., 2013; Saidian et al., 2015a), CT-scanning (Milliken et al., 2013), mercury intrusion (Howard, 1991; Rivera et al., 2014; Saidian et al., 2015a), nitrogen adsorption (Kuila et al., 2012; Saidian et al., 2015a), and NMR (Sondergeld et al., 2010; Jiang et al., 2013; Rylander et al., 2013; Rivera et al., 2014, Saidian et al., 2015b). Amongst these methods, only the NMR technique allows us to assess pore size distributions in the laboratory and at downhole conditions. NMR experiments are a two-part process: data acquisition requiring fit-for-purpose pulse sequences and data processing with carefully designed mathematical inversions. Before using the methods developed for high-
porosity rocks, we need to assess whether the specific settings and assumptions can be applied and how they need to be modified for mudrock applications.

The low-field (2 MHz) NMR signal is produced by the hydrogen nuclei present in the pore fluid of porous formations. The concentration of hydrogen is correlated to the porosity of the rock (Kenyon, 1997). Since NMR signals from the minerals cannot be detected by the low-field NMR tool, porosity can be calculated directly without making assumptions about the mineral constituents (Dunn et al., 2002). The relaxation rate of the hydrogen nuclei subjected to an oscillating magnetic field provides information about both the pore structure and the saturating pore fluid (Kenyon, 1992). Pore size distribution by analyzing T₁ and T₂ time distributions (Kenyon, 1997), bound and free fluid volume calculations by defining time cut offs (Timur, 1969, Straley et al., 1997 and Coates et al., 1999), permeability estimation using the time distribution spectra (Timur, 1969, Howard et al., 1993 and Kenyon, 1997), fluid typing, saturation (Hürlimann et al., 2002) and viscosity (LaTorraca et al., 1999 and Hirasaki et al., 2003) estimation based on fluid relaxation times are some of the common applications of NMR downhole data for conventional rocks such as sandstones and carbonates. However, successful rock and fluid characterizations from NMR data rely on high quality data and data processing. In unconventional rocks, these tasks are more challenging due to small pores, high surface to volume ratio (Saidian et al., 2015a), presence of kerogen and bitumen, occurrence of both mineral-hosted and organic-hosted pores, and abundance of iron bearing minerals such as pyrite (Passey et al., 2010).

NMR signals are acquired using pulse sequences consisting of radio frequency pulses and delay times. Choosing the appropriate acquisition parameters demands an
understanding of the pulse sequence, pore structure and fluid properties. For example, the relaxation time of a bulk fluid is inversely proportional to its viscosity (Hirasaki et al., 2003) and is reduced on contact with the grain surfaces in porous media (Dunn et al., 2002). This decrease in relaxation rate depends on the pore characteristics such as pore size, connectivity, mineralogy and surface area to volume ratio (Saidian et al., 2015b). NMR data acquisition in fast relaxing systems, such as low porosity rocks requires instruments with high sensitivity and modified pulse sequence timings. In the first part of our paper, we discuss the specific differences in acquisition design for high-porosity sandstones and low-porosity mudstones.

Even the highest quality NMR data must be processed prior to any interpretation of, for example, porosity and pore size distributions. Typically, an inverse Laplace transform (Butler et al., 1981 and Dunn et al., 1994) is applied to account for the relaxation rates superimposed in the NMR raw decay data in the form of a multi-exponential decay. A single exponential decay is usually suitable for inversion of most low viscosity bulk fluids (Dunn et al., 1994), while fluid saturated porous media often require a multi-exponential decay. In fast relaxing and low porosity rocks, the inversion is usually compromised due to low signal to noise ratio and fast decay of the NMR signal. A second part of our paper deals with inversion parameters for high-porosity sandstones and low-porosity mudstones.

Given the increasing application of NMR studies in low-porosity, tight rocks, a discussion of the challenges associated with NMR data acquisition and processing in low-porosity, tight rocks, though essential, is lacking. Note that we do not intend to present new techniques or pulse sequences for NMR data acquisition in unconventional
rocks or introduce a new inversion algorithm. Our goal was to identify the data acquisition, analysis and interpretation challenges for low-porosity, tight formations and emphasize factors that increase accuracy and reliability of NMR measurements in these samples. We focused on two most common NMR downhole measurements, namely, the transverse relaxation time ($T_2$), mainly used for pore size distribution measurement, and 2d diffusion-$T_2$ (D-$T_2$) maps, used for fluid identification based on diffusion coefficient differences between reservoir fluids (Hürlimann et al., 2002). We compare NMR response in a sandstone sample and a mudrock sample and show how different acquisition parameters affect the NMR response of each rock. We also use 1D simulation software to investigate the road blocks during mathematical inversion for mudrock samples. We assess the challenges in diffusion measurement by simulating the diffusion response in mudrocks with two analytical models of simplified pore geometries such as spheres.

2.3 NMR Data Acquisition and Processing

Before discussing the challenges associated with NMR measurements in shales, we briefly introduce the pulse sequences, inversion algorithms and theoretical models to be used in this study. We focus here on the pulse sequences of two most common downhole NMR measurements: $T_2$ relaxations and D-$T_2$ maps, the theoretical basis and assumptions of the inversion algorithms and the theoretical diffusion models underlying the simulation software used here.

2.3.1 CPMG Pulse Sequence for $T_2$ relaxations

$T_2$ measurements are based on the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Figure 2-1) (Carr and Purcell, 1954; Meiboom and Gill, 1958). Briefly, this
pulse sequence consists of one 90° (π/2) pulse followed by a number of 180° (π) pulses (number of echoes) separated by echo spacing (echo time or TE). The loss in magnetization after the 90° pulse is termed as the free induction decay (FID). The coherence of the spins after each 180° or π pulse are recorded as pulse spin echoes or simply, echoes (Figure 2-1). The CPMG pulse sequence produces a number of spin echoes (number of echoes) that constitute the spin echo train data. This echo train is the raw data for T₂ distributions. Pulse length and amplitude, TE and number of echoes are the main parameters that need to be designed according to rock and fluid properties.

Figure 2-1: Schematic of the CPMG pulse sequence. This pulse sequence is the most common sequence to measure the T₂ distribution. FID is the free induction decay, π and π/2 are the 180 and 90 degrees pulses, TE is the echo spacing which is the time between two consecutive 180 degrees pulses. Echo train (the dashed line) is the raw data for T₂ distribution measurement.

We simulated the effect of signal to noise ratio, echo spacing, smoothing parameter (With software courtesy of Magritek™) by designing T₂ distributions and their corresponding echo train data. We modeled various T₂ distributions by changing the number and the relaxation rate of the T₂ peaks. We used the non-negative least square (NNLS) inversion to invert the echo train data to produce the T₂ distribution. The simulation software allowed us to create uni- and bi-modal T₂ distributions at different...
relaxation rates and study the effect of acquisition parameters on the T$_2$ distributions inverted from echo train data.

### 2.3.2 Pulsed Field Gradient (PFG) Pulse Sequences

Self-diffusion (henceforth referred as diffusion) is a random translational motion of the molecules that is driven by internal kinetic energy (Price, 1997). We will limit our analysis to the hydrogen nuclei as it is the most important for oil and gas industry NMR applications. Diffusion measurements using pulsed field gradient (PFG) (Figure 2-2a), stimulated pulse field gradient (PFGST) (Tanner, 1970) and diffusion editing (Hürlimann et al., 2002) have been used to identify fluid saturations (Freedman et al., 2002, Hürlimann et al., 2002,) and characterize the pore structure in reservoir rocks (Mitra and Sen, 1992, Latour et al., 1995, Hürlimann et al., 2002, Pape et al., 2006). The diffusion coefficient is calculated using Equation 2-1 (Stejskal and Tanner, 1965) and is proportional to the attenuation of magnetization from FID to the first echo (Figure 2-2a).

\[
\ln \left( \frac{E}{E_0} \right) = -D\delta^2\gamma^2 g^2 \left( \Delta - \frac{\delta}{3} \right)
\]  

(2 – 1)

where $E_0$ and $E$ are the magnetizations of the FID and spin echo (Figure 2-2a), respectively, $D$ is the diffusion coefficient, $\delta$ is the gradient pulse duration, $\gamma$ is the magneto gyric ratio of the spins ($2.675 \times 10^{-8}$ rad s$^{-1}$ T$^{-1}$ for hydrogen nuclei), $g$ is the gradient pulse amplitude, $\Delta$ is the time duration between the gradient pulses (diffusion time).

In wireline logging, diffusion measurements are combined with CPMG measurements (Figure 2-2b) to produce a 2d map of fluid diffusivity and transverse relaxation (D-T$_2$ maps) (Sun and Dunn, 2005, Toumelin et al., 2006). This pulse sequence combines two phenomena: the T$_2$ distributions and the translational diffusion
coefficients of the fluid molecules. The chemical properties of water and oil are captured in the 1d $T_2$ distributions while the diffusion coefficient measures the reduction in the bulk diffusion coefficient of the fluid due to restrictions of the molecules by the pore walls (Hürlimann and Venkataramanan, 2002). The D-T maps are produced with a two dimensional inverse Laplace transform (Hürlimann et al, 2002, Venkataramanan et al., 2002, Aichele et al., 2007; Song, 2010).

Figure 2-2: Schematic of the (a) PFG and (b) PFG-CPMG pulse sequences. Diffusion coefficient can be measured using PFG (a) pulse sequence and when combined with CPMG (b) it can be utilized for fluid typing and saturation calculation. $\pi$ and $\pi/2$ are the 180 and 90 degrees pulses, $\Delta$ is the diffusion time which is the time between gradient pulses, $\delta$ is the gradient pulse duration, $g$ is the gradient pulse amplitude, TE is the echo spacing which is the time between two consecutive 180 degrees pulses.

For comparison, we also modeled spin echo attenuations due to translational spin diffusion with two analytical solutions of the Bloch equations for idealized spherical
pore geometries: Gaussian Phase Distribution (GPD) and Short Gradient Pulse (SGP) (Bloch, 1946; Torrey, 1956).

GPD assumes that the phase distribution is Gaussian and the attenuation due to translational motion of the spins in a magnetic field gradient can be modeled using Equations 2-2 to 2-4 (Murday and Cotts, 1968). The SGP approximation (Equation 2-5) assumes that the spin motion is negligible in pulse gradient duration and spin diffusion does not occur (Balinov et al., 1993).

\[ E(g) = \exp\left(-\frac{2\gamma^2 g^2}{D^2}\right) \times \sum_{n=1}^{\infty} \frac{2\alpha_n^2 D\delta - 2 + 2L(\delta) - L(\Delta - \delta) + 2L(\Delta) - L(\Delta + \delta)}{\alpha_n^6 (R^2 \alpha_n^2 - 2)} \]  

(2 - 2)

\[ L(t) = \exp(-\alpha_n^2 Dt) \]  

(2 - 3)

\[ (\alpha_n R)J_{3/2}(\alpha_n R) - \frac{1}{2}J_{3/2}(\alpha_n R) = 0 \]  

(2 - 4)

where \( E(g) \) is the signal attenuation at each gradient step, \( \gamma \) is the magnetogyric ratio, \( g \) is the gradient amplitude, \( D \) is the diffusion coefficient of the fluid, \( \delta \) is the gradient pulse length, \( \Delta \) is the diffusion time, \( R \) is the idealized spherical pore radius, \( \alpha_n \)'s are the solutions of the Equation 2-4, and \( J \) is the Bessel function of the first kind.

SGP assumes the gradient pulse length is equal to zero and self-diffusion does not occur during the pulsing period. The attenuation can then be modeled as (Balinov et al., 1993) using Equation 2-5.

\[ E(g) = \frac{9[q \cos(q) - \sin(q)]^2}{(q)^6} - 6(q)^2 \sum_{n=0}^{\infty} \left[J_n'(q)^2 \right] \sum_{m} \frac{(2n + 1)\alpha_{nm}^2}{\alpha_{nm}^2 - n^2 - n} \times \exp\left(\frac{\alpha_{nm}^2 D\Delta}{R^2} \right) \frac{1}{[\alpha_{nm}^2 - (\gamma g\delta R)^2]^2} \]  

(2 - 5)
where \( q = \gamma g \delta R \) and \( j_n \) is the spherical Bessel function of the first kind. \( \alpha_{nm} \) is the \( m^{th} \) root of the equation \( j'_n(\alpha) = 0 \) and can also be expressed in terms of the Bessel function of the first kind \( n j_{n+\frac{1}{2}}(\alpha) - \alpha j_{n+\frac{3}{2}}(\alpha) = 0 \).

In the GDP and the SGP models, the spin echo attenuation is a function of pore radius. The rest of parameters are either known or are acquisition parameters specified in the experiment design. We use both models to estimate the spin echo attenuations and the reliability of diffusion measurements in mudrocks.

### 2.3.3 Signal Processing

The raw echo train data and data are registered as voltage decay (in \( \mu \text{V} \)) as a function of time (in ms or s). The amplitude decays are results of relaxation of spins in an echo train data or attenuation of spins due to incoherency in a magnetic field gradient. The commonly-used \( T_2 \) distributions are obtained by mathematically inverting the “most likely” or best representation of the \( T_2 \) times that would produce the echo train data or the diffusion coefficient that would cause the attenuation (Coates et al., 1999). In this section, we briefly introduce the inversion for \( T_2 \) distribution; the other measurements including 1d and 2d maps follow the same mathematical principles.

For simple systems, such as low viscosity bulk fluids, a single exponential function adequately describes the relaxation phenomena in the echo train data. More complex systems, such as fluid-saturated porous media, require a multi-exponential function to model the relaxations creating an ill posed mathematical problem which has a trivial solution (Whittall and MacKay, 1989; Buttler et al., 1981).

Assuming full polarization of all the hydrogens before CPMG sequence, we can present the echo train data in the form of a summation in:
\[ g_i = \frac{M(t_i)}{M_0} = \sum_{j=1}^{m} f_j e^{-\frac{t_i}{T_j}} + \epsilon_i \quad i = 1, \ldots, n \] (2 – 6)

In which \( g_i \) is \( i \)th echo amplitude, \( M(t_i) \) is the magnetization at \( t=t_i \), \( M_0 \) is the magnetization at \( t=0 \), \( f_j \) is the amplitude for each predefined \( T_j \), \( t_i \) is experiment time, \( T_j \) is the predefined relaxation step and \( \epsilon_i \) is the error.

Since \( f_j \) and \( T_j \) are both unknown, nonlinear inversion algorithms use an iterative method to solve for both unknowns simultaneously, requiring initial estimates to start the iteration. This iterative approach imposes limitations on the number of relaxation times to prevent problems such as divergence or convergence to a local minimum (Whittall and MacKay, 1989). In the linear approach, however, we assume a number of \( T_j \) values and solve Equation 2-6 for \( f_j \) values by minimizing the error (Dunn et al., 2002).

In Equation 2-6, the \( T_j \)'s represent different pore sizes and the \( f_j \)'s are the volume of the pores (porosity) with characteristic relaxation time (pore size) of \( T_j \). Since \( f_j \)'s are representation of porosity at each \( T_j \), the solution to the problem cannot be negative. The problem can be solved using Non Negative Least Square (NNLS) approach proposed by Lawson and Hanson (1974). This approach results in distribution of discrete delta functions, which are sharp spikes at different \( T_j \) values. Although this solution minimizes the error in Equation 2-6, it does not represent the continuous pore size distributions of porous rocks. To impose this criterion, a second constraint of continuity and smoothness of the distribution is imposed on the solution. Both constraints and their implementation to solve the Equation 2-6 form the basis for various linear inversion algorithms. The general form of the regularized equation is shown in Equation 2-7.
\[ \phi(f) = \frac{1}{2} \sum_{i=1}^{n} \left( \sum_{j=1}^{m} f_j e^{-\frac{t_i}{T_j}} - g_i \right)^2 + \alpha R(f_j) \]  

(2-7)

where \( R(f_j) \) is the regularization or penalty function and \( \alpha \) is the smoothing parameter. Each inversion algorithm uses different regularization functions and requires a different solution.

The right hand side of Equation 2-7 has two parts. The first part is the conventional least square fitting and the second part is the regularization component. Without regularization, the \( T_2 \) distributions are modeled as sharp, unstable, and non-reproducible peaks. The smoothing parameter \( \alpha \), creates a balance between stability of the produced peaks and over-weighting the regularization function. Indiscriminate increases in \( \alpha \) increase the weight of the regularization function and over-smooth the distribution (Casanova et al., 2011). Proposed solutions of this problem, regardless of the inversion type and solution algorithm, should minimize the misfit factor shown in Equation 2-8.

\[ \chi^2 = \sum_{i=1}^{n} \left( \sum_{j=1}^{m} f_j e^{-\frac{t_i}{T_j}} - g_i \right)^2 \]  

(2-8)

Statistically, \( \chi^2 \) is expected to correspond to the number of echoes in the experiment. The optimal smoothing parameter can be obtained by plotting \( \chi^2 \) as a function of \( \alpha \) (Casanova et al., 2011). Alternatively, the smoothing parameter can be calculated (Dunn et al., 1994). We use the Dunn et al. (1994) approach to calculate the “optimum smoothing parameter”

We now discuss the specific challenges in mudrocks for data acquisition and for choosing appropriate parameters in data inversion. We also investigate the reliability of
restricted diffusion in mudrocks by comparing experimental data with analytical models of the diffusion phenomena.

2.4 Discussion

In this study we aim to discuss the most important aspects of NMR data acquisition and analysis in unconventional rocks. In all cases we compare two cases: a sandstone case and a shale case with long and short relaxation times, respectively. We investigate the significance of different parameters on data acquisition and inversion for each case. Both experimental results and simulations are utilized to compare both cases.

2.4.1 NMR Acquisition

NMR data are acquired using pulse sequences. We discuss features of the pulse sequences as well as instrument limitations that might prevent high resolution data acquisition in mudrocks.

2.4.1.1 Echo Spacing (TE)

Echo spacings (TE) specify the timing of the 180° pulses as well as initiation of spin echo amplitude data acquisition. Minimizing TE in the CPMG sequence can improve the NMR signal by allowing acquisition of fast relaxing components and by diminishing diffusion effects.

The sooner the acquisition starts, the more spin echoes are detected, and the higher the signal to noise ratio achieved (Coates et al., 1999). Furthermore, the early time signals, significant in samples with fast relaxing hydrogens, such as in heavy oils and mudrocks, can be captured. In Figure 2-3, we compare the effect of echo spacing on capturing the fast relaxing components of a sandstone (Figure 2-3a) and a mudrock
The echo train acquired with a TE = 60 µs shows a peak at 0.4 ms which is diminished when the TE is increased to 200 and 400 µs. The increased TE had negligible effect on the T$_2$ distributions of the high porosity sandstone (Figure 2-3a) since the short relaxation times represent less than 3% of the total porosity. In the low porosity mudrock however, larger TE fail to measure spins that generate the 0.4 ms peak because they decay before the acquisition starts. These spins account for more than 34% of the total porosity.

Figure 2-3: T$_2$ distribution measured with TE of 60 µsec, 200 µsec and 400 µsec for (a) sandstone and (b) mudrock samples. Acquiring data with longer TE disregards the fast relaxing components in the T$_2$ distribution for mudrocks (a). Long TE also increases the diffusion effect by imposing an extra relaxation and reduces the peak amplitude for sandstone (b).

Spin diffusion in pore space due to magnetic field inhomogeneity and presence of internal gradients imposes an additional spin relaxation: the diffusion induced relaxation (Hürlimann, 1998). Since performing the experiment without magnetic gradients is practically impossible, minimizing TE can reduce diffusion induced relaxations (Saidian et al., 2015a). At low frequencies (2 MHz), the diffusion induced relaxation is negligible in mudrocks due to their small pore sizes, regardless of the
diffusion coefficient variations of the saturating fluids or the magnetic susceptibility variations in the pore space (Washburn, 2014). Consequently, the relaxation peak at 10 ms in the mudrock does not change with increased TE (Figure 2-3a). However, the sandstone (Figure 2-3b) shows significant diffusion effects; at TE = 400 µs, the peak amplitude around 200 ms is reduced by 5% of the total porosity.

2.4.1.2 Radio Frequency (RF) Pulses and Acquisition Delays

Variations in the duration, amplitude and frequency of RF pulses due to practical limitations compromise the data acquisition timing of the NMR signal. Several delay times are associated with both transmitting the pulse and acquiring the NMR signal: free ringing, damping and group delays. We briefly discuss the definition, source and the effect of each delay on acquisition of the NMR signal (Mitchell et al., 2014).

Ideally, the probe should recover immediately after transmitting the RF pulse and start acquiring data. However, the energy in the RF pulser coil does not dissipate instantly and leads to acoustic ringing (Buess and Petersen, 1978; Peshkovsky et al., 2005). The induced RF signal in the coil caused by excitation of internal metallic parts of the probe due to initial pulsing is called acoustic ringing (Morris and Toohey, 1985); it can last up to several milliseconds depending on the magnet strength and quality factor and the pulse frequency (Buess and Petersen, 1978). Acoustic ringing interferes with NMR signals from the sample as its frequency overlaps with the RF pulse and the Larmor frequency. Ringing effects can be eliminated by simply delaying acquisition until the ringing decays. A damping pulse can expedite the ringing decay process. However, since the damping pulse might create free ringing as well, an additional damping delay is required to eliminate that ringing as well. The time required for the probe to recover
from the various free ringing is called the “ringing and damping delay” or “probe dead time” (Mitchell et al., 2014).

The NMR signal is digitally filtered to improve signal to noise ratio (SNR) (Moskau, 2001). The RF pulse transmitted by the probe and the signal received from the sample are filtered to narrow the frequency range and improve data quality. Each filtering process imposes a filtering time delay, known as “group delay”.

The group delays and the probe dead time together determine when signal acquisition from the sample can start; it is the minimum practical TE of an NMR instrument. Although minimizing the TE is desirable in samples with fast relaxing hydrogen nuclei, choosing too small a delay time to achieve minimum TE results in appearance of unwanted signals such as ringing effect. The interference from these unwanted signals is significant in mudrocks where the actual signal is weak due to low porosity or decay of fast relaxing hydrogens during the delay times. Figure 2-4 shows the effect of variation of total delay on the acquired FID signal for a mudrock and a sandstone. At low acquisition delay (30 µs), the interference from free ringing for both samples is captured by the receiver. The acoustic ringing amplitude is negligible for the sandstone with a high NMR signal (Figure 2-4a). On the other hand, for the mudrock (Figure 2-4b), the acoustic ringing is as high as 25% of the actual signal from the sample. This extra amplitude can be interpreted as the signal and, if not accounted for, result in overestimation of porosity and micropore volume. An acquisition delay larger than 90 µs eliminates acoustic ringing for both samples (Figure 2-4).
2.4.1.3 Background Signal

Low field NMR signals originate from hydrogen nuclei in the sample. Hydrogen atom contamination in the test environment, e.g. from sample containers, plastic or Teflon wraps and ambient moisture, might also produce a detectable signal. A common practice is to capture the background signal by repeating the same experiment on the sample container and wraps without the sample and subtracting the background noise from the original signal. To avoid adding noise to the data, the SNR of the background signal must match or exceed that of the sample.

![FID signal for a mudrock sample with (a) 30 µsec and (b) 95 µsec delays (damping and acquisition delay combined). The probe acoustic ringing is shown by the circle in figure (a) for short delay. At low acquisition delay (30 µs) the acoustic ringing for both samples is captured by the receiver. For the sandstone (a) the acoustic ringing amplitude is negligible whereas for the mudrock (b) the acoustic ringing is about 25% of the signal. Increasing the acquisition delay to 90 µs eliminates the acoustic ringing for both samples.](image)

In high porosity rocks, with high amplitude NMR signals, background noise is negligible compared to the main signal. In low porosity rocks, the contribution from the background noise is significant and can be interpreted as a real signal and lead to
overestimation of porosity and micro-pore volume. Figure 2-5 displays the NMR signal and Figure 2-6 shows the $T_2$ distributions before and after background removal for a

![Figure 2-5: Original and background subtracted echo train data for (a) Sandstone and (b) Mudrock sample. As shown the background signal amplitude is negligible for Sandstone sample but it changes the mudrock signal significantly after subtraction.](image)

![Figure 2-6: $T_2$ distributions for before and after background subtraction for (a) Sandstone and (b) Mudrock samples. The changes in sandstone spectrum are negligible, but for the mudrock, a major part of the fast relaxing components have been removed.](image)
high porosity sandstone (Figure 2-5a; Figure 2-6a) and a low porosity mudrock (Figure 2-5b; Figure 2-6b). Note that the change in the signal amplitude at early times for the mudrock sample is significant (up to 60% of the total porosity), whereas it is smaller for the sand sample (less than 6% of the total porosity).

2.4.1.4 Number of Echoes

Depending on the sample properties, such as fluid viscosity or pore size distribution of the rock, the time required for the echo train to decay to noise level varies. Enough echoes for a specific TE value are required to capture all different hydrogen nuclei with different relaxation rates. Figure 2-7 shows that the echo train decays are different in a sandstone and a mudrock sample although both samples are saturated with the same fluid. Due to differences in the pore structure and mineralogy, hydrogen nuclei in the mudrock sample relax faster than in the sandstone. At any given TE time, it is best practice to increase the number of echoes until the echo train data decays to noise level. Similar to acquiring data with long TE which discounts fast relaxing components, acquiring data with insufficient number of echoes leads to discounting slow relaxing hydrogen and incomplete $T_2$ distribution.

2.4.2 Signal Processing

Appropriate mathematical inversion is required for accurate analysis and interpretation of NMR data, regardless of SNR and data quality. The reliability of any inversion can be compromised by acquisition parameters, sample properties and instrument limitations. We discuss here the factors that affect the inversion process, such as smoothing, SNR and relaxation rate.
Figure 2-7: The echo train data acquired with 60 µsec TE for (a) Sandstone and (b) Mudrock. As we see in both figures the echo train amplitude (solid black line) reaches to noise level (light gray line) at the end of the experiment.

2.4.2.1 Smoothing Parameter

We use the regularization function to produce a smooth $T_2$ distribution to represent the pore size distribution of a natural rock. The smoothing parameter ($\alpha$ in Equation 2-7) is the regularization weight; it plays a significant role in the $T_2$ distribution shape. Without regularization, the inversion produces discrete delta functions. Figure 2-8 shows the original $T_2$ distribution used to produce the echo train data and the inversion results with different smoothing parameters is also shown for comparison. Decreasing the smoothing parameter from 1 to 0.05 (Figure 2-8a to 2-8c) changes the distribution from a broad single peak biased by the regularization function (Figure 2-8a) to sharp and discrete peaks which are similar to discrete delta functions (Figure 2-8c). The optimum smoothing parameter is the compromise between instability of the delta-
type result and bias by over-smoothing. In the following section, we discuss how SNR and relaxation rate affect the smoothing parameter value.

![Diagram](image.png)

**Figure 2-8**: Effect of smoothing parameter on the inversion result. Smaller smoothing parameters lead to sharp and thin peaks in the $T_2$ distribution, while larger smoothing parameters broaden the spectrum and combine the peaks in the original spectrum to one broad peak.

### 2.4.2.2 Signal to Noise Ratio

Signal to noise ratio (SNR) is a measure of the quality of the NMR data. It is the ratio of the initial magnetization amplitude in echo train data to the average noise amplitude. Doubling the number of experiments (NMR scans) increases the SNR by a factor of $\sqrt{2}$. We simulated synthetic $T_2$ distributions with similar shapes, TEs and
number of echoes but with variable relaxation rates and SNR. The mudrock and the sandstone spectra can be differentiated by fast (Figure 2-9a) and slow (Figure 2-9a) relaxation rates, respectively. We inverted the echo train data using various smoothing parameters to reproduce either the original spectrum (solid curves in Figure 2-9) or the spectrum with most similarity to the original spectrum. Figure 2-9 shows that (a) For sandstone (Figure 2-9a), the original spectrum is reproduced for high SNR scenarios (>> 10 SNR). (b) For mudrock sample (Figure 2-9b), the original spectrum was not recovered even at the high SNR of 1000. (c) All the inverted spectra for the mudrock are unimodal. (d) Lower SNR (< 10) signals yield inversion artifacts at fast relaxing times that might be interpreted as micro porosity. (e) The total amplitude calculated from $T_2$ distributions remained unaffected by the SNR values.

Our simulation results show that for fast relaxing samples such as mudrocks, regardless of the quality of the data, the original $T_2$ distribution cannot be reproduced by the inversion process. Also the inverted $T_2$ distribution does not show the bimodal or multi-modal distribution of the pore structure in mudrocks and inversion artifacts appeared at short relaxation times might be interpreted as micro-porosity.

2.4.2.3 Relaxation Rate

To investigate why the inversions failed to reproduce the $T_2$ spectrum for the mudrock (Figure 2-9b), we simulated synthetic echo train data for a fast and a slow relaxing scenario each with a uni- and a bi-modal spectrum. The TE, number of echoes and SNR were kept constant. The smoothing parameter used to simulate the original $T_2$ distribution is denoted as “simulated smoothing parameter”, while the smoothing parameter calculated using the method of Dunn et al. (1994) is denoted as “optimum
Figure 2-9: Comparison of a synthetic T₂ distribution for (a) Sandstone and (b) Mudrock. The original T₂ spectra are shown as solid curves and the inverted spectra are shown as dashed curves. For the sandstone (a) the original shape of the T₂ distribution is reproduced by inversion. But for the mudrock, due to fast relaxation and proximity of two peaks, even at SNR of 1000 the original shape of the T₂ distribution is not reproduced.

Figure 2-10 shows both original and inverted T₂ spectra for unimodal distributions at three different relaxation rates calculated using the simulated smoothing parameter. All the peaks, regardless of the relaxation rates, were reproduced by inversion. Comparison of real and optimum smoothing for in Figure 2-11 shows that the optimum smoothing parameter is up to 3 orders of magnitude higher than real smoothing parameter. The difference is larger for faster relaxation peaks. Increasing the relaxation rate at a constant TE time reduces the number of data points in the echo train data. Consequently, the inversion algorithm uses a limited number of points to reproduce the distributions. In this case, higher smoothing parameter is calculated to increase the
weight of the regularization function and the resulting distribution is biased by this function.

Figure 2-10: Original and inverted $T_2$ spectra for single peak distributions at three different relaxation rates. In this figure only the results of inversion using real smoothing parameter are shown. As it is shown all the peaks regardless of the relaxation rates are reproduced by inversion.

Figure 2-11: Comparison of real and optimum smoothing in shows that the optimum smoothing parameter is systematically higher than real smoothing parameter up to 3 orders of magnitude. The difference is higher for faster relaxation peaks.

Figure 2-12 shows the results for the simulation of bimodal distributions for two different samples with high and low relaxation rates. The inversion successfully reproduced both peaks of the spectrum with low relaxation rate; in the fast relaxation
spectrum, the peaks are not accurately resolved after inversion. Similar to the unimodal scenario (Figure 2-11), the simulated smoothing parameter is smaller than optimum smoothing parameter (Figure 2-13), and this difference increases with increasing relaxation rate.

Figure 2-12: Original and inverted $T_2$ spectra for double peak distributions at two different relaxation rates. In this figure only the results of inversion using real smoothing parameter are shown. The inversion process gave a mismatch for fast relaxation peak.

Figure 2-13: Comparison of real and optimum smoothing parameter. It shows that the optimum smoothing parameter is systematically higher than real smoothing parameter up to 3 orders of magnitude. The difference is higher for faster relaxation peaks.
The simulation results show that for mudrocks using the optimum smoothing parameter results in a broad distribution due to over-smoothing the spectrum. Multimodal distribution is an indication of presence of different pore sizes or fluids with different viscosities in the rock. Over-smoothing of the distribution masks the T2 spectra by broadening and combining the peaks and hinders the proper interpretation the NMR T2 distributions.

2.4.3 Restricted Diffusion

Restricted diffusion measurements presented as 2d D-T maps, are commonly used for pore characterization, fluid typing, saturation and viscosity determination. There are two main challenges associated with restricted diffusion measurement in mudrocks: the gradient pulse amplitude and the diffusion timing. In this section we discuss these two challenges and the reliability of diffusion measurements in mudrocks by simulating the restricted diffusion phenomena in spherical pores utilizing GPD and SGP models and experimental data for a mudrock sample.

2.4.3.1 Gradient Amplitude

Diffusion measurements are based on the attenuation of the spin echo in a magnetic gradient (the reduction of the magnetization from $E_0$ to $E$ in Figure 2-2a and 2-b). This attenuation is the result of change in spin phases and Brownian motion of the spins in the porous media. The phase change of the spins is a function of the spin location in the magnetic field. Significant phase change or translational motion of the spins in the pores is required for the signal attenuation to be detectable by an NMR instrument. The translational motion of the spins in mudrocks is limited because of the abundance of nano- and micro-scale pores in these rocks, so the gradient amplitude
has to be strong enough to create a detectable phase change across a single pore.

We simulated the spin echo attenuation in a spherical pore using GPD (Figure 2-14) and SGP (Figure 2-15) models with a fluid diffusion coefficient of 2.5 m²/s, gradient pulse duration of 1.5 ms and diffusion time of 50 ms. We varied the pore radii from 1 to 50 µm for the pulse gradient amplitude of 0 to 0.5 T/m to model low frequency NMR experiments (Figure 2-14a and Figure 2-15a). We also varied the pore radii from 0.05 to 5 µm for the gradient pulse amplitude of 0 to 20 T/m to model a high frequency NMR experiments (Figure 2-14b and Figure 2-15b). Common practice for a reliable diffusion measurement is more than 90% signal loss due to diffusion (Bruker™ Diffusion NMR Manual, 2009). Our simulations show that although the SGP model demonstrates higher attenuation for the same acquisition parameters, both models confirm that the attenuation is negligible for 1 µm radius at gradient pulse amplitude of 0.5 T/m (Figure 2-14a and Figure 2-15a). Also the attenuation for pore radii of 5 and 10 µm was not high enough for a reliable diffusion measurement at this gradient pulse amplitude (Figure 2-14a and Figure 2-15a). Simulations of signal attenuation at gradient pulse amplitudes up to 20 T/m (Figure 2-14b and Figure 2-15b) indicated significant attenuation for pores larger than 1 µm radius for GPD model (Figure 2-14b) and larger than 500 nm for SGP model (Figure 2-15b). Since downhole and low field NMR instruments are limited to gradients below 0.5 T/m, the measured diffusion coefficient is only sensitive to the large pores where the majority of the attenuation occurs.

2.4.3.2 Diffusion Time

Diffusion time (Δ in Figure 2-2) is the delay time between two gradient pulses. The translational diffusive motion of the spins during this time period imposes the
Figure 2-14: The simulation results of signal simulation in spheres with various radii as a result of diffusion of the fluid assuming Gaussian phase distribution (GPD) of the spins for gradient amplitude of (a) 0 to 0.5 T/m and (b) 0 to 20 T/m. The fluid diffusion coefficient is 2.5 m²/s, gradient pulse duration and diffusion times are 1.5 and 50 ms, respectively.

Figure 2-15: The simulation results of signal simulation in spheres with various radii as a result of diffusion of the fluid assuming short gradient pulse (SGP) duration for gradient amplitude of (a) 0 to 0.5 T/m and (b) 0 to 20 T/m. The fluid diffusion coefficient is 2.5 m²/s, gradient pulse duration and diffusion times are 1.5 and 50 ms, respectively.
required signal attenuation for diffusion measurements. A similar phenomenon to acoustic ringing happens is the probe when the gradient pulses are applied. This phenomenon is denoted as eddy current which takes place in different metallic parts of the probe.

The eddy currents create gradient artifacts which vary in amplitude depending on the direction of the applied gradient pulse (Chan et al., 2014). The eddy current’s effect on NMR signal can be minimized by applying the gradient pulses with a finite ramp time (the time required for the pulse to reach its maximum amplitude) and extending the data acquisition until the eddy currents are decayed (stabilization delay). The minimum diffusion time for a reliable PFG pulsing is determined by the ramp times, stabilization delays and minimum time required for spins to diffuse in the porous media. Typically, in low field NMR measurements, the diffusion time is commonly higher than 10 ms. Relaxation of the spins during diffusion time rules out the contribution of these spins in diffusion measurement. The signal loss due to relaxation before data acquisition for sandstones (Figure 2-7a) is less than 10% of the total signal whereas in mudrocks (Figure 2-7b) is more than 90% of the total signal. To show the effect of diffusion time on diffusion measurement we compared the T$_2$ distribution and D-T$_2$ map for a mudrock sample (Figure 2-16). The D-T$_2$ maps is acquired with diffusion time of 13 ms and maximum gradient amplitude of 0.5 T/m. T$_2$ spectrum showed bimodal distribution with dominant peaks at 0.8 and 60 ms (Figure 2-16a). The signal on the left side of dashed red line in Figure 2-16a is not captured in D-T$_2$ map and the T$_2$ distribution measured by the D-T$_2$ pulse sequence shows only the 60 ms peak. The fast relaxing spins (0.8 ms peak) were relaxed during the diffusion time.
2.5 Conclusions

Tight, low-porosity rocks (also called shales or mudrocks) present unique challenges in NMR data acquisition and signal processing. We have presented errors and pitfalls in NMR experimental design and data processing for such rocks. We have shown that:

- Data acquisition should prevent signal interferences from RF pulses and increase NMR data quality by eliminating signals not originating from the sample. Left uncorrected, these interferences and unwanted signals can be interpreted as microporosity in mudrocks.

- Inversion of NMR data for mudrocks is more challenging than for conventional rocks mainly because of the fast relaxation of the hydrogen nuclei in these rocks. Overestimation of the smoothing parameter, peak broadening and lack of resolution to

![Mudrock T2 Distribution](image1)

Figure 2-16: (a) T\textsubscript{2} distribution and (b) D-T\textsubscript{2} for a mudrock sample. The signal on the left side of dashed line in is not captured in D-T\textsubscript{2} map due to signal decay during diffusion time. The T\textsubscript{2} distribution (a) shows a bimodal distribution but the D-T\textsubscript{2} map (b) does not show the peak at faster times. All the spins with relaxation faster than the red dashed line relaxation time decayed in the D-T\textsubscript{2} experiment before the data acquisition started.
identify bi or multi-modal distributions are consequences of fast relaxing signal in mudrocks. These effects can lead to over interpretation of the $T_2$ distribution in mudrocks.

- In the current state of the logging technology, downhole restricted diffusion experiments are not reliable for fluid typing and saturation measurements in mudrocks: The pulse gradient amplitude for low frequency instruments is not high enough, and the signal decays significantly due to relaxation of the spins before the acquisition of the spin echo starts.

This study provides insight about NMR data acquisition and signal processing challenges in mudrocks. It highlights the necessary precautions for acquiring NMR data. It also indicates how the rock and fluid properties in mudrocks might compromise the data quality and reliability.

2.6 Acknowledgments

This paper is dedicated to the memory of Dr. Michael L. Batzle. The authors would like to thank Sophie Godeferoy, Brett Ryland and Paul T. Callaghan from Victoria University of Wellington for providing the inverse Laplace transform program for 2d inversions. We also thank OCLASSH and Center for Rock Abuse sponsors for providing support and samples.

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CHAPTER 3

A Comparison of Measurement Techniques for Porosity and Pore Size Distribution in Shales (Mudrocks): A Case Study of Haynesville, Eastern European Silurian, Niobrara, and Monterey Formations

A paper published in the AAPG Memoir 110: Imaging Unconventional Reservoir Pore Systems

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“There is nothing constant in this world but inconsistency.”
- Jonathan Swift

3.1 Abstract

Porosity and pore size distribution (PSD) are required to calculate reservoir quality and volume. Numerous inconsistencies have been reported in measurements of these properties in shales (mudrocks). We investigate these inconsistencies by evaluating the effects of fine grains, small pores, high clay content, swelling clay minerals and pores hosted in organic content. Using mudrocks from the Haynesville, Eastern European Silurian, Niobrara and Monterey formations, we measured porosity and pore or throat size distribution using subcritical nitrogen (N2) gas adsorption at 77.3 K, mercury intrusion (MI), water immersion (WI), and helium porosimetry based on Gas Research Institute standard methodology (GRI). We used scanning electron microscope (SEM) images to understand the pore structure at a microscopic scale. We separated
the samples from each formation into groups based on their clay and TOC contents and further investigated the effects of geochemical and mineralogical variations on porosity and PSD. We find that differences in the porosity and PSD measurement techniques can be explained with thermal maturity, texture and mineralogy, specifically clay content and type and total organic carbon (TOC) variations. We find that porosity and PSD measurement techniques can provide complementary information within each group provided the comparison is made between methods appropriate for that group. Our intent is to provide a better understanding of the inconsistencies in porosity measurements when different techniques are used.

3.2 Introduction

Thanks to new technologies such as hydraulic fracturing and horizontal drilling in the last decade, unconventional reservoirs gained oil and gas industry’s attention as valuable resources for energy production. Passey et al. (2010) defined “unconventional reservoirs” as a wide range of hydrocarbon-bearing rocks that are not economically producible without stimulation techniques. Although the term unconventional reservoir lacks adequate lithologic definition, in this paper, we refer to tight oil, or gas-producing reservoirs which may or may not be organic rich and are often called “shales”. In today’s terminology, shale reservoirs are either siliciclastic or carbonate mudrocks and need not necessarily contain clay minerals. Although alternate terms have been used for shale reservoirs such as unconventionals, self-resourcing rocks, organic-rich rocks and mudstones, the term shale has endured. In this work we use the term mudrock to refer to these reservoirs.
Mudrocks are fine-grained rocks with more than 50% of its particles less than 62.5 µm (Folk, 1974, Friedman 2003, and Javadpour, 2005). Like other sedimentary rocks, they are composed of a wide range of minerals such as clay, quartz, feldspar, carbonates, and heavy minerals such as pyrite (Passey et al., 2010). Besides mineral components, mudrocks may contain organic matter as a significant component of the rock (Bohacs et al., 2013).

Porosity and pore size distribution (PSD) are used for reservoir evaluation, permeability prediction (Nelson, 2009), and elastic property calculations (Kuila and Prasad, 2011). A major challenge in estimating transport and storage capacity of mudrocks is the poor understanding of their pore properties including size, distribution and pore hosting components such as organic matter, different clays and other fine gain minerals (Nelson, 2009, Chalmers et al., 2012, Loucks et al., 2012, Kuila et al., 2014a, Kuila et al., 2014b). Lack of accessibility of the investigating fluid to the pore system is the main deterrent to reliable and accurate laboratory measurements. Limited accessibility can be due to extremely low permeability, insufficient cleaning (leaving residual oil behind due to low permeability), complicated mineral surface-fluid interactions, or insufficient equilibration time.

It is important to not only quantify pore space with visual techniques such as Scanning Electron Microscopy (SEM) (for example, Lemmens et al., 2010, Bernard et al., 2012, Curtis et al., 2012, Alcantar-Lopez and Chipera, 2013, Milliken et al., 2013, Zargari et al., 2013) or CT-Scanning (Coshell et al., 1994, Wildenschild and Sheppard, 2012,) but also with non-visual techniques. Non-visual techniques can be used for quantitative analysis of the samples. Some examples of non-visual techniques are
nitrogen gas adsorption (N2) (Echeverria et al., 1999, Chalmers et al., 2012, Kuila et al., 2012), mercury intrusion (MI) (Howard, 1991), water immersion porosimetry (WI) (Howard, 1991, Kuila et al., 2014a) and nuclear magnetic resonance (NMR) (Sondergeld et al., 2010b, Jiang et al., 2013, Rylander et al., 2013, Rivera et al., 2014, Saidian et al., 2015).

Porosity and PSD are commonly measured with techniques such as mercury intrusion and helium expansion. These approaches yield consistent values for conventional rocks (Hossain et al., 2011). For mudrocks, however, the methods to measure porosity and PSD need careful selection. Large variations in their pore sizes and shapes can result in up to 50% inconsistency in porosity values (Howard, 1991; Katsube and Scromeda, 1991; Katsube et al., 1992; Dorsch and Katsube, 1996, Sondergeld et al., 2010b). Discrepancies in results arise because the techniques are based on specific physical phenomena (e.g. surface adsorption and pore condensation in N2 technique, intrusion into capillary in MI technique) and use of different investigating fluids to access the pore space. These differences can be exploited considering the fact that each technique measures different aspects of the pore space. A combination of methods can help fully characterize complex pore spaces. Furthermore, within each technique, repeatability can be compromised due to inconsistent pretreatment methods such as grinding and sieving, laboratory conditions such as relative humidity and temperature, and millimeter scale heterogeneity which hinders the ability to produce equivalent sample aliquots for multiple measurements (Passey et al., 2010; Kuila, 2013). Differences in porosity values measured by different laboratories or under different pretreatment conditions are well documented (Passey et
al, 2010, Sondergeld et al., 2010b, Comisky et al., 2011). A methodical comparison of porosity values in mud rocks determined by various techniques that examines the compositional, textural and geochemical reasons for data variations is lacking.

The main objective of our work is to understand various pore sensing techniques on the basis of textural, mineralogical and geochemical differences. We present porosity obtained from helium expansion, mercury intrusion, water immersion and nitrogen adsorption. We also present PSD data obtained from mercury intrusion and nitrogen adsorption. We investigate the controlling factors on the results of each experimental method and evaluate data variations together with textural, mineralogical and geochemical differences. Further, we compare porosity values measured with various techniques with the PSDs measured with three different techniques. Finally, we provide recommendations for a new approach for PSD comparison in mudrocks.

In this study we use the pore size classification suggested by Rouquerol et al. (1994). In this classification micro, meso and macro pores have <2 nm, 2-50 nm and >50 nm pore width, respectively. All the pore or throat size distributions are plotted using the diameter or width of the pores. Although diameter and pore width might not be the same in some cases such as elongated pores, it should be noted that the PSD inversion methods used in this paper assumes a non-intersecting cylindrical pore geometry, therefore the pore dimension should be treated as ‘equivalent cylindrical diameter’ irrespective of the actual pore shape.

3.3 Materials

Below we briefly describe the dominant mineralogy, thermal maturity, organic matter type, and organic matter content for the samples used for this study. The details
of each sample set have been presented by Rivera, 2014 and Godinez; 2014 (Monterey), Kuila, 2013 (Haynesville, Niobrara, and Eastern European Silurian).

3.3.1 Haynesville Formation

34 samples were taken from Upper Jurassic Haynesville Formation (Kuila, 2013). The samples were clay-rich (up to 73 wt% mainly illite-smectite group of clays with <5% to 9% swelling smectitic layers) with moderate amounts of quartzo-feldspathic constituents (average of 26 wt%) and a variable amount of carbonate (1 to 11 wt%) (Figure 3-1a). The carbonate mineralogy is mostly calcite, except significant amounts of dolomite (up to 44 wt%) was observed in 2 samples. In the Haynesville sample set the TOC varied between 0.5-6.3 wt%; the kerogen was in the gas window based on the \( T_{\text{max}} \) up to 542 °C and HI which varied from 19 to 57 with an average of 36. Presence of a low temperature S2 peak(or shoulder) between 350-400 °C in the RockEval pyrogram (Kuila et al., 2014a) suggests presence of bitumen in the samples (Clementz, 1979; Wilhelms et al., 1991). Figure 3-2a and 3-2b show SEM images for two Haynesville samples having different mineralogy. Figure 3-2a shows silt-sized quartz, calcite and plagioclase particles surrounded by a mixture of illite and clay-sized quartz. Organic matter is dispersed between clay-sized particles. Figure 3-2b represents a dolomite rich sample with intergranular spaces filled with a mixture of quartz and clay minerals as well as organic matter.

3.3.2 Eastern European Silurian Formation

22 samples were taken from the Eastern European Silurian gas play in Eastern Europe (henceforth referred as Silurian) (Kuila, 2013). The samples contained up to 52 wt% quartz and up to 57 wt% clay which is mostly illite (Figure 3-1b). The kerogen was
thermally mature in the gas window and TOC ranged between 1-6 wt%. No pyrogram peaks were observed in the Rock Eval results up to 550 °C (Kuila et al., 2014a) which confirmed the absence of any pyrolyzable kerogen in these samples (Clementz, 1979; Wilhelms et al., 1991).

Figure 3-1: Mineralogy of (a) Haynesville, (b) Silurian, (c) Niobrara (Chalk, Marl and Fort Hays), and (d) Monterey samples measured by QXRD and color-coded by TOC. See the sample descriptions for more information. The TOC values for Monterey samples used in this study were not available. The chalk (dashed blue circle) and marl (red solid circle) rock types are shown in (c) based on clay content and total carbonate content.
Figure 3-2: SEM images (Backscattered Electron Images) for two Haynesville samples. (a) Silt-sized quartz, calcite and plagioclase particles surrounded by a mixture of illite and clay-sized quartz. Organic matter is dispersed between clay-sized particles. (b) Dolomite rich sample with intergranular spaces filled with a mixture of quartz and clay minerals as well as organic matter. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Pl=Plagioclase, Ilt=Illite, Chl=Chlorite, OM=Organic Matter.
Figure 3-3: SEM images (Backscattered Electron Images) for two Silurian samples. (a) and (b) Silt-size particles such as quartz, pyrite, and dolomite are surrounded by a matrix of illite and chlorite. Organic matter is dispersed between clay particles. Qz=Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Pl=Plagioclase, Ilt=Illite, Chl=Chlorite, OM=Organic Matter, TiO2=Titanium Dioxide.
The HI varied from 0 to 9 with an average of 3 indicating extremely high maturity of these samples. Texturally, the silt-size particles such as quartz, pyrite, and dolomite are surrounded by a matrix of illite and chlorite and organic matter is dispersed between clay particles (Figure 3-3a and 3-3b).

### 3.3.3 Niobrara Formation

22 marl and chalk samples came from a well in the Berthoud Field, Larimer County, CO, USA (Kuila, 2013), specifically from the Fort Hays limestone and the overlying Smoky Hill members of the Niobrara formation. They were calcite-rich rocks with moderate amounts of clay (up to 35 wt% with an average of 16.5 wt%), quartz (average of 11 wt%) and pyrite (Figure 3-1c). The clays are mainly mixed layer illite/smectite with 14-95 % (average of 31%) estimated smectite fraction. Type II kerogen was thermally mature and was in the oil window based on average $T_{\text{max}}$ of 436 °C and HI which varied from 119 to 386 with an average of 306. TOC varied between 0.1 and 5.3 wt% SEM images for two samples are shown in Figure 3-4a and 3-4b. Figure 3-4a shows relatively more homogeneous intercrystalline pore distribution which is filled with organic matter. Figure 3-4b shows larger intercrystalline pores filled with organic matter. Note that the larger intercrystalline pores are within the peloid structures.

### 3.3.4 Monterey Formation

A combination of 12 sidewall and conventional core samples were taken from an oil producing well drilled at the western flank of the southern San Joaquin Basin in California. The samples were predominantly quartz phase porcellanites containing moderate amounts of clay (up to 24 wt% with an average of 8 wt%) and pyrite (up to 7
Figure 3-4: SEM images (Backscattered Electron Images) for two Niobrara samples. (a) shows relatively more homogeneous intercrystalline pore distribution which is filled with organic matter. (b) shows larger intercrystalline pores filled with organic matter. Note that the larger intercrystalline pores are within the peloid structures. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Hem= Hematite, Pl=Plagioclase, Ilt=Illite, OM=Organic Matter, TiO₂=Titanium Dioxide, Ms=Muscovite.
Figure 3-5: SEM images (Backscattered Electron Images) for two Monterey samples. (a) and (b) moderate carbonate and dominant quartz grains with presence of organic matter filling up the intergranular and intercrystalline pores. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Hem=Hematite, Pl=Plagioclase, OM=Organic Matter.
wt% with an average of 3 wt%). A smaller sample set (3 samples) were calcite-rich (Figure 3-1d). TOC varied from 0.85-4.95 wt%. Kerogen was Type II with thermal maturity in the oil window based on average $T_{\text{max}}$ of 438 °C and the hydrogen index (HI) varying from 184 to 473 with an average of 374. SEM images of Monterey samples (Figure 3-5) show moderate amount of carbonate and dominant quartz grains with the presence of organic matter filling up the intergranular and intercrystalline pores.

3.4 Methods

In this section, we describe the pretreatments, investigating fluids, and methods as well as the associated challenges for each measurement technique. In the results and discussion part we will investigate how these challenges and limitations affect the porosity measurement for different sample sets. Table 3-1 lists the experiments that were performed for different sample sets.

Table 3-1: Summary of the disadvantages of each measurement technique and the resulting effect on porosity measurements.

<table>
<thead>
<tr>
<th>Method</th>
<th>Haynesville</th>
<th>Monterey</th>
<th>Niobrara</th>
<th>Silurian</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRI</td>
<td>23</td>
<td>NA</td>
<td>NA</td>
<td>9</td>
</tr>
<tr>
<td>Helium Injection (HE)</td>
<td>NA</td>
<td>11</td>
<td>NA</td>
<td>9</td>
</tr>
<tr>
<td>Water Immersion (WI)</td>
<td>34</td>
<td>12</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>Mercury Intrusion (MI)</td>
<td>13</td>
<td>12</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Nitrogen Adsorption (N2)</td>
<td>22</td>
<td>12</td>
<td>22</td>
<td>19</td>
</tr>
</tbody>
</table>

3.4.1 Helium Expansion using the Gas Research Institute (GRI) Method and Helium Injection under Confining Stress

The porosity was measured by a commercial laboratory using the Gas Research Institute (GRI) helium porosimetry technique on crushed rock samples. Due to sample limitations only Silurian and the Haynesville samples were used for these measurements. The porosity was also measured using CMS300™ for cylindrical
Monterey samples. In the GRI technique, bulk rock volume is measured by mercury immersion using Archimedes’ principle and crushed rock grain volume is measured by Boyle’s Law (Luffel and Guidry, 1992; Luffel et al., 1992; GRI-95/0496).

Helium expansion, using either crushed or intact samples, measures pores that are connected and accessible by helium gas. Luffel and Guidry (1992) suggested 30 minutes as the equilibration time for shales as opposed to 1 minute for conventional rocks. In nano-darcy permeability rocks, temperature fluctuations can compromise pressure equilibration and decrease the measurement accuracy. On the other hand, using crushed samples allows the gas to access isolated pores that might be inaccessible otherwise. Sondergeld et al. (2010b) and Passey et al. (2010) reported very high disparities in the porosity and permeability values measured by different laboratories using same samples. Kuila et al. (2014a) provided a thorough discussion of the GRI technique and investigated the effect of pretreatment and laboratory conditions on the final grain density and porosity results. For example, the Dean-Stark extraction pretreatment with a hot solvent typically boiling toluene can create porosity in thermally mature samples, such as the Niobrara and Monterey, by dissolving bitumen and lead to porosity overestimation.

3.4.2 Water Immersion (WI)

In this study, we used the adapted protocol of water immersion for mudrocks developed by Kuila et al. (2014a). In this adapted protocol, approximately 5 grams of rock chips were first vacuum dried at 200 °C for approximately 12 hours and then weighed in air. It is assumed that the existing water and the hydrocarbon in the samples were evaporated after vacuum drying. They were then saturated and weighed again in
water. This protocol of using intact samples and measuring grain density at low humidity increases the repeatability of the experiment (Kuila et al., 2013).

Immersion porosity measurements assess the pores available to the saturating fluid (water or oil). Thus, the fluid type, the pore surface wettability, and the saturation method affect the porosity values. Also presence of swelling clays such as smectite would affect the accuracy of this technique.

3.4.3 Mercury Intrusion (MI)

In MI porosimetry, small intact rock chips were heated up to 200 °C for 12 hours and degassed for 30 minutes at 50 µmHg to remove water and volatile hydrocarbons. Mercury was then injected in the sample at discrete pressure steps from 0.14 to 420 MPa. Pressure was considered equilibrated when the injection rate fell below 0.001 µl/g/s. The Washburn model (Washburn, 1921), assuming cylindrical capillary tube model was used to convert the pressure data to TSD. A conformance correction, for example, the Bailey method from Comisky et al. (2011) was applied to high pressure measurements to account for sample compressibility. The total porosity of the samples was calculated by measuring the bulk volume of the sample submerged in the mercury and the pore volume measured by the volume of intruded mercury. Since MI can only measure the volume of pores with throat-diameter larger than 3.6 nm (at 420 MPa), a significant portion of the pore space in fine-grained rocks is neglected.

3.4.4 Nitrogen Adsorption (N2)

This technique has traditionally been used to measure total specific surface areas (TSSA) in conventional reservoir rocks. Due to practical limitations, N2 technique can only measure the volume of pores with a dimension less than 200 nm (Gregg and
Sing, 1983). 1-3 grams of samples were crushed, sieved through a 40 mesh (420 µm) sieve, and then degassed under vacuum at 200 °C until the outgassing rate was less than 0.005 Torr/min over a 15 minute interval. Nitrogen was injected into the analysis chamber and adsorption of nitrogen to the degassed sample started. The adsorption took place under constant temperature of liquid nitrogen. Pressure and adsorbed quantity of nitrogen were recorded as isotherms and were used to calculate PSD. We used the Barrett, Joyner and Halenda (BJH) inversion (Barrett et al., 1951) as recommended by Kuila (2013) for mudrocks. This inversion method calculates the PSD assuming non-connecting cylindrical pores. The pore volume was calculated by measuring the amount of nitrogen adsorbed in the sample. The Harkins and Jura (1944) thickness curve was utilized for both BJH inversion and micropore (pores with width smaller than 1.7 nm) volume calculation with t-plot analysis. The total pore volume was calculated by combining the micropore volume and the total volume measured for pores with width of 1.7 nm to 200 nm. We used this technique to measure PSD and pore volume in all samples.

3.5 Results

We analyzed samples representing major lithology types (Figure 3-1): predominantly carbonate (Niobrara); predominantly quartz (Monterey); predominantly clay (Haynesville); and a mineral mixture (Silurian). Each sample set has varying amounts of clay and TOC contents. This richness of data allowed us to analyze and explain porosity mismatches between the methods for mineralogy, PSD, and measurement condition effects.
3.5.1 Haynesville Formation

Porosity values are measured by N2, WI, GRI and MI techniques (Figure 3-6). The following observations can be made from this figure:

- MI porosities are lower than that measured by N2 and WIP (Figure 3-6a and 3-6b).
- WI and N2 porosities are comparable within 2 p.u. difference (Figure 3-6c).
- GRI and N2 porosities are comparable within 2 p.u. difference (Figure 3-6d).
- Except some low clay content samples that show higher GRI porosity, the WI and GRI porosity show similar porosities within 2 p.u. difference (Figure 3-6e). The porosity value increases with clay content, however, there is no systematic trends of clay content with the trends observed in the comparative porosity cross plots.

The PSD measured using the N2 technique show significant variation with mineralogy and organic content. Figure 3-7a and 3-7b show the PSD color-coded by clay and TOC content, respectively. Samples with high clay (low TOC) show large amplitudes at the small mesopore range (< 10nm). Samples with low clay (high TOC) show large amplitudes at the big mesopores (10-50 nm) and macropore range (>50 nm). MI TSD was also measured for a subset of Haynesville samples (Figure 3-8). The incomplete shape of MI TSDs suggest that there are pores with throats smaller then 3.6 nm which are not assessed by this technique. There are also a pores with throats larger than 20 nm.

3.5.2 Silurian Formation

We measured the porosity of the Silurian samples using WI, MI, N2 and GRI techniques (Figure 3-9). The following observations can be made:

- MI, N2 and WI measurements show an increase in porosity with increase in TOC
MI porosity is significantly lower when compared to porosities measured by WI and N2 techniques (Figure 3-9a and 3-9b).

WI and N2 porosities are comparable within 2 p.u. difference (Figure 3-9c).

GRI porosity, in general, is lower compared to WI and N2 porosities (Figure 3-9d and 3-9e).

We measured PSD using N2 (Figure 3-10) and TSD using MI (Figure 3-11) techniques for all Silurian samples. The N2 PSDs are color-coded by both clay (Figure 3-10a) and TOC (Figure 3-10b) contents. We make the following observations:

- Significant variation in amplitude of the small mesopore range (<10 nm) is observed.
- The big mesopore (10-50 nm) and macropore range (>50 nm) show similar distributions for all samples with small variations in amplitude.
- The PSD from N2 for some of the high TOC samples (Figure 3-10b) suggests presence of micropores (<2nm). TOC and clay content do not show a clear effect on the PSD.
- The incomplete shape of MI TSD results (Figure 3-11) suggest that there are pores that are not accessible using the MI technique.
- Clay content does not show an effect on the MI peak amplitude (Figure 3-11a) whereas for some high TOC samples the MI peak amplitude is higher (Figure 3-11b).

3.5.3 Niobrara Formation

Figure 3-12 shows the comparison between porosity values measured using the N2, MI and WI techniques. The samples with clay content less than 10 wt% are chalk and the rest are marl rock type (Figure 3-1c). We make the following observations for
Figure 3-6: Porosity comparison for Haynesville samples. The porosities are measured by (a) WI and MI, (b) N2 and MI, (c) WI and N2, (d) N2 and GRI and (e) WI and GRI. Data points are color-coded by clay content. Note that not all the measurements are performed for all samples. (a) and (b) MI underestimates the porosity when compared with WI and N2. (c) WI and N2 show comparable porosity values within 2 p.u. (d) and (e) GRI and N2 show similar porosity values within 2 p.u. and (e) Except some low content samples that show higher GRI porosity, the WI and GRI porosity show similar porosities within 2 p.u. difference.
Figure 3-7: N2 PSD spectra of Haynesville samples color-coded by (a) clay content and (b) TOC content. Samples with high clay and low TOC show high amplitudes at small mesopore range (< 10 nm) and samples with low clay and high TOC show high amplitudes at big mesopores (10-50 nm) and macropores range (>50 nm).

samples with a wide distribution of pore sizes and variable clay content such as the Niobrara samples:

- N2 and WI porosities does not show any consistent trend; the N2 porosity is lower for some samples while others show comparatively lower WI porosities  (Figure 3-12a).
- WI and MI porosities are comparable within 2 p.u. for chalk type. WI overestimates the porosity for marl rock type with higher clay content (Figure 3-12b).
- N2 shows higher porosity for marl samples and MI shows higher porosity for chalk samples (Figure 3-12c).

We used the N2 and MI techniques to measure PSD (Figure 3-13) and TSD (Figure 3-14) for Niobrara samples, respectively:

- The shapes of the PSD (Figure 3-13) for low clay content, chalk samples show increasing PSD amplitude which suggests the presence of pores larger than 200 nm. The high clay content, marl, samples show a dominant pore size of 80-100 nm.

Figure 3-8: MI throat size distributions for Group 2 Haynesville samples which have the highest macropore volume compared to other groups. The MI porosity was highly underestimated compared to other techniques. This implies that the throat size distributions do not assess the whole pore space.
Figure 3-9: Porosity comparison for Silurian samples. The porosities are measured by (a) WI and MI, (b) N2 and MI, (c) WI and N2, (d) WI and GRI and (e) N2 and GRI, all color-coded by TOC content. (a) to (c) MI, N2 and WI measurements show an increase in porosity with increase in TOC. (a) and (b) MI highly underestimates the porosity compared to WI and N2 techniques (c) WI and N2 porosities are comparable within 2 p.u. difference. (d) and (e) GRI generally underestimates the porosity compared to WI and N2 in these samples.
Figure 3-9: Continued.

Figure 3-10: The pore size distribution measured by N2 technique for Silurian samples color-coded by (a) clay content and (b) TOC content. (a) and (b) Significant variation in amplitude in small mesopore range (<10 nm) is observed. The big mesopore (10-50 nm) and macropore range (>50 nm) show similar spectra with small variations in amplitude. TOC and clay content do not show a clear effect on the PSD spectra.
Figure 3-11: The throat size distribution measured by MI technique for Silurian samples color-coded by (a) clay content and (b) TOC content. The MI TSD results suggest that there are pores that are not accessible by MI technique. (a) and (b) Clay content does not show an effect on the MI peak amplitude whereas for some high TOC samples the MI peak amplitude is higher.

- Similar to N2 PSD data, the MI TSD data (Figure 3-14) show two different sets of distributions. One set shows a PSD with a dominant pore size 80-100 nm (low clay content, chalk) and the other set shows an abundance of small pores smaller than 20 nm (high clay content, marl) (Figure 3-14).

- The shape of MI TSDs for marl samples indicates the presence of pores that are not accessible by mercury.

### 3.5.4 Monterey Formation

Porosity values were measured for Monterey samples using WI, MI, HE and N2 techniques (Figure 3-15). We make the following observations:

- WI, MI and HE porosities show comparable values within 2 p.u. difference (Figure 3-15a to 3-15c).

- HE and WI show the best correlation (Figure 3-15b).

- N2 significantly underestimates the porosity for high porosity (>5 p.u.) samples.
Figure 3-12: Porosity comparison for Niobrara samples. The porosities are measured by (a) WI and N2, (b) WI and MI, and (c) MI and N2, all color-coded by total clay content. Note that not all the measurements are performed for all samples. (a) Comparing N2 and WI samples shows that N2 underestimates the porosity for some samples and WI overestimates the porosity for other samples. (b) WI and MI porosities are comparable within 2 p.u. for low clay content (<10 wt%) samples and WI overestimates the porosity for high clay samples (>10 wt%). (c) N2 shows higher porosity for high clay content samples and MI shows higher porosity for low clay samples.
Figure 3-13: The PSD for Niobrara samples using N2 technique, color-coded by clay content. Some of the spectra (low clay content, chalk) show an increasing PSD amplitude which suggest the presence of pores larger than 200 nm. The other group of spectra (high clay content, marl) shows a dominant pore size of 80-100 nm.

Figure 3-14: The TSD measured by MI technique, color-coded by clay content. The MI TSD data show two different sets of spectra. One set shows a PSD spectrum with a dominant pore size 80-100 nm (low clay content, chalk) and the other set shows abundance of small pores smaller than 20 nm (high clay content, marl). The shape of MI spectra for high clay samples indicates the presence of pores that are not accessible by mercury.
• N2 and HE show comparable values (within 1 p.u.) for low porosity samples (<5 p.u.).

• The comparative porosity trends do not show any systematic correlation with clay content.

We measured PSD and TSD for Monterey samples using N2 (Figure 3-16) and MI (Figure 3-17) techniques, respectively:

• The N2 pore size amplitude (Figure 3-16) for pores larger than 10 nm varies significantly and shows no correlation with the clay content.

• The amplitude for micropores (<20 nm) and small mesopores (<10 nm) is negligible except for one high clay content sample (Figure 3-16).

• The MI TSDs (Figure 3-17) also show a significant variation in both amplitude and throat size.

• Similar to N2 PSDs, clay content does not show any correlation with the shape and amplitude for these distributions.

3.6 Discussion

The main driver for this comparative study was to analyze the differences in each method and to exploit these differences to learn more about the samples honoring the mineralogical and geochemical properties of each sample set. Samples were chosen from different formations. Haynesville and Silurian formations are highly mature (gas window) with low hydrogen index (average of 36 and 3, respectively). The Niobrara and Monterey samples are less mature (oil window) with high hydrogen index (average of 306 and 374). For each sample set, we considered the results in terms of the effect of thermal maturity, TOC and clay content and type on the porosity, PSD and pore types.
We recognized the strengths and drawbacks of each method as listed in Table 3-2 for porosity and PSD measurement. Here, we discuss our results and evaluate the benefits and applicability of each technique for organic-rich mudrocks.

Figure 3-15: Porosity comparison for Monterey samples. The porosities are measured by (a) MI and WI, (b) HE and WI, (c) HE and MI, (d) N2 and WI, (e) N2 and MI, and (f) N2 and HE, all color-coded by total clay content. (a) to (c) WI, MI and HE porosities show comparable values within 2 p.u. difference. (b) HE and WI show the best correlation. (d) to (f) N2 significantly underestimates the porosity for high porosity (>5 p.u.) samples. N2 shows comparable values (within 2 p.u.) for low porosity samples (<5 p.u.). Clay content does not affect the porosity measurements.
Figure 3-15: Continued.

Figure 3-16: Pore size distribution spectra measured for Monterey samples using N2 technique, color-coded by clay content. The N2 pore size amplitude for pores larger than 10 nm does not vary significantly and shows no correlation with the clay content. The amplitude for small mesopores (<10 nm) is small except for one high clay content sample.
Figure 3-17: Throat size distribution spectra measured for Monterey samples using MI technique color-coded by clay content. The MI throat size distributions show a significant variation in both amplitude and throat size. Clay content does not show any correlation with the spectra and amplitude either.

3.6.1 Comparison of Porosity Measured by Different Techniques

As mentioned in Table 3-2 MI technique measures the porosity for pores with a throat diameter larger than 3.6 nm. Underestimation of MI porosity values for Haynesville (Figure 3-6a and 3-6b) and Silurian (Figure 3-9a and 3-9b) is because of the high thermal maturity (low HI) and the abundance of small organic matter (OM)-hosted pores in these samples. OM-hosted pores are in the mesopore (2-50 nm) and small macropore size (50-200 nm) range and not all accessible by MI technique. MI porosity values for low clay content (< 10 wt%) Niobrara (Figure 3-12b) and Monterey samples (Figure 3-15a and 3-15c) are comparable with other techniques (within 2 p.u.). The porosity in these samples are mainly intercrystalline and accessible by mercury.

WI porosity measures the pores that are filled with distilled water. The presence of swelling clays in the samples causes overestimation of porosity. Mineralogy of Niobrara samples showed presence of swelling clays (mixed layer illite/smectite). The clay content in other sample sets mainly consisted of Kaolinite and illite which are much
less swelling. The effect of swelling clays in Niobrara samples can be seen when WI is compared against N2 (Figure 3-12a) and MI (Figure 3-12b). In more thermally mature samples such as Haynesville (Figure 3-6c) and Silurian (Figure 3-9c) and low clay content samples such as Monterey (Figure 3-15a and 3-15b) the clay swelling is not significant and WI porosity is comparable with other techniques within 2 p.u. difference.

Table 3-2: Summary of the disadvantages of each measurement technique and the resulting effect on porosity measurements.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Disadvantage</th>
<th>Effect on Porosity Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRI</td>
<td>- Hot solvent extraction removes soluble bitumen</td>
<td>- Creates artificial porosity and causes overestimation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Causes higher grain volume and porosity underestimation</td>
</tr>
<tr>
<td>Water Immersion</td>
<td>- Clay minerals can swell with water</td>
<td>- Porosity overestimation in smectite rich samples</td>
</tr>
<tr>
<td></td>
<td>- Water might not fill organic-hosted pores and these pores might be hydrophobic</td>
<td>- Partial saturation of organic-hosted pores and porosity underestimation</td>
</tr>
<tr>
<td>Mercury Intrusion</td>
<td>- Does not measure pores associated with throat smaller than 3.6 nm</td>
<td>- Misses pores with throat smaller than 3.6 nm and causes porosity underestimation</td>
</tr>
<tr>
<td></td>
<td>- Clay tactoid pores are missed</td>
<td>- Causes porosity underestimation in clay-rich samples</td>
</tr>
<tr>
<td>Nitrogen Adsorption</td>
<td>- Does not measure pore bodies larger than 200 nm</td>
<td>- Misses pore bodies larger than 200 nm and causes porosity underestimation</td>
</tr>
<tr>
<td></td>
<td>- Gas might get sorbed in certain minerals or organic matter</td>
<td></td>
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</tbody>
</table>

As mentioned in Table 3-2 water might not be able to fill the hydrophobic organic hosted pores. We can not directly observe this phenomena in the porosity data presented in this study but there are some indications of the effect of hydrophobic pores on WI porosity measurement. For example there is higher scatter in the WI-N2 porosity comparison for Haynesville (Figure 3-6c) and Silurian (Figure 3-9c) samples compared
to the HE-WI porosity comparison for Monterey samples (Figure 3-15b). Monterey samples are in the oil window and intercrystalline pores are the dominant pore types, but Haynesville and Silurian are in the gas window and OM-hosted pores form the dominant pore type which is hydrophobic.

Since the N2 adsorption technique can only measure volumes of pore with diameter less than 200 nm, the comparable N2 porosity for Haynesville (Figure 3-6c and 3-6d) and Silurian (Figure 3-9c) with WIP indicates that these dominance of fine pores in these samples. This is consistent with high degree of compaction and maturation these particular rocks have undergone. High clay (>10 wt%) Niobrara samples also show the presence of OM-hosted pores. The N2 technique is able to measure the bulk of porosity in high clay (>10 wt%) Niobrara samples while the MI technique could not measure the fine OM-hosted pores and intra-tachoidal clay pores (Kuila and Prasad, 2013) and WI overestimates the porosity due to swelling effect. OM-hosted pores are not abundant in the low porosity (< 5 p.u.) Monterey samples. The similarity of N2 porosity with other techniques (Figure 3-15d to 3-15f), for low porosity Monterey samples indicate dominance of intercrystalline pores with a diameter smaller than 200 nm.

GRI porosity was measured for Haynesville samples and a limited number of Silurian samples. The higher scatter in low clay (<35 wt%) Haynesville samples (Figure 3-6e) is likely due to hot solvent extraction prior to GRI measurements. These low clay Haynesville samples have higher OM matter in them (discussed later). Removal of soluable organic matter increases the porosity measured by the GRI technique. This effect is ruled out for Silurian samples since no soluble bitumen was observed in these
samples. The underestimation of GRI for Silurian samples might be due to inaccessibility of gas to the micropores. The HE technique successfully measures porosity for the Monterey samples since few micropores (in OM or clay) are present in these samples. Note that the lack of complete cleaning prior to the HE measurements could result in underestimation of porosity measured by this technique.

Table 3-3 lists the key properties of each formation/sample set and the recommended porosity measurement techniques. Comparison of porosity values measured by different techniques show that when the N2 and MI techniques measure comparable porosity with other techniques, the PSD assessed by these techniques can be used to study the pore structure. For example the N2 PSD can be used to study the pore structure for highly mature gas window samples (Haynesville and Silurian), Clay-

<table>
<thead>
<tr>
<th>Formation/Subsample</th>
<th>Key Characteristic</th>
<th>Recommended Measurement Technique</th>
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<tbody>
<tr>
<td>Haynesville</td>
<td>- No swelling clays - Small pores - Low soluble bitumen - Pore connectivity</td>
<td>- Water Immersion - Nitrogen Adsorption - Helium Expansion (GRI)</td>
</tr>
<tr>
<td>Silurian</td>
<td>- No swelling clays - Small pores - Low permeability</td>
<td>- Water Immersion - Nitrogen Adsorption - Helium Expansion (GRI)</td>
</tr>
<tr>
<td>Niobrara-Marl (Clay &gt;10 wt%)</td>
<td>- Small pores - High TOC - High swelling clay content</td>
<td>- Nitrogen Adsorption</td>
</tr>
<tr>
<td>Niobrara-Chalk (Clay &lt;10 wt%)</td>
<td>- Large pores - Low swelling clay content - Low TOC</td>
<td>- Mercury Intrusion - Water Immersion</td>
</tr>
<tr>
<td>Monterey-Low Porosity (&lt; 5 p.u.)</td>
<td>- Small pores - Very low clay content</td>
<td>- Water Immersion - Nitrogen Adsorption - Helium Injection</td>
</tr>
<tr>
<td>Monterey-High Porosity (&gt; 5 p.u.)</td>
<td>- Large pores - Very low clay content</td>
<td>- Water Immersion - Helium Injection - Mercury Intrusion</td>
</tr>
</tbody>
</table>
rich oil window samples (Niobrara with clay content more than 10 wt%), and oil window tight samples (Monterey samples with porosity lower than 5 p.u.). MI TSD can not be used in gas window samples (Haynesville and Silurian), but it is an appropriate technique for studying the pore structure in oil window low clay (<10 wt%) Niobrara and high porosity Monterey (>5 p.u.) samples.

### 3.6.2 Composition Controls on Pore Structure

The N2 PSDs for the Haynsville samples in Figure 3-7 are divided into 5 groups based on the PSD distribution shapes (Figure 3-18). These groups have unique mineralogical characteristics highlighting that mineralogical composition control pore-structure in these Haynesville mudrocks. The crossplot between the TOC and clay content for the Haynesville samples (Figure 3-19) shows an inverse correlation between TOC and clay content (Hammes and Frébourh, 2012).

Clay content cut offs for different groups are defined as <35 wt%, 35-50 wt%, 50-60 wt% and >60 wt%. Group 5 samples are dolomite rich samples with >30 wt% dolomite content. Group 1 samples (Figure 3-18a) show dominant pore size of 20 nm. These samples have high TOC and an abundance of OM-hosted pores (Figure 3-20). Group 2 to 5 (Figure 3-18b to d) show an increase in the small mesopore size range (<10 nm) and decrease in the big mesopore (10-50 nm) and macropore size (>50 nm) range. Group 2 samples have slightly lower TOC and higher clay content compared to Group 1. They show an abundance of OM-hosted pores and the presence of intercrystalline pores in clay minerals (Figure 3-21).SEM images for Group 3 samples (Figure 3-22) confirm the N2 PSD results (Figure 3-18c) which demonstrate both intercrystalline (<10 nm) and OM-hosted pores (some >10 nm). Group 4 samples are
Figure 3-18: N2 PSD spectra of Haynesville samples for (a) Group 1, (b) Group 2, (c) Group 3, (d) Group 4 and (e) Group 5. The samples are grouped based on the PSD shape. The distributions can be divided in two parts; pores smaller than 10 nm and larger than 10 nm. From Group 1 to 4 the amplitude of small pores increases and the amplitude of large pores decreases. Group 5 samples are dolomite rich and behave differently compared to the rest of groups.
Figure 3-19: Correlation between TOC and clay content for Haynesville samples. The samples can be divided in five groups based on the TOC and clay content. Clay content cut offs for different groups are defined as <35 wt%, 35-50 wt%, 50-60 wt% and >60 wt%. Group 5 samples are dolomite rich samples with more than 30 wt% dolomite content.

Clay rich (60-80 wt%) and show an abundance of small mesopores (<10 nm) measured by N2 PSD (Figure 3-18d). SEM images (Figure 3-23) show that intercrystalline pores in clay minerals are the dominant pores in these samples. Group 5 samples are dolomite rich (>30 wt%) with a very low TOC content (<1.5 wt%). The spaces between dolomite grains are filled with a mixture of clay and quartz particles which host the intercrystalline pores in these samples (Figure 3-24).

N2 PSD for Silurian samples (Figure 3-10) show relatively similar amplitudes for large mesopores (10-50 nm) and macropores (>50 nm). The PSD amplitude for pores with a diameter smaller than 10 nm varies significantly. The TOC-Clay content crossplot for the Silurian samples (Figure 3-25) shows two different trends; low clay-low TOC samples (Group 1) and high clay-high TOC samples (Group 2). In Group 1 the amplitude for pores with a diameter less than 10 nm increases as the clay content
Figure 3-20: SEM images (Backscattered Electron Images) of Haynesville samples in Group 1. These samples are TOC rich (> 6 wt%) and show dominant pore size of 20 nm (Figure 3-18a). As a result of thermal maturation lots of pores are developed within the organic matter. Note that the pore sizes are mainly less than 200 nm. Qz=Quartz, Cal=Calcite, Ill=Illite, OM=Organic Matter.
Figure 3-21: SEM images (Backscattered Electron Images) of Haynesville samples in Group 2. These samples have slightly lower TOC and higher clay content compared to Group 1. Although OM-hosted pores are the dominant pore types, the images demonstrate presence of intercrystalline pores in clay minerals. Qz=Quartz, Py=Pyrite, Ilt=Illite, Chl=Chlorite, OM=Organic Matter.
Figure 3-22: SEM images (Backscattered Electron Images) of Haynesville samples in Group 3. These samples have a combination of organic- and mineral-hosted pores. The N2 PSD results (Figure 3-18c) also indicates the presence both intercrystalline (< 10 nm) and OM-hosted pores (> 10 nm). As a result of thermal maturation lots of pores are developed within the organic matter. Qz=Quartz, Ilt=Illite, OM=Organic Matter.
Figure 3-23: SEM images (Backscattered Electron Images) of Haynesville samples in Group 4. These samples are clay rich (60-80 wt%) and show an abundance of small mesopores (<10 nm) measured by N2 PSD (Figure 3-18d). The SEM images show that intercrystalline pores in clay minerals are the dominant pores in these samples. Qz=Quartz, Ilt=Illite.
Figure 3-24: SEM images (Backscattered Electron Images) of Haynesville samples in Group 5. These samples are dolomite rich (> 30 wt%) with very low TOC content (< 1.5 wt%). The space between dolomite grains are filled with a mixture of clay and quartz particles which host the intercrystalline pores in these samples. Although the organic content is minimal in this Group, organic-hosted pores are developed where OM is present. Quartz, Calcite, Dolomite, Pyrite, Illite.
Figure 3-25: The relationship between clay and TOC content for Silurian samples. The samples can be divided in two groups. Group 1 which has clay and TOC content lower than 48 and 1.8 wt%, respectively and Group 2 which has TOC and Clay content higher than the mentioned values. In Group 1 the TOC is relatively constant whereas in Group 2 the TOC and clay content have inverse correlation.

increases (Figure 3-26a). However in Group 2 the peak amplitude for pores smaller than 10 nm increases as the TOC increases (Figure 3-26b). The SEM images for a sample from Group 1 (Figure 3-27) show the presence of both OM-hosted pores and intercrystalline pores. However, Group 2 sample SEM images show an abundance of OM-hosted pores. The intercrystalline pores are filled with organic matter which hosts the majority of the pores (Figure 3-28).

Although both Haynesville and Silurian are in the gas window and show relatively similar TOC-Clay content correlations, there are key differences between the pore structure of these samples:

- The clay content varies between 30 to 60 wt% for the Silurian samples and 20-80 wt% for the Haynesville samples.

- The dominant pore type for the Silurian samples is OM-hosted and the pore
structure is dictated mainly by TOC, whereas for the Haynesville samples both clay content and TOC control the pore structure.

- Silurian samples belong to a geologically older formation than the Upper Jurassic Haynesville samples.

N2 PSD for the Niobrara samples are divided into two groups based on the PSD shapes (Figure 3-29). The PSD of the Group 1 samples (Figure 3-29a) shows the presence of pores larger than 200 nm that were not assessed by the N2 technique. The PSD of the majority of Group 2 samples (Figure 3-29b) show that the dominant pore size is close to 100 nm. Group 1 samples belong to Chalk rock types (clay content < 10%) and Group 2 samples belong to the Marl rock types. TOC-Clay correlation for these samples (Figure 3-30) demonstrates that the Group 1 samples show TOC less than 2 wt% and clay content less than 10 wt%. Group 2 samples show variable TOC.

Figure 3-26: The pore size distribution measured by N2 technique for (a) Group 1 color-coded by clay content and (b) Group 2 color-coded by TOC. Increasing in clay content for samples in Group 1 (a) results in increase in pore size distribution amplitude at 3 nm pore size range. The samples of Group 2 (b) do not follow the same trend. The highest amplitudes belong to the samples with the highest TOC content and samples with either high clay or TOC content show higher amplitude at 1.7-5 nm pore size range.
Figure 3-27: SEM images (Backscattered Electron Images) of Silurian samples in Group 1. Both OM-hosted and intercrystalline pores are present in these samples. In this group the amplitude for pores with diameter less than 10 nm increases as the clay content increases (Figure 3-26a). Qz=Quartz, Il=Illite, OM=Organic Matter.
Figure 3-28: SEM images (Backscattered Electron Images) of Silurian samples in Group 1. The intercrystalline pores are filled with organic matter which holds the majority of the pores. The organic hosted pores are in the mesopore range. The size of the pores and possibly lack of connectivity limits the capability of the porosity and pore size distribution measurements to assess the pores. Qz=Quartz, Ill=Illite, OM=Organic Matter.
Figure 3-29: Examples of PSD measured by the N2 technique for samples from (a) Groups 1 and (b) Group 2, all color-coded by clay content. The PSD of the Group 1 samples (a) shows presence of pores larger than 200 nm that were not assessed by the N2 technique. The PSD of the majority of Group 2 samples (b) shows that the dominant pore size lies around 100 nm.

Figure 3-30: The Niobrara samples are divided in two groups based on their TOC contents. Group 1 has low TOC (<2 wt%) and low clay (<10 wt%) content group 2 has high clay content (>10 wt%). Clay and TOC content control the porosity and pore size distribution in Niobrara samples.

content with clay content higher than 10 wt%. In Group 1 samples the pores are mainly intercrystalline and reside in the clay minerals that fill the space between calcite grains (Figure 3-31).
Figure 3-31: SEM images (Backscattered Electron Images) of Niobrara samples in Group 1 (chalk sample). Quartz, calcite and clay particles fill the space between calcite grains and form the intercrystalline pore structure. Minimal organic matter and organic-hosted pores are present in this sample (TOC of 0.1 wt%). The intercrystalline pores form a connected network which is accessible to displacement fluids for porosity measurements. Qz=Quartz, Cal=Calcite, Ilt=Illite.
Figure 3-31a shows how quartz, calcite and clay particles fill the space between calcite grains and form the intercrystalline pore structure. Minimal organic matter or organic-hosted pores are present in this sample (0.1 wt% TOC). Figure 3-31b shows a connected network of intercrystalline pores which are accessible to investigating fluids for porosity measurements. A major group of pores in the Group 2 samples (Figure 3-32) reside in the organic matter and show smaller sizes compared to Group 1. A significant amount of TOC is visible in this sample which fills the intercrystalline pores (Figure 3-32a). Figure 3-32b shows the organic-hosted porosity. As shown by the annotations in this figure the pores are smaller than 100 nm. Small pore size and lack of connectivity limit the accessibility of the investigating fluids to these pores for porosity measurements.

The clay content range (20-40 wt%) and TOC-Clay content cross plot for the Group 1 Niobrara samples (Figure 3-30) are similar to the Group 2 Haynesville samples (Figure 3-19). The N2 PSD measured for these samples are also similar (Figure 3-18b and Figure 3-29b). Since both groups of samples have high TOC and an abundance of OM-hosted pores, this similarity confirms that in these samples 100 nm is the abundant pore width for these pore types.

Based on the porosity comparisons presented in Figure 3-15, we divided the Monterey samples into two groups; Group 1 with low porosity samples (< 5 p.u.) and Group 2 with high porosity samples (>5 p.u.). N2 PSD data for both groups are shown in Figure 3-33a and 3-33b, respectively. Both groups show very low amplitudes at small mesopores range (<10 nm), except one high clay sample in Group 1. N2 PSD of Group 1 samples represent the whole pore structure whereas the Group 2 PSD only
Figure 3-32: SEM images (Backscattered Electron Images) of Niobrara samples in Group 2 (marl sample). Significant amount of TOC is visible in this sample which fills the intercrystalline pores. The OM-hosted pores are developed in the organic matter. As shown by the annotations, the pores are smaller than 100 nm and possibly not connected. Both small pore size and lack of connectivity limit the accessibility of the displacement fluids to these pores for porosity measurements. Cal=Calcite, Ilt=Illite, Py=Pyrite, OM=Organic Matter.
Figure 3-33: Pore size distribution spectra measured for Monterey samples using N2 technique for (a) Group 1 (porosity <5 p.u.) and (b) Group 2 (porosity >5 p.u.). Since samples in Group 1 (a) show more comparable N2 porosity values when compared with HE and MI techniques we can consider the spectra in (a) a suitable representation of pore size distribution for these samples. N2 measures a highly underestimated porosity for Group 2 samples, so N2 spectra (b) does not represent the whole pore space.

represents pores smaller than 200 nm. Since the Monterey samples have very low clay content there is no correlation between the PSD and clay content for either groups. The PSD are mainly a function of the intercrystalline pores in the quartz phase. Group 1 samples have intercrystalline pores in the clay phase and interacrystalline pores within the quartz and calcite grains (Figure 3-34).

The intercrystalline space is filled with organic matter (bitumen, or secondary organic matter) which holds very low OM-hosted porosity. Group 2 samples show larger intercrystalline pores compared to Group 1 samples. The pores are developed in the space between quartz grains and are partially filled with authigenic illite and secondary organic matter (Figure 3-35).

Although the N2 technique does not assess the whole pore space for either Group 1 Niobrara (Figure 3-29a) or Group 2 Monterey (Figure 3-33b) samples, the N2
Figure 3-34: SEM images (Backscattered Electron Images) of Monterey samples in Group 1. These samples have intercrystalline pores in clay phase and interacrystalline pores within the quartz and calcite grains which are exposed due to polishing. The intercrystalline space is filled with organic matter which holds very low OM-hosted porosity. Qz=Quartz, Cal=Calcite, Dol=Dolomite, Ilt=Illite, Py=Pyrite.
Figure 3-35: SEM images (Backscattered Electron Images) of Monterey samples in Group 2. These samples show larger intercrystalline pores compared to Group 1 samples. The pores are developed in the space between quartz grains. Qz= Quartz, Ilt= Illite, OM= Organic Matter.
PSD shapes are different. Since MI TSD is the appropriate technique for pore structure characterization for these samples we will discuss the main reason for this difference in the following section.

TSD for Group 2 Haynesville samples (Figure 3-8) indicates that there are pores with throat diameter smaller than 3.6 nm that are not assessed by the MI technique (We did not measure the MI TSD for the samples in other groups). Based on N2 PSD results, Group 2 samples have the highest macro-pore volume amongst all groups in this sample set (Figure 3-18b). Underestimation of porosity and incomplete TSD for Group 2 samples implies that the MI results for other groups, with smaller pore sizes, will be underestimated as well.

Similar to Haynesville samples, Silurian MI TSD also showed that there are pores with throat diameter smaller than 3.6 nm that are not reached by the mercury (Figure 3-11). The MI TSDs for Group 1 samples (Figure 3-36a) do not demonstrate the same clay content dependency as N2 distributions for these samples (Figure 3-26a). On the other hand MI TSDs amplitude of Group 2 samples (Figure 3-36b) increases with increasing TOC, similar to N2 PSD (Figure 3-26b).

TSDs assessed by the MI technique for Groups 1 and 2 Niobrara samples are shown in Figure 3-37a and 3-37b, respectively. For the samples in Group 1 (Figure 3-37a) mercury successfully accessed the pores which were not accessible by N2 (Figure 3-29a). On the other hand, the throat size distributions for Group 2 show that there were pores associated with throats smaller than 3.6 nm.

MI PSD show more heterogeneity in the Monterey samples (Figure 3-38) compared to the Niobrara samples (Figure 3-37). The dominant TSDs for Monterey
samples vary significantly from less than 20 nm for Group 1 samples (Figure 3-38a) to more than 200 nm for Group 2 samples (Figure 3-38b). Besides heterogeneity, Group 2 samples show a wider range of TSD for individual samples, whereas in Group 1, Niobrara samples MI TSD shows a more uniform PSD with variable amplitudes (Figure 3-37a).

Figure 3-36: The throat size distribution of Silurian samples measured by MI technique for (a) Group 1 color-coded by caly and (b) Group 2 color-coded by TOC. (a) The MI spectra for Group 1 samples do not demonstrate the same clay content dependency as N2 spectra for these samples (Figure 3-26a). (b) On the other hand MI spectra amplitude of Group 2 samples increases with increasing TOC, similar to N2 PSD (Figure 3-26b).

### 3.7 Conclusions

The porosity and PSD were measured for four sample sets from different formations ranging from high thermal maturity (gas window Haynesville and Silurian) to low maturity (oil window Niobrara and Monterey). The clay content and TOC vary significantly within each sample set. Based on the results presented in this study the following conclusions can be drawn:
Figure 3-37: Throat size distributions of Niobrara samples assessed by MI technique for samples in (a) Group 1 and (b) Group 2, color-coded by clay content. (a) For Group 1 samples mercury successfully assessed the pores which were not accessible by N2 (Figure 3-29a). (b) On the other hand for samples in Group 2 mercury did not reach the small pores hosted by the organic matter, these pores were assessed by N2 (Figure 3-29b).

Figure 3-38: Throat size distribution of Monetery samples measured using MI technique for (a) Group 1 and (b) Group 2, color-coded by clay content. The dominant throat size distributions for Monterey samples vary significantly from less than 20 nm for Group 1 (a) and more than 200 nm for Group 2 samples (b).

- Using samples from different formations and maturities, we have shown that without a priori knowledge regarding thermal maturity, TOC, clay type and content porosity and PSDs in mudrocks cannot be assessed or studied using a single method. Our
assessments of pore size sensitivity for each technique emphasize the significance of combining various techniques to describe the full pore topology in organic-rich mudrocks.

- The main reasons for inconsistency in measured porosities in mudrocks are low permeability and lack of pore connectivity, presence of hydrophobic pores that limit accessibility of investigating fluids to micro and mesopores, as well as inconsistent pretreatment protocols.

- MI technique underestimates the porosity for thermally mature samples (Haynesville and Silurian) with an abundance of OM-hosted pores. It also underestimates the porosity in less mature Niobrara samples when TOC is high (Marl) and tight Monterey samples (<5 p.u.).

- WI provides reliable porosity when samples are thermally mature or when no or minimal swelling clays are present. The possible effect of hydrophobic pore on partial saturation of the samples should be considered.

- N2 technique is appropriate for porosity and PSD assessment for thermally mature samples (Haynesville and Silurian) or samples with an abundance of OM-hosted pores (Niobrara). It also successfully assesses the low porosity Monterey samples but fails to capture pores at the high end of the distribution of pore sizes.

- The reliability of the measured porosities depends on the accessibility of the investigating fluid to the pores. Thus, pore accessibility or wettability of the solid to the probe fluid can be investigated by comparing the PSDs measured by different techniques. A combination of methods is required to reliably measure porosity and PSD in mudrocks.
3.8 Acknowledgements

This paper is dedicated to the memory of Dr. Michael L. Batzle. We would like to thank Dr. Douglas McCarty, Dr. Arkadiusz Derkowski, Benjamin Harrell and Cesar Mapeli for their help with the experiments and fruitful discussions. We thank Chesapeake Energy Reservoir technology Center and Don Harville for their collaboration. We also thank OCLASSH and Center for Rock Abuse groups for support and funding of the research. Special thanks to the AAPG Bulletin/Memoir reviewers Dr. Terri Olson, Dr. Quinn Passey and Dr. Jeremy Dahl for valuable comments and suggestions which significantly improved the quality of this work.

3.9 References


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CHAPTER 4

Effect of Mineralogy on Nuclear Magnetic Resonance Surface Relaxivity:
A Case Study of Middle Bakken and Three Forks Formations

A paper accepted by the Journal of Fuel
Milad Saidian and Manika Prasad

“The essential element in personal magnetism is a consuming sincerity - An overwhelming faith in the importance of the work one has to do.”
- Bruce Barton

4.1 Abstract

Porosity and pore size distribution (PSD) are crucial for reserve and producibility estimation and production planning. PSD properties are evaluated in the subsurface from nuclear magnetic resonance (NMR) logs and require knowledge about surface relaxivity. In common practice, surface relaxivity is considered to be a constant. We present a case study of the Middle Bakken and Three Forks formations to evaluate surface relaxivity using porosity, PSD and total specific surface area data. To avoid error propagation from the input parameters to surface relaxivity estimates, we first acquired reliable porosity and PSD by combining different techniques. We analyzed the data using information on mineralogy, mass magnetic susceptibility (MMS) and scanning electron microscopy. We find that:
- Surface relaxivity depends on paramagnetic mineral content, magnetic susceptibility and distribution in natural rocks.
- We found a linear correlation between surface relaxivity ($\rho \ [\mu m/s]$) and illite content ($f_{il} \ [wt\%]$) distributed in the matrix $\rho=0.067 \times f_{il}+0.56$ with high correlation coefficient ($R^2=0.79$).
- Clay bound water cut off times lie between 2.13 - 2.23 ms for $T_1$ and 1.34 - 1.40 ms for $T_2$ distributions based on our mineralogy-guided calculations. Using a typical value of 3 ms resulted in more than 100% error in clay bound porosity calculation especially for high clay content samples.

Our results can be used to improve the interpretation of NMR logs for surface relaxivity, PSD and clay content evaluation. The correlation between surface relaxivity and distributed clay content can be used to calculate surface relaxivity from the clay content measured from mineralogy logs such as Elemental Capture Spectroscopy (ECS) or using gamma ray which is the main indication of the clays.

4.2 Introduction

Logging data acquisition and interpretation play a significant role in reserve and producibility estimation and production planning. Reliable petrophysical models require accurate estimation of petrophysical properties such as porosity and pore size distribution (PSD). NMR logging is widely used to measure the porosity and PSD in the form of longitudinal ($T_1$) and transverse ($T_2$) relaxation times (Timur, 1969).

The parameter to convert NMR time distributions to PSD is the surface relaxivity. Surface relaxivity is attributed to the paramagnetic impurities on the surface of the grains which interact with hydrogen nuclei and impose an additional relaxation (Korringa
et al., 1962). There are numerous studies that show an increase in surface relaxivity by increasing the paramagnetic content such as manganese and iron (Foley et al., 1996; Keating and Knight, 2007) or iron bearing minerals such as pyrite, pyrrhotite and siderite (Keating and Knight, 2010). However, these studies were performed by increasing the paramagnetic content in synthetic unconsolidated samples. Iron bearing minerals and iron oxides have significant effect on surface relaxivity. However, the common practice is to calculate the surface relaxivity for a limited number of samples from a well or formation and use the average value for all samples regardless of variations in rock composition. This is not a very accurate way of calculating surface relaxivity because significant inconsistencies in calculated values are observed and the reported values can vary up to one order of magnitude for the same rock type or porous material. The $T_1$ surface relaxivities gathered by Dunn et al. (2002) for sandstone and quartz samples vary from 0.013 to 46 µm/s. Hürlimann et al. (1994) measured $T_1$ surface relaxivity of 2.6 and 11 for two limestone samples. They also reported surface relaxivities of 4.1 and 16 µm/s for Fontainebleau sandstone whereas Fleury (2007) reported $T_2$ surface relaxivity of 11.7 and 3.5 µm/s for Fontainebleau samples with similar permeability ranges (< 13% permeability difference) using the same measurement technique. The main conclusions from these comparisons are (a) There is no universal surface relaxivity value for carbonate or sandstone samples and, (b) Samples from the same formation or rock type do not necessarily have the same surface relaxivity. Using the reported values for sandstone and carbonate rocks for other samples might result in significant errors in PSD calculations.
Calculation of surface relaxivity using theoretical models is not possible since requires an estimation of the electron-spin relaxation times for the paramagnetic impurity. This information is not available for the electron-spins on the surface of the rocks (Kleinberg et al., 1994). Available methods in the literature to estimate surface relaxivity in reservoir rocks can be divided in three types; (a) By iteratively varying surface relaxivity to match NMR relaxation times with pore or throat size distribution measurements from other techniques, such as mercury intrusion capillary pressure (MICP) (Marschall et al., 1995, Kleinberg, 1996, Kenyon, 1997, Rivera et al., 2014), nitrogen adsorption (Rivera et al., 2014), and image analysis (Howard et al., 1993, Kenyon, 1997; Jiang et al., 2013). (b) Estimations of surface relaxivity using rock surface area measured by cation exchange capacity (CEC) (Sen et al., 1990), nitrogen gas adsorption (Sen et al., 1990, Hossain et al., 2011, Hürlimann et al., 1994), and image analysis (Hossain et al., 2011). (c) Estimation of surface relaxivity solely relying on combination of NMR measurements, namely relaxation time distribution measurements using CPMG or IR pulse sequences and restricted diffusion measurements pulse sequences such as pulse field gradient (PFG) and pulse field gradient stimulated echo (PFGSE) (Mitra, 1992, Latour et al., 1993, Hürlimann et al., 1994, Slijkerman and Hofman, 1998).

Type (c) measurements are not suitable for unconventional and tight samples because NMR data acquisition and interpretation especially diffusion measurements are more complicated in these rocks due to the presence of small pores and fast relaxation of hydrogens (Saidian and Prasad, 2015). Type (a) and (b) measurements are indirect measurement of the surface relaxivity and depend on other measurements such as
pore volume (porosity), surface area and PSD. Saidian et al. (2015a) showed that there are significant inconsistencies in porosity and PSD measurement in shales using different techniques and reliability of these measurements depend on the clay content and type, thermal maturity and total organic carbon. Choosing reliable techniques for porosity and PSD is a prerequisite for an accurate calculation of the surface relaxivity.

There are numerous studies focusing on the variation of surface relaxivity in synthetic unconsolidated porous media. However, there is not a thorough study that presents measurement of the surface relaxivity in unconventional rocks using different techniques and investigate the effect of mineralogy and paramagnetic impurities on the surface relaxivity. A more reliable surface relaxivity can be used in log analysis by providing a correlation between the mineralogy and surface relaxivity and consequently a more accurate PSD calculation and petrophysical interpretation.

In this study we measured the porosity for 12 samples from Middle Bakken and Three Forks formations using various techniques such as nitrogen adsorption (N2), NMR, helium injection (HE), water immersion (WI) and mercury intrusion (MI). Based on a systematic comparison of porosity values we investigated the reliability of PSD measured by MI, NMR and N2 techniques. Then we calculated the surface relaxivity by correlating different measured PSDs with NMR responses as well as measuring the surface to volume ratio (SVR) using N2 technique. The effect of paramagnetic impurities such as illite, chlorite and pyrite content on surface relaxivity is investigated and clay bound cut off values are reported for log interpretation applications.
4.3 Materials

Twelve samples were taken from Middle Bakken and Three Forks formations. Samples were carbonate rich, mainly dolomite (up to 78 wt%) with moderate amount of clay (up to 36 wt%) and quartz and feldspar (up to 46 wt%) (Table 4-1). The samples were not organic rich and the clay is mainly illite. Table 4-1 shows the detailed mineralogy of each sample. The samples were saturated with 25000 ppm KCl brine for WIP and NMR measurements to eliminate any possible clay swelling.

Table 4-1: Mineralogy of the Bakken samples. Kspar stands for K-Feldspar, Q+K+P stands for combination of Quartz, K-feldspar and Plagioclase contents.

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4.4 Methods

We measured porosity and PSD using multiple techniques such as NMR, MI, N2, HE and WI. The core samples were cleaned and dried prior to each experiment. In the following, we explain the experimental procedure and data acquisition parameters for each technique.
4.4.1 Nuclear Magnetic Resonance (NMR)

$T_1$ and $T_2$ distributions as well as porosity were measured using inversion recovery and Carr-Purcell-Meiboom-Gill (CPMG) (Carr and Purcell, 1954; Meiboom and Gill, 1958) pulse sequences, respectively. The samples were fully brine (25000 ppm KCl brine) saturated and the measurements were performed using a 2 MHz Magritek Rock Core Analyzer®. All $T_2$ distributions were measured using 100 µs echo spacing (TE), 3000 ms polarization time, 2500 number of echoes and minimum 100 signal to noise ratio (SNR). The $T_1$ distributions were measured using 20 logarithmically spaced wait times ranging from 0.07 to 3000 ms. $T_1$ and $T_2$ distributions were generated using inverse Laplace non-negative least square fitting (Lawson and Hanson, 1974 and Buttler et al., 1981) of inversion recovery and echo train raw data, respectively. The smoothing parameter was calculated using the methodology described by Dunn et al. (1994).

Assuming very long bulk relaxation rate (compared to surface relaxation), negligible diffusion induced relaxation and fast diffusion regime in individual pores the NMR responses can be related to pore size using the following equation (Coates et al., 1999; Dunn et al., 2002):

$$\frac{1}{T_i} = \frac{1}{T_{is}} = \rho_i \frac{S}{V} = \rho_i \frac{c}{R}$$

(4 - 1)

where subscript “$i$” denotes 1 or 2 for $T_1$ and $T_2$ relaxations, respectively, $\rho$ is the surface relaxivity, $S$ is the rock surface area, $V$ is the pore volume, $R$ is the pore radius and $c$ is the constant which is 1, 2 or 3 for planar, cylindrical and spherical pores, respectively.
4.4.2 Mercury Intrusion (MI)

Porosity and pore throat size distribution (TSD) were measured using MI technique. Small rock chips were heated up to 200 °C and degassed to remove all the water. The mercury was injected with uniform pressure steps ranging from 0.14 to 420 Mpa (14.7 to 60000 psi). The conversion from pressure data to TSD was done using the Washburn (1921) model assuming a bundle of non-connected capillary tubes. A conformance correction, for example, the Bailey method from Comisky et al. (2011) was applied to high pressure measurements to account for mineral compressibility.

4.4.3 Nitrogen Adsorption (N2)

Nitrogen adsorption technique was used to measure total specific surface area (henceforth referred as surface area), total pore volume (henceforth referred as pore volume) and PSD for all samples. The samples were crushed and sieved (40 mesh equivalents to 420 µm) and then degassed under vacuum at 200 °C until the outgassing rate was less than 0.005 Torr/min over a 15 minutes interval. Nitrogen was injected in to the degassed sample and the pressure-volume data were recorded at constant temperature (Langmuir isotherms). The Barrett, Joyner and Halenda (BJH) inversion (Barrett et al., 1951) was used to calculate the PSD assuming non-connected cylindrical pores. The PSD spectra calculated using BJH span from 1.7 nm to 200 nm. Due to technical limitations N2 technique does not assess pores larger than 200 nm in width (Gregg and Sing, 1983). The Harkins and Jura (1944) thickness curve was utilized for both BJH inversion and micropore (pores smaller than 1.7 nm) volume calculation with t-plot analysis.
4.4.4 Water Immersion (WI)

Porosity was measured using water immersion technique. The Archimedes' principle was used to measure the bulk and grain volumes. The original protocol for this measurement was developed at the American Petroleum Institute (API RP40). In this study, we used the adapted protocol for mudrocks developed by Kuila et al. (2014). Five grams of rock chips were first dried and weighed in air. This weight was measured using a Mettler Toldeo® moisture analyzer at 200 °C for 15 min to exclude the weight of possible adsorbed moisture. Then the samples were saturated and weighed again in air and submerged in water.

4.4.5 Helium Injection (HE)

Porosity was measured using cylindrical cores under 800 psi net confining stress using a CMS 300® instrument. Inert helium gas was used as the displacement fluid for porosity measurements to avoid any chemical reaction between the gas and the rock matrix.

4.4.6 Cation Exchange Capacity (CEC)

Based on the laboratory procedure provided by the vendor the CEC was measured using the Co(III)-hexamine$^{3+}$ cation exchange, spectrophotometric technique. CEC values were converted to "smectite equivalent" by assuming a theoretical CEC of 95-100 meq/100g of the smectitic surfaces of illite-smectite and common pure smectites. The CEC surface area was calculated from the "smectite equivalent" values assuming a theoretical surface area of 800 m$^2$/g of pure smectite.
4.4.7 Bulk Magnetic Susceptibility (BMS)

The bulk magnetic susceptibilities (henceforth referred as susceptibility) were measured for all samples using a Kappabridge (KLY-4S\textsuperscript{TM}) magnetic susceptometer applying a 200 A/m magnetic field. The samples were cylindrical core plugs and were cleaned and dried prior to the measurement. The susceptibility was measured at laboratory condition.

4.5 Results

Based on Equation 4-1 to calculate surface relaxivity we need reliable values of porosity (pore volume), surface area and PSD. In this section we present the result of various measurements to achieve the required values. We performed a detailed analysis of porosity and PSD for 12 samples with variable clay content ranging from 0 to more than 36 wt%.

4.5.1 Porosity Measurement

We measured porosity using MI, WI, NMR, N2 and HE techniques (Table 4-2). Comparison of porosity showed that all techniques measure the same value within 2 p.u. difference.

Figure 4-1 shows the linear correlation between NMR porosity and the clay content. Similar correlation was also observed for other measurement techniques with higher scatter. This correlation can be used for clay content calculations using porosity measurement both at laboratory and downhole conditions. Clay content can be also calculated using NMR T\textsubscript{2} distributions. We used a mineralogy-based model and calculated the cut off times of 2.13-2.23 ms and 1.34-1.40 ms for T\textsubscript{1} and T\textsubscript{2} distributions, respectively. Figure 4-2a and 4-2b show the cross plot of the calculated clay bound
water volume measured from $T_1$ and $T_2$ distributions, respectively, and the clay content from XRD data. These values are much lower than the common 3 ms $T_2$ cut off time that is used for clay bound water volume calculations (Straley et al., 1997).

Table 4-2: Summary of all results and calculations. Sample Mass (N2 Exp): the mass of crushed sample used in N2 experiments, TSSA: total specific surface area, TPV: total pore volume, N2 ADS DLM: logarithmic average of the PSD calculated from N2 adsorption branch, MI D_{LM}: logarithmic average of PSD calculated from MI, BMS: Bulk Magnetic Susceptibility. The grain density in this table is an average of WI and XRD calculated grain densities.

<table>
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<th>N2 Porosity</th>
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<th>WI Porosity</th>
<th>HE Porosity</th>
<th>NMR Porosity</th>
<th>Grain Density</th>
<th>N2 BET TSSA</th>
<th>TPV</th>
<th>CEC</th>
<th>CEC TSSA</th>
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<th>$T_{1,M}$</th>
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Figure 4-1: Linear correlation between NMR porosity and clay content. This correlation can be used for clay content calculations using porosity measurement both at laboratory and downhole conditions.

Figure 4-2: Cross plot of the calculated clay bound water volume measured from (a) $T_1$ distributions using a cut off time of 2.13-2.23 ms and (b) $T_2$ distributions using a cut off time of 1.34-1.40 ms. These values are much lower than the common 3 ms (Straley et al., 1997) used for clay bound water volume calculations. Using this typical value results in more than 100% error in clay bound porosity calculation especially for high clay content samples.
4.5.2 PSD and Surface Area Measurement

The samples were divided in two groups based on the clay content. Group 1 with low clay content (<10 wt%) and Group 2 with high clay content (>10 wt%). Figure 4-3 shows the PSD measured by nitrogen adsorption technique. Group 1 distributions (Figure 4-3a) show lower amplitudes both at meso (2-50 nm) and macro-pore (>50 nm) size ranges. Whereas Group 2 distributions demonstrate a dominant peak at 20-40 nm ranges. Some samples in Group 2 show a small peak in 2-5 nm range as well; the peak can be attributed to clay tactoid pores (Kuila, 2013 and Saidian et al., 2015a). The clay effect on total specific surface area distribution is also shown in Figure 4-4. For Group 1 samples the surface area distribution shows lower amplitudes in < 5nm range compared to Group 2 samples. The peaks at this pore size range are attributed to the clay minerals (mainly illite and chlorite).

Figure 4-3: Pore size distribution measured by nitrogen adsorption for (a) Group 1 and (b) for Group 2 samples. Group 2 samples show higher amplitudes due to higher porosity. The higher amplitude for pores in less than 10 nm range is due to higher clay content in Group 2 samples.
Figure 4-4: Surface area distribution measured by nitrogen adsorption for (a) Group 1 and (b) Group 2 samples. Group 1 shows lower surface area compared to Group 2. The highest surface area amplitude for Group 2 samples in smaller pores which can be allocated to clays.

The MI TSD was also measured for all samples (Figure 4-5). Group 1 samples show broader spectra and larger throat size (10-400 nm) but lower amplitudes compared to Group 1 which shows smaller throat size with narrow throat size range (10-100 nm) and higher amplitudes. Figure 4-6 and Figure 4-7 show the $T_1$ and $T_2$ distributions measured for Bakken samples respectively.

The $T_2$ distributions for Group 1 (Figure 4-6a) show bimodal spectra with dominant peaks at 1-3 ms and 10-20 ms, whereas the distributions for Group 2 show a unimodal distribution at 1-3 ms. The wider spectra for samples in group 1 indicate the presence of a wider range of pore sizes and also larger pores in these samples. The logarithm mean for each spectrum, calculated by Equation 4-2 (Saidian et al., 2015b), is commonly used to represent the $T_1$ or $T_2$ distribution. Figure 4-8 shows the correlation between $T_{1LM}^{-1}$ and $T_{2LM}^{-1}$.

$$T_{nLM} = \exp\left(\frac{\sum \ln(T_{ni}) \times \phi_i}{\sum \phi_i}\right)$$  \hspace{1cm} (4 - 2)
where $n$ is 1 and 2 for $T_1$ and $T_2$ relaxation times, respectively, $T_{nLM}$ is the logarithmic mean of time distribution. If the $T_n$ distribution spectrum is plotted using $i$ number of points (bins), the $i^{th}$ bin has a $T_n$ time ($T_{ni}$) and an amplitude which is the porosity associated with that bin ($\phi_i$).

**Figure 4-5:** The throat size distribution measured by mercury intrusion for (a) Group 1 and (b) Group 2 samples. Group 1 shows higher throat size (10-100 nm) compared to Group 2 (3-80 nm).

**Figure 4-6:** Transverse relaxation time ($T_2$) for (a) Group 1 and (b) Group 2 Bakken samples. The $T_2$ distribution in Group 1 (a) shows bimodal spectra with dominant peaks at 1-3 ms and 10-20 ms, whereas the distributions for Group 2 (b) show a unimodal distribution at 1-3 ms.
Figure 4-7: Longitudinal relaxation time ($T_1$) for (a) Group 1 and (b) Group 2 Bakken samples. The $T_1$ distribution in Group 1 (a) shows bimodal spectra with dominant peaks at 2-4 ms and 10-30 ms, whereas the distributions for Group 2 (b) show a unimodal distribution at 2-4 ms.

Figure 4-8: $T_1$-$T_2$ cross plot for Bakken samples. Since $T_1$ acquisition at downhole condition is time consuming this correlation between $T_1^{-1}$ and $T_2^{-1}$ can be used to estimate $T_1$ value from available $T_2$ distributions. It also can be used to convert $T_2$ surface relaxivity to $T_1$ surface relaxivity and vice versa.
4.6 Discussion

In common practice the surface relaxivity is considered constant throughout a formation or well. Previous studies showed that there are significant inconsistencies in measured or calculated surface relaxivities for similar rock type or formation. In this section we improve our understanding of surface relaxivity and the parameters that affect its value by (a) Calculating the surface relaxivity using different techniques, (b) Studying the effect of rock composition and paramagnetic minerals on surface relaxivity, (c) Investigating the inconsistencies in surface relaxivity values and making recommendation for appropriate applications.

4.6.1 Surface Relaxivity Calculation

There are different approaches to calculate the surface relaxivity. In this section we calculate the surface relaxivity using two approaches: correlating NMR response with PSD or TSD measured by other techniques and Calculation be combining NMR data and SVR using Equation 4-1.

Surface to volume ratio (SVR) is required for surface relaxivity calculation using Equation 4-1. Since all porosity values measured by different techniques are comparable (within 2 p.u. difference) we used the surface area and pore volume measured by N2 technique for surface relaxivity calculation. It is found that the SVR for Group 1 samples (indicated by dashed line circle in Figure 4-9) varies between 170-360 \( \mu m^{-1} \), whereas, for the high clay content samples of Group 2 (indicated by solid line circle in Figure 4-9) the SVR is more consistent and in the range of 225-275 \( \mu m^{-1} \). The SVR for Group 1 samples depend on the pore size, whereas, SVR in Group 2 samples is dominated by clay particles (mainly illite). Clays are distributed in pores and mask the
effect of pore size on the surface area measurement. Both $T_1$ and $T_2$ surface relaxivities ($\rho_1 N_2 \text{ SVR}$ and $\rho_2 N_2 \text{ SVR}$, respectively) calculated using Equation 4-1 are listed in Table 4-3. Note that the correlation between $T_1$ and $T_2$ can be used to convert the values from $T_1$ to $T_2$ surface relaxivity since the SVR is constant in both calculations. Henceforth we only discuss the $T_2$ surface relaxivity and same correlations and conclusions are applicable to $T_1$ surface relaxivity.

Table 4-3: Calculated surface relaxivity using different techniques. $\rho_1$ and $\rho_2 N_2 \text{ SVR}$: $T_1$ and $T_2$ surface relaxivity, respectively using N2 SVR, $\rho_2 \text{ CEC SVR}$: $T_2$ surface relaxivity, using CEC SVR, $\rho_2 \text{ Visual N2}$: $T_2$ surface relaxivity using visually correlating $T_2$ distribution and PSD from N2, $\rho_2 \text{ Visual MI TSD}$: $T_2$ surface relaxivity using visually correlating $T_2$ distribution and TSD from MI, $\rho_2 \text{ N2 ADS } D_{LM}$: $T_2$ surface relaxivity using logarithmic average of pore size form N2 adsorption, $\rho_2 \text{ MI } D_{LM}$: $T_2$ surface relaxivity using logarithmic average of pore size form MI TSD.

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<th>$\rho_2 N_2 \text{ SVR}$</th>
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<th>$\rho_2 \text{ Visual N2 PSD}$</th>
<th>$\rho_2 \text{ Visual MI TSD}$</th>
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Figure 4-9: Surface to volume ratio (SVR) measured by N2 technique. The surface to volume ratio for low clay content samples of Group 1 (indicated by dashed circle) varies between 170-360 µm⁻¹, whereas, the high clay content samples of Group 2 (indicated by solid circle) show a more consistent SVR in the range of 225-275 µm⁻¹.

We also calculated the surface relaxivity by combination of NMR time average ($T_{2LM}$) and average diameter of the pores measured by MI and N2 ($\rho_2$ MI $D_{LM}$ and $\rho_2$ N2 $D_{LM}$, respectively) using Equation 4-1 and visual correlation of NMR time distributions with N2 adsorption PSD and MI TSD ($\rho_2$ Visual N2 PSD and $\rho_2$ Visual MI PSD) as described by Marschall et al. (1995) (Table 4-3). In all calculations the pores are assumed cylindrical and the constant value, $c$, in Equation 4-1 is considered 2.

The values calculated using the comparative approach depends on the technique that the NMR distributions are correlated with. Different PSD measurement techniques presumably measure the same property in the rock but due to differences in mechanisms and measurement physics the measured PSD distributions do not show to the same property of the porous media (Saidian et al., 2015a). However, the
distributions can be compared qualitatively, for example, NMR, MI and N2 distributions for samples in Group 1 (Figure 4-3a to 4-7a) showed a wider distribution of pores and throats compared to the samples in Group 2 (Figure 4-3b to 4-7b).

Based on surface relaxivities calculated in this section we make two important observations: (a) all the measurement methods show that the surface relaxivity varies for different samples and assuming a constant surface relaxivity for a formation, rock type or well regardless of the factors such as rock composition is not accurate. (b) Surface relaxivities calculated by different techniques are not equal. In the following sections we investigate the effect of rock composition on surface relaxivity and also explain the sources of discrepancy in surface relaxivity values calculated by different techniques.

4.6.2 Effect of Paramagnetic Minerals on Surface Relaxivity

Fluid-solid interaction (surface relaxation) is usually the dominant relaxation mechanism in porous materials (Dunn et al., 2002). This interaction is quantified by the surface relaxivity both for longitudinal and transverse relaxations. Korringa et al. (1962) allocated the longitudinal relaxation of the nuclei at the solid surface to the relaxation of spins at two surface sites: magnetic and non-magnetic. In their theory the spins were temporarily adsorbed to these sites. Kleinberg et al. (1994) extended their model to account for surface relaxation during transverse relaxation as well. Under a series of assumptions the model for both longitudinal and transverse relaxations is reduced to (Korringa et al., 1962; Kleinberg et al., 1994; Foley et al., 1996):

\[
\frac{1}{T_i} = \left( \frac{S h}{V} \right) (n_M) \frac{1}{T_{iM}}
\]

(4 – 3)
where \( i \) is 1 or 2 to denote longitudinal or transverse relaxation times, respectively, \( h \) is the thickness of spin layer that is affected by surface sites, \( n_M \) is the ratio of number of magnetic surface sites to the total number of surface sites and \( T_{im} \) is characteristic relaxation of nuclei at magnetic surface sites. Combining Equations 4-1 and 4-3, the surface relaxivity can be written as:

\[
\rho_i = \frac{h n_M}{T_{im}} \quad (4 - 4)
\]

The surface relaxivity can be assumed solely a function of the concentration of the magnetic sites if: (a) All the spins relax at the same rate once contacted a magnetic site and (b) the spin layer thickness affected by the surface effect is constant (Foley et al., 1996). For simplicity we refer to the non-magnetic sites as the host mineral and the magnetic ions, compounds or minerals as magnetic impurity or simply impurity.

There are numerous studies on the effect of concentration of various magnetic impurities on the surface relaxivity of synthetic porous materials (e.g. Kenyon and Kolleeny, 1995; Foley et al., 1996; Bryar et al., 2000; Keating and Knight, 2007; Keating and Knight, 2008). In the following we discuss the observations that were made in these studies and compare them with our observations in this study:

**Observation 1: Most of the impurities that are abundant in soil or near-surface depths (oxidizing environments) have very high magnetic susceptibilities.**

In most cases the impurities discussed in the literature are ferromagnetic minerals with very high magnetic susceptibility e.g. magnetite, goethite and pyrrhotite. Due to the chemical alteration (digensesis), metamorphism, presence of sulphide-reducing bacteria and changes in oxygen content and acidity (PH) (Tarling and Hrouda, 1993) commonly the impurities in oil and gas producing formations such as Middle
Bakken and Three Forks are mainly the paramagnetic minerals e.g. pyrite, illite, montmorillonite (smectite) and Fe-chlorite (Chamosite) (Table 4-4) with orders of magnitudes lower magnetic susceptibility. Other minerals, formation brine and hydrocarbons are diamagnetic (Table 4-4) and do not contribute to the enhanced relaxation of the spins at the surface of the minerals.

**Observation 2: The magnetic susceptibility of the porous media monotonically increases with the magnetic impurity concentration.**

Ferromagnetic minerals tend to dominate the magnetic properties of the rock such as magnetic susceptibility, when they form more than 0.1 vol% of the rock and the magnetic susceptibility of rock exceeds $5 \times 10^{-3}$ SI. In their absence, paramagnetic minerals that form more than 1 vol% of the rocks control the magnetic susceptibility of the rock and this value is usually less than $5 \times 10^{-4}$ SI (any value in between is a combination of paramagnetism and ferromagnetism) (Tarling and Hrouda, 1993). In the mentioned studies the samples contained a single type of impurity, however, in natural rocks a mixture of paramagnetic minerals with variable iron contents are present. To account for this variation as well as variation in paramagnetic mineral content, we calculated the iron content of each sample considering the amount of iron in mineral molecular structures (Figure 4-10). The iron is concentrated mainly in chlorite (chamosite), pyrite and illite with 29.43, 46.55 and 1.43 wt% iron content in their molecular structure, respectively (webmineral.com, 2015). Although pyrite mineral have the highest iron content and susceptibility, illite and chlorite dominate the susceptibility due to higher content compared to pyrite content (Table 4-1). Figure 4-11 shows that pyrite does not affect the susceptibility (Figure 4-11a) due to low concentration and
combination of illite and chlorite clays dominates the susceptibility (Figure 4-11b) in these samples. These observations are in controversy with the other studies that showed higher concentration of iron bearing minerals increases the susceptibility because in this study we have a more complex system due to presence a combination of paramagnetic minerals with various content and distribution.

Table 4-4: The magnetism and magnetic susceptibility of different minerals, fluids and compounds that are abundant in rock samples from oil and gas producing formations. Ferro, Para and Dia stand for ferromagnetic, paramagnetic, and diamagnetic materials. aDearing (1999), bDunlop and Özdemir (1997), cTarling and Hrouda (1993), and dIvakhnenko, 2006. The brine and the hydrocarbon magnetic susceptibilities are for different fluids from various reservoirs. Since the density values are not unique only mass susceptibility is reported. All mineral density values are from webmineral.com (2015).

<table>
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<th>Mass Susceptibility (10^{-6}\text{m}^3/\text{kg})</th>
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<td>Hydrocarbon Fluids (^d)</td>
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Figure 4-10: The iron content for each sample calculated by the iron content in the molecular structure of each mineral.

Figure 4-11: Cross plot of susceptibility and iron content for (a) pyrite, (b) chlorite and illite minerals. The susceptibility is dominated by the presence of chlorite and illite (mainly chlorite). Due to very low pyrite content (<1 wt%) this mineral does not affect the susceptibility significantly.
**Observation 3:** The impurities were distributed evenly throughout the porous material by mixing of the grains/powders or chemically coating of the host mineral grain surfaces.

Besides the impurity concentration (paramagnetic mineral content) which affects the surface relaxivity the distribution of the impurities also play a significant role. In the previous studies the impurities were evenly distributed throughout the porous media by chemical coating or mixing of the host minerals. In natural rocks paramagnetic minerals are not distributed uniformly. Pyrite is mainly scattered in the porous media in the form of individual nodules whereas clays can be distributed in the pore space as pore filling material. Scanning electron microscopic (SEM) images revealed that the illite clays (Figure 4-12a and 4-12b) and to a much lesser extent chlorite clays (Figure 4-12c) are present in the pore space between the dolomite and quartz grains. Energy dispersive X-ray spectroscopy (EDS) of the illite grains confirmed the presence of iron in illite minerals (Figure 4-12d). Distribution of the illite clays in the pore space and their high surface area compared to chlorite and pyrite increases the effect of illite paramagnetic properties on the fluid-rock interaction and consequently surface relaxivity.

**Observation 4:** The surface relaxivity increases monotonically with increasing the impurity concentration.

In near surface NMR studies, the surface relaxivity increases with impurity concentration linearly. By further increasing the impurity concentration and consequently internal gradient, the fast diffusion regime no longer exists in the pores and the correlation deviates from linearity.
Figure 4-12: (a-c) Scanning electron microscopic (SEM) images and (d) energy dispersive X-ray spectroscopy (EDS) for Middle Bakken and Three Forks samples. Illite is distributed in the pore space between large dolomite and quartz grains (a-b). Chlorite is also seen in the space between the dolomite grains, however, due to low chlorite content it is not abundant (c). The EDS data for illite grains show that iron is present in all clays especially illite which has the highest volume.

As mentioned earlier, in paramagnetic rocks, due to low magnetic susceptibility (compared to ferromagnetic rocks) at low NMR frequencies (e.g. 2 MHz) the internal gradient is negligible and pores stay at the fast diffusion regime. As mentioned earlier in our samples the only paramagnetic mineral that has high concentration (wt%) and is distributed in the pore space is illite. The plots of $\rho_2 N2$ SVR as a function of different minerals (Figure 4-13) confirm that the surface relaxivity has the best correlation with illite (Figure 4-13a) compared to chlorite and pyrite which is consistent with the SEM
results (Figure 4-12). Note that this correlation does not imply that chlorite and pyrite do not affect the surface relaxivity value and mainly applies when the illite clays are distributed in the pore space. More studies are required to investigate the effect of laminated clay content on the surface relaxivity values.

The result of this section reveals that correlating susceptibility and surface relaxivity is not a correct approach (Figure 4-13b) since susceptibility value is dominated by chlorite and illite iron (Figure 4-11) content whereas the surface relaxivity is dominated by illite content (Figure 4-13a). This is controversial to the previous studies that showed both surface relaxivity and susceptibility are linearly correlated to the impurity concentration.

Figure 4-13: Correlation between the $T_2$ surface relaxivity ($\rho_2 N2 SVR$) and (a) illite, (b) susceptibility. The plots of $\rho_2 N2$ SVR as a function of different minerals confirm that the surface relaxivity has the best correlation with illite. Note that this correlation does not imply that chlorite and pyrite do not affect the surface relaxivity value. Correlating BMS and surface relaxivity (b) is not a correct approach since BMS value is dominated by chlorite and illite iron (Figure 4-11) content whereas the surface relaxivity is dominated by illite content (a).
Other surface relaxivity values (Table 4-3) have an increasing trend with illite content but with higher scatter and lower correlation coefficients. Similar increasing trends imply that the effect of paramagnetic minerals on surface relaxivity does not depend on calculation method.

4.6.3 Application of Surface Relaxivity

The main source of discrepancy is correlating NMR data with different SVR, PSD or TSD measurement techniques. As mentioned earlier these techniques use different mechanisms and physics to assess the same rock property. N2 measurements are based on condensation of N2 in pores with different sizes at different pressures which provide information about the pore body size distribution (Figure 4-3). MI measurements are based on the pressure that is required to pass the mercury through pore throats (Figure 4-5). In both MI and N2 experiments the investigating fluid has to enter the pore space from the exterior of the sample.

As oppose to NMR measurements, in which the sample is fully saturated with the displacement fluid (in most cases water or brine) prior to the measurement and no displacement occurs throughout the experiment. The main issue with NMR measurements is the coupling of micro and macro-pores by exchange of spins between the pores through translational diffusive motion. The level of coupling depends on the surface relaxation, fraction of microporosity, the size of micro and macro pores and the diffusion coefficient (Anand and Hirasaki, 2005). In shales the pores are most likely in the coupled state and the $T_2$ response is highly affected by the pore coupling (Washburn, 2014). Anand and Hirasaki (2005) derived the coupling constant for a simplified 2d model of one micropore adjacent to a macro-pore without considering the
effect of their distribution. The distribution of pores affects the coupling of the pores in a way that in samples with clay laminations the coupling between micro and macro-pores is weaker than samples with distributed clays (Saidian and Prasad, 2013). At highly coupled condition the $T_2$ and $T_1$ distributions are unimodal (Figure 4-6b and 8b, respectively) and highly dominated by micropores since they contain the highest surface area (Figure 4-4).

The other source of discrepancy is assuming similar surface relaxivity for individual pores in the porous media. Theoretically surface relaxivities vary in different pores in the same sample based on the hosting mineral type and the distribution of paramagnetic impurities (Arns et al., 2006; Keating and Knight, 2012). Measuring this value for individual pores is not practical and a constant surface relaxivity is assumed for PSD or TSD calculation purposes.

We converted the $T_2$ distributions of two samples from Groups 1 and 2 to PSD using different calculated surface relaxivities (Figure 4-14 and Figure 4-15, respectively). The following observations can be made: (a) The PSDs calculated from N2 VIS and N2 SVR are similar for both samples. (b) MI VIS and MI DLM also result in similar TSDs. (c) For Group 1 samples the MI TSD data cannot be visually correlated with other techniques whereas the MI TSDs for Group 2 samples are comparable with NMR and N2 data. Note that the value of visually calculated surface relaxivities is biased since there are no specific criteria for a visual good match. This issue is amplified for Group 1 samples which show different distribution shapes for all three techniques.
Figure 4-14: Different calculated and measured PSD for a sample from Group 1. (a) PSD measured by N2 and NMR converted using the calculated surface relaxivities by combining NMR and N2 measurements. (b) TSD measured by MI and NMR converted using the calculated surface relaxivities by combining NMR and MI measurements.

Figure 4-15: Different calculated and measured PSD for a sample from Group 2. (a) PSD measured by N2 and NMR converted using the calculated surface relaxivities by combining NMR and N2 measurements. (b) TSD measured by MI and NMR converted using the calculated surface relaxivities by combining NMR and MI measurements.
Choosing the appropriate value for practical purposes mainly depends on the application of the PSD or TSD measurements. For example saturation height modeling by correlating MI TSD and NMR data is a common practice in log interpretation and saturation calculation (Lowden et al., 1998; Altunbay et al., 2001). In this case the surface relaxivities that are calculated by visual correlation between MI TSD and $T_2$ distribution should be utilized. For permeability calculation using SVR and characteristic pore radius using models such as Kozeny-Carman, the surface relaxivity calculated using Equation 4-1 and the measured SVR from N2 technique is recommended. We suggest the following steps to utilize the suitable surface relaxivity value for log interpretation purposes:

**Step 1**: Understand how petrophysical properties of interest (permeability, saturation, elastic properties, etc.) are related to PSD/TSD.

**Step 2**: Find the suitable correlation to tie core petrophysical properties to the measured PSD/TSD in the laboratory.

**Step 3**: Calculate the surface relaxivity using PSD/TSD data accordingly.

**Step 4**: Find a correlation between the calculated surface relaxivity and paramagnetic content of the samples considering the distribution of the minerals and their iron content.

**Step 5**: Evaluate the mineralogy of the formation and calculate the surface relaxivity using the correlation in step 4.

**Step 6**: Convert the $T_2$ or $T_1$ distributions to PSD or TSD and calculate the petrophysical property of interest using the correlation in step 2.
4.7 Conclusions

The porosity, pore size distribution and NMR response were measured for 12 Middle Bakken and Three Forks samples. The surface relaxivity was calculated for all samples using different methods. Correlating the surface relaxivity to “distributed” clay content and eventually gamma ray readings at downhole conditions is a novel application of the gamma ray logs in petrophysical characterization of the rocks. Based on the results presented in this study the following conclusions can be drawn:

- Assuming a constant surface relaxivity for a rock type, formation or well is not accurate and factors such as the content and distribution of paramagnetic mineral should be considered for surface relaxivity calculation.
- We found a linear correlation between surface relaxivity \( \rho [\mu \text{m/s}] \) and illite content \( f_{\text{ill}} [\text{wt}%] \) distributed in the matrix \( \rho=0.067 \times f_{\text{ill}}+0.56 \) with high correlation coefficient \( R^2=0.79 \).
- Although chlorite and pyrite encompass the highest iron content, illite is uniformly distributed in the pore space and is the paramagnetic impurity that dominates the surface relaxation of hydrogen nuclei at the fluid-grain interface.
- Clay bound water cut off times lie between 2.13 - 2.23 ms for \( T_1 \) and 1.34 - 1.40 ms for \( T_2 \) distributions based on our mineralogy-guided calculations. Using typical value of 3 ms resulted in more than 100% error in clay bound porosity calculation especially for high clay content samples.

4.8 Acknowledgements

This paper is dedicated to the memory of Dr. Michael L. Batzle. We acknowledge Kurt Livo, Cesar Mapeli and Rana Elghonimy from Colorado School of Mines, Gerhard
Heij and Dr. Douglas Elmore from University of Oklahoma, Tomasz Topor from Polish Academi of Science and Douglas McCarthey from Chevron ETC for their help in performing some of the measurements. We also acknowledge OCLASSH and Fluids consortiums at Colorado School of Mines for support and funding of the project.

4.9 References


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CHAPTER 5

Effect of Paramagnetic Mineral Content and Distribution on Nuclear Magnetic Resonance Surface Relaxivity in Organic-Rich Niobrara and Haynesville Shales

A paper accepted by the Geophysics

Milad Saidian, Kurt Livo, and Manika Prasad

“Might and wrong combined, like iron magnetized, are endowed with irresistible attraction.”

- Nathaniel Hawthorne

5.1 Abstract

Surface relaxivity is required to convert nuclear magnetic resonance (NMR) relaxation times to pore size distributions (PSD). In current practice, a constant value of surface relaxivity is used for an entire well, formation, or rock type, regardless of compositional and textural variations. This approach might result in significant errors in PSD calculation in the presence of paramagnetic minerals that affect surface relaxivity values. We present surface relaxivity calculations for Niobrara and Haynesville samples calculated from measurements of surface to volume ratio and from measurements of the average pore radius. We measured the transverse relaxation time ($T_2$) with a low field (2 MHz) NMR instrument. We also measured porosity and PSD using nitrogen adsorption (N2). The total specific surface area was measured using N2 and cation exchange capacity (CEC) equivalent surface area. We find that:
• Paramagnetic impurities, chlorite and illite-smectite, distributed in the matrix dominate the NMR response and the calculated surface relaxivity
• Surface relaxivity is linearly correlated with paramagnetic distributed clay content
• The technique that was used to measure the surface area and pore volume, as well as the method used to calculate the surface relaxivity play a significant role.
• Presence of smectites increases uncertainty in surface to volume ratio and consequently in surface relaxivity calculations

Our surface relaxivity - clay correlations can be used to calculate surface relaxivity from mineralogy or gamma ray logs and to invert NMR logs and laboratory data to PSD.

5.2 Introduction

NMR logs are widely used to calculate porosity and pore size distribution (PSD) both at laboratory and at downhole conditions. With known surface relaxivity (SR), NMR time distributions, the time domain NMR data can be transformed to size domain PSD (Kenyon et al., 1997). The surface relaxation results from interactions between paramagnetic sites and hydrogen nuclei in the pore space (Korringa et al., 1962) which increases with paramagnetic minerals content (Saidian and Prasad, 2015a).

The paramagnetic ion content, magnetic susceptibility and the surface relaxivity are linearly correlated for synthetic unconsolidated sand packs (Foley et al., 1996). Increasing the concentration of paramagnetic ions and minerals increases the surface relaxivity in unconsolidated sand packs (Keating and Knight, 2007; 2008; 2010). Surface relaxivity cannot be calculated directly for rock grain surfaces due to lacking information on spin-electron interaction on the surface of the grains (Kleinberg et al., 1994). A practical approach is to calculate surface relaxivity using indirect methods, e.g.
by measuring the surface to volume ratio (Keating and Knight, 2007; Hossain et al., 2011) or by correlating NMR time distributions with PSD assessed from other techniques such as mercury intrusion (MI) (Marschal et al., 1995; Rivera et al., 2014) and nitrogen adsorption (N2) (Saidian and Prasad, 2015a). Surface relaxivity calculated using these methods with a limited number of samples is averaged and used for the entire well, formation or rock type regardless of mineralogical variations. This constant value approach results in differences of up to two orders of magnitude in surface relaxivity values for similar rock types (Dunn et al., 2002).

We calculated the surface relaxivity by measuring the $T_2$ and surface to volume ratio as well as measuring the average pore radius using N2 technique for organic rich samples from the Niobrara and the Haynesville formations. We calculated the surface to volume ratio using the total specific surface area (or simply surface area) measured by cation exchange capacity (CEC) and N2 techniques. We find that paramagnetic mineral content and their distribution control surface relaxivity.

5.3 Materials and Methods

We used 19 Niobrara and 16 Haynesville samples from oil and gas producing organic rich shales, respectively. Tables 5-1 and 5-2 show the mineralogy of the Haynesville and Niobrara sample sets, respectively. For more information about the samples sets see Kuila, 2013 and Saidian et al., 2015.

We used porosity, pore size distribution (PSD), and cation exchange capacity (Kuila, 2013; Saidian et al., 2015). Transverse relaxation time ($T_2$) distributions were measured using Carr-Purcell-Meiboom-Gill (CPMG) (Carr and Purcell, 1954; Meiboom and Gill, 1958) pulse sequence. The samples were saturated with de-ionized water and

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measured using a 2 MHz Magritek Rock Core Analyzer®. $T_2$ distributions were generated using inverse Laplace non-negative least square fitting of echo train raw data (Lawson and Hanson, 1974; Buttler et al., 1981).

All three, bulk, surface, and diffusion induced relaxation mechanisms contribute to the relaxation of the hydrogen nuclei in porous media described by $T_2$ decay. Assuming slow bulk relaxation (compared to the other relaxation mechanisms), fast diffusion regime in the pores, and negligible diffusion induced relaxation, the $T_2$ relaxation can be correlated to the surface properties and pore volume of the rock using the following equation (Coates et al., 1999):
Table 5-2: Mineralogy of the Niobrara sample set. Q+Plag+F: combination of quartz, plagioclase and feldspar content, I-S: illite-smectite mixed layer, TOC: total organic carbon (Kuila, 2013).

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$$\frac{1}{T_2} \approx \frac{1}{T_{2s}} = \rho_2 \frac{S}{V} = \rho_2 \frac{c}{R}$$  \hfill (5 - 1)

where $T_{2s}$ is the $T_2$ relaxation due to surface properties and pore volume, $\rho_2 = T_{2s}$ surface relaxivity, $S =$ rock surface area, $V =$ pore volume, $R =$ pore radius, and $c$ is a constant $= 1, 2$ or $3$ for planar, cylindrical and spherical pores, respectively. We used Equation 5-1 to calculate surface relaxivity from calculated surface to volume ratio, $T_2$, and pore radius with different techniques.
5.4 Results and Discussion

Surface relaxivity calculated with Equation 5-1 requires input on surface area, pore volume, T$_2$ distribution and PSD. The value and reliability of surface relaxivity calculations depend on the technique and its reliability to measure these parameters in organic rich shales. Saidian et al. (2015) showed that reliability of the porosity and PSD measurements in organic rich shales depends on clay type and content, TOC, and thermal maturity of the samples.

In the following section, we study (a) the effect of presence of paramagnetic minerals on the T$_2$ response, (b) calculation of surface relaxivity (Equation 5-1) using surface area data from N2 and CEC measurements and by comparing the T$_2$ response with the logarithmic average of the PSD measured by N2 technique (Equation 5-1), (c) the effect of presence of organic matter on surface relaxivity and (d) comparison of the measured surface relaxivities using different techniques. The petrophysical properties and the calculated surface relaxivities are listed in Tables 5-3 and 5-4 for Haynesville and Niobrara samples, respectively. Note that data are missing for a few samples.

5.4.1 NMR Response and Mineralogy

The surface relaxivity and surface to volume ratio are the main parameters that control the T$_2$ response in Equation 5-1. In Niobrara and Haynesville samples, the paramagnetic minerals that might affect the surface relaxivity value and T$_2$ response are pyrite, chlorite and illite-smectite. In order to understand what minerals have the dominant effect on NMR response, we compared T$_{2LM}$ with different paramagnetic minerals (Figure 5-1 and Figure 5-2). We find that:
Table 5-3: Petrophysical properties and calculated surface relaxivities for Haynesville sample set. WI PHI: water immersion porosity, N2 PHI: nitrogen adsorption porosity, SR N2 TSSA: surface relaxivity calculated using nitrogen surface area, SR CEC TSSA: surface relaxivity using CEC surface area, SR N2 DLM: surface relaxivity calculated using comparison of $T_{2Lm}$ and nitrogen adsorption DLM. Grain density is calculated based on XRD mineralogy and TOC content (Kuila, 2013; Saidian et al., 2015).

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<th>CEC</th>
<th>CEC TSSA</th>
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- Chlorite is the dominant paramagnetic constituent for Haynesville samples (Figure 5-1a); $T_{2Lm}$ and the paramagnetic illite (Figure 5-1b) content appear uncorrelated.
- In the Niobrara samples, the content of illite-smectite mixed layer clays (Figure 5-2a) is the only paramagnetic constituents that affect the $T_2$ response.
- Although pyrite has significant effect on magnetic properties, pyrite content and NMR response appear uncorrelated for both sample sets (Figure 5-1c and 5-2b).
Table 5-4: Petrophysical properties and calculated surface relaxivities for Haynesville sample set. WI PHI: water immersion porosity, MI PHI: mercury intrusion porosity, N2 PHI: nitrogen adsorption porosity, SR N2 TSSA: surface relaxivity calculated using nitrogen surface area, SR CEC TSSA: surface relaxivity using CEC surface area, SR N2 DLM: surface relaxivity calculated using comparison of $T_{2LM}$ and nitrogen adsorption DLM. Grain density is calculated based on XRD mineralogy and TOC content (Kuila, 2013; Saidian et al., 2015).

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We explain these observations by considering the level of paramagnetism of the mineral constituents and their distributions. In both sample sets, the clay minerals are distributed in the pore space (Figure 5-3) and host a significant portion of the pores (Saidian et al., 2015a) while pyrite is present as discrete nodules. The paramagnetic
Figure 5-1: Correlation between $T_{2LM}$ and (a) chlorite content, (b) I-S content, and (c) pyrite for Haynesville samples. $T_{2LM}$ has strong correlation with chlorite content. The correlation is due to the distribution of clays and higher paramagnetism of chlorite clay compared to illite.

distributed clays have high surface areas which increases the probability of spin collisions. In Haynesville samples, although illite is more abundant, the higher paramagnetism of chlorite (Tarling and Hrouda, 1993) dominates the magnetic properties of the rock and the NMR response.
Figure 5-2: Correlation of $T_{\text{2LM}}$ and (a) I-S content, (b) pyrite content. $T_{\text{2LM}}$ has a strong correlation with I-S content because the illite and smectite clays are distributed in the pore space.

### 5.4.2 Surface Relaxivity Calculation

Reliable surface area and porosity measurements are crucial for surface relaxivity calculation. Saidian et al. (2015a) showed that the N2 technique is reliable for porosity and PSD measurement in the Haynesville formation and the marls of the Niobrara formation, whereas other techniques such as MI are need for the Niobrara chalk samples. The N2 method, using Brunauer–Emmett–Teller (BET) theory (Brunauer et al., 1938) measures only the external surface area of clay minerals while the CEC method measures both internal and external surface areas. Consequently, CEC surface area values are larger than N2-BET surface area. The illitic Haynesville samples (Figure 5-4) show a linear correlation between surface area values from both techniques, whereas Niobrara samples show higher scatter for clay-rich samples due to presence of smectite clays with high internal surface areas (Passey et al., 2010). XRD data confirm that smectite content is negligible for Haynesville samples because the
formation is thermally mature (gas window); Niobrara samples with lower thermal maturity (oil window) have significant smectite content (up to 95% of the I-S mixed layer).

Figure 5-3: SEM images of (a) Haynesville and (b) Niobrara sample. Chlorite and illite fill the pores in the Haynesville samples (a) and have the highest influence on surface relaxivity. In Niobrara samples (b) the illite-smectite clays fill the pore space and are the dominant paramagnetic impurity.
We calculated the surface relaxivity using both N2-BET and CEC surface area values and the total pore volumes (or simply pore volume) from Saidian et al. (2015) for each sample set. Surface relaxivity for the Haynesville samples calculated with both, the N2-BET and the CEC surface areas are linearly correlated with the chlorite content (Figure 5-5). The scatter in these plots might be due to pyrite effects on surface relaxivity. The correlation between surface relaxivities and I-S content is significantly weaker for Niobrara samples (Figure 5-6) mainly because of (a) uncertainty in porosity or pore volume measurement (Saidian et al., 2015), (b) presence of smectite clay with significant internal surface area that cannot be measured by N2 technique (Figure 5-6a shows larger scatter at higher I-S content), and (c) uncertainty in T_{2LM} measurement due to the fast relaxation of the hydrogens in pores (Saidian and Prasad, 2015b).

![Figure 5-4](image.png)

**Figure 5-4:** Cross plot of CEC TSSA and N2 TSSA for (a) Haynesville and (b) Niobrara samples color-coded with total clay content. Linear correlation for Haynesville is due to abundance of clays with minimal internal surface area. Lack of correlation for Niobrara samples is due to the presence of smectite with high internal surface area.
Figure 5-5: Comparison between chlorite content and surface relaxivity calculated using (a) N2 TSSA and (b) CEC TSSA for Haynesville samples. Surface relaxivity correlates with the paramagnetic impurity (chlorite) of how TSSA was measured.

Figure 5-6: Comparison between I-S content and surface relaxivity calculated using (a) N2 TSSA and (b) CEC TSSA for Niobrara samples. Lack of correlation is due to uncertainty in porosity estimation (Saidian et al., 2015) and high internal surface areas in smectite clay.
5.4.3 Effect of Organic Matter

To our knowledge, the magnetic susceptibility of kerogen is largely unknown. Using hydrocarbon fluids from different parts of the world, Ivakhnenko (2006) showed that paramagnetism of the oils increases with increasing density and with residue yield of oil distillation. Assuming that the kerogen has a density of greater than 1 and remains unchanged at 342 °C (less than $T_{\text{max}}$ of 434 °C which is the onset of bitumen and oil generation (Dellisanti et al., 2010)), we used the susceptibility value of $-0.9 \times 10^{-8}$ SI m$^3$/kg from this study. Due to the diamagnetic nature of kerogen, theoretically, in the absence of paramagnetic impurities, there should be no significant distinctions between the relaxation of hydrogen in pores hosted in organic matter (OM) and those hosted in diamagnetic minerals. However, kerogen can affect the NMR response and surface relaxivity calculation indirectly: (a) Hydrogen bearing structure of the kerogen imposes an extra relaxation due to hetero-nuclear coupling of the hydrogens in the pore space and the structural hydrogens in the kerogen (Washburn, 2014). (b) Kerogen is usually associated with pyrite and other trace minerals with high magnetic susceptibility (Passey et al., 2010). (c) Kerogen can host a significant portion of the pores in organic rich shales especially in gas window (Milliken et al., 2013). The nanometer sized OM-hosted pores have large surface areas and in turn increase the surface relaxation. Magnetic properties of the kerogen need to be studied further to better understand its effects on surface relaxivity.

5.4.4 Comparison and Application of Calculated Surface Relaxivities

We calculated the surface relaxivity using Equation 5-1 for Haynesville samples by calculating the logarithmic mean of the radius (R) measured by N2 PSD. Due to
uncertainty in Niobrara surface relaxivity calculations, this analysis was not performed for Niobrara samples. Figure 5-7a and 5-7b show cross plots of surface relaxivity calculated by the average radius method with surface relaxivity calculated by N2 surface area and CEC surface area, respectively. The mismatch in surface relaxivity values is due to errors in the measurements and in the methodology that is used for surface relaxivity calculation. Despite the mismatch in surface relaxivity values, the similar trends imply that regardless of the calculation method, surface relaxivity values increase with paramagnetic mineral content.

![Figure 5-7](image)

Figure 5-7: Correlation between the surface relaxivity calculated by average radius method with (a) CEC TSSA and (b) N2 TSSA. The surface relaxivity values are not consistent but show similar trends.

Paramagnetic impurity content and distribution dominate the surface relaxivity values. The main sources of inconsistency lie in the measurements of pore volume, surface area and PSD, namely the methodology, physical principles, and probing fluids. For example N2 technique only measures the external surface area of the clays
whereas the CEC technique measures the surface area of internal structure of the clays. This internal surface area might not represent the surface area that affects the NMR response. The key for an accurate NMR log interpretation is the correlation between surface relaxivity (regardless of the calculation method) and the clay content in oil and gas producing rocks. Choosing the appropriate technique for surface relaxivity calculation depends on the NMR PSD application. For example for saturation height modeling using the surface relaxivity calculated by comparing NMR data and mercury intrusion data is recommended. The correlation between the CEC surface relaxivity and the mineralogy can be used to calculate the CEC value using downhole NMR log data. The effect of clay content on surface relaxivity that is established in this work implies that gamma ray logs can be used for clay content calculation and also used for surface relaxivity calculation which is a novel application of the gamma ray logs.

5.5 Conclusions

Correlation between the surface relaxivity calculated using CEC and N2 techniques and clay content can be used for NMR log interpretation using gamma ray logs which is a novel application for these logs. Our surface relaxivity calculations for organic rich Niobrara and Haynesville shale samples by combining NMR and calculated surface to volume ratio show that:

- Level of magnetism, concentration, and distribution of paramagnetic minerals affect the surface relaxivity values regardless of the calculation method.
- Surface relaxivities calculated with surface areas from CEC and N2 methods were comparable when smectite clay content with high internal surface areas was low.
- Diamagnetic kerogen does not affect the surface relaxivity and mainly OM-hosted
pores, high CEC and large surface area of the kerogen affect the surface relaxivity and NMR measurements.

5.6 Acknowledgements

This paper is dedicated to the memory of Dr. Michael L. Batzle. The authors acknowledge OCLASSH and Fluids consortium for their support and funding. We also thank Leo Alcanter-Lopez and Chesapeake Energy for providing the FESEM images.

5.7 References


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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

“We are not certain, we are never certain. If we were, we could reach some conclusions, and we could, at last, make others take us seriously.”

- Albert Camus

The main objective of this thesis was to provide a thorough understanding of the way that fluid and rock surface interact in the porous media. This interaction is the key providing a precise representation of the pore size distribution at laboratory and downhole conditions using the NMR technique. To make this happen, we had to take some steps back and make sure that, first of all, our techniques and procedures to acquire, analyze and interpret the NMR data that have been used for conventional rock application are valid or not. Also, how should we tailor our learning points and knowledge from conventional rock to the new challenges that we are faced with unconventional rocks? The second step was to make sure that we have a good understanding of the pore structure in shales and also of the tools that we use to characterize their structure. Choosing the right porosity, pore size distribution and surface area measurement technique is crucial for NMR data interpretation. Reliable measurements cannot be achieved without knowledge of rock mineralogy, geochemistry and texture.

The next step was to study the rock-fluid interaction at the surface of the grain in the form of surface relaxivity which is the key to convert the NMR time distribution data
to pore size distribution. For this purpose we studied the magnetic properties of the individual minerals also as a mixture forming a natural rock. We looked at how the mineral type, content and distribution affect the magnetic properties of the rock and consequently the surface relaxivity. In the following we provide the main conclusions for every step that we took in this thesis to advance our understanding of the NMR response in rock. We also provide recommendations for future study in the subject of this thesis.

6.1 Conclusions

The followings present the main conclusions of this thesis. I divided this section to three conclusions based on the main subjects of the thesis.

6.1.1 Challenges in NMR Acquisition, Analysis and Interpretation

- Data acquisition should prevent signal interferences from pulses and increase NMR data quality by eliminating signals not originating from the sample. Left uncorrected, these interferences and unwanted signals can be interpreted as microporosity in mudrocks.

- Inversion of NMR data for mudrocks is more challenging than for conventional rocks mainly because of the fast relaxation of the hydrogen nuclei in these rocks which can lead to over interpretation of the $T_2$ distribution in mudrocks.

- In the current state of logging technology, downhole restricted diffusion experiments are not reliable for fluid typing and saturation measurements in mudrocks: The pulse gradient amplitude for low frequency instruments is not high enough, and the signal decays significantly due to relaxation of the spins before the acquisition of the spin echo starts.
6.1.2 Porosity and Pore Size Distribution Measurement in Shales

- Without a priori knowledge regarding thermal maturity, TOC, clay type and content porosity and PSDs in mudrocks cannot be assessed or studied using a single method. Our assessment of pore size sensitivity for each technique emphasizes the significance of combining various techniques to describe the full pore topology in organic-rich mudrocks.

- The reliability of the measured porosities depends on the accessibility of the investigating fluid to the pores. Thus, pore accessibility or wettability of the solid to the probe fluid can be investigated by comparing the PSDs measured by different techniques. A combination of methods is required to reliably measure porosity and PSD in mudrocks.

6.1.3 Effect of Rock Composition and Texture on Surface Relaxivity

- Assuming a constant surface relaxivity for a rock type, formation or well is not accurate and factors such as the content and distribution of paramagnetic mineral should be considered for surface relaxivity calculation.

- Level of magnetism, concentration, and distribution of paramagnetic minerals affect the surface relaxivity values in natural rocks regardless of the surface relaxivity calculation method. Correlating the surface relaxivity to “distributed” paramagnetic minerals such as clay content and eventually gamma ray readings at downhole conditions is a novel application of the gamma ray logs in petrophysical characterization of the rocks.
6.2 Recommendations for Future Studies

In this study we were able to shed light on NMR measurement challenges in shales, porosity and pore size distribution and also rock composition and texture effect on surface relaxivity in shales. In this section, we would like to introduce some of the questions whose investigation was beyond the scope and time limit of this PhD thesis.

- In this study we focused on the effect of "distributed" paramagnetic minerals on the surface relaxivity of the rock. However, we did not perform any experiments, except limited number of synthetic unconsolidated samples, to study the effect of laminated paramagnetic mineral distribution on NMR response and surface relaxivity of the rock. More studies with synthetic and natural samples with distributed and dispersed paramagnetic minerals are required to fully understand both aspects of the subject.

- We calculated a single surface relaxivity for rock samples and correlated this value to their paramagnetic impurity. Assuming single surface relaxivity might not be an accurate assumption especially in samples with laminated paramagnetic impurity distribution which have minimal diffusional coupling effect.

- The magnetic properties of paramagnetic minerals such as illite, illite-smectite, chlorite and pyrite vary significantly depending on the level of purity of the mineral, digenesis, and pressure-temperature condition through the geologic time. There is a wide range of magnetic susceptibility reported in the literature for the same mineral. The inconsistency is higher for stronger paramagnetic minerals such as chlorite and pyrite. A thorough study is required to measure the magnetic susceptibility for different oil and gas producing formations for magnetic susceptibility calculations.
To our knowledge magnetic properties of kerogen are not reported in the literature. In this study we estimated its magnetic susceptibility by extrapolating the data for crude oil which might not be a reliable approach. A thorough study of the magnetic properties of the kerogen and the effect of parameters e.g. kerogen type and maturity on magnetic properties is required.
APPENDIX A

Qualitative and Quantitative Reservoir Bitumen Characterization:
A Core to Log Correlation Methodology

A paper published in *the Interpretation*

Milad Saidian, Torben Rasmussen, Mosab Nasser, Andres Mantilla, Rick Tobin

“The invalid assumption that correlation implies cause is probably among the two or three most serious and common errors of human reasoning”
- *Stephen Jay Gould*

A.1 Abstract

Reservoir bitumen is a highly viscous, asphaltene-rich hydrocarbon that can have important effects on reservoir performance. Discriminating between producible oil and reservoir bitumen is critical for recoverable hydrocarbon volume calculations, and production planning, yet the lack of resistivity contrast between the two makes it difficult, if not impossible, to make such differentiation using conventional logs. However, the Nuclear Magnetic Resonance (NMR) response in bitumen-rich zones is dominated by short transverse relaxation times ($T_2$) and low apparent fluid hydrogen index ($HI_{app}$), providing an opportunity to identify the presence of reservoir bitumen. Therefore, NMR logging technology becomes crucial in the characterization of reservoirs where the presence of bitumen may be of concern. In this study we used NMR and other log data to identify and quantify the occurrence of reservoir bitumen in a carbonate reservoir. A
thorough petrophysical evaluation was performed using a full suite of logs, formation pressure measurements and laboratory core analysis data.

We discuss several quick methods to identify intervals with a higher chance of reservoir bitumen presence. The short transverse relaxation times ($T_2$) and consequently lower $T_2$ logarithmic mean time values are characteristics of bitumen-rich zones. Another characteristic is low HI$_{app}$ in these zones and consequently lower NMR porosity estimates when compared to porosity estimates from the density and neutron tools. We analyzed two dimensional longitudinal-transverse relaxation time ($T_1$-$T_2$) maps for core samples at different depths to confirm the presence of reservoir bitumen in some wells using laboratory low-field NMR data. We observed a high $T_1/T_2$ ratio at various depths which is an indication of high molecular weight hydrocarbons (HMWHC). The presence of bitumen at the same depths was confirmed by thin section analysis, and is the likely cause for failed formation pressure testing attempts at those depth intervals. Partial cleaning of reservoir bitumen-rich core plugs, results in helium injection porosity estimates that are too low, and closer to the NMR porosity than to density porosity, the latter being more consistent with actual values. In addition the grain density calculated by helium injection is significantly lower than the grain density estimated from Elemental Capture Spectroscopy (ECS) and X-Ray Diffraction (XRD) techniques. Disregarding these effects complicates the core to log correlation, which is common practice for porosity calculations using the density log. A volumetric rock model was used to reconcile core and log data as well as to calculate the saturation of reservoir bitumen. The methodologies for reservoir bitumen characterization introduced here can be applied successfully in different reservoirs for more reliable and precise reservoir
evaluation and production planning.

A.2 Introduction

The reservoir bitumen formation mechanism is not fully understood. This is reflected in the terminology of HMWHCs where different terms are used to infer different chemical and physical (Dumont et al. 2012) properties or engineering applications. Lomando (1992) lists a series of terminologies that are used in the literature to address these hydrocarbons: solid hydrocarbon, pyrobitumen, dead oil, black sands, asphaltic sands, tar mats and solid bitumen. Due to the complex nature of heavy hydrocarbons, Lomando (1992) prefers to use the term reservoir bitumen since it is a descriptive term and avoids confusion with source rock bitumen and kerogen, and is general enough to cover a wide range of heavy hydrocarbons. There are numerous other definitions and nomenclatures for different heavy hydrocarbons based on properties such as color, reflectance, fluorescence, micro-solubility, isotropy, anisotropy, softening point and density (For more information about these terminologies and their definitions see Tissot and Welte, 1984, Jacob, 1988, Larsen and Kidena, 2002, Nascimento and Gomes, 2004). In this work, we use the term reservoir bitumen as defined by Lomando (1992) and refer to any hydrocarbon other than reservoir bitumen as light hydrocarbon. In the reservoir of interest there was no indication of gas, and we do not consider gas in this study.

Reservoir bitumen is an immobile hydrocarbon that can have significant effects on reservoir quality and production mechanism. When reservoir bitumen is present in significant amounts, identifying the occurrence and quantifying its saturation as well as understanding its distribution in the reservoir, are of paramount importance for
geological and engineering modeling, and for making economic decisions. Its presence leads to overestimation of reserves, if not accounted for. The extent of reduction in porosity and permeability of the rock as a result of precipitation of the reservoir bitumen can be as destructive as the damage caused by carbonate and silica cement (Lomando, 1992). The effect of reservoir bitumen on flow behavior should be investigated in the context of mobility, fluid viscosity and distribution in the pore space. When HMWHCs are distributed in the pore space and coexist with light and producible hydrocarbons, reservoir bitumen is likely to block pore throats. Conceptually Dumont et al. (2012) suggest that heavy asphaltene nano-aggregates precipitate on grain surfaces and block some of the pore throats as they segregated in the reservoir by gravity. Precipitated asphaltenes interrupt the migration of the remaining asphaltene aggregates to deeper parts of the reservoir, leading to the formation of asphaltene-rich hydrocarbon patches.

Differentiating reservoir bitumen and light oil using conventional logs such as neutron, density and resistivity tools is difficult, if not impossible, due to the lack of resistivity and density contrast between light hydrocarbons and bitumen. The use of advanced logging tools such as NMR and Elemental Capture Spectroscopy (ECS), in conjunction with other logs and core data allows for the differentiation between reservoir bitumen and other hydrocarbon types in the pore space. Nascimento and Gomes (2004) used resistivity logs at different depths of investigation and identified tar mat-saturated zones by mud invasion profile interpretation. Akkurt et al. (2009) defined the missing porosity concept and excessive bound fluid to identify tar mat-saturated zones using triple combo and NMR logs. Missing porosity refers to the portion of porosity not detectable by the NMR logging tool but detectable by other tools such as density and
neutron tools. Due to short relaxation times of the tar mats the signal from tar and bound water overlap in NMR response and results in overestimation of the bound fluid.

In this work we discuss the effects of the presence of reservoir bitumen on experimental results such as low-field NMR 1D and 2D experiments, helium injection porosity and grain density, and thin section images. We present a quick look method using core data, formation pressure data, and log data to qualitatively identify the reservoir bitumen rich zones, and at the same time we use NMR porosity and density porosity log data in a volumetric rock model to quantify the reservoir bitumen saturation in the reservoir. Finally we present the results of application of both the qualitative and the quantitative methodologies in two reservoir bitumen saturated wells.

A.3 Effect of Reservoir Bitumen on Laboratory Data

Reservoir bitumen affects laboratory measurements in different ways. In this section we introduce different experiments that were performed to characterize the core samples. We also discuss the possible effect of reservoir bitumen on results.

A.3.1 NMR porosity

The porosity estimate from NMR is a measure of the number of hydrogen nuclei in a porous medium. Since in a subsurface reservoir system hydrogen is mostly present in water and hydrocarbons, the concentration of hydrogen molecules controls the relationship between the NMR response and fluid volume, and ultimately the inferred porosity of the rock. Commonly, the reference fluid for this conversion is fresh water, and the property that defines the concentration of the hydrogen is the $H1_{app}$. $H1_{app}$ is the ratio of hydrogen nuclei detected by NMR in a known volume of the fluid to hydrogen nuclei detected by NMR in the same volume of water. Although, chemically the $H1$ for
viscous hydrocarbons is close to one, $H_{\text{app}}$ can be smaller than one depending on oil viscosity and NMR acquisition parameters such as echo spacing (LaTorraca et al., 1999). Hence, without correction for low $H_{\text{app}}$ in heavy oil and HMWHC saturated rocks, the NMR derived porosity is underestimated. Presence of gas would also affect NMR porosity because $H_{\text{app}}$ of the gas is less than one and varies depending on the pressure and temperature condition (for more information see Akkurt et al., 1996).

A.3.2 NMR $T_1$ and $T_2$ distributions

Three relaxation mechanisms control the transverse relaxation ($T_2$) time for different rock and fluid combinations. These mechanisms; bulk fluid relaxation, surface relaxation, and diffusion relaxation act in parallel and can be modeled by Equation A-1 (Coates et al., 1999). Depending on fluid viscosity, chemical composition, rock mineralogy and NMR acquisition parameters, one, two or all three relaxation mechanisms dominate the relaxation of hydrogen molecules.

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$

Where, $T_2$ is the transverse relaxation time in ms, $T_{2B}$ is the bulk fluid relaxation in ms, $T_{2S}$ is the surface relaxation in ms and $T_{2D}$ is the fluid diffusion relaxation in ms.

The fluid diffusion effect is negligible when the NMR response is acquired using short echo spacing (TE) (Carr and Purcell, 1954). Bulk fluid relaxation depends highly on the fluid properties such as viscosity and chemical composition, varies linearly with temperature, and can be modeled with Equation A-2:

$$T_{2B} \approx a \frac{T}{\mu}$$
where $a$ is a constant in cP/$^\circ$K/ms that depends on fluid chemistry, $T$ is temperature in $^\circ$K, and $\mu$ is fluid viscosity in cP. Note that Equation A-2 applies only to the fluids. Bulk relaxation of the gas depends on the pressure and temperature condition.

Surface relaxation is dominated by the interactions between fluid and pore surfaces and can be modeled using Equation A-3 (Coates et al., 1999):

$$\frac{1}{T_{2s}} = \rho_2 \frac{S}{V} = \rho_2 \frac{c}{R}$$

(A - 3)

in which $\rho_2$ is the surface relaxivity ($\mu$m/ms), $S$ is the surface area ($\mu$m$^2$), $V$ is the pore volume ($\mu$m$^3$), $R$ is the pore body radius ($\mu$m), and $c$ is the pore shape constant which is 1, 2 or 3 for planar, cylindrical and spherical pores, respectively (Machado et al., 2011).

Similar theory is applied to $T_1$ distribution except that diffusion relaxation in Equation A-1 does not exist in $T_1$ experiments. Also $T_1$ is usually significantly higher than $T_2$ for heavy hydrocarbons. High $T_1/T_2$ ratio is characteristic for heavy hydrocarbons and is used to differentiate reservoir bitumen from lighter hydrocarbons. Hirasaki et al. (2003) showed that both $T_1$ and $T_2$ decrease linearly by increasing oil viscosity for samples with viscosity lower than 200 cP. For more viscous samples both $T_1$ and $T_2$ reach plateau values and $T_1$ tend to be higher than $T_2$ by up to one order of magnitude or more.

We modeled the effect of bulk fluid relaxation and surface relaxivity on the $T_2$ response for different pore sizes by combining Equations A-1 to A-3. Figure A-1a shows the effect of bulk fluid relaxation time (assuming spherical pores with a constant surface relaxivity of 9 $\mu$m/s) on the $T_2$ response as a function of pore body size. If the pores are saturated with low viscosity fluid (<3 cP) the effect of pore size on the relaxation time is significant and the time distribution can be considered a representation of the pore sizes for pore
radii less than 100 μm. This is due to the fast spin diffusion inside individual pores which equilibrates the spin density and consequently all the spins in each pore relax with a common relaxation rate (For more information see Brownstein and Tarr (1979) and Dunn et al. (2002)). When pores are saturated with a high viscosity fluid such as reservoir bitumen (in Figure A-1a viscosity of 3000 cP is modelled) the resulting T₂ is dominated by the bulk fluid relaxation and no effect from the pore size is observed. In such cases the average T₂ value can be used to estimate the fluid viscosity using empirical correlations (Hirasaki et al., 2003).

Figure A-1b shows the effect of surface relaxation on the T₂ response for different pore body size for a rock sample saturated with a fluid with viscosity of 3000 cP. The surface relaxivity reported in the literature for carbonates is 1 to 7 μm/s and for sandstones 6.4 to 25 μm/s (Chang et al., 1994, Marschall et al., 1995, Freedman et al., 1997). For pore sizes bigger than 0.3 μm, changing the surface relaxivity (which can be translated to mineralogy of the rock) does not have any significant effect on the T₂ time since it is highly dominated by the presence of high viscosity (short relaxation) reservoir bitumen.

Based on the results shown in Figure A-1 in reservoir bitumen saturated intervals, the NMR response is dominated by bulk relaxation regardless of the rock mineralogy and it no longer represents the pore size distribution of the rock. Although reservoir bitumen compromises the conventional application of the NMR logs, its effect on NMR response can be used to identify the reservoir bitumen saturated intervals.

In this section we show how the aforementioned theories about the effect of reservoir bitumen on T₁ and T₂ responses apply in NMR experimental results and interpretation. Figure A-2 shows T₁ (dashed line) and T₂ (solid line) distributions for two
core samples from different sections of a reservoir at both “native state” and “cleaned and brine saturated” conditions. The samples are measured at laboratory condition using a 2 MHz NMR instrument. Sample 1 (Figures A-2a, and A-2c) is taken from a reservoir bitumen saturated interval and sample 2 (Figures A-2b and A-2d) is taken from a water saturated interval. In Figure A-2a, the dominant $T_1$ and $T_2$ peaks are at 12 and 0.7 ms, respectively. As mentioned earlier, short $T_2$ time and high $T_1/T_2$ ratio in this sample are indications of the presence of heavy hydrocarbons such as reservoir bitumen. Sample 2 (Figure A-2b) shows $T_1$ and $T_2$ distributions with similar bimodal shapes. Higher average $T_2$ value (24.4 ms) and lower $T_1/T_2$ ratio for the dominant peaks, compared to the same values in Figure A-2a, indicate the presence of water and light hydrocarbon such as native oil or synthetic mud.

Figure A-1: Effect of (a) bulk fluid relaxation time and (b) surface relaxation on the $T_2$ response (constant surface relaxivity of 9 $\mu$m/s) at each pore body size. In (a) the $T_2$ response is highly dominated by the fluid with very low bulk relaxation (high viscosity). The response is not sensitive to the pore size and will be highly suppressed to shorter relaxation times. (b) When the rock is saturated with a high viscosity fluid (constant bulk relaxation of 5 ms or approximately 3000 cP) the surface relaxation does not affect the NMR response for pores larger than 0.3 $\mu$m which shows the dominant effect of fluid bulk relaxation on the response.
Figure A-2: (a and b) $T_1$ (dashed line) and $T_2$ (solid line) distributions measured at laboratory condition at native state condition. (c and d) Samples were cleaned by hot solvent extraction and the measurements were repeated at brine saturated condition. Sample 1 is reservoir bitumen saturated and sample 2 is from a water saturated zone. High $T_1/T_2$ in sample 1 at native state is an indication of presence of reservoir bitumen. This ratio in Sample 2 is smaller, due to the presence of a lighter phase such as oil based mud or water. In brine saturated condition (c) long relaxing components ($T_1/T_2$ of 1) have been added to the spectrum of sample 1 (solid arrows in c), but still the $T_1$ and $T_2$ distributions are affected due to incomplete extraction and presence of reservoir bitumen residues ($T_1/T_2$). The peaks which correspond to the reservoir bitumen residues are indicated by dashed arrows in c. In sample 2 after extraction there is no sign of presence of mud or light hydrocarbon and $T_1$ and $T_2$ distributions are similar.
Subsequent to the fresh state measurements, all the samples were cleaned by hot solvent extraction. Then they were saturated with brine and the same NMR experiments were performed. The NMR responses for both samples (Figures A-2c and A-2d), show significant differences compared to the response at native state conditions (Figures A-2a and A-2b, respectively). By cleaning the samples and re-saturating with brine, new peaks at higher relaxation times appeared in the spectra. The peaks at 300 ms with equal $T_1$ and $T_2$ times in Figure A-2c and Figure A-2d (indicated by solid arrows) are due to replacement of part of the reservoir bitumen with brine. An important observation in Figure A-2c is the presence of the peak with short $T_2$ and high $T_1/T_2$ ratio (shown by dashed arrows) after cleaning of the sample. The presence of these peaks suggests that the cleaning process did not remove all the reservoir bitumen in the pore space. This has been observed in almost all the core samples taken from the reservoir bitumen rich intervals regardless of the volume of the residue in different samples.

A.3.3 NMR T$_1$-T$_2$ maps

Non-uniform pore size distribution in heterogeneous reservoir rocks and presence of different fluids with variable viscosity and hydrogen index (HI) make it difficult, if not impossible, to fully characterize the fluids in the porous media using just 1D $T_1$ and $T_2$ distributions. $T_1$-$T_2$ correlation maps are used to differentiate the heavy and/or viscous phase from the light phase using the differences in $T_1/T_2$ of the fluids (for more information about $T_1$-$T_2$ maps, acquisition and inversion see Song et al., 2002).

We use this property in $T_1$-$T_2$ correlation 2D maps, to differentiate high viscosity from low viscosity hydrocarbons. $T_1$-$T_2$ maps are acquired at native state for Sample 3
(Figure A-3a) which is taken from a reservoir bitumen saturated interval and sample 4 (Figure A-3b) is taken from a light oil saturated interval. The portion of the data that falls on, or close to, the one to one correlation line (black solid line in Figures A-3a and A-3b) represents the light fluids such as light oil, mud or water in the porous media.

Deviation of the data from this line is directly related to the viscosity of the hydrocarbon. The high amplitude data components, indicated as “heavy HC”, for sample 3 (Figure A-3a) are due to the presence of reservoir bitumen in this sample. The $T_1$-$T_2$ correlation map for Sample 4 (Figure A-3b) shows that the sample is saturated with light hydrocarbon and water.

![T$_1$-T$_2$ correlation maps](image)

Figure A-3: $T_1$-$T_2$ correlation maps for (a) reservoir bitumen saturated sample and (b) light fluid saturated sample. The red dashed-dotted line is the minimum relaxation time measureable with the NMR instrument which is 100 μs. Any data point on the left side of this line is either noise or a mathematical inversion artifact. The black solid line is the 1:1 ratio line and the color bar is normalized signal intensity. Presence of data components with short $T_2$ and very high $T_1/T_2$ ratio in (a) indicates the presence of reservoir bitumen in the sample. All the components on the 1:1 ratio lines in (a) and (b) correspond to light hydrocarbon and/or water responses.

**A.3.4 Helium injection porosity**

Helium injection porosity and air/liquid permeability measurements are common practices in conventional core analysis. Such data is used by petrophysicists for
porosity and permeability core to log correlation. Core samples undergo a multi stages extraction-cleaning process in the laboratory to clean out oil, mud and water in the core before the measurements. At the first stage of cleaning, a Dean-Stark extraction-distillation unit was used to extract the water, using toluene for 48 hours. The solvent was replaced by chloroform to extract the oil then samples were oven dried at 105 °C until constant weight was reached. An attempt was made to remove the heavier components of the oil using higher polarity solvents such as methylene chloride and tetrahydrifuran. As shown earlier in Figures A-2a and A-2c, despite the multistage cleaning there are still indications of presence of reservoir bitumen in the pore space.

Partial cleaning of the samples is due to the insolubility or partial solubility of the HMWHC in polar solvents. Another reason is the blockage of the pore throats by the reservoir bitumen which prevents the solvent from reaching parts of the pore space (Wilhelms et al., 1994). In both cases using high polarity solvents and increasing the cleaning time would increase the efficiency of the cleaning process. Figure A-4a shows the core helium porosity and density log evaluated total porosity data for samples that are taken from a well that has no indication of reservoir bitumen presence (henceforth we refer to this well as well 1) The density log total porosity is calculated without consideration of the possibility of bitumen in the pore space. A more thorough discussion of how to incorporate the bitumen in the density log total porosity evaluation will be presented later.

The porosity values from density and helium injection are in good agreement for well 1. We performed the same comparison for a set of samples taken from a well and its side track that are affected by the presence of reservoir bitumen (henceforth we refer
to this well and its side track as Well 2 and Well 2ST, respectively) The results are shown in Figure A-4b, in which core helium porosity is systematically lower than the log density total porosity. This is due to the presence of reservoir bitumen residue in the cores even after two stage extraction.

![Figure A-4: Density porosity and helium porosity cross plot (a) light oil saturated well (Well 1) and (b) reservoir bitumen saturated well (Well 2) and its side track well (Well 2ST). Both porosity values are in good agreement in (a) but helium injection systematically underestimates the porosity values in (b).](image)

As mentioned earlier, similar to helium porosity, NMR log porosity calibrated with fresh water shows lower porosity than density derived total porosity. The NMR log porosity (calibrated using HI of 1 for water) and helium injection porosity data for well 2 and its side track are shown in Figure A-5. Although both porosity values underestimate the rock porosity compared to density log total porosity, they show better agreement than Figure A-4b. This comparison shows a common source of error, which is the presence of reservoir bitumen, for both NMR log and helium injection measurements. The possibility of pore throat blockage by reservoir bitumen due to partial sample
cleaning discussed above could cause an additional porosity deficit when He-injection porosity values are compared to NMR porosity values. However, only an unknown fraction of the reservoir bitumen in the pore space is spatially configured to result in isolated pockets of pore space undetectable by the He-injection measurement. On the other hand, the cleaning procedure before the He-injection measurement might result in removal of an unknown amount of reservoir bitumen, thus increasing the He-injection porosity compared to NMR log porosity. It is likely that some of the scatter seen in Figure A-5 is related to these opposite effects, which we consider relatively small but have not been able to quantify.

Figure A-5: Cross plot of NMR log porosity and Helium injection porosity values for reservoir bitumen saturated well and its side track well (Wells 2 and 2ST, respectively). Both NMR log and helium injection porosities are affected by presence of reservoir bitumen in the pore space. Due to the underestimation of the porosity in both measurements, helium injection porosities are in better agreement with NMR porosity than with density porosity values.
A.3.5 Grain density measurement

Grain density measurement using helium injection is a reliable way to calibrate the grain density measured by the ECS log and calculate the total porosity using density logs (Wilhelms et al., 1994). Evaluating the total porosity using constant mineralogy and fluid type often results in poor estimation of porosity, especially in heterogeneous systems (Elseth et al., 2001). Presence of low density (compared to mineral densities) reservoir bitumen residue in the pore space due to partial cleaning, reduces the helium injection grain density (Wilhelms et al., 1994) since during the measurement the bitumen is part of the solid matrix rather than a saturating fluid.

Another method to determine the grain density is using XRD data. This method quantifies the mineralogy of the rock based on the angle of diffraction of the scattered X-ray beam, after collision with the crystalline structure of the mineral. Decrease in the crystal size or lack of crystallinity will reduce the intensity of the diffracted beam (for more information see Ruessink and Harville, 1992). Thus XRD results are not affected by the reservoir bitumen regardless of the saturation due to the non-crystalline structure. Note that XRD is not a direct grain density measurement technique and in this study we use the mineral constituents of the rock determined by XRD and grain density values for pure individual minerals to calculate the grain density using Equation A-4.

\[ \rho_g = \frac{100}{\sum (wt\%_{min}/\rho_{min})} \]  

(A - 4)

where \( \rho_g \) is the grain density of the rock sample in gr/cm\(^3\), \( wt\%_{min} \) is the weight percent fraction of each mineral, and \( \rho_{min} \) is the density of the pure mineral in gr/cm\(^3\).
Figure A-6 shows a comparison between grain density evaluated by XRD and helium porosity measurements. In well 1 (Figure A-6a), the XRD and helium injection grain density result in similar values. In wells 2 and 2ST, (Figure A-6b), the XRD grain density is higher than and shows no correlation with the calculated grain density by helium injection. In Wells 2 and 2ST the presence of varying amounts of low density reservoir bitumen residue has affected the grain density whereas the XRD method only considers the hydrocarbon free grain density. Using helium injection grain density values for core-log correlation without considering the effect of reservoir bitumen residue, results in underestimation of the total calculated using the density log. There are other sources of grain density estimates such as ECS logs and Multimineral analysis which theoretically are reservoir bitumen independent and can be used for core to log correlation of the grain density for a more precise density porosity calculation. Figure A-7 shows a schematic of which parts of the reservoir rock are detected by different log and core laboratory measurement techniques.

**A.3.6 Petrographic analysis**

Petrographic analysis of thin-sections can be used to detect the presence of reservoir bitumen in reservoir rocks. It can provide direct confirmation of the presence of reservoir bitumen in reservoirs. In thin section, reservoir bitumen is recognized as a solid cement that occurs in a variety of geometries, including meniscus pore wall coatings (Figures A-8a and A-8b), solidified droplet shapes, pore-bridging ribbons (Figures A-8c and A-8d), and as complete or nearly complete pore filling material (Figure A-8e).
Figure A-6: Cross plot of grain density calculated by helium injection and XRD data for (a) light oil saturated well (Well 1) and (b) reservoir bitumen saturated well and its side track (Wells 2 and 2ST, respectively). In Well 1, (a), the XRD and helium injection grain density result in similar values whereas in Wells 2 and 2ST, (b), the XRD grain density (not affected by HC remnants) is systematically higher than the calculated grain density by helium injection data (which is affected by the HC residues). Using helium injection grain density values for core-log correlation without considering the effect of reservoir bitumen residue results in underestimation of the porosity calculated using density log.

Figure A-7: Volumetric rock model that shows the portion of the rock and fluid for different measurements. (a) Density log measures the bulk density of the rock including all the minerals and the fluids in the pore space. (b) NMR porosity includes the light fluids and part of the heavy hydrocarbons such as reservoir bitumen indicated by “???” sign in the figure. (c) Helium injection calculated grain density includes both rock matrix and the hydrocarbon remnants which are the results of incomplete extraction. (d) XRD and ECS log measure the weight fraction of each mineral constituent in the matrix. By assuming a density value for each individual mineral the grain density can be calculated.
Figure A-8: In thin sections, reservoir bitumen is recognized as a solid cement that occurs in a variety of geometries, including (a) pore-lining, meniscus bitumen in dolomite reservoir facies, (b) meniscus bitumen pore linings in limestone, (c) pore-lining bitumen and pore-bridging ribbon of bitumen in limestone facies, (d) pore-lining and pore-bridging bitumen in oncoidal limestone facies, (e) pore-filling bitumen with dessication cracks in a skeletal limestone. Examples of each bitumen geometry are annotated and shown using dashed boxes. In all cases, reservoir bitumen has reduced the pore volume and decreased the permeability by restricting pore throats. (f) shows a limestone sample which is not damaged by the presence of reservoir bitumen. The blue color in all images is the epoxy that has been used for thin section preparation.
Reservoir bitumen is opaque in transmitted plane light or cross polarized light, and blackish-brown to black in reflected light. Desiccation cracks may appear within the bitumen fill (Figure A-8e) originating from either natural shrinkage or laboratory-induced desiccation resulting from the cleaning and drying process. In ultraviolet light bitumen will appear black, non-reflective, and will not show any sign of fluorescence. An example of a clean, non-bitumen saturated thin section is shown in Figure A-8f.

Reservoir bitumen is difficult to confuse with other types of solid opaque cements like pyrite or iron oxides. Pyrite does not occur in meniscus, droplet, ribbon shaped or pore wall coating morphologies, and in reflected light it will exhibit a characteristic gold color. Also iron oxides are readily distinguished from bitumen by their characteristic rust to red colors in reflected light.

In order to preserve bitumen for petrographic observation, the core plugs used to make thin sections should be cleaned enough to remove brine, moveable (liquid) oil, and drilling mud, but not so aggressively cleaned that the solid components are removed. If thin sections are made from core plug end trims, the cleaning procedure used should match the protocol used for routine core analysis so that the visual evidence observed in thin sections matches the core analysis data results quantitatively. The protocol used can vary depending on desired results. Three levels of cleaning may be used: (1) Non-aggressive cleaning to remove brine and drilling mud while preserving all of the oil components (volatile liquid oil stain and solid bitumen). In thin section, oil stain will appear as a thin brown coating that may fluoresce in UV light, while the solid bitumen will be opaque, black and non-fluorescent. (2) Additional solvent cleaning to remove the volatile liquid stain, leaving behind only the solid bitumen in the pores. This
will yield a thin-section view with porosity estimates that should reasonably match core analysis results as well as downhole NMR porosity calculations. (3) Highly aggressive, longer-duration cleaning (especially at high temperatures) to remove all hydrocarbon components.

This method yields a clean, open pore system showing no evidence of hydrocarbon migration. Thin-section estimates of porosity in this case may match uncorrected, un-calibrated density log estimates, but will not likely match NMR log results. However, the thin-section porosity values can be used to estimate the total potential porosity elsewhere where solid bitumen might be absent.

Petrographic work can be integrated into the bitumen assessment process described in this study in three basic ways: (1) qualitative visual confirmation of downhole log results, (2) quantitative measurement of volume % solid bitumen, volume % pore space, and volume % solid minerals, (3) determination of relative and/or absolute oil charge timing. Relative timing may include timing versus other diagenetic burial events, and may include initial charge, recharge, flushing, and biodegradation events. Absolute geologic timing may be interpreted for single or multiple events, and may include information about temperature, pressure and depth conditions that existed in the reservoir strata. In this study we use the petrographic analysis of the thin sections for qualitative visual confirmation of the presence of the reservoir bitumen.

A.4 Reservoir Bitumen Quick Identification Method

As discussed earlier, presence of reservoir bitumen in the rock has a significant effect on the laboratory and downhole NMR responses as well as laboratory tests such as thin sections, porosity and grain density measurements. Any of these indicators
taken individually might not be sufficient to positively identify reservoir bitumen, but taken together the agreement of all or some of these indicators provide a stronger indication of the presence of reservoir bitumen. We used these effects to develop a quick identification method to differentiate the reservoir bitumen and light fluid saturated intervals. The following describes the step wise workflow for reservoir bitumen identification.

**Step 1: T<sub>2</sub> distribution**

For a proper interpretation of the T<sub>2</sub> distributions, fluid saturations and viscosities are required. Equation A-1 provides a correlation to calculate the approximate bulk relaxation for oils using viscosity and reservoir temperature.

As described earlier (Figure A-1), in reservoir bitumen saturated intervals, the short bulk T<sub>2</sub> relaxation of the bitumen dominates the T<sub>2</sub> spectrum. Therefore visual inspection of the T<sub>2</sub> distribution enables a first assessment of fluid type.

**Step 2: Density (total)-NMR porosity**

Presence of low H<sub>1</sub><sub>app</sub> fluids, such as high viscosity hydrocarbons or gasses, reduces the estimated porosity from the NMR tool. Plotting density porosity and NMR porosity on the same scale helps us identify the zones where NMR shows a deficit in porosity. Due to uncertainties associated with grain density and liquid phases especially in high clay content, heterogeneous and thinly layered reservoirs, it is challenging to define a universal threshold for NMR-Density porosity difference as an indication of presence of reservoir bitumen. Precise depth matching in reservoirs with rapidly variable porosity with depth is crucial prior to Density-NMR porosity comparison. A slight mismatch could result in a significant porosity deficit and misinterpretation of an interval.
as reservoir bitumen rich.

**Step 3: Density (total) porosity-\(T_{2LM}\) cross over**

For light hydrocarbon or water saturated rocks (assuming \(HI_{app}\) of 1 for both fluids), the \(T_2\) distribution can be considered a representation of the pore size distribution, and the \(T_2\) logarithmic mean (\(T_{2LM}\)), calculated by Equation A-5, will be an indication of the pore size that dominates the porosity of the rock.

\[
T_{2LM} = \exp\left(\frac{\sum \ln(T_{2i}) \times \phi_i}{\sum \phi_i}\right)
\]

in which \(T_{2LM}\) is the logarithmic mean of \(T_2\) distribution measured in ms. If the \(T_2\) distribution spectrum is plotted using \(i\) number of points (bins), the \(i^{th}\) bin has a \(T_2\) time \((T_{2i})\) and an amplitude which is the porosity associated with that bin \((\phi_i)\).

\(T_{2LM}\) and density porosity cross over is an indicator of whether the \(T_2\) response is dominated by rock or fluid properties. In clay free intervals saturated with light oil and water we expect to see an increase in \(T_{2LM}\) as a result of increase in porosity. Presence of reservoir bitumen shifts the \(T_2\) distribution towards shorter relaxation times, and consequently \(T_{2LM}\) decreases significantly and does not follow the porosity variation. Density porosity, regardless of the bitumen content, captures the variations in porosity. Fluid and rock effects on \(T_2\) distribution can be separated by plotting density porosity and \(T_{2LM}\) on the same track. They should be scaled so that they approximately overlap in water or light hydrocarbon saturated intervals (for example 30 to 0 p.u for porosity and 0 to 700 ms on linear scale for \(T_{2LM}\)).

**Step 4: Grain density comparison**

Plotting different grain density data sets on the same track helps to confirm the presence of reservoir bitumen in the intervals that have low helium injection calculated
grain densities, compared to other measurements such as XRD, ECS or multimineral analysis.

**Step 5: Petrographic screening**

Available thin-sections were used to visually confirm the presence of solid pore-filling bitumen. We created a log where we assigned a value of 1 for petrographic images that show the presence of bitumen (Figures A-8a to A-8e) and a value of 0 for reservoir bitumen free images (Figure A-8f).

**Step 6: Downhole pressure test**

Downhole formation pressure tests are used to measure the fluid mobility at different depths. Taken independently, formation pressure tests are not an indication of the presence of reservoir bitumen. A dry or failed pressure test can be either due to low permeability of the rock or high viscosity of the fluid. In this study we assigned 0 to the failed or dry pressure tests and 1 to the tests that recorded a pressure build up.

### A.5 Reservoir Bitumen Quantification: Volumetric Model

In the previous section a stepwise quick, but qualitative, identification method for reservoir bitumen was presented. In this section we discuss a volumetric model to quantify the saturation of the reservoir bitumen and refine the total porosity estimation for hydrocarbon volume calculation purposes.

Figure A-9 shows a schematic of the reservoir rock model developed. The question mark in Figure A-9 indicates that the cleaning process in the core laboratory will remove an unknown amount of the reservoir bitumen present in the reservoir. It is assumed that this portion of the hydrocarbon is undetectable by the NMR logging tool in the reservoir. The amount of removed bitumen is expected to be small, therefore, the
matrix density values reported from helium injection core analysis \( (\rho_{macore}) \) will be smaller than the matrix density of the reservoir rock \( (\rho_{ma}) \). Likewise, the bitumen in the reservoir is non-moveable so it is effectively part of the rock, and the log derived apparent reservoir matrix density, \( (\rho_{mares}) \), is close to \( \rho_{macore} \), as detailed later. The limestone reservoirs under consideration here are essentially shale free, and there was no shale included in the model.

![Reservoir Rock Model](image)

Figure A-9: Reservoir rock model annotated with relevant density and porosity labels used in the text. The question mark indicates that the cleaning process will remove an undefined amount of the reservoir bitumen, which is itself undetectable by the NMR logging tool in the reservoir.

Total porosity calculated from the density log using a standard matrix density will include the part of the pore space occupied by bitumen. The total porosity value including the volume of bitumen \( (\phi_{max}) \) is larger than the core analysis derived value and the total porosity value from an NMR log which does not detect the bitumen (Figure A-7).
The effect of the presence of reservoir bitumen on the evaluation of porosity can be quite significant. Consider a reservoir with matrix density $\rho_{ma} = 2.75$ gr/cm$^3$ with two different porosity values, $\phi_{max} = 0.25$ and $\phi_{max} = 0.10$ and varying amount of reservoir bitumen. The water saturation ($S_{wt}$) in the two situations is 20% and 40%, respectively. If the total porosity is calculated from the density log without acknowledging the presence of varying amounts of reservoir bitumen, the total porosity will be significantly higher than the NMR porosity, even for moderate amounts of reservoir bitumen (Figure A-10). This suggests that the combination of the total porosity estimation from the density log and the NMR porosity can be used to quantify the amount of reservoir bitumen.

Figures A-10a and A-10b show the effect on porosity estimates of varying amounts of reservoir bitumen in the pore space in the two examples, respectively. It is interesting to note that for Bitumen saturations larger than, e.g. 20% the difference between the evaluated total porosity and the NMR porosity becomes significant (>15%). The effective reservoir matrix density ($\rho_{mares}$) which decreases rapidly with increasing bitumen saturation can be derived from the model equations presented below to be compared to core analysis matrix density ($\rho_{macore}$) values which should also include the reservoir Bitumen assuming the Bitumen has not been removed in the core cleaning process.

When logging the reservoir it is assumed that the NMR tool and the density tool (measuring $\rho_B$) respond to the same fluid in the pore space due to their similar measurement depths of investigation, i.e. the relevant water saturation for the model is $S_{xo}$. We will denote the saturation of NMR detectable hydrocarbon and non NMR
detectable hydrocarbon $S_{HC}$ and $S_{RB}$, respectively. All saturations are with reference to $\phi_{max}$, which is the porosity of all the non-mineral portions of the rock (Figure A-9). With the model and nomenclature given in Figure A-9 the following relationships can be derived:

$$\rho_{fl} \phi_{fl} = S_{xo} \phi_{max} \rho_{W} + (\phi_{fl} - S_{xo} \phi_{max}) \rho_{HC}$$  \hspace{1cm} (A - 6)

$$\rho_{B} = \rho_{fl} \phi_{fl} + \rho_{RB} \phi_{RB} + \rho_{ma} (1 - \phi_{fl} - \phi_{RB})$$  \hspace{1cm} (A - 7)

where $\rho_{fl}$ and $\phi_{fl}$ are the density and porosity of the fluids that are detectable by NMR, respectively. $\rho_{W}$ and $\rho_{HC}$ are the densities of water and light hydrocarbons in the rock, respectively. Assuming $\phi_{fl} = \phi_{NMR}$ (the logged NMR porosity in Figure A-9), we can

Figure A-10: Effect on porosity estimates of varying amounts of bitumen in the pore space in two examples (a) PHI_MAX=0.10 and Swt=0.40 and (b) PHI_MAX=0.25 and Swt=0.20. The black dotted lines indicate the total porosity evaluated without consideration of the presence of the reservoir bitumen, i.e. considering all hydrocarbon (oil and reservoir bitumen) as oil for oil density calculation. The solid brown lines are the porosity that can be detected by an NMR tool which cannot detect the "solid" reservoir bitumen. The dashed-dotted blue lines indicate the reservoir matrix density ($\rho_{mares}$), i.e. the combined density to the mineral volume and the varying amount of reservoir bitumen. Dashed green lines are the difference between total porosity and NMR porosity. For Bitumen saturations larger than 20% the difference between the evaluated total porosity and the NMR porosity becomes significant (>15%). The reservoir matrix density ($\rho_{mares}$) decreases rapidly with increasing Bitumen saturation.
rearrange Equation A-6 and Equation A-7 for $\rho_{fl}$ and $\phi_{RB}$ which is reservoir bitumen porosity and eventually calculate $S_{RB}$ which is reservoir bitumen saturation:

$$\rho_{fl} = \frac{S_{xo}\phi_{max}\rho_W + (\phi_{NMR} - S_{xo}\phi_{max})\rho_{HC}}{\phi_{NMR}} \quad (A-8)$$

$$\phi_{RB} = \frac{\rho_B - \phi_{NMR}\rho_{fl} - \rho_{ma}(1 - \phi_{NMR})}{\rho_{RB} - \rho_{ma}} = \phi_{max} - \phi_{NMR} \quad (A-9)$$

$$S_{RB} = \frac{\phi_{RB}}{\phi_{max}} \quad (A-10)$$

To solve for the bitumen content an iterative approach is used. First the total porosity ($\phi_t$) from the density log is calculated following an iterating approach using density porosity log data and Archie’s equation (or any appropriate water saturation model) using an initial guess for $\rho_{fl}$ until stable values of $\phi_t$, water saturation (including $S_{xo}$), and total fluid density ($\rho_{fl}$ in Equation A-11) are obtained. In the first calculation there is no attempt to include the effect of bitumen. In the presence of bitumen the initial calculated value of $\phi_t$ will be too small (compared to $\phi_{max}$) as bitumen is denser than the moveable oil and the bitumen will be treated as moveable oil. The next step is to calculate Equations A-8 to A-10 above using $\phi_t$ for $\phi_{max}$. The total porosity calculation is now repeated with the modification that the fluid density $\rho_{fl}$ is calculated using $S_{RB}$ and the associated $\rho_{RB}$ in the following manner:

$$\rho_{fl} = S_{xo}\rho_W + (1 - S_{xo} - S_{RB})\rho_{HC} + S_{RB}\rho_{RB} \quad (A-11)$$

The total porosity $\phi_t$ and $S_{xo}$ are then fed into Equations A-8 to A-10 and the process is repeated.

In addition to the standard log evaluation, the above procedure results in an estimate of $S_{RB}$. Here we use $S_{RB}$ as a bitumen indicator for values larger than 0.25. $S_{RB}$ can also be used to calculate the fraction of pore space of the reservoir that is occupied by bitumen and as a guide to the distribution of the bitumen.
It is possible to derive an estimate of the apparent reservoir matrix density ($\rho_{m\text{ares}}$), i.e. including the bitumen as:

$$\rho_{m\text{ares}} = \frac{\phi_R \rho_B + (1 - \phi_{\text{NMR}} - \phi_R) \rho_m}{1 - \phi_{\text{NMR}}} = \frac{\rho_B - \rho_f \phi_{\text{NMR}}}{1 - \phi_{\text{NMR}}} \quad (A - 12)$$

The apparent reservoir matrix density ($\rho_{m\text{ares}}$) should compare favorably to the helium injection derived matrix density ($\rho_{m\text{core}}$) values which also include the effect of bitumen.

Figure A-11 illustrates the robustness of the method. Figure A-11a is a cross plot of core analysis matrix density ($\rho_{m\text{core}}$) for whole core and plug samples from Well 2 plotted against the result of a multimineral model ($\rho_{\text{Multim}}$) which includes Quartz, Calcite, and Dolomite. Figure A-11b the same core data ($\rho_{m\text{core}}$) plotted against the calculated $\rho_{m\text{ares}}$ using the method described above. The match is not perfect but the trend is clear, and the method properly includes apparent matrix density values as low as 2.45 g/cc.

Figure A-11: Well 2 core analysis matrix density ($\rho_{m\text{core}}$) plotted against two log based matrix density estimates: (a) using a multimineral based log estimate of matrix density not including the effect of bitumen and (b) using the approach given here including the effect of reservoir bitumen.
As discussed above density derived values for total porosity will be smaller than the “true” total porosity of the model, \( \phi_{max} \) (Figure A-9), if the bitumen is not properly included in the fluid density that enters the total porosity calculation. This is because the bitumen is treated as belonging to the fluid in the pore space. Incorporating the bitumen will actually increase the evaluated total porosity as compared to a standard evaluation, not accounting for bitumen, and make the agreement with core derived values even poorer. The NMR porosity, on the other hand, should be in much better agreement with the core derived values as the NMR log does not respond to the bitumen part which in this context can be considered solid (Figure A-5). Figure A-12 illustrates the increase in total porosity from density log when bitumen is included (PHIT) as compared to not included (PHIT_NO_RB_EFFECT) in the evaluation of a bitumen rich section of Well 2. It can be seen that including the effect of bitumen can increase the evaluated total porosity significantly.

Track 6 is the crossover of \( T_{2LM} \) (T2_LogM) and total porosity (PHIT) logs. In light fluid and water saturated intervals total porosity and \( T_{2LM} \) should follow the same trend. We plot them on opposite scales to for visual convenience. In zone A of well 3 (Figure A-14) which is a water saturated interval two logs clearly show similar trends. As porosity increases the \( T_{2LM} \) increases as well, which shows the dominant effect of pore structure on NMR data. In zones B of both wells porosity log shows significant variations whereas \( T_{2LM} \) log shows a constant low average time. This is an indication of the high viscosity fluid effect on NMR response (Step 3).

Track 6 is the crossover of \( T_{2LM} \) (T2_LogM) and total porosity (PHIT) logs. In light fluid and water saturated intervals total porosity and \( T_{2LM} \) should follow the same trend.
We plot them on opposite scales to for visual convenience. In zone A of well 3 (Figure A-14) which is a water saturated interval two logs clearly show similar trends. As porosity increases the $T_{2LM}$ increases as well, which shows the dominant effect of pore structure on NMR data. In zones B of both wells porosity log shows significant variations whereas $T_{2LM}$ log shows a constant low average time. This is an indication of the high viscosity fluid effect on NMR response (Step 3).

Track 6 is the crossover of $T_{2LM}$ (T2_LogM) and total porosity (PHIT) logs. In light fluid and water saturated intervals total porosity and $T_{2LM}$ should follow the same trend. We plot them on opposite scales to for visual convenience. In zone A of well 3 (Figure A-14) which is a water saturated interval two logs clearly show similar trends. As porosity increases the $T_{2LM}$ increases as well, which shows the dominant effect of pore structure on NMR data. In zones B of both wells porosity log shows significant variations whereas $T_{2LM}$ log shows a constant low average time. This is an indication of the high viscosity fluid effect on NMR response (Step 3).
Track 6 is the crossover of $T_{2LM}$ ($T2\_LogM$) and total porosity (PHIT) logs. In light fluid and water saturated intervals total porosity and $T_{2LM}$ should follow the same trend. We plot them on opposite scales to for visual convenience. In zone A of well 3 (Figure A-14) which is a water saturated interval two logs clearly show similar trends. As porosity increases the $T_{2LM}$ increases as well, which shows the dominant effect of pore structure on NMR data. In zones B of both wells porosity log shows significant variations whereas $T_{2LM}$ log shows a constant low average time. This is an indication of the high viscosity fluid effect on NMR response (Step 3).

A.6 Case Study and Discussion

The explained methodologies for quick identification and volumetric modeling were applied to two wells with reservoir bitumen saturated intervals. The reservoir under consideration was pre-salt Cretaceous carbonate, more specifically an aptian lacustrine microbial limestone, located in the deep water Campos basin off shore Brazil. Several wells with varying amounts of reservoir bitumen have been drilled in the area. In this paper we only discuss wells with high levels of reservoir bitumen. The wells were drilled with oil base mud and were logged with wire line standard triple combo suites, NMR, ECS and formation pressure tests. The logging operations were carried out successfully and the data quality is good for all reservoir sections discussed here.

The log tracks for well 2 and well 3 are shown in Figure A-13 and Figure A-14, respectively. Details of each log track are given in Table A-1. In well 2 (Figure A-13) three zones have been observed. At the top and bottom there are two low resistivity water saturated intervals (zones C and A, respectively). Zone B in Figure A-13 with low gamma ray (GR), high resistivity (RSHAL and RT) and high density porosity (PHIT) is
shown. The resistivity, density and neutron logs at this interval show all the characteristics of a prolific oil saturated reservoir. This is similarly observed in the top interval (zone B) of Well 3 shown in Figure A-14.

![Graph showing PHIT effect](image)

Figure A-12: Illustration of the effect of including the bitumen in the total porosity (PHIT) calculation as opposed to not including bitumen in the calculation (PHIT_NO_SHC_EFFECT) for Well 2.

Table A-1: Log track definitions for wells 2 and 3 in Figure A-13 and A-14, respectively.

<table>
<thead>
<tr>
<th>Track #</th>
<th>Log and Core Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>True Vertical Depth Sub Sea</td>
</tr>
<tr>
<td>2</td>
<td>Gamma Ray</td>
</tr>
<tr>
<td>3</td>
<td>Shallow (RSHAL) and Deep (RT) Resistivity</td>
</tr>
<tr>
<td>4</td>
<td>NMR T₂ Distribution</td>
</tr>
<tr>
<td>5</td>
<td>NMR (PHIT_NMR), and Core Helium Injection (Por_Core) Porosity</td>
</tr>
<tr>
<td>6</td>
<td>Density Porosity (PHIT) and T₂ Logarithmic Mean (T₂ LogM)</td>
</tr>
<tr>
<td>7</td>
<td>Effective (RHO_MARES), XRD calculated (GD_XRD) matrix density, Helium Injection (GD), Multimineral Model (RHOMA_QUA)</td>
</tr>
<tr>
<td>8</td>
<td>Pressure Test (Good Press and Failed Press) and Thin Section Analysis (thin Section)</td>
</tr>
<tr>
<td>9</td>
<td>Timur-Coates Model NMR (KTIM_NMR) and Helium Injection (K_Core) Permeability</td>
</tr>
<tr>
<td>10</td>
<td>Reservoir Bitumen (S_SHC) and Water Saturation (SWT)</td>
</tr>
</tbody>
</table>
Figure A-13: Log and core data for well 2. Log track details are given in Table 1. The well shows three zones: Zone A is a mixed water/oil/bitumen saturated zone, Zone B is a bitumen saturated zone, and Zone C is water saturated. Quick identification steps are shown in different log tracks. Detailed discussion for each track is given in the results and discussion section.

We followed the stepwise quick identification for both wells to differentiate reservoir bitumen saturated intervals. In the following after discussing each log track, the corresponding quick identification step will be addressed.

Track 4 in both wells shows the changes in NMR T2 distribution (T2_DIST) when the NMR logging tool enters zones B of both wells. We observed that the presence of heavy hydrocarbon dominates the NMR response and shifts the distribution towards faster relaxation times (Step 1).

The brown fill in Track 5 indicates the areas that NMR porosity (PHIT_NMR) is underestimating the porosity in comparison to density porosity (PHIT). Helium injection porosity data (Por_Core) is also shown. As shown earlier in Figure A-5, they are closer
to NMR porosity due to reservoir bitumen effect (Step 2).

Track 6 is the crossover of $T_{2LM}$ ($T2_{LogM}$) and total porosity (PHIT) logs. In light fluid and water saturated intervals total porosity and $T_{2LM}$ should follow the same trend. We plot them on opposite scales to for visual convenience. In zone A of well 3 (Figure A-14) which is a water saturated interval two logs clearly show similar trends. As porosity increases the $T_{2LM}$ increases as well, which shows the dominant effect of pore structure on NMR data. In zones B of both wells porosity log shows significant variations whereas $T_{2LM}$ log shows a constant low average time. This is an indication of the high viscosity fluid effect on NMR response (Step 3).

Figure A-14: Log and core data for well 3. Log track details are given in Table 1. The well shows two layers, a water saturated layer at the top (indicated as zone A) and an oil saturated interval (indicated as zone B). Quick identification steps are shown in different log tracks. Detailed discussion for each track is given in the results and discussion section.
Track 7 presents laboratory and downhole grain density measurements. In zones B the helium injection grain density (GD), which is affected by the presence of reservoir bitumen residue, shows a systematically lower grain density compared to other measurements such as XRD calculated (GD_XRD in well 2) and multimineral analysis (RHOMA_QUA) which are reservoir bitumen independent (Step 4).

Track 8 shows both thin section analysis (Thin Section) and pressure test results (Good_Press and Failed_Press). In the majority of the thin sections in zones B, reservoir bitumen has been observed and the pressure test results are “Dry”. It is an indication of very low fluid mobility either due to low permeability or high fluid viscosity. In order to differentiate permeability and fluid viscosity effects on the failed pressure tests we plotted the helium injection permeability results (K_Core) in Track 9. The high core permeabilities indicate that the failure in pressure tests is most likely due to the fluid viscosity effect (Steps 5 and 6). Note that the permeabilities measured by helium injection methods are also affected by reservoir bitumen residue and are only indicators of permeability in these intervals.

92 ms is the common time cut off for capillary bound water volume using NMR log in Timur-Coates permeability model for carbonate rocks (Coates et al., 1999). In zones B, the majority of the NMR T₂ distribution (Track 4) falls below the cut off time and results in underestimation of the permeability calculated by Timur-Coates model (KTIM_NMR in Track 9). NMR permeability models are developed assuming T₂ distribution is a representation of pore size distribution. As mentioned earlier, in reservoir bitumen saturated intervals the distribution is highly dominated by the short bulk relaxation of the reservoir bitumen.
After identifying the reservoir bitumen saturated intervals, the volumetric model presented in this paper was used to calculate the saturation of reservoir bitumen. The results of the model are shown in Track 10. As observed the saturation of the reservoir bitumen is not constant throughout the wells. The results of the model have been used directly in field scale reserve calculations.

A.7 Conclusions

One of the main challenges in reservoirs with reservoir bitumen is understanding of the distribution and the effect that reservoir bitumen has on individual log and core measurements. In this work, thorough petrophysical modeling, using all available data was performed for two wells.

NMR logging is the state of the art method used to differentiate between light and heavy/immobile hydrocarbons. In reservoir bitumen saturated intervals, the NMR T$_2$ distribution is dominated by the bulk fluid relaxation and is not a representation of the pore size distribution, so the empirical permeability models using NMR data become unreliable. Helium injection grain density from core analysis is underestimated due to the presence of reservoir bitumen residue. Since it is the common source of core-log calibration for density log porosity calculation, using this grain density data results in the underestimation of total porosity calculated from the density log. Other sources of porosity such as NMR and helium injection also underestimate the total porosity of the rock.

The devised volumetric model is able to explain and quantify the results of the core analysis data when reservoir bitumen is present in the reservoir. The technique described here can be applied to different reservoirs, regardless of lithology and
producing fluid type, for more reliable and precise reservoir evaluation and production planning.

A.8 Acknowledgement

The authors would like to thank Amir Hussain Rangwala, Vitaly Mayer, Mai Kristine Borre and Bill Morgan for discussions and comments. Also we would like to acknowledge Maersk Oil Houston Inc., BP and Anadarko for permission to publish this work as well as OCLASSH research group from Colorado School of Mines for their support to finalize the paper.

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APPENDIX B

Measurement of the Water Droplet Size in Water-in-Oil Emulsions Using Low Field Nuclear Magnetic Resonance for Gas Hydrate Slurry Application

A paper published in the Canadian Journal of Chemistry

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B.1 Abstract

Turbulent flow in the oil and gas pipelines often results in the formation of a water-in-oil (W/O) emulsion. Small water droplets in the pipeline provide large total surface area for hydrate formation at the water/gas saturated oil interface, which can lead to full conversion of water to gas hydrate. As a result, this may prevent the formation of large hydrate aggregates that can cause hydrate particle settling and eventually plugging. It is thus of particular interest to determine the water droplet size of an emulsion. Since water droplet size of the emulsion provides information about the hydrate particle size in the slurry, it is crucial to determine the water droplet size in a W/O emulsion. In this work, the water droplet size of model W/O emulsion systems were measured using two techniques: Diffusion-Transverse Relaxation ($T_2$) experiments using low field Nuclear Magnetic Resonance (NMR) and optical microscopy image analysis techniques. The $T_2$ distribution of the emulsion was also measured. The water volume fraction was varied from 10 – 70 vol.%. The NMR and microscopy image analysis results show the droplet size ranging from 3.5 to 4.5 µm and 2 to 3 µm, respectively. Both techniques show a minimum 2 and 4 µm at 50 vol.% water cut. There
are two main reasons for the small difference in droplet size distribution (DSD) measured using these techniques: NMR provides DSD of the entire emulsion sample as opposed to an optical microscopy technique that only capture a small sample of the emulsion. In addition, since the NMR method does not require sample preparation, the characteristics and properties of the emulsion are maintained. On the contrary, using microscopy images, the sample is compressed between two glass slides. This will disturb the properties of the emulsion. By combining the diffusion-$T_2$ and $T_2$ distributions, the surface relaxivity was determined to be $0.801 \, \mu\text{m/s}$ for the oil/water emulsion. The DSD obtained from the NMR method in this work was compared with microscopy analysis, and results show there is reasonable agreement between the two methods. This paper provides a comparison of the two methods that can be used to determine the water droplet size of W/O emulsions. This study indicates that a relatively simple quantitative NMR method can be utilized to determine the water droplet size of W/O emulsions before gas hydrate formation, and hence can be used to assess the gas hydrate slurry properties and plugging risk of W/O systems.

B.2 Introduction

Gas hydrates (also known as clathrate hydrates) are crystalline compounds in which small gas molecules such as methane, ethane, propane and cyclopentane are enclathrated by hydrogen-bonded water molecules (Sloan and Koh, 2008). The water molecules form a network of hydrogen bonds around the gas molecules thereby forming water cages. Gas hydrates typically form at high pressure and low temperature (e.g. $10 \, \text{MPa}$, $277 \, \text{K}$ for methane hydrates) (Sloan and Koh, 2008). At these conditions, hydrates can form and plug subsea oil/gas pipelines and are considered a nuisance.
Figure B-1 shows a conceptual schematic of hydrate formation in pipelines for an oil-dominated system (i.e. where oil is the continuous phase). Hydrate formation begins with water being emulsified in the oil phase forming a water-in-oil (W/O) emulsion. As explained below, this emulsion may or may not be desirable depending on the size of the water droplets. Next, at appropriate pressure and temperature condition, a thin hydrate shell will grow around the water droplets (Sloan and Koh, 2008). If the water droplet is in the µm size range, gas molecules are able to penetrate through the shell. In this case, hydrates will grow inward forming fully converted hydrate particles that can prevent hydrate agglomeration and pipeline blockage. However, this hydrate shells can create a gas diffusion barrier between the oil and the water phase if water droplets are bigger than µm size range (Sloan and Koh, 2008). Then there will be capillary attraction forces between hydrate particles due to water bridging (from unconverted free water) that cause the particles to agglomerate forming large hydrate aggregates (Sloan and Koh, 2008). Since these aggregates may then form a blockage in the pipeline, it is crucial to determine the water droplet size in an emulsion and eventually the hydrate particle size in a slurry.

Figure B-1: Conceptual schematic of hydrate plug formation in pipeline for oil dominated system (redrawn from (Turner, 2006) and (Turner et al., 2009).
There are several methods being employed by researchers and operators to determine droplet size of the emulsion such as microscopy (Delgado-Linares et al., 2013), and Nuclear magnetic resonance (NMR) (Aichele et al., 2007; Opedal et al., 2009; Fridjonsson et al., 2012). Each method has its own advantages and disadvantages. For instance, the microscopy imaging method is relatively simple and fast. The size of the droplet is measured by analyzing optical microscopy images of the emulsion. However, in this method, only a small sample of the emulsion is analyzed (e.g. ~250 water droplets) and thus the method may not reflect the actual condition in pipelines. Another method to determine the DSD of emulsions is using NMR. This method has gained interest since it is non-destructive and can measure a considerable amount of sample.

In this paper, the DSD of the system is determined by studying the diffusion of the system using NMR, specifically by taking advantage of the differences in relaxation times for oil and water. In this work, we present a method for the conversion of the $T_2$ distribution signal to droplet size distribution.

B.3 Materials and Methods

In this section we introduce the sample preparation methodology as well as the techniques that we used to characterize the samples. We also present the acquisition parameters that were chosen to perform the experiments.

B.3.1 Emulsion Preparation

The model water-in-oil emulsion consists of a mineral oil, a mixture of surfactants and deionized water. The mineral oil in this work was Crystal Plus mineral oil 70T purchased from STE Oil Company Inc. The oil is a Newtonian fluid with a viscosity of 20
cP at 25 °C and density of 0.857 g/cm³ at 20 °C. The chemical composition of the mineral oil is given in Table S1.

The surfactant mixture consists of a nonionic surfactant, Sorbitan Monooleate (known as Span 80) and an ionic surfactant, Sodium Di-2-Ethylhexylsulfosuccinate (known as AOT). The molecular structures of the surfactants are shown in Figure B-2. The concentration of surfactant in the model W/O emulsions is 5 wt.% with respect to the total mass of the emulsion. Furthermore, the ratio concentration of the surfactants used in this work is 90 wt.% of Span 80 and 10 wt.% of the AOT. Span 80 was purchased from Sigma Aldrich. It has a reported molecular weight of 428.61 g/mol and Hydrophilic Lipophilic Balance (HLB) value of 4.3 (Peixinho et al. 2010). AOT surfactant was purchased from Fischer Scientific and has a reported molecular weight of 444.56 g/mol. The water volume fraction (also known as water cut) for this model emulsion system ranges from 10 to 70 vol.%

![Molecular structure of the surfactants](image)

Figure B-2: Molecular structure of the surfactants used in this work, (a) Span 80 and (b) AOT.

In this work, 30 ml of emulsion sample was prepared by first, dissolving the pre-weighed surfactant mixture in the mineral oil at low heat (∼50°C) and medium stirring.
This was done using a hotplate and a magnetic stirrer. Next, the sample was cooled to room temperature. Once cooled, the sample was stirred at 8000 rpm using a high-speed homogenizer (Virtis Sentry Cyclone IQ2 Homogenizer), while water was added slowly using a syringe. (Sjöblom et al., 2010). The total stirring time depends on water cut of the emulsion. For emulsions with water cuts ≤ 50 vol. %, the system was stirred for 3 minutes where water was added during the first minute. As for 60 and 70 vol.% water cut emulsions, the system was stirred for 6 minutes and water was added during the first 4 minutes. A longer stirring time was required for the high water cut system to allow water to be added slowly into the system. This method ensures that W/O emulsion will be produced.

B.3.2 Microscopy Droplet Size Measurement

The water droplet size of the emulsion was measured using an optical microscope (Olympus IX71) connected to a digital camera (Olympus XM10). The microscope images were analyzed using ImageJ. At each water cut investigated, a minimum of 250 water droplets were measured and the mean droplet size was calculated and reported in this work.

B.3.3 NMR Droplet Size Measurements

The NMR measurements were performed using a 2 MHz Magritek Rock Core Analyzer. All measurements are at room temperature and pressure. Two main pulse sequences are used to measure the NMR response for the emulsion samples. In this section, the pulse sequences and the analysis techniques are discussed.
B.3.3.1 Carr-Purcell-Meiboom-Gill (CPMG) Pulse Sequence

The CPMG pulse sequence (Figure B-3) was introduced by Carr and Purcell (1954) and then modified by Meiboom and Gill (1958) to measure the transverse relaxation time ($T_2$) of hydrogen nuclei in fluid samples. The $T_2$ relaxation mechanism is a combination of three relaxation mechanisms (Equation B-1): bulk relaxation ($T_{2B}$), surface relaxation ($T_{2S}$), and diffusion induced relaxation ($T_{2D}$) (Dunn et al., 2002).

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}} \quad (B - 1)$$

By minimizing the echo spacing (TE in Figure B-3) the diffusion induced relaxation becomes negligible compared to bulk and surface relaxations (Coates et al., 1999). Surface relaxation is a function of surface relaxivity and the ratio of surface area to the volume. Assuming spherical-shaped droplets for the discontinuous phase (water in this study), Equation B-1 can be rewritten as (Equation B-2):

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{\rho S}{V} = \frac{1}{T_{2B}} + \frac{\rho S}{r} \quad (B - 2)$$
In which $\rho$ is the surface relaxivity, $S$ is the surface area, $V$ is the volume, $r$ is the droplet radius. This equation can be solved for droplet radius, which is the main focus of this study (Aichele et al., 2007):

$$r = 3\rho \left( \frac{1}{T_2} - \frac{1}{T_{2B}} \right)^{-1} \quad (B-3)$$

Bulk and $T_2$ distributions in Equation B-3 can be measured for the emulsion, the only parameter that is required for droplet size calculation is the surface relaxivity.

All the NMR measurements were performed using a 2 MHZ Magritek Rock Core Analyzer at room temperature and pressure. The $T_2$ distributions were measured with 400 $\mu$s echo spacing, 50000 number of echoes, constant pulse length of 20$\mu$s for both 90 and 180 degrees pulses and minimum signal to noise ratio (SNR) of 250.

**B.3.3.2 Pulsed Field Gradient-CPMG Pulse Sequence**

The Pulsed Field Gradient-CPMG pulse sequence consists of a pulse field gradient (PFG) followed by a CPMG pulse sequence (Figure B-4). This pulse sequence correlates two phenomena: the translational diffusion coefficient of water molecules restricted by droplet walls (replicated in the diffusion measurement) and the chemical properties of water and oil (replicated in the $T_2$ measurement). A two dimensional distribution function accounts for these phenomena and an inverse Laplace transform is used to produce the D-$T_2$ maps. We used non-negative least square (NNLS) algorithm for 2d inversion of D-$T_2$ data (Lawson and Hanson, 1974). More information about D-$T_2$ data acquisition and mathematical inversion can be found in (Hürlimann et al., 2002; Venkataramanan et al., 2002; Song, 2010). The smoothing parameter for the inversion has been chosen by the method described by (Dunn and LaTorraca, 1994).
Discontinuous phase diffusion coefficient can be measured using only PFG pulse sequence (Packer and Rees, 1972; Hirasaki and Pena, 2003; Johns 2009; Fridjonsson et al., 2012). PFG pulse sequence measures the diffusion coefficient of a combination of both continuous and discontinuous phases. There are two methods to measure the discontinuous diffusion coefficient: In the first approach differentiating the diffusion coefficient requires knowledge of the fraction of the continuous phase (Packer and Rees, 1972; Hirasaki and Pena, 2003; Johns 2009; Fridjonsson et al., 2012, Fridjonsson et al., 2014) which is usually unknown in cases such as oil and gas production wells and pipelines. The second approach is to use very long diffusion times to allow the continuous phase NMR signal to decay during this time period (Hirasaki and Pena 2003; Johns 2009; Opedal et al., 2009; Lingwood et al., 2012; Sørland et al., 2013). The disadvantages of this approach are compromising the signal to noise ratio since a major portion of the signal decays due to relaxation before the data acquisition and also applicability only in cases that the continuous phase relaxation is faster than the discontinuous phase.

![Diagram of PFG-CPMG pulse sequence](image)

Figure B-4: Schematic of the PFG-CPMG pulse sequence (modified from 5). This pulse sequence is used to measure the D-T2 maps. π and π/2 are the 180 and 90 degrees pulses, Δ is the diffusion time which is the time between gradient pulses, δ is the gradient pulse duration, TE is the echo spacing.
In this study we used 2D D-T₂ maps, even though the experiment time is longer than PFG experiments. Using 2D maps we can differentiate the water and oil diffusion responses based on their respective T₂ distributions. The 2D maps were measured using 30 ms diffusion time, 5 ms gradient pulse duration, 0.5 T/m maximum gradient and 40 gradient steps. The CPMG part of the pulse sequence is ran using the CPMG pulse sequence for 1d T₂ experiments. Figure B-5 shows an example of the 2D map specifically the 20% water cut emulsion.

Figure B-5: (a) 2D D-T₂ map for 20 vol.% water cut emulsion and (b) corresponding Diffusion coefficient and T₂ distribution extracted from 2D map. In (a) Both water and oil responses are shown distinctively, but separate D and T₂ responses were not able to resolve the differences. The water line is the diffusion coefficient measured for bulk water used in this study and the oil line is calculated based on the correlation by Lo et al. (2002).

The diffusion values are converted to radius using the following approach. The water molecules are restricted by the droplet walls; as a result the measured diffusion is lower than the bulk water diffusion. This reduction in diffusion coefficient value depends on the droplet size and the PFG acquisition parameters. Murday and Cotts (1968) developed a model to relate the echo-signal attenuation to the diffusion coefficient of the fluid in a sphere with specific radius considering the experimental acquisition
parameters (Murday and Cotts 1968). We use this model to calculate the droplet radius using measured diffusion coefficients.

**B.4 Results and Discussions**

In this section we present the results of bubble size distribution using multiple techniques such as microscopy and NMR.

**B.4.1 Microscopy Droplet Size Measurements**

Figure B-6 shows the microscopy images of the water-in-oil emulsions prepared using mineral oil 70T at 10 and 50 vol.% of water cut. Analysis of the microscopy images shows that the numerical average droplet size of this emulsion system is in the range of 2 – 3 μm across all water cut emulsions investigated in this work (Figure B-7). It is to be mentioned here that at each water cut a minimum of 250 water droplets were measured. From these measurements, the average droplet size and its standard deviation was calculated. The error bar in Figure B-7 represents the standard deviation in the measurements. This average droplet size is in agreement with a typical water-in-crude oil emulsion system reported by us and other researchers (Noïk et al. 2002).

The microscopy water droplets size measurement shows that there is minimal change in the size of the water droplets across the water cuts investigated in this work. It is likely that the water droplet size does not change due to the high concentration of surfactant used in this work (Lingwood et al., 2012). Our study shows that the critical concentration of aggregation (CCA), which is, the concentration at which inverse micelles form was measured to be 0.1 wt.% for all water cuts (Delgado-Linares et al., 2013). Thus, the emulsions used in this work were prepared at concentrations above the CCA.
Figure B-6: Microscopy images of mineral oil 70T emulsion system at (a) 10 vol.% and (b) 50 vol.% water cut. Red lines indicate the boundary.

Figure B-7: Microscopy droplet size measurement for mineral oil 70T emulsions at various water cuts (vol.%).

**B.4.2 NMR Droplet Size Measurements**

Figure B-8 shows the T$_2$ distribution for bulk oil and water as well as all the emulsions measured using the CPMG pulse sequence (Figure B-3). Bulk responses show a clear distinction between oil and water T$_2$ distributions (Figure B-8a). When water is emulsified in the oil phase, the T$_2$ response for the discontinuous phase (water
droplet) is affected by the emulsion properties. Figure 8b shows the T<sub>2</sub> response for emulsion samples. The T<sub>2</sub> relaxation times for oil do not change by varying the water cut because oil is the continuous phase. T<sub>2</sub> response for water varies depending on the water cut. The surface relaxivity for the emulsions can be calculated by solving Equation B-3 for ρ. We used the T<sub>2</sub> distribution of the water phase for samples with water cut of 50-70 vol% since they show a distinct peak for water phase. The average surface relaxivity is 0.801 µm/s (Hirasaki and Pena 2003; Fridjonsson et al., 2012). By having this surface relaxivity value, droplet size of any T<sub>2</sub> distribution for this mineral oil and water system can be calculated using Equation B-3. Using this calculated surface relaxivity, the droplet size derived from T<sub>2</sub> distributions and Equation B-3, varies from 3.3 to 4.7 µm which is close to the range of the droplet size measured by diffusion method. The difference is because for low water cut samples (10 to 30 vol%) samples the water T<sub>2</sub> distribution is not distinct from the oil distribution.

Figure B-8: T<sub>2</sub> distribution for (a) bulk oil and water and (b) emulsions at various water cuts.
Figure B-9 shows the numerical average water droplet size across all water cut emulsions studied in this work determined from NMR investigations. As can be seen in Figure B-9, the average droplet size is ~ 4 μm. In this figure, the error bar represents the smallest and largest water droplets detected in these measurements from T$_2$ data. Similarly to the microscopy analysis, the size of water droplets shows minimal change with change in the water cut of the system. As mentioned earlier, the relatively constant water droplet size across the water cuts is likely to be due to the high concentration of surfactant used in this study. However, it should be mentioned here that the minimum water droplet size observed at 50 vol.% water cut is relatively small and thus not significant.

![Figure B-9: NMR droplet size measurements for mineral oil 70T emulsions at various water cuts.](image-url)
B.4.3 Comparison between NMR and Microscopy Results

Figure B-10 shows the comparison of the water droplet size obtained from the two methods used in this work: NMR and optical microscopy measurements. From Figure B-10, the size of the water droplet reported in both methods is in the same order of magnitude, with the NMR method showing a slightly larger droplet size (average of 1 μm larger) as compared to the optical microscopy method. The difference in the size of the water droplet reported by both methods is currently being investigated. Some of the expected error from optical microscopy method includes poor edge detection due to the shadow effects.

Furthermore, it can be seen in Figure B-10 that in both methods, the trend of the water droplets across all water cuts studied is relatively similar; both show a minimum droplet size at 50 vol.% water cut. This shows that the NMR method proposed here is able to measure the water droplet size in emulsion systems. In addition, it should be noted that when comparing the two methods, larger deviation was observed for the microscopy method results as compared to the NMR method. It is thought that this large deviation in the size of the water droplet measured is due to the optical microscopy method that was used. In optical microscopy, actual position of the droplets in the z-axis (vertically) could not be determined. Consequently, the droplets that are far from the lens appear smaller in the pictures taken. The size of the droplets was measured regardless of the vertical position of the droplets size and the result was taken into the calculation of the average droplet size. This resulted to a smaller average droplet size.
Figure B-10: Comparison of NMR and Microscopy water droplet size for all water cuts (vol. %).

**B.5 Conclusions**

Our results have shown that Diffusion-Transverse Relaxation \( (T_2) \) experiments using a low field NMR method can be used to measure the DSD of an emulsion sample. The results obtained from this method were compared with the results obtained from microscopy image analysis techniques. The investigations show that the average droplet size obtained from NMR is on average 1 μm larger as compared to the microscopy technique. However, both methods show a similar trend across the water cuts investigated in this work. There are relatively small changes in the size of the water droplets across the water cuts studied here. The method also allows the determination of average surface relaxivity for water droplets in an oil continuous phase and was calculated to be 0.801 μm/s. The determination of average surface relaxivity of this model emulsion system, allows direct calculation and determination of average water
droplet size in this model system without performing diffusion test. This NMR method will be immensely useful in determining the droplet size of water-in-oil emulsions, and hence provides a simple quantitative approach to assessing gas hydrate slurry formation and hydrate plugging risk.

B.6 Acknowledgement

The authors would like to thank Sophie Godeferoy, Brett Ryland and Paul T. Callaghan from Victoria University of Wellington for providing the inverse Laplace transform program for 2D inversions. The authors would also like to thank Dr. John Ripmeester and Evan McCarney for all the valuable discussion and input that he has provided on this work. Additionally, Ahmad AA Majid would like to thank Universiti Malaysia Pahang and Malaysian Ministry of Education for sponsoring his studies.

B.7 References


