A STUDY ON RESTORATION AND COMPOSITE ARRANGEMENT OF CORE SAMPLES FOR SCAL EXPERIMENTS

By

©Edison Amirtharaj Sripal

A thesis submitted to the school of Graduate Studies in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Faculty of Engineering and Applied Science
Memorial University of Newfoundland

May 2023

St. John's, Newfoundland
Canada

Abstract

Special core analysis (SCAL) programs are designed to meet explicit requirements for the specific reservoir type and lithology. The success of a SCAL program relies on qualitative determination of the petrophysical parameters (density logs, resistivity logs, etc.) and dynamic parameters (wettability, relative permeability, etc.). Since wettability is critical for capillary pressure and relative permeability experiments, coreflood tests cannot be performed until wettability tests have been completed and analyzed. This research develops an optimal method for wettability restoration in reservoir rocks and validation of the appropriate arrangement of the aged core plugs in a composite core arrangement for a successful SCAL program.

An important aspect of preliminary core preparation for SCAL experiments is the restoration of the core sample to its original wettability. The prevalent method for restoration of a core sample, to either strongly oil-wet or weakly oil-wet, is largely dictated by increasing or decreasing the aging time at reservoir temperature. There is no consistent or reliable method ascribed for a specific sedimentary core sample to restore it to its original state that is obtained from preserved core samples. In this study, we identify brine salinity, restoration temperature, and restoration time (age in number of days) as important parameters contributing to wettability. The objective of this work is to determine the optimum level of these independent variables (brine salinity, temperature, and age) for restoring wettability. Additionally, the Box Behnken model of surface response methodology was applied to analyze the effects of these parameters on wettability restoration. Wettability was experimentally validated using a combination of contact angle measurement, USBM tests and SEM imaging (at low vacuum conditions). A seminal effort in applying SEM-MLA image analysis for wettability determination was also explored. The study shows a comprehensive influence of brine salinity,

aging time, and temperature towards wettability restoration. Further, a systematic approach was applied to quantify the degree of uncertainty linked to a) wettability estimation and b) the aging procedure to control wettability in Berea, Silurian dolomite, and chalk. With comprehensive experimental work, we were able to alter the wettability of chalk samples.

Core samples from different depths of an exploration well are often used as composite cores for routine and special core analysis to evaluate the potential of a reservoir. The question is whether or not the order of the core plugs in the composite core makes a difference in the absolute and relative permeability measurements. The seminal work by Huppler (1969) proposed ordering individual core samples harmonically in a composite core in order to match the overall permeability. Langaas (1998) proposed ordering the core samples in decreasing permeability for effective relative permeability measurements, based on a theoretical framework of North Sea sandstones. In this work, we tested the methods proposed by Huppler and Langaas experimentally. The orientation of the core samples was tested for permeability and relative permeability and compared with the theoretical model developed by Langaas. In addition to the experimental work, simulations were performed with four different composite cores and the representative recovery factor was compared to provide the appropriate composite core arrangement.

Acknowledgments

I would like to sincerely acknowledge the support of my family, near and far, for their unwavering support. I would like to give special thanks to my wife Leela Christy, she has been my emotional anchor not only in this Ph.D. endeavor but throughout the last 20 years. I would like to thank my sons Casimir and Abran for their understanding. My son Abran was the fountain of my motivation for this work. If not for his constant accompaniment to the lab during holidays, weekends, and late nights, this PhD work would have been a less memorable experience.

This work could only have been accomplished by the mutual collaboration of many people. I would like to thank Dr. Lesley James. I would like to thank my collaborators Dr. Saeed Jafari and Dr. David Grant for their support in publishing the articles. I would like to thank my colleagues in the Hibernia Enhanced Oil Recovery Research Group for providing all the help.

Co-Authorship Statements

The following people have contributed to the work undertaken as part of this thesis:

Candidate	Edison Sripal	Memorial University
Author 1	Lesley James	Memorial University
Author 2	David Grant	Memorial University
Author 3	Saeed Jafari Daghlian Sofla	Memorial University

Contribution of work by co-authors for each paper:

Paper 1: Application of an Optimization Method for the Restoration of Core Samples for SCAL Experiments **Presented in Chapter 3**

Author contributions:

Design and identification of the research topic	Candidate, Author 1
Practical aspects of the research	Candidate, Author 1
Data analysis	Candidate
Manuscript preparation	Candidate, Author 1

Paper 2: Application of an SEM Imaging and MLA Mapping method as a tool for Wettability restoration in Reservoir Core samples SCAL Experiments Presented **in Chapter 4**

Author contributions:

Design and identification of the research topic	Candidate
Practical aspects of the research	Candidate, Author 1, Author 2
Data analysis	Candidate
Manuscript preparation	Candidate, Author 2

Paper 3: Composite Core- An experimental approach in evaluating ordering criteria for individual cores in composite Presented **in Chapter 5**
Author contributions:

Design and identification of the research topic	Candidate, Author 1
Practical aspects of the research	Candidate, Author 1
Data analysis	Candidate, Author 3
Manuscript preparation	Candidate, Author 3

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1 CHAPTER ONE

Introduction and Overview

Routine (RCAL) and Special Core Analysis (SCAL) data are important for reservoir characterization, and for secondary and tertiary production optimization. RCAL tests include porosity, permeability, lithology, and initial fluid saturation. SCAL tests include wettability, capillary pressure, relative permeability measurements, and coreflooding tests, which often take several months to conduct in order to represent actual flow conditions exhibited in the field. In order to produce quality SCAL data, it is important to select representative cores from each stratum representing the different bedding layers in the reservoir [1]. An important consideration to ensure quality and reliability in SCAL experiments is the restoration of wettability of the core samples. Incomplete core sample restoration may lead to unrealistic estimates of residual oil saturation, which further affects relative permeability and capillary pressure measurements.

Reservoirs are generally considered to be oil-wet and this can be achieved either from native or restored states [2, 3]. Obtaining native-state core samples is challenging both economically and operationally. It requires suspending production, protecting the sample from drilling fluids, and preventing any evaporation or contamination [3-5]. Hence, laboratory experiments are routinely performed on restored-state core samples. The restoration process typically involves cleaning the core sample of any drilling fluid using various solvents rendering it water-wet. The cleaned samples are then saturated with brine at reservoir conditions before they are brought to connate water saturation by saturating it with crude oil to capillary pressure. The oil/brine saturated cores are aged at reservoir conditions. The literature is inundated with various aging strategies, but the conundrum is the lack of a commonly accepted aging process for either sandstones or carbonates [5-8]. In this work, we investigate the effect of three parameters that are generally agreed upon as contributing to the aging process [3-7]: brine salinity, aging time, and aging temperature.

The development of appropriate geological and reservoir simulation models relies significantly on routine and specialized core analysis (SCAL) data. Laboratory relative permeability experiments are carried out on composite cores made by stacking a series of smaller core plugs of length ~1.5 - 2 inches. The resulting composite core is considered as a single core with average physical properties. In the laboratory, composite cores are regularly used to perform coreflooding experiments to determine recovery factors and residual oil saturations after flooding [9].

1.1 Motivation

A common SCAL program can last for months if not for years [1]. A significant portion of this time is spent on aging the reservoir cores and validating the wettability. Any significant reduction in the time required to validate wettability would significantly contribute to reducing cost and effort to characterize the reservoir. In this work, we try to determine the optimal parameters for aging and the threshold duration beyond which the aging does not change the wetting state. This work was attempted on three different rock types such as Berea, Silurian Dolomite, and chalk to assess ageing overall in very different mineral compositions.

The important question in composite core arrangement is what ordering of cores is appropriate for coreflooding experiments. Huppler's [10] criteria of harmonic average of the permeability is often considered the industry norm for composite core preparation. However, there is no consensus [1, 9-11] on choosing either an increasing permeability or decreasing permeability along the flow direction. Often experiments are performed with a composite core composed of samples with decreasing permeability along the flow direction to reduce the time of experimentation and reduce cost. The decreasing permeability allows one to perform the experiment in very short time and thus minimize the expenditure. The assumption is that capillary forces are low in a high permeability system, which is provided by placing the highest permeability cores at the inlet end of the composite.

1.2 Problem statement

The objectives of this work is to examine core preparation techniques to ensure consistent and reliable routine and specialized core analysis procedures. Specifically, we verified a consistent and reliable process for restoring wettability in reservoir rocks for SCAL experiments, developed a new technique to determine wettability and evaluated the appropriate composite arrangement of cores for coreflooding experiments.

1.2.1 Optimal conditions for wettability restoration

1. Identify the parameters that contribute to aging and develop a framework to optimize the aging process for wettability restoration of reservoir rocks for SCAL experiments. In this work we determine the optimal value of the three parameters (aging time, temperature and brine salinity) that are generally agreed upon as contributing to the aging process [2, 8].
2. Determine the appropriate statistical design of experiments such that it provides an understanding of the parametric effects controlling the process with minimum number of experiments. For this work we chose to apply the Box Behnken response surface method (DOE) to optimize the input parameters i.e., aging time, temperature and brine salinity for the desired output parameter i.e., wettability. For a complex experimental

work involving multiple parameters of interest, response surface modeling provides an estimate of the interaction of the input parameters and the effects associated with it, the result a shape of the response surface under investigation

3. Develop a comprehensive suite of wettability measurement experiments using statistical design of experiments (DOE) as a framework. In order to get reliable results from DOE it is important to determine the low limit and high limit of the input parameters such that all practically possible results could be included in the statistical analysis.

1.2.2 New method for wettability validation

The second part of the wettability work is specifically framed for establishing an alternate method for evaluating wettability in reservoir rocks specifically Berea, Silurian Dolomite and chalk.

1. Develop a fast and effective alternative method for wettability measurement in reservoir rocks. For this work we used low vacuum SEM-MLA imaging with core samples saturated with oil and brine
2. Determine the threshold beyond which the aging does not change the wetting state of outcrop chalk, Berea and Silurian dolomite. The main objective is to evaluate to what degree the wettability in chalk can be controlled in the lab.

1.2.3 Composite Core Arrangement

There is no consensus on the ideal orientation of the composite core and the industry is divided in choosing the order of the smaller core plugs in the composite core [9,10].

1. In this work, we attempt to experimentally determine the appropriate method for stacking cores in a composite core made of large permeability range with different porosity and relative permeability of individual cores. Coreflood experiments were performed with reservoir cores and fluids.
2. Coreflood simulations were carried out using different composite core arrangement to understand the effect of mobility ratio on the recovery factor. The objective was to provide a comparative study between experimental and simulated results and recommend the appropriate composite core arrangement

1.3 Thesis structure

Chapter 1 presents the motivation of the study, states the problem and provides the structure of the thesis.

Chapter 2 presents the literature review on wettability and coreflooding with composite core arrangement. This chapter also covers the basic principles in wettability and the experimental methods applied to validate wettability and relative permeability measurements. The experimental methods covered in this chapter are primarily the ones that were carried out in the laboratory.

Chapter 3 been published in the journal Petrophysics. In this paper, we try to determine the optimal value of the three parameters that are generally agreed upon as contributing to the aging process [2, 11]: brine salinity, aging time, and aging temperature. A statistical approach was used to find the optimal values of these parameters to ensure oil-wet characteristics in reservoir rocks for coreflooding experiments.

Chapter 4 has been published in the Journal of Minerals as the special issue on "The Application of Automated SEM-Based Identification of Detrital, Diagenetic and Indicator Mineral Phases". This chapter discusses the application of SEM-MLA as an alternative method of wettability validation by analysing the oil content in reservoir rocks. A suite of Berea, chalk and Silurian dolomite were used for this work, and it was demonstrated that SEM-MLA is effective in comparing wettability data against contact angle and USBM method.

Chapter 5 has been published by the Global Journal of Science and Engineering. This chapter discusses the different orientation of core samples in a composite core for coreflooding experiments. A comparison study between experimental simulation on different composite core arrangement is presented with a recommendation for decreasing permeability arrangement of core samples for reliable coreflooding data.

Chapter 6 contains a summary, conclusions, and recommendations for future work.

1.4 References

1. American Petroleum Institute, 1960, Recommended practice for core analysis procedure: New York, API-RP40, 1st ed. 55p
2. Hirasaki, G.J., Rohan, J.A., Dubey, S.T., & Niko, H., "Wettability Evaluation During Restored-State Core Analysis," (1990), Paper SPE-20506, Presented at the SPE Annual Technical Conferences and Exhibition, New Orleans, Louisiana, USA, 23-26 September.
3. Anderson, W.G., "Wettability Literature Survey - Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability". Journal of Petroleum Technology, (1986) 38, 10, 1125-1144.
4. Anderson, W.G.: "Wettability Literature Survey-Part 2: Wettability Measurement," JPT (Nov. 1986) 1246-62. Anderson, W.G: "Wettability Literature Survey-Part 3: The Effects of Wettability on the Electrical Properties of Porous Media," JPT (Dec. 1986) 1371-78.

5. Anderson, W.G.: "Wettability Literature Survey-Part 4: The Effects of Wettability on Capillary Pressure," JPT (Oct. 1987) 1283-1300.
6. Anderson, W.G.: "Wettability Literature Survey-Part 5: The Effects of Wettability on Relative Permeability," JPT(Nov. 1987) 1453-68
7. Anderson, W.G.. Wettability Literature Survey-Part 6: The Effects of Wettability on Waterflooding. J Pet Technol 39 (1987): 1605–1622. doi: https://doi.org/10.2118/16471-PA
8. Tang. G.Q, and N.R. Morrow, "Influence of Brine composition and Fines Migration on Crude Oil/Brine/Rock Interactions and oil recovery. Journal of Petroleum Science and Engineering. (1999) 24 (2-4):99-111
9. Huppler, J., 1969. Waterflood relative permeabilities in composite cores. J. Pet.Technol. (United States) 21
10. Langaas, K., Ekrann, S., Ebeltoft, E., 1998. A criterion for ordering individuals in a composite core. J. Pet. Sci. Eng. 19 (1), 21–32. https://doi.org/10.1016/S0920-4105(97)00032-6
11. Zekri, A.Y., Almehaideb, R.A., 2006. Relative permeability measurements of composite cores—an experimental approach. Pet. Sci. Technol. 24 (6), 717–736 https://doi.org/10.2118/77939-MS

2 CHAPTER TWO

Literature Review

2.1 Wettability and Aging

The wettability of reservoir rock determines, to a large extent, the location, flow, and distribution of oil, gas and water in a reservoir. These factors, in turn, influence the production of oil and gas, recovery by waterflood, and the performance of enhanced oil recovery processes. An improved understanding of the factors that influence reservoir wettability is vital to provide more accurate predictions of reservoir behavior. Although numerous studies [3-12] have attempted to determine the conditions that control reservoir wettability, many aspects of the process remain unclear to this date. The effect of factors such as temperature, brine composition and pH, initial water saturation, rock mineral composition, crude oil composition, etc. have been investigated, but studies have often produced conflicting or indeterminate results [3, 4-6]. The primary difficulty in using the available literature to discern the factors governing wettability alteration is that varied methods and materials have been used, which make comparisons between studies difficult, if not impossible.

Aging time and temperature are generally considered to be the two most important factors contributing to the aging process. Anderson [4, 5] indicated that 1000 hours (40 days) of aging at reservoir temperature is sufficient for wettability equilibrium based on experiments performed using Berea plugs where wettability changed from water-wet to moderately oil-wet in 40 days. Morrow [11-14], in various water flooding and imbibition studies on Berea samples, observed lowest USBM wettability index values with water when the samples were aged at 80 to 90ºC for 10 days. Torsater [15] identified that short-term imbibitions were significantly reduced by shortened aging time but aging at high temperature (90ºC) yielded more recovery. Carbonates, being natural slightly oil-wet, were shown to display oil-wet attributes when aged for only 2 days at 90ºC [16]. Graue et al. [17] reported that a stable wettability was obtained for chalk samples aged more than 14 days using brine and crude oil. A similar work was reported on Rordal chalk samples [18].

During the aging process, it is important to saturate the core with brine prior to oil to ensure the wettability effects due to brine chemistry are not ignored. Numerous studies have been reported in the literature describing the effect of brine salinity on aging by changing the concentration and composition. The brine salinity with higher concentrations of monovalent and divalent ions like Na and Ca affects wettability. They can reduce the solubility of the crude surfactants and promote adsorption at the mineral surface causing the system to become more oil wet. Tang and Morrow [11] identified that increasing brine salinity had a significant effect on altering wettability in Berea sandstone. Vijapurapu et al. [19] investigated the effect of various dilutions of brine on oil wettability and found that there was a threshold brine concentration for wettability alteration. Chattopadhyay [20] varied the concentration of brine (4% to 20% NaCl) and found increasing wettability altering behavior with increasing NaCl concentration. Similar trends were observed by Jadhunandan and Morrow (1995) [21] on Berea, exhibiting more oil-wet characteristics when aged with increasing brine salinity.

In addition to the above-mentioned parameters, many different oils and minerals have been utilized in various studies, and compositional effects have also been found to play an important role in determining system wettability. In addition, many studies [4-7] have investigated the effects of crude oil fractions by fractionating the crude and then dissolving the fraction in a suitable solvent. Asphaltene and resin fractions that are re-dissolved in a solvent, however, are in a very different environment than that provided by the crude. A dominant factor in the wettability alteration is the surface adsorption of asphaltenes which is further controlled by brine -oil composition, rock chemistry and rock fluid interactions.

Wettability is of paramount importance in oil recovery from low permeability chalk as it controls the flow and distribution of fluids [22]. Another impediment is that there is no standard method for the measurement of wettability. Many different techniques have been employed to assess the wettability of a system, and each measure somewhat different properties. The most common quantitative methods are contact angle measurement and fluid imbibition/displacement procedures such as the Amott and USBM methods. According to Anderson [4,5], for an oil-brine-rock system, the rock is classified as water-wet if the contact angle between a water droplet and rock is $< 75^{o}$, intermediate-wet if the contact angle is between 75-100^{o} and oil-wet if the contact angle is 105-180^{o}. This wettability characterization, using the contact angle method, has been successfully applied on carbonates [11], sandstones and shales [22]. USBM wettability index is calculated from the drainage and imbibition capillary pressure curves. Robin [13] demonstrated a qualitative differentiation between oil-wet to water-wet capillary pressure curves. For a reservoir rock to be deemed oil-wet, the wettability index has to be -1. Lately, USBM wettability methods are increasingly applied to understand the wettability nature of shale formations in unconventional oil production [3, 23, 25]. In addition to the above two methods, digital imaging methods like SEM analysis are increasingly applied for wettability characterization. CRYO SEM and ESEM methods [26-29] were initially used to analyse wettability in rocks and packed glass beads that were saturated with reservoir fluids. But these analyses were not accurate as it often compromised the sample integrity due to extreme changes in the physical state because of cooling and polishing. In a seminal effort, we applied SEM-MLA method by testing the sample without any changes in its physical state [30]

2.2 Basic Principles

Wettability can be defined as the tendency of a fluid to spread on and preferentially adhere to, or wet, a solid surface in the presence of other immiscible fluids. Wettability of a porous medium governs the relative distribution of fluids in the pores and has considerable influence on the conditions in which reservoir fluids flow, changing the this wettability state subsequently leading to the recovery of hydrocarbons. Although strongly water-wet and truly oil-wet reservoirs do exist, most reservoirs are at a wettability state intermediate between water-wet and oil-wet [30-31]. Wettability is measured using reservoir fluid samples, the wettability is reported in terms of a certain wettability index, signifying the degree of water, oil wetness, or intermediate wetness. There are several methods for quantitatively measuring the wettability of a rock/fluid system. The most commonly applied methods are (a) contact angle method, (b) Amott's test, and (c) USBM method [31].

2.2.1 Contact Angle Measurement

Contact angle measurement involves the direct observation of wetting angles on small rock samples by microscopic observation. One of the most popular methods for measuring the contact angle is the 'sessile drop method', which involves depositing a liquid drop on a smooth solid surface and measuring the angle between the solid surface and the tangent to the drop profile at the drop edge. Figure 2-1 shows a schematic diagram of a liquid drop spreading on a solid surface. As shown in Figure 2-1, as the contact angle decreases, the wetting characteristics of the liquid increase. Complete wettability would be evidenced by a zero contact angle, and complete non-wetting (oil-wet) would be evidenced by a contact angle of 180°. Table 2-1 is a summary of the contact angle ranges within which a rock surface is considered water-wet, oil-wet or neutrally wet [31].

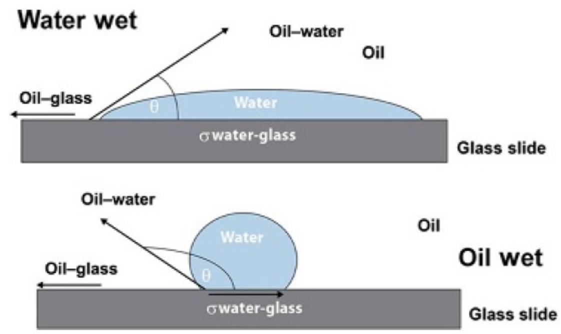


Figure 2-1: Illustration of wettability measurement through contact angle [31]

Table 2-1: Wettability classification according to contact angle measurement [31]

	Water Wet	Neutrally Wet	Oil Wet
Minimum	0º	60-75º	105-120º
Maximum	60-70º	105-120º	180º

2.2.2 Amott Test

The Amott test determines wettability based on the displacement properties of the oil-water-rock system including natural and forced displacement of oil and water from a given core sample [31].

1. The test begins with a residual oil saturation in the core obtained by forced displacement of oil (Primary Drainage). The average wetting characteristic of the core sample following a procedure that involves four displacement operations as demonstrated in Figure 2-2.
2. Immersion of the core sample in oil to observe the spontaneous displacement of water by oil (spontaneous drainage) carried out in the Amott cell.
3. Forced displacement of water by oil by applying a high displacement pressure (forced drainage) carried out in the refrigerated centrifuge.

4. Immersion of the core sample in water to observe the spontaneous displacement of oil by water (spontaneous imbibition) carried out in the Amott cell.

5. Forced imbibition (displacement) of oil by water carried out in the refrigerated centrifuge.

The volume of water and oil released in the spontaneous and forced displacement steps are recorded. The core sample wettability is determined as follow

$$\boldsymbol{\partial_W = V_{WS}/V_{WT}} \tag{1}$$

$$\boldsymbol{\partial_O = V_{OS}/V_{OT}} \tag{2}$$

where,

V_{WS} = Volume of water spontaneously displaced by oil (spontaneous imbibition),

V_{WF} = Volume of water released by forced displacement of water by oil (Forced imbibition),

V_{WT} = V_{WS}+V_{WF} Volume of water from spontaneous and forced displacement,

V_{OS} = Volume of oil spontaneously displaced by water (Spontaneous drainage),

V_{OF} = Volume of oil released by forced displacement of oil by water (forced drainage),

V_{OT} = V_{OS}+ V_{OF} = Volume of oil from spontaneous and forced displacement, and

∂_W and ∂_O are used as used at wettability indices.

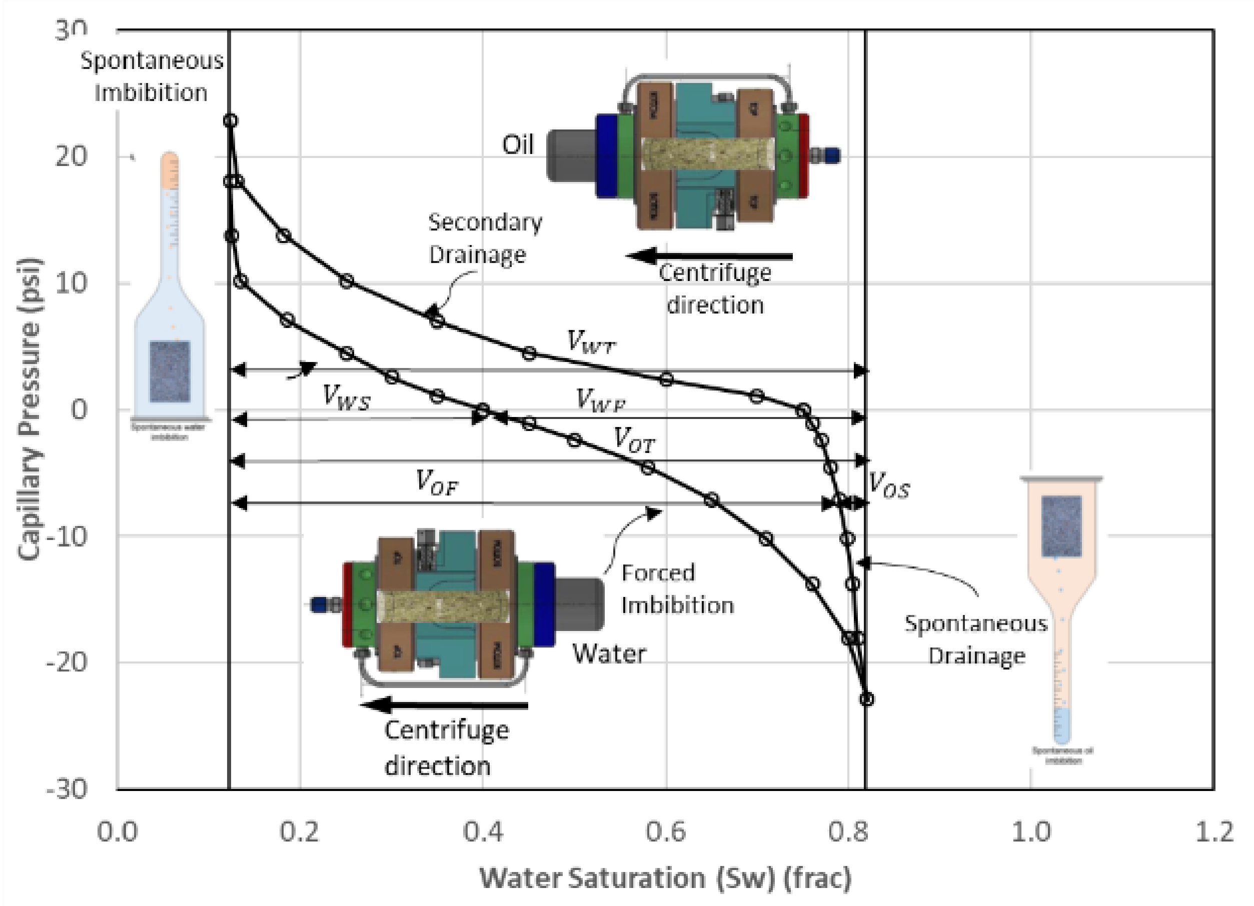


Figure 2-2: Schematic of wettability measurements throughout the Amott test

The wetting preferences of the tested core samples are characterized according to the general criteria shown in the Table 2-2 below:

Table 2-2: Wettability ratios by Amott test [31]

Displacement Ratio	Water Wet	Neutral Wet	Oil Wet
δ_O	0	0	Positive
δ_W	Positive	0	0

In addition to the criteria outlined in Table 2, a distinction is also made between strong and weak oil or water wetting preferences of the core sample, i.e. δ_O approaching 1 indicates strong oil wetness whereas a value of δ_O approaching 0 indicates weak preference for oil wet [31].

2.2.3 USBM Wettability Measurement

The U.S. Bureau of Mines (USBM) method is entirely conducted in a centrifuge apparatus. The test begins by establishing the connate water saturation in the core plug sample. Irreducible water saturation in the core sample is obtained by centrifuging the water saturated sample under the displacing oil phase at high speeds. The displacement of water by oil is monitored and centrifugation is continued until equilibrium is achieved, which is indicated by zero fractional water production or by a plateau in the cumulative water production versus time curve [32]. The volume balance is used to calculate the irreducible water saturation. Once the core sample is prepared at irreducible water saturation, wettability determination begins with the first step in which cores are placed in brine and centrifuged at incrementally increasing speeds. This step is also known as the water drive as brine displaces oil from the core (Figure 2-3). Water saturation is determined at each constant speed of the centrifuge [33, 34]. Capillary pressure is calculated from the equation below:

$$\boldsymbol{P_C} = \frac{\Delta\rho}{2}\left[\frac{2\pi N}{60}\right]^2 (\boldsymbol{R_{EXT}}^2 - \boldsymbol{R_{INT}}^2) \tag{3}$$

where,

$\boldsymbol{P_C}$ = Capillary pressure in Pascal,

$\boldsymbol{\Delta\rho}$ = Density difference between the wetting fluid and non-wetting fluid in Kg/m^3,

$\boldsymbol{N}$= rotations speed in revolutions per minute (rpm),

$\boldsymbol{R_{EXT}}$ = Distance between the rotating axis and the outer face of the core sample in m, and

$\boldsymbol{R_{INT}}$ = Distance between the rotating axis and the inner face of the core sample in m.

In the second and final step, the core is placed in oil and centrifuged. During this oil drive step, oil displaces brine from the core. The water saturation and the capillary pressures are calculated at each incremental centrifugation speed in a manner similar to first step [34]. After completion of these two steps, the capillary pressure is plotted against the water saturation as indicated in the curve in Figure 2-3.

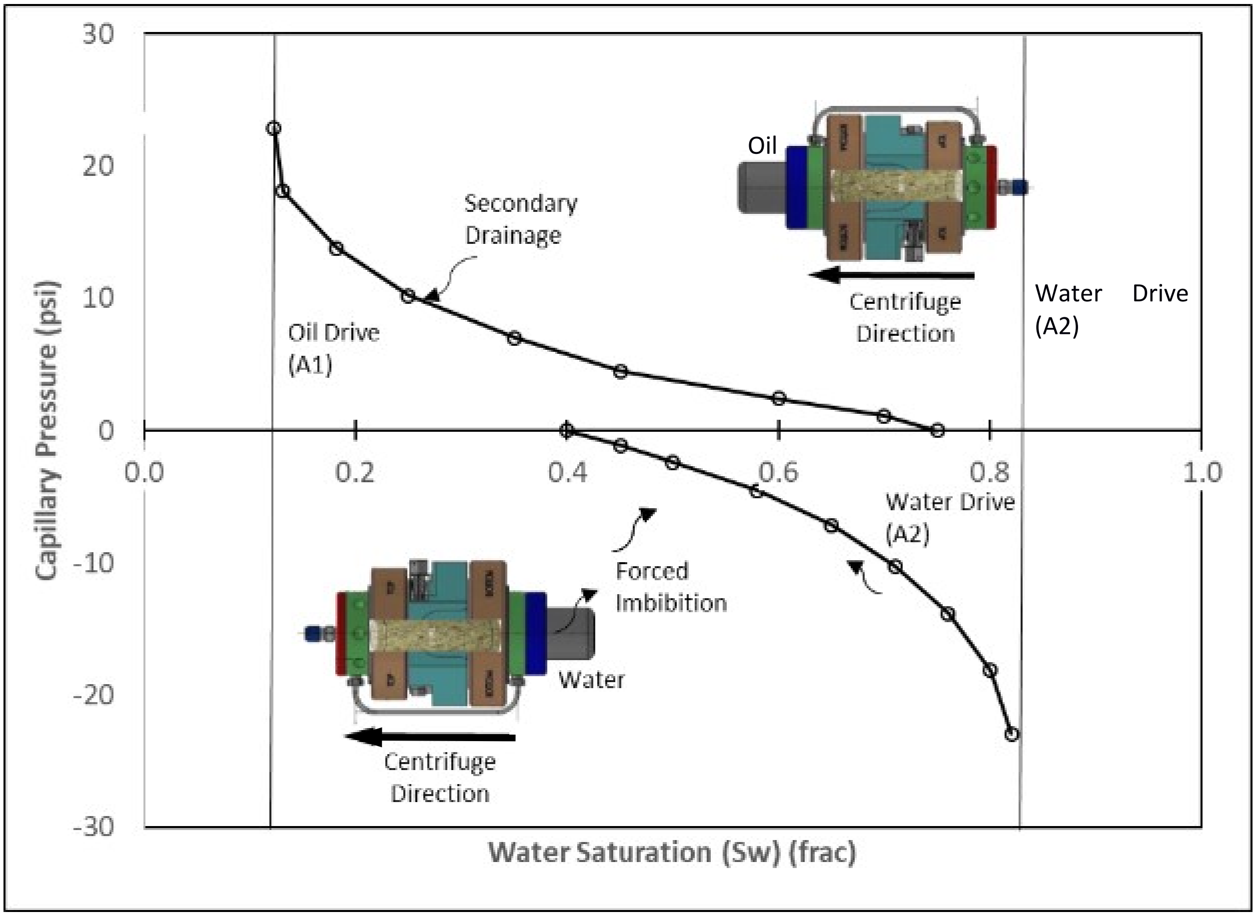


Figure 2-3: Schematic of wettability measurement by USBM method

The USBM wettability index (I_{USBM}) is then calculated from the ratio of the area under the two effective pressure curves according to the following equation

$$\boldsymbol{I_{USBM}} = \mathbf{log}\left(\frac{A_1}{A_2}\right) \quad (4)$$

where

A_1 = area under the oil curve, and

A_2 = area under the water curve.

If $I_{USBM} > 0$, the core is water wet, and if $I_{USBM} < 0$, the core is oil wet.

2.3 Composite core arrangement

The ability of two or more fluids to flow through a reservoir depends on several factors, such as absolute permeability and fluid saturations in the formation. Relative permeability is the function used to describe the saturation dependence of multi-phase flow. This affects numerous reservoir characteristics such as displacement efficiency, watercut, reservoir pressure gradients, well production and injection strategies. Relative permeability is the most dominant parameter controlling reservoir performance, but it is difficult and expensive to measure. The alternative to using single large cores is selected core plugs acting as composite core through as special core analysis program. An important aspect of using composite core samples for lab scale experiments is to determine the relative permeability, which determines the recovery of fluids from reservoir simulated through coreflooding experiments.

Coreflooding and more specifically relative permeability experiments, are generally conducted at steady state or at unsteady state conditions. In the steady state method, a fixed ratio of fluids are injected until the pressure and saturation equilibria are reached. The steady state method is laborious, time consuming and more expensive, which is often circumvented by taking the unsteady state relative permeability measurements route. The advantage of unsteady state relative permeability measurements over steady state experiments is that they do not explicitly depict the reservoir flow mechanism of one fluid displacing another [35]. The steady state method is preferred by some investigators as unsteady state experiments are difficult to process, as data is limited to a smaller range of saturations and/or fluid flow conditions, making extrapolation (relative permeability models) over the entire saturation range uncertain. Additionally, experiments are performed at higher flow rates to overcome the capillary pressure gradient effects, which results in non-uniform sweep and limited saturation range.

Civan and Donaldson [36] overcome the requirement of running unsteady state experiments at high flow rates by accounting for capillary pressure effects using a semi-analytical approach. This semi-analytical approach is not immune to the errors arising from numerical differentiation and integration [37].

Empirical models coupled with history matching was often used a tool to determine and tune the continuous relative permeability function as a way to overcome complexities involved in experimental and interpretation methods [38]. The limited range of experimental data from unsteady state methods is extrapolated and fit over the entire saturation range by choosing a relative permeability model and matching coreflooding and simulation production data [39]. The relative permeability curve obtained form these methods provided the data for the complete saturation range [40, 41].

Huppler [1] developed an introductory work on composite core arrangement for coreflooding experiments based on the permeability of individual cores. The sequence of ordering of the cores was based on the criterion that average permeability between two adjacent cores must be close to the harmonic average of the overall permeability. As an example, a composite core will be ordered as 100, 40, 80, and 60 mD with a combined harmonic average of ~62 mD. It must be noted that Huppler neglected capillary effects and considered equal relative permeability and porosity for all the core plugs in the composite core. Alternately, a sequence of decreasing permeability in the composite core was proposed by Langaas et al. [2] based on a numerical study of sandstone samples from the North Sea. The permeability of the cores ranged from 400 to 1000 mD with the assumption that porosity and relative permeability were the same for all core plugs. Considering capillary effects with a water-to-oil ratio of 0.4:2.4 and an injection rate of 2.53 ml/min, three different sequence types were studied, i.e ascending, descending, and the Huppler criteria. Unsteady state core flooding experiments were simulated, and relative permeability was calculated using the JBN (Johnson, Bossler & Naumann) method [42]. Based on this simulation work, Langaas et al. proposed that ordering by decreasing permeability along the flow direction, i.e the sample at the inlet has the highest permeability and the sample at the outlet has the lowest permeability, provided the best estimate for residual oil saturation. Langaas also tried varying the water viscosity from 0.4 to 14 cP and found no real change in the shape of the relative permeability curves and, as expected, oil recovery increased (decreasing S_{or}) with increasing water viscosity. Watson [41] and Ohen [42] proposed a cubic spline representation of relative permeability data for matching results from unsteady state method using composite cores.

Zekri et al. [35] extended Langaas' numerical study to an experimental approach. Zekri et al. performed unsteady state relative permeability experiments on a suite of carbonate cores from the United Arab Emirates (UAE) with permeabilities ranging from 0.55 to 30 mD. The composite core order was compared based on recovery factor alone. Decreasing permeability order resulted in the highest recovery factor when the water-to-oil viscosity ratio was 1:15. In a similar approach, Mohammadi et al. [41] proposed ordering cores with increasing permeability along the flow direction to produce a high recovery factor for a waterflood experiment on carbonate cores. It should be noted that ordering the composite cores to achieve the highest recovery factor is an artificial criterion and the criterion should perhaps be more realistically based on injection and production well placement and reservoir drainage strategies [43].

Siddiqui et al. [12] proposed a comprehensive protocol to select representative core plug samples for SCAL experiments based on a combination of reservoir zonation, heterogeneity analysis and application of RQI (Reservoir Quality Index) techniques. This set of stringent requirements are generally compromised as the bedding planes being along the small dimension of the whole core so that only short core samples are available for laboratory experiments. These are due to restriction imposed by monitoring authorities like CNLOPB to extract only small core plugs from the large 6" cores. The results from experiments using short cores of few inches long often result in poor material balance accuracy due to infrequent flaws in the core and a greater influence of undesired end effects. Composite cores are constructed by series arrangement of small core plugs (~1.5 - 2") drilled parallel to the bedding plane [12] to overcome all these shortcomings. It often involves having capillary bridges between samples to overcome capillary end effects under triaxial compression to increase the relative accuracy of volume measurements [44].

2.3.1 Relative Permeability Measurement

Relative permeability on core samples can be determined by three test methods

1. Unsteady state method
2. Steady state method
3. Centrifuge

2.3.1.1 Unsteady State Method

The unsteady state permeability measurement is a dynamic displacement test. The main objectives of this test are to define the end-point effective permeability, determine the incremental production data and a section of the relative permeability curves. The core sample to be tested is placed in a coreholder under a predetermined net confining stress (net overburden pressure). Prior to starting the test, the core sample should be pre-conditioned to achieve representative initial water saturation and wettability. The experiment is performed at reservoir condition i.e. constant temperature, overburden pressure and back pressure (reservoir pressure). In this test initially single phase is injected at the inlet of the core and the displaced phase is produced at the outlet of the core at the same rate as the injected phase. This process continues until the injected phase is produced at the outlet of the core. The point at which the injected phase is first observed exiting the outlet face is called breakthrough. After breakthrough, both injected and displaced phases are produced and the displaced phase production becomes a curve. The initial "end-point" effective permeability (to oil or gas at S_{wi}) is measured. Fluid injection is often performed at a constant pressure or constant rate until about 99% water cut. The final end-point effective permeability to the displacing phase is measured at the residual saturation of the displaced phase [47]. If end points only are required, only total production volumes are recorded. For relative permeability curves, incremental production data (vs. injection volumes) must be acquired. End-point permeability is determined using Darcy's law. The intermediate relative permeability data are determined either analytically using JBN or Jones and Roszelle methods [48-51] or numerically (via coreflood simulation). Odeh and Dotson [33] suggested a modification of Jones and Roszelle graphical technique that accounts for capillary end effects. Tao and Watson [55] completed an extensive analysis of propagation of errors through the JBN (Johnson, Bossler & Naumann) method. Additionally, Tao and Watson proposed numerical routines for improving the accuracy of JBN method.

2.3.1.2 Steady State Method

The steady state permeability test is also a dynamic displacement test. The main objective is to define the intermediate relative permeability curves, especially at low saturation values of the displacing phase. In the steady state test, a sequence of fixed ratios of fluids are injected into the core until saturation and pressure equilibrium is established at each ratio. Both end points and intermediate relative permeability to both phases are calculated using Darcy’s law once fluid flow reaches steady state (i.e. stable differential pressure and stable saturation). This technique assures that flow and saturation equilibrium are achieved before making the final readings of flow rate and pressure differential. Differential pressure, injection rates and/or production rates are recorded throughout the test. Saturations are determined by volumetric or gravimetric measurements [53].

2.3.1.3 Centrifuge Method

The centrifuge can be used to generate relative permeability data. The main advantages of the centrifuge method are faster and more efficient drainage, and the ability to measure low relative permeability values closer to residual saturations. But, the disadvantage is that only relative permeability of the displaced phase is generated. For example, water displacing oil is used to produce the imbibition relative permeability to oil K_{ro} and oil displacing water is used to produce drainage K_{rw}. The table below summaries the advantages and disadvantages between different methods [53].

Table 2-3 Pc methods – Advantages and Disadvantages

Method	Advantages	Disadvantages
Centrifuge	• Applicable to most rock types • Simple and quick • Non-destructive test • Uses synthetic reservoir fluids	• Most expensive method • Raw production data needs to be corrected by the test lab
Porous Plate	• Best method to achieve a uniform saturation profile • Uses synthetic reservoir fluids • Non-destructive test	• Time-consuming to achieve a complete Pc curve • Time allowed to achieve equilibrium can completely govern the resultant curve
Mercury Porosimetry	• Low-cost technique • Rapid tests	• Not representative of reservoir fluids • Test is destructive (mercury remains in sample)

The centrifuge technique for measuring relative permeability is a simple extension of the centrifuge technique for measuring capillary pressure where the fluid produced as a function of time for each rotational speed is analyzed to determine the relative permeability curves. Data collection is the same as the capillary pressure experiment except that the frequency of data capture is greatly increased, particularly just after the speed of rotation is changed.

The technique uses a series of pre-selected rotational speeds. The centrifuge is rapidly accelerated to the first speed and held at that speed until production ceases. The centrifuge is then rapidly accelerated to each successive speed, allowing for production to cease at each step. This experiment is therefore the same as that used to determine capillary pressures; however, in addition to measuring the equilibrium production at each speed, production is measured as a function of time throughout the experiment. The equilibrium points at the end of each speed period may be analyzed independently of the transient stages to determine the capillary pressure. The transient stages of the curve are very sensitive to relative permeabilities.

Therefore, multi-speed experiments can be used to determine both capillary pressures and relative permeabilities [54, 56].

Two techniques are used to analyse production data to obtain relative permeability curves: the Hagoort (1980) [50] method and numerical simulation. The Hagoort method is based on three assumptions: i) that the effects of capillary pressure are negligible except near the equilibrium point (a correction procedure is available); ii) that the acceleration is uniform along the sample; and iii) that the mobility of the non-wetting component is infinite. The preferred technique is to use the simulation of the production data together with a relevant capillary pressure.

2.4 References

1. Huppler, J., 1969. Waterflood relative permeabilities in composite cores. J. Pet.Technol. (United States) 21
2. Langaas, K., Ekrann, S., Ebeltoft, E., 1998. A criterion for ordering individuals in a composite core. J. Pet. Sci. Eng. 19 (1), 21–32. https://doi.org/10.1016/S0920-4105(97)00032-6
3. Hirasaki, G.J., Rohan, J.A., Dubey, S.T., & Niko, H., "Wettability Evaluation During Restored-State Core Analysis," (1990), Paper SPE-20506, Presented at the SPE Annual Technical Conferences and Exhibition, New Orleans, Louisisana, USA, 23-26 September.
4. Anderson, W.G., "Wettability Literature Survey - Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability". Journal of Petroleum Technology, (1986) 38, 10, 1125-1144.
5. Anderson, W.G.: "Wettability Literature Survey-Part 2: Wettability Measurement," JPT (Nov. 1986) 1246-62.
6. Anderson, W.G: "Wettability Literature Survey-Part 3: The Effects of Wettability on the Electrical Properties of Porous Media," JPT (Dec. 1986) 1371-78.
7. Anderson, W.G.: "Wettability Literature Survey-Part 4: The Effects of Wettability on Capillary Pressure," JPT (Oct. 1987) 1283-1300.

8. Anderson, W.G.: "Wettability Literature Survey-Part 5: The Effects of Wettability on Relative Permeability," JPT(Nov. 1987) 1453-68
9. Anderson, W.G.. Wettability Literature Survey-Part 6: The Effects of Wettability on Waterflooding. J Pet Technol 39 (1987): 1605–1622. doi: https://doi.org/10.2118/16471-PA
10. American Petroleum Institute, 1960, Recommended practice for core analysis procedure: New York, API-RP40, 1st ed. 55p.
11. Tang. G.Q, and N.R. Morrow, “Influence of Brine composition and Fines Migration on Crude Oil/Brine/Rock Interactions and oil recovery. Journal of Petroleum Science and Engineering. (1999) 24 (2-4):99-111.
12. Siddiqui, S., Okasha, T. M., Funk, J. J., & Al-Harbi, A. M. (2006, December 1). Improvements in the Selection Criteria for the Representative Special Core Analysis Samples. Society of Petroleum Engineers. doi:10.2118/84302-PA
13. Zhou, X., Morrow, N.R., & Ma, S. (2000). Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding. Society of Petroleum Engineers. doi:10.2118/62507-PA
14. Zhou, X, Torsaeter, O, Xie, X, & Morrow, N.R. (1995). The Effect of Crude-Oil Aging Time and Temperature on the Rate of Water Imbibition and Long-Term Recovery by Imbibition. Society of Petroleum Engineers. doi:10.2118/26674-PA
15. Torsater, O, Engeset, B, Hendraningrat, L, & Suwarno, S, Improved Oil Recovery by Nanofluids Flooding: An Experimental Study. Society of Petroleum Engineers. (2012) 163335
16. Alotaibi, M.B., Azmy, R., & Nasr-El-Din, H.A. (2010, January 1). Wettability Challenges in Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/129972-MS
17. Graue, A., Viksund, B.G., & Baldwin, B.A., “Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk,” (1999), Society of Petroleum Engineers. doi:10.2118/55904-PA
18. Zangiabadi, B., Korsnes, R.I., Madland, M.V., Hildebrand-Habel, T., Hiorth, A., & Kristiansen, T.G., “Mechanical Properties of High And Lower Porosity Outcrop Chalk At Various Wetting States,” (2009), Presented at Asheville 2009, the 43rd US Rock

Mechanics Symposium and 4th US-Canada Rock Mechanics Symposium, Asheville, NC, 28 June-1 July

19. Vijapurapu, C.S., & Rao, D.N. (2003). Effect of Brine Dilution and Surfactant Concentration on Spreading and Wettability. Society of Petroleum Engineers. doi:10.2118/80273-MS
20. Chattopadhyay, S, Jain, V, & Sharma, M.M. (2002). Effect of Capillary Pressure, Salinity, and aging on Wettability Alteration in Sandstones and Limestones. Society of Petroleum Engineers. doi:10.2118/75189-MS
21. Jadhunandan, P.P., & Morrow, N.R. Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems. Society of Petroleum Engineers. (1995) 22597
22. Alvarez, J. O., & Schechter, D. S. (2016, April 11). Altering Wettability in Bakken Shale by Surfactant Additives and Potential of Improving Oil Recovery During Injection of Completion Fluids. Society of Petroleum Engineers. doi:10.2118/179688-MS
23. Andersen, P.O., Ahsan, R., Evje, S., Bratteli, F., Madland, M.V., & Hiorth, A., “A Model for Brine-Dependent Spontaneous Imbibition Experiments with Porous Plate,” (2013), Society of Petroleum Engineers. doi:10.2118/164901-MS
24. Fogden, Andrew and Evgenia V. Lebedeva. "Changes in Wettability State Due to Waterfloodin." Petrophysics 53 (2012): 420–429Lichaa, P.M., Alpustun, H., Abdul, J.H., Nofal, W.A., and Fuseni, A.B.: “Wettability Evaluation of a Carbonate Reservoir Rock,” Advances in Core Evaluation IIIReservoir Management, Worthington, P.F. and Chardaire-Riviera, C. (eds.), Gordon and Breach Science Publishers, Great Britain (1992).
25. Loahardjo, N, Winoton, & Morrow, N.R. (2013). Oil Recovery from Bentheim Sandstone by Sequential Waterflooding and Spontaneous Imbibition. Society of Petrophysicists and Well-Log Analysts.
26. Kumar, M., Fogden, A., Senden, T., & Knackstedt, M.A., “Investigation of Pore-Scale Mixed Wettability,” Paper SPE-129974, SPE Journal, (2012), 17, 1, 20–30. doi: 10.2118/129974-PA.
27. Dodd Nicole, Marathe, Rohini, Middleton, Jill, Fogden, Andrew, Carnerup, Anna, Knackstedt, Mark, Mogensen, Kristian, Marquez, Xiomara, Frank, Soren, Bounoua, Noureddine, and Rashed Noman. "Pore-Scale Imaging of Oil and Wettability in Native-State, Mixed-Wet Reservoir Carbonates." Paper presented at the International Petroleum

Technology Conference, Doha, Qatar, January 2014. doi: https://doi.org/10.2523/IPTC-17696-MS\

28. Robin, M., Combes, R., Degreve, F., & Cuiec, L., "Wettability of Porous Media from Environmental Scanning Electron Microscopy: From Model to Reservoir Rocks", (1997), Paper SPE-37235, Presented at the International Symposium on oilfield Chemistry, Houston, Texas, USA, 18-21 February.
29. Schmatz, J., Klaver, J., Jiang, M., & Urai, J.L., "Nanoscale Morphology of Brine/Oil/Mineral Contacts in Connected Pores of Carbonate Reservoirs: Insights on Wettability From Cryo-BIB-SEM," (2017), Society of Petroleum Engineers. doi:10.2118/180049-PA
30. Sripal, E., and James, L.A., "Application of an Optimization Method for the Restoration of Core Samples for SCAL Experiments," Petrophysics, (2018) 59, 1, 72-81.
31. McPhee C., Reed, J., & Zubizarreta, I., Core Analysis: A Best Practice Guide, Elsevier, Amsterdam, Netherlands, (2015), 64, 313-345
32. Forbes,P.L., 1997, Centrifuge Data Analysis Techniques: An SCA Survey on the Calculation of Drainage Capillary Pressure Curves from Centrifuge Measurements, paper SCA 1997 – 14, Presented at The International Symposium of the Society of Core Analysts, Calgary, Canada.
33. Forbes,P.L, Chen, Z.A., and Ruth D.W., " Quantitative Analysis of Radial Effects on Centrifuge Capillary Pressure Curves," Paper SPE 28182, Presented at the 69th SPE annual conference in New Orleans, LA, 25-28 September 1994.
34. Ranjan, R.R., "Theoretically Corret Analyticl Solution for Calculating Capillary Pressure Saturation From Centrifuge Experiments," Paper presented at the SPWLA 1986 annual loggin symposium. June 9-13.
35. Zekri, A.Y., Almehaideb, R.A., 2006. Relative permeability measurements of compositecores—an experimental approach. Pet. Sci. Technol. 24 (6), 717–736 https://doi.org/10.2118/77939-MS
36. Civan, F., Donaldson, E., 1989. Relative permeability from unsteady-state displacements with capillary pressure included. SPE. Form. Eval. 4 (2), 189 –193. https://doi.org/10.2118/16200-PA

37. Hussain, F., Cinar, Y., Bedrikovetsky, P.G., 2010. Comparison of methods for drainage relative permeability estimation from displacement tests. In: SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers
38. Aziz, K., Settari, A., 1979. Petroleum Reservoir Simulation. Applied Science Publ. Ltd., London, UK.
39. Brooks, R.H., Corey, A.T., 1964. Hydraulic properties of porous media and their relation to drainage design. Trans. ASAE 7 (1), 26 – 0028. https://doi.org/10.13031/2013.40684
40. Ghazanfari, M., Khodabakhsh, M., Kharrat, R., Rashtchian, D., Vossoughi, S., 2006.Unsteady state relative permeability and capillary pressure estimation of porousmedia. In: XVI International CMWR Conf., Denmark.
41. Watson, A., Richmond, P., Kerig, P., Tao, T., 1988. A regression-based method for estimating relative permeabilities from displacement experiments. SPE. Res. Eng. 3 (03), 953–958. https://doi.org/10.2118/15064-PA
42. Johnson, E., Bossler, D., Naumann, V., 1959. Calculation of relative permeability from displacement experiments. Trans. AIME 216, 370 –372.
43. Alamooti A.M., Ghazanfari. M., Masihi. M., investigating the relative permeability behaviour in presence of capillary effect in composite core systems. Journal of Petroleum Science and Engineering 160 (2018) 341 – 350 350.
44. Tarek, A., 2007. Reservoir Engineering Handbook. Elsevier
45. Li, K., Shen, P., Qing, T., 1994. A new method for calculating oil-water relative permeabilities with consideration of capillary pressure. Mech. Pract. 16 (2), 46–52.
46. Richmond, P., Watson, A., 1990. Estimation of multiphase flow functions from displacement experiments. SPE Res. Eng. 5 (1), 121-127. https://doi.org/10.2118/18569-PA.
47. Hassler, G.L., & Brunner, E. “Measurement of capillary pressures in small core samples,” Trans. AIME, (1945) 160, 114-123.
48. Jones, S., Roszelle, W., 1978. Graphical techniques for determining relative permeability from displacement experiments. J. Pet. Technol. 30 (05), 807 –817. https://doi.org/10.2118/6045-PA
49. Corey, A.T., 1954. The interrelation between gas and oil relative permeabilities. Prod. Mon. 19 (1), 38–41.

50. Hagoort, J.: “Oil Recovery by Gravity Drainage”, SPEJ, June 1980, p 139-150
51. Honarpour, M., Koederitz, F., Herbert, A., 1986. Relative Permeability of Petroleum Reservoirs. CRC Press, Boca Raton, Fl.
52. Buckley, S.E., Leverett, M., 1942. Mechanism of fluid displacement in sands. Trans. AIME 146 (01), 107 –116.https://doi.org/10.2118/942107-G
53. Bursey.B.J., Mohagheghian. E. , Sripal. E. and James. L.A., Prediction of centrifuge capillary pressure using machine learning techniques, paper SCA 1997 – 14, Presented at The International Symposium of the Society of Core Analysts, Austin, USA.
54. Toth, J., Bodi, T., Szucs, P., Civan, F., 1998. Practical method for analysis of immiscible displacement in laboratory core test.
55. Ruth D and Wong S., 1991 "Calculation of Capillary Pressure Curves from data obtained by the Centrifuge method.'" The Log Analyst, V 31, no.5, 575-582.
56. Forbes P., 1991, Simple and accurate methods for converting centrifuge data into drainage and imbibiton capillary pressure curves, SCA-107, in 5th Annual Conference Transactions: Society of Professional Well Log Analysts, SCA Chapter-at-large v3, 15p

3 CHAPTER THREE

Application of an Optimization Method for the Restoration of Core Samples for SCAL Experiments (Paper 1, Published)

This chapter is an edited version of the article **published in Petrophysics**; Sripal, Edison, and L. A. James. "Application of an Optimization Method for the Restoration of Core Samples for SCAL Experiments." Petrophysics 59 (2018): 72–81.

Abstract

An important aspect of preliminary core preparation for SCAL experiments is the restoration of core sample to its original wettability. The prevalent method for restoration of core sample to either strongly oil-wet or weakly oil-wet is largely dictated by increasing or decreasing the time of ageing at reservoir temperature. There is no consistent or reliable method ascribed for a specific sedimentary core sample to restore to its original state which is obtained from preserved core samples. In this study we have identified three important parameters, brine salinity, restoration temperature, and restoration time (age in number of days) as contributing to wettability. The objective of this study was to determine the optimum level of these independent variables (brine salinity, temperature, and age) for restoring wettability. In this paper we extend the Box Behnken model of surface response methodology to analyze wettability determined via three methods: contact angle, USBM, and a new method using SEM-MLA over extended ranges of brine salinity (10,000, 100,000 and 200,000 ppm total dissolved salts), temperature (60, 90 and 120° C), and age of conditioning (2, 4 and 8 weeks). The samples for this study included 15 Berea sandstone samples aged in crude oil and brine of varying salinity. The wettability was experimentally validated using contact angle measurements, USBM tests, and a novel SEM-MLA imaging (at low vacuum conditions). A seminal effort in applying SEM-MLA image analysis for wettability determination was also explored. Linear regression models were developed and the adequacy of predicting the output variables (wettability) to nearly all conditions were verified. The study showed a comprehensive influence of brine salinity, aging time, and temperature towards wettability restoration. Further 2-D and 3-D surface plots were generated to show the interaction between the three independent variables in establishing a wettability value.

KEYWORDS: Enhanced Oil Recovery, Wettability, SEM-MLA, USBM

3.1 Introduction

Specialised Core Analysis (SCAL) data, specifically capillary pressure (P_c) and relative permeability (K_r) are important for reservoir characterization, production optimization and simulation. In this study, we developed an optimization methodology to restore wettability in core samples for SCAL experiments as laboratory experiments are routinely performed on core samples from restored state [4]. In practice, aging strategies vary between organizations and there is no one commonly accepted restoration process. In this paper we try to determine the optimal value of the three parameters that are generally agreed upon as contributing to the aging process [2, 15]: brine salinity, aging time, and aging temperature. Hibernia light crude oil with API gravity of 35, asphaltene content of < 1% and total acid number of 0 was used for saturating the core samples. The crude oil composition is presented in Table 3-1. Berea core sample with 80% quartz content and less than 2% clay content was used for this study.

Table 3-1: Hibernia crude oil composition

Composition of Hibernia Crude Oil			
Component	Mass fraction	Mole fraction	Volume fraction
CO2	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000
C1	0.0000	0.0000	0.0000
C2	0.0000	0.0000	0.0000
C3	0.0002	0.0009	0.0003
i-C4	0.0003	0.0012	0.0005
n-C4	0.0018	0.0070	0.0026
i-C5	0.0028	0.0086	0.0040
n-C5	0.0054	0.0165	0.0075
C6	0.0163	0.0427	0.0206
C7+	0.9732	0.9231	0.9646

Aging time and temperature are generally accepted to be the two most important factors contributing to the aging process. Anderson (1986) indicated that 1,000 hours (40 days) of aging at reservoir temperature is sufficient for wettability equilibrium. Additionally during the aging process, it is important to saturate the core with brine prior to oil to ensure the wettability effects due to brine chemistry are not ignored. Numerous studies [5, 13] have demonstrated the effect of increased brine salinity on oil wet characteristics exhibited in Berea sandstone.

Wettability is generally quantified by contact angle measurements or by USBM method or both. For a reservoir rock to be deemed oil-wet, the contact angle in an oil-brine-rock system should be > 105^{o} (Anderson 1986) or wettability index to be -1. USBM wettability index is calculated from the drainage and imbibition capillary pressure curves and Robin (2001) demonstrated a qualitative differentiation between oil-wet to water-wet capillary pressure curves. Lately, USBM wettability methods are increasingly applied on understanding the wettability nature of shale formations in unconventional oil productions [3, 6, 8]. In addition to the above two methods, digital imaging methods like SEM analysis are increasingly applied for wettability characterization. CRYO SEM and ESEM methods [7, 9, 10, 11] were initially used to analyse wettability in rocks and packed glass beads that were saturated with reservoir fluids. But these analyses were not accurate as it often compromised the sample integrity due to extreme changes in the physical state because of cooling and polishing. In a seminal method, we have applied SEM-MLA method by testing the sample without any changes in its physical state.

We have extended the range of three input parameters that influence wettability to address the gaps that were identified in the past work [12]. Additionally, we have extended the model to include three response factors instead of one for determining wettability, they include contact angle measurement, USBM wettability index and organic content from SEM-MLA analysis

3.2 Experiment Methodology

For this study we have chosen statistical design of experiments (DOE) as it provides an understanding of the parametric effects controlling a process with the benefit of a decrease in the number of experiments required. Box Behnken response surface methodology was applied to optimise the input parameters i.e., aging time, temperature and brine salinity for the desired output parameter that is wettability. Box Behnken requires only 15 trials for a three factor experiment and providing maximum efficiency for a surface model. The box Behnken model is simplified model compared to other existing models such as central composite design. In this study we have extended the model to include three response factors: contact angle measurement, USBM wettability index method and organic content (%) from SEM-MLA analysis. Table 3-2 summarises the experimental plan and the real values for input parameters. Trials at optimal levels were duplicated twice to ensure repeatability. Design Expert ® software was used for the DOE, response surface model analysis, and input parameters optimisation.

Table 3-2: Experimental measurement for Berea sandstone

Berea Sample	Porosity (%)	Salinity (ppm)	Temp (°C)	Time (weeks)	Contact Angle (°)	SEM-MLA Oil %	Wettability Index (USBM)
B1	18.45	10,000	60	4	108	0.1	0.282
B2	18.19	10,000	120	4	70	0.2	0.424
B3	19.71	200,000	60	4	87	1.2	-0.013
B4	20.69	200,000	120	4	95	1.3	0.034
B5	18.24	10,000	90	2	98	0.59	0.778
B6	18.24	10,000	90	8	65	0.07	0.519
B7	18.12	200,000	90	2	75	1.81	0.113
B8	21.13	200,000	90	8	98	0.53	-0.651
B9	18.40	100,000	60	2	82	1.57	0.165
B10	18.45	100,000	60	8	70	0.39	-0.660
B11	18.52	100,000	120	2	103	2.54	0.681
B12	19.46	100,000	120	8	105	1.58	-0.613
B13	18.00	100,000	90	4	112	1.02	0.2881
B14	18.60	100,000	90	4	110	1.39	0.1870
B15	18.47	100,000	90	4	102	1.72	0.1249

A wider range of brine salinities from 10,000 to 200,000 ppm were used for this work which was markedly different from 60,000 to 120,000 ppm that was used in the previous study [12]. The composition of brine includes some divalent calcium and magnesium ions and the complete composition is presented in Table 3-3. The aging period was increased from 6 weeks to 8 weeks with the maximum aging temperature changed from 90 to 120°C. Hibernia (offshore Newfoundland) dead crude oil with 5.9 cP viscosity and 878 kg/m^3 density was used for saturation. The oil was filtered and degassed by vacuuming it for 48 hours to prevent any gas production during the drainage. During the aging process the core samples were circulated with few pore volumes of oil on a weekly basis. Berea Sandstone used for this work came from Cleveland Quarries with porosity in the range of 18 - 20% and gas permeability ~150 mD.

Table 3-3: Brine Properties

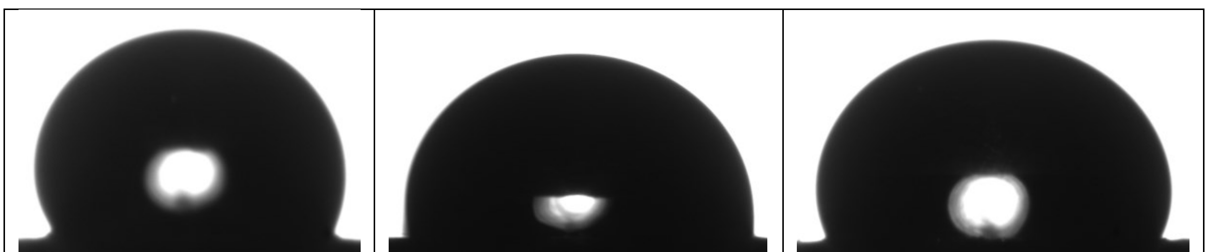
Brine Salinity (ppm)	Density (kg/m^3)	Viscosity (cP)	IFT with air (mN/m)
10,000	1010	1.05	70.8
100,000	1070	1.21	22.4
200,000	1140	1.50	5.32

Brine Composition: NaCl 84.38%; $CaCl_2*2H_2O$ 12.32%; $MgCl_2*6H_2O$ 2.57%; KCl 0.4%; Na_2SO_4 0.32%

The core samples for testing were initially cut to 6.3 cm length with two 5 mm sections cut from the top and bottom of the core. A Whatman© grade 1 filter paper was placed between the core and cut sections. The idea was to use the core sample for capillary pressure measurement (USBM wettability measurement) and the thin section being used for contact angle measurement and SEM-MLA analysis. The samples were then sonicated for 60 minutes and dried in an oven for 24 hours before being saturated with the representative brine as outlined in the experimental plan.

In the first stage of experiment, the core samples were brought to connate water condition and oil saturation. The brine saturated samples (thin section+ core + thin section) were loaded into a core holder at overburden pressure of 3000 psi and centrifuged in drainage mode. A Whatman© grade 1 filter paper was placed between the thin sections and the core sample, wrapped in a teflon tape and held in place using a viton sleeve. The core sample and the sections are held in place by the end pieces of the centrifuge coreholder and a overburden pressure of 3000 psi is applied. A Rotosilenta 630RS refrigerated centrifuge from Vinci Technologies was used for this purpose. The drainage test with oil displacing brine was carried out in 7 centrifugation steps starting from 500 rpm to a maximum of 3,500 rpm with 3 hours of equilibration time per rpm step.

After centrifuging, the core holders were disassembled to inspect the oil saturation in the core samples. The samples were again loaded in the core holder and the overburden pressure was adjusted prior to placing them in the oven for aging. Once the aging was completed, the top (thin) section of the core sample was loaded in a Vinci IFT 700 instrument to measure the contact angle by sessile drop method using brine as the drop fluid. The measured contact angles for the aged Berea Sandstone are listed in Table 3-2. Figure 3-1 shows representative contact angles for the brine sessile drop in the presence of air for some of the aged rock samples.



Berea 1 (108^{O}) | Berea 7 (75^{O}) | Berea 14 (110^{O})

Figure 3-1: Contact angle measurements for Berea.

In the second stage, the bottom (thin) section of the aged core sample was carefully removed and secured in a glass container to ensure no oil gets vaporized from the pores due to exposure and was utilised for SEM-MLA analysis. FEI Quanta 650 FEG scanning electron microscope, equipped with Bruker high throughput energy dispersive x-ray (EDX) system and backscattered electron detectors was used for this purpose. Imaging on the flat sample surfaces was carried out at very low vacuum conditions (0.6 Torr) to prevent evaporation of fluids [7].

Additionally, the samples were not subject to any metallic or carbon coating on the surface, except for liquid graphite coating on the sample holder. Instrument conditions and parameters include a high voltage of 25 kV, spot size of 5.75, working distance of 13.5 mm, 10 nA beam current, 16 µs BSE dwell time, 10 pixel minimum size (400 pixel frame resolution for 1mm HFW), and 12 ms spectrum dwell for EDX. Each of these MLA acquisitions was completed using version 3.1.4.683 MLA™ software and took between 3-4 hours per sample. Minerals and fluids in the core sample were calculated through a custom classification script that accounted for porosity and minerals. The mineralogy was determined using GXMAP measurement mode within FEI Mineral Liberation AnalyzerTM software, equipped on a FEI Quanta 650 Field Emission Gun (FEG) SEM. Each mineral identified must be within a 80% match to a known standard x-ray. For the determination of porosity, the "Pores" were determined using a custom classification, in which material that had a greyscale of certain range, where Back Scatter Emission is 0 – 30) was scripted to be "Pores" instead of background material. This darker material of "Pores" was not matched to any x-ray standard. The results for individual samples were acquired as digital map of the minerals and a data table listing their mineral composition (Table 3-4). Figure 2 is an example of mineral map and BSEM image (black colour around the sample is not part of the rock image) of a sample aged for 4 weeks at 90^{o}C. The minerals identified from the mineral map are listed in Table 3-4. Wettability assessment was based on the organic (oil) content of the sample in direct comparison to brine and mineral composition prior to saturation. The organic content for each sample is listed in Table 3-2.

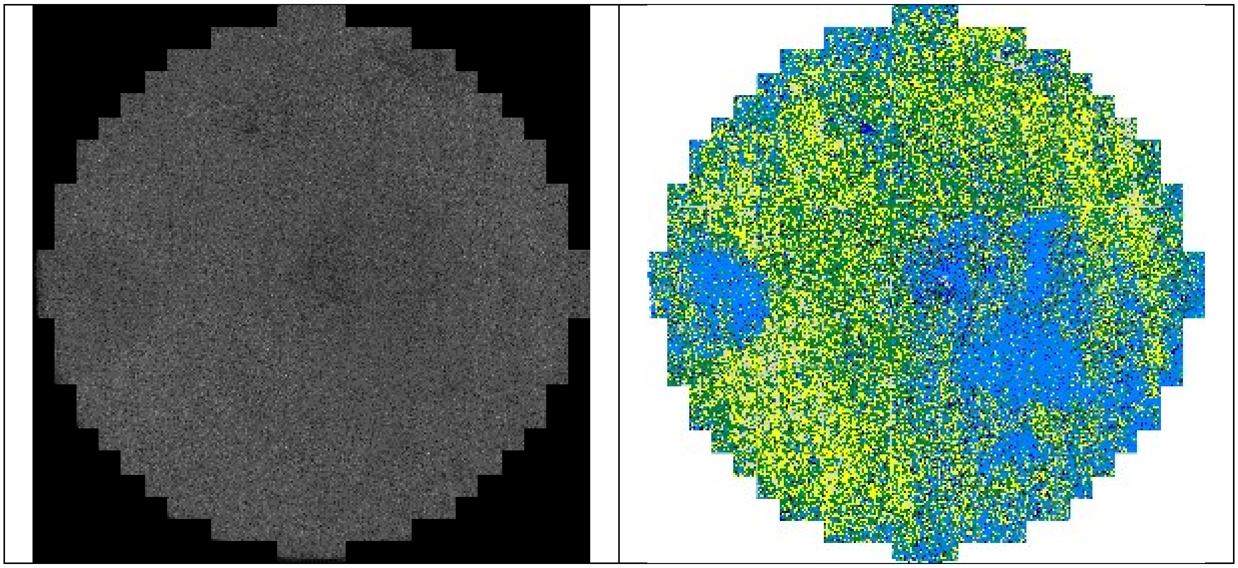


Figure 3-2: (a) BSEM images of Berea sample 15 (b) Mineral map of Berea sample 15

Table 3-4: Mineral list from the SEM-MLA analysis of Berea 15

Mineral list from SEM-MLA of Berea 15 (Mineral Map)		
Colour	Mineral	Area (%)
	Quartz	30.09
	Halite	27.93
	Unknown	29.24
	Others	5.64
	Pores	3.66
	Oil	1.72
	Plagioclase	1.12
	Feldspar	0.35
	Chlorite	0.19
	Clay	0.02
	Fe-minerals	0.02
	Zircon	0.01
	Mica	0.01

After the primary drainage test was completed, the imbibition step was started to force brine into the aged core sample to displace oil. The core samples were loaded in the core holder (in imbibition mode) with overburden pressure of 3000 psi. The receiving tubes were filled with the representative brine for each sample and the samples were centrifuged from 500 rpm to 3500 rpm in seven steps of 3 hours duration in each step. At the end of the imbibition test, the secondary drainage step was carried out by forcing oil through the brine saturated samples. The secondary drainage process was also carried out in seven steps. The secondary drainage data and the imbibition data were analysed and the area under each curve was calculated. Figure 3-3 is the capillary pressure curves generated for samples saturated with oil at different brine concentration (drainage) and displacement of oil under different brine concentrations (imbibition). The USBM wettability index was calculated based on the area under the curve for both secondary drainage (A_1) and primary imbibition (A_2) using the formula W = log (A_1/A_2). Typically the wettability index ranges from > 0 for water wet to <0 for oil wet and 0 for neutrally wet. In comparison with the contact angle measurement, the USBM method provides a macroscopic average of the core plugs used in this study [8]. The wettability index calculated for the 15 samples are listed in Table 3-2.

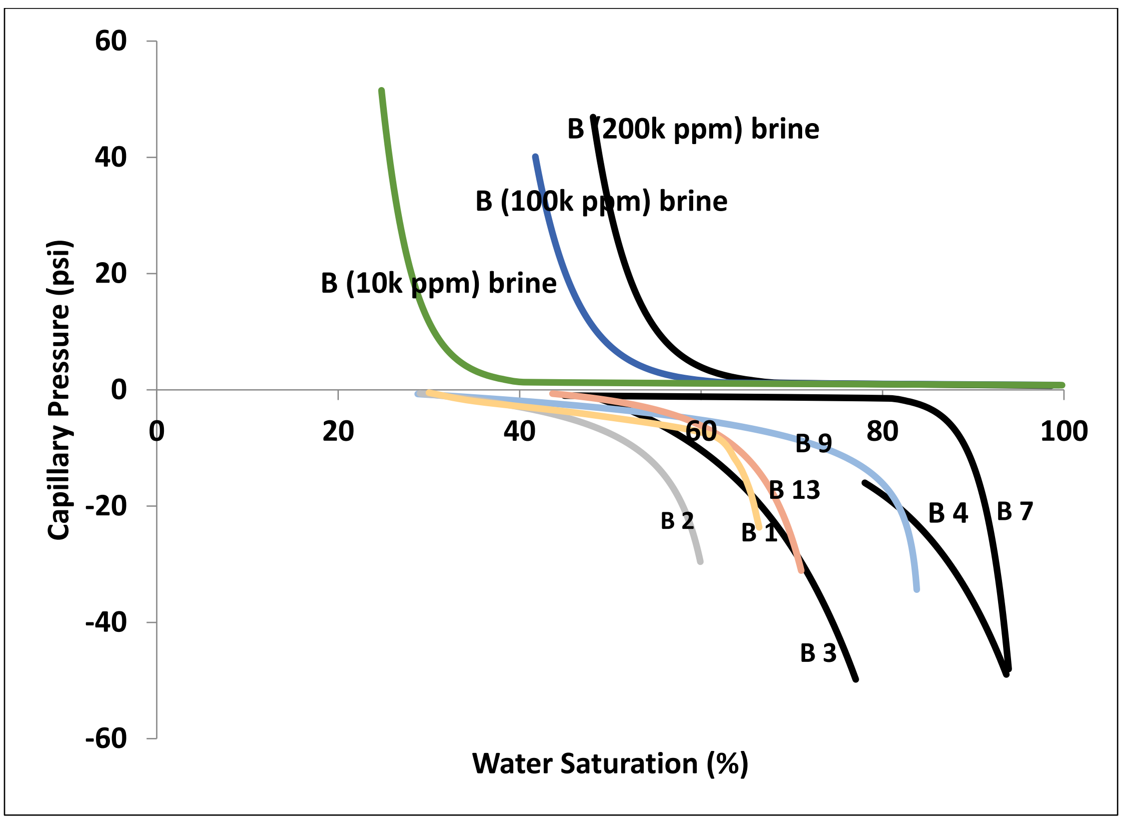


Figure 3-3: Capillary pressure curves for Berea samples (Primary Imbibition and Primary Drainage)

3.3 Results and Discussion

Box Behnken response surface methodology, with three factors and three responses, was chosen to investigate and optimise the core restoration (wettability) process. The experimental results are shown in Table 3-2 and Design Expert ® Software was used for statistical analysis. The optimal aging conditions were predicted using a first order polynomial model which was fitted to correlated relationships between brine salinity, aging temperature and time (input variables) and contact angle, wettability index and organic content i.e., oil content (responses). The experimental data was analysed by multiple regression analysis through least squares method. Analysis of Variance (ANOVA) was applied to compute regression coefficients of the linear and higher order (quadratic and polynomial) models with interaction effects. Statistical validation of the model was done using F-test where a "fitted" model is deemed significant if the probability level is low, i.e. p-value ≤ 0.05. The regression model was used to develop the response surface plots in order to visualise the relationship between the three input variables and responses. Finally, the developed models were used to suggest optimal conditions for aging. The experimental sequence was randomized in order to minimise bias and variability in measurements.

The results of the analysis of variance (ANOVA) tests were carried out individually for the three response factors i.e. contact angle, USBM wettability index and organic content from SEM-MLA and are presented in Tables 3-5, 3-6 and 3-7, respectively. For the contact angle measurement and organic content using SEM-MLA, the ANOVA test indicated only the quadratic model to be significant over other models. This is evidenced by the overall model p-values of 0.0464 and 0.0095, respectively. The resultant quadratic equations for the model developed using contact angle is presented in Equation 1. Aging time was the only significant parameter affecting wettability. Brine salinity and temperature were found to influence wettability only when they were considered with aging time, but independently they were found to be inadequate in influencing contact angle measurement.

$$Contact\ Angle = 65.12 - 3.62 \times 10^{-4}\,[Salinity\ (ppm)] + 0.59[Temp\ (°C)] + 13.38[Age\ (Weeks)] + 0.031[Temp\ x\ Age] - 1.843[Age^{2}] \quad \textbf{(1)}$$

Table 3-5: ANOVA test results for Berea Sandstone (Contact Angle)

Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value (Prob > F)**
Model	0.42	9	0.047	4.95	0.0464
A-Salinity	8.5E-003	1	8.5E-003	0.90	0.3863
B-Temperature	6.5E-005	1	6.5E-005	6.8E-003	0.9372
C-Age	0.082	1	0.082	8.65	0.0322
AB	0.070	1	0.070	7.35	0.0422
AC	0.12	1	0.12	12.16	0.0175
BC	4.9E-003	1	4.9E-003	0.52	0.5042
A2	0.061	1	0.061	6.45	0.0519
B2	0.013	1	0.013	1.41	0.2890
C2	0.097	1	0.097	10.20	0.0242

Table 3-6:ANOVA test results for Berea Sandstone (USBM Wettability Index)

Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value (Prob > F)**
Model	2.77	3	0.92	48.00	<0.0001
A-Salinity	0.26	1	0.26	13.65	0.0035
B-Temperature	0.066	1	0.066	3.41	0.0919
C-Age	2.45	1	2.45	127.00	<0.0001

Table 3-7: ANOVA test results for Berea Sandstone (SEM-MLA Wettability Analysis)

Analysis of variance table [Partial sum of squares - Type III]					
Source	Sum of Squares	df	Mean Square	F Value	p-value (Prob > F)
Model	6.28	9	0.70	10.38	0.0095
A-Salinity	0.52	1	0.52	7.68	0.0393
B-Temperature	0.18	1	0.18	2.63	0.1659
C-Age	0.14	1	0.14	2.13	0.2039
AB	1.10	1	1.10	16.39	0.0098
AC	0.17	1	0.17	2.48	0.1758
BC	0.40	1	0.40	5.91	0.0593
A2	2.12	1	2.12	31.55	0.0025
B2	0.83	1	0.83	12.42	0.0168
C2	0.25	1	0.25	3.72	0.1118

In the case of the USBM wettability index, a linear model was found to be best suited for predicting the experimental outcome which is confirmed from very low p-value of <0.0001. Among the three parameters, aging time was found to have the highest F value thereby significantly influencing the restoration process. The linear model equation using USBM wettability index (USBM WI) is shown in Equation 2.

$$USBM\ WI = 0.782 - 1.9 \times 10^{-6}[Salinity\ (ppm)] + 3.02[Temp\ (℃)] - 0.179[Age] \quad \textbf{(2)}$$

In order to evaluate the significance of each input parameter on the outcome wettability measurement, F-tests were conducted on the three models. In the model based on contact angle measurement, aging time had higher F-values compared to temperature and salinity. Whereas in the model considering wettability by SEM-MLA, temperature and salinity had higher F-values respectively. For the model developed based on wettability index, aging time was the significant factor contributing to the restoration process. Additionally, p-values for input parameters in all three cases were calculated to be less than the model F-value which is an indication that the statistical models are statistically significant. A diagnostic test was carried out to compare the experimental data with the model predicted results. Figure 3-4 shows a plot of experimental versus predicted values for both contact angle and USBM wettability index. Both analyses showed strong agreement between the experiment and model data as observed through most data points lying close to or on the diagonal line. A similar trend with predicted and actual values was observed in the organic content using SEM-MLA, but the results are withheld as we are progressing with further analysis.

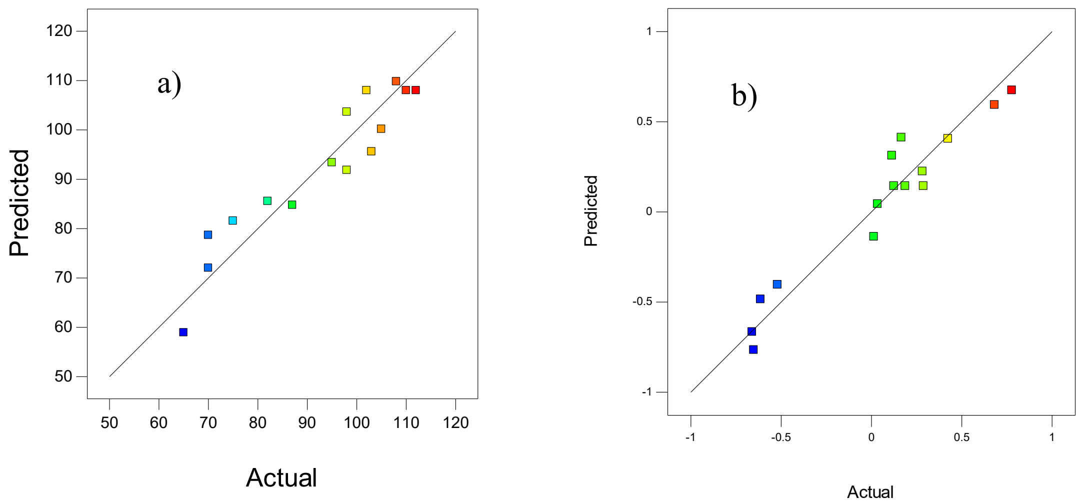
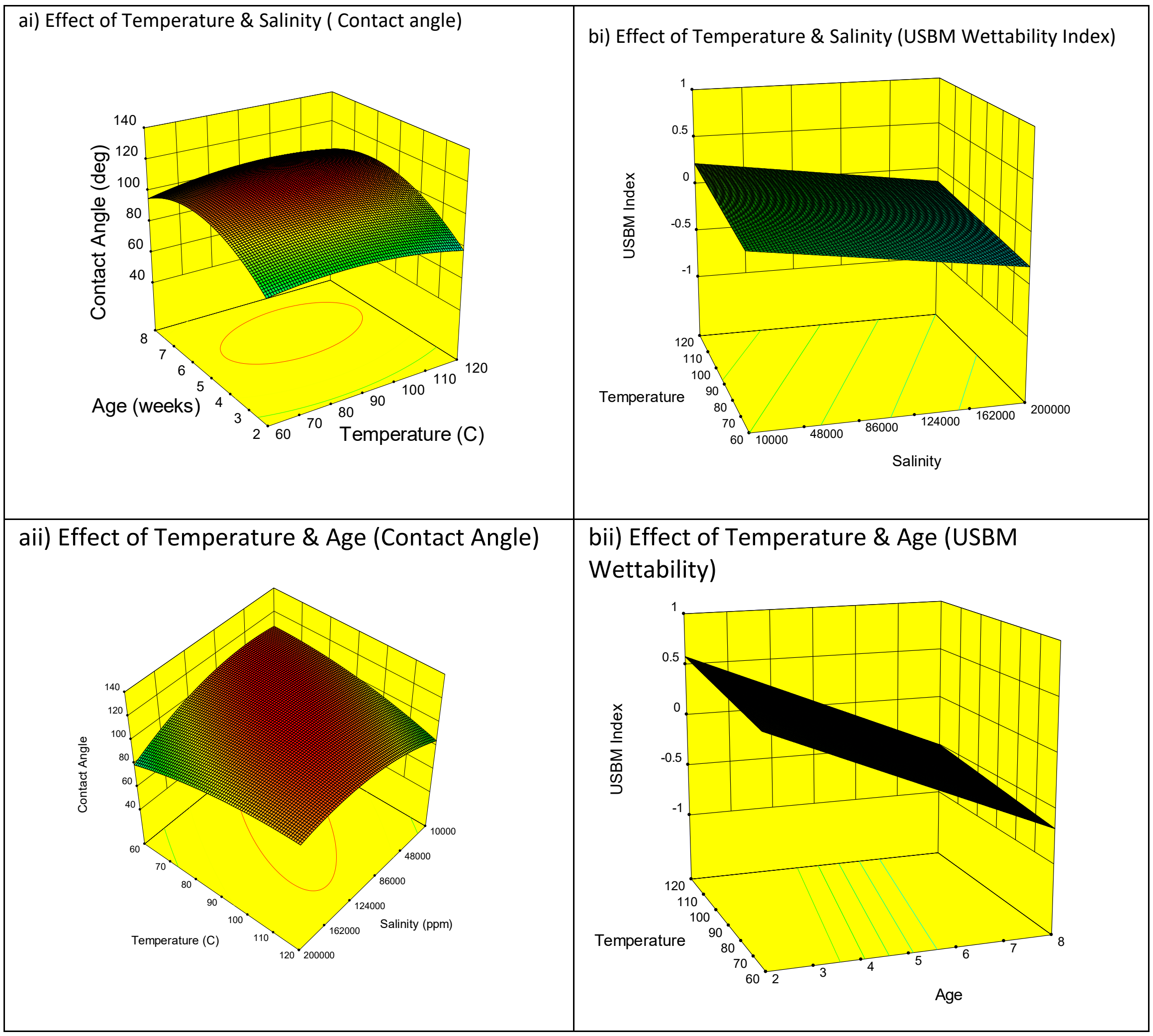


Figure 3-4: Predicted vs Actual for Berea Sandstone (a) Contact Angle (b) USBM Wettability Index

From the developed statistical model we were able to produce 3-D response surface plots and 2-D contour plots for the three input parameters (aging time, temperature and salinity) against contact angle. Figure 3-5 represents the contour plot and 3-D RSM. The 2-D and 3-D plots provide an understanding of the interaction between two input parameters (e.g age and salinity), while keeping the third parameter constant (temperature). The time of aging was found to be the most significant factor in impacting the aging process as observed through contact angle measurement. As the aging period was extended from 2 weeks to 8 weeks, the contact angle increased indicating a shift from intermediate oil-wet to strongly oil-wet characteristics. A similar trend was reported by Morrow (2000) and Anderson (1986) where strong oil wet characteristics was observed when aging time was extended to more than 40 days. Increase in temperature was aiding oil-wet behavior whereas increasing brine salinity resulted in decreasing contact angle hence more water-wet behavior. This is in close agreement with published work [14, 15] on wettability alteration in sandstone when the brine concentration was increased from 0.3 % to 20%.



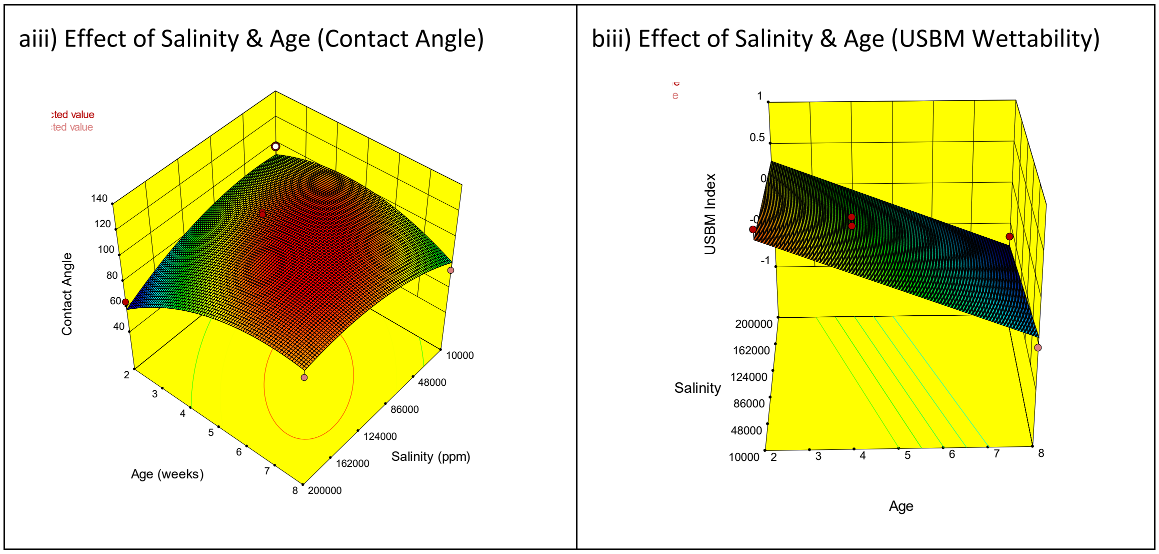
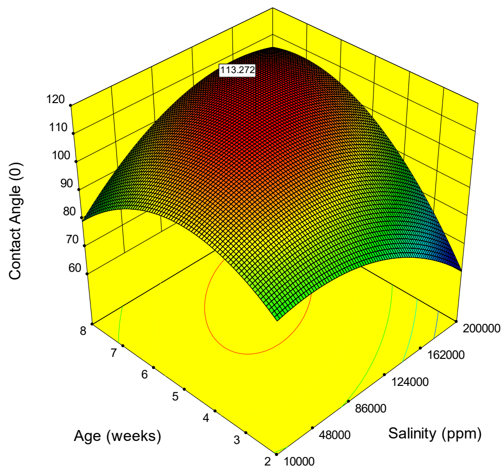


Figure 3-5: Contact angle 3D surface models & 2D contour plots of temperature, salinity and age

Optimisation: The regression models developed using three different wettability characterizations were utilised for optimising the input parameters such as temperature, aging time and brine salinity. As previously mentioned, the wettability criterion for an oil-rock-brine system with a contact angle >105° is considered oil-wet. Applying the optimisation criteria of maximizing the contact angle, numerical solutions were generated to establish the optimum value for Brine Salinity, Temperature and Time to be 104,257 ppm, 95°C & 5.5 weeks, respectively, for restoring wettability. The results are graphically represented via 3D response surface in Figure 3-6, where the peak points region is observed in both 2-D and 3D plots. In the case of wettability index, the optimal conditions for restoration were found to be aging time of 6.2 weeks, brine salinity of 115,000 ppm and temperature of 99°C. The optimal values were determined by setting a criteria of wettability index in the range of 0 to -0.6. The optimisation methodology was applied in SEM-MLA analysis by implementing the criteria of maximizing the organic content. The organic content (oil %) assed was found to be largely underestimated as compared to our trial tests. Hence the optimisation results are not being published until further an analysis is completed on SEM-MLA analysis of aged core samples.



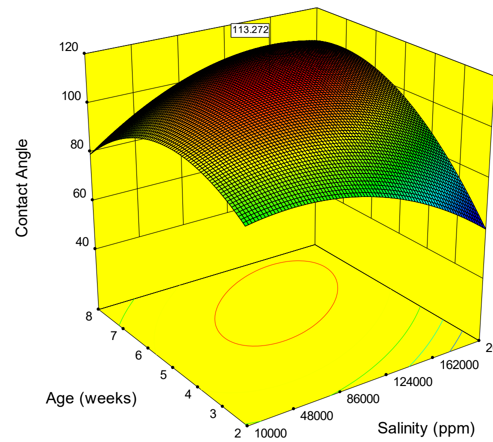


Figure 3-6: Optimum Ageeing Conditions (contact angle, 5.5 weeks, 95°C, 104,257 ppm)

3.4 Conclusion

Response Surface Modelling (RSM) using three factor Box Behnken Design was successfully applied to study and optimise brine salinity, temperature of aging and aging time for wettability restoration in core samples.

1. A suite of 15 Berea sandstones were prepared and aged following Box Behnken design of experiments. Wettability was validated based on three response factors i.e., contact angle, USBM wettability index and organic content using SEM-MLA analysis.
2. The experimental results were analyzed statistically using a regression model and analysis of variance (ANOVA). The ANOVA results for the three response factors showed high coefficient of determination values, ensuring a fit of the developed mathematical model with the experimental data.
3. Applying the optimization methodology, the optimum value of input parameters for restoring oil-wet conditions using contact angle measurement was calculated as brine salinity at 104,257 ppm, temperature at 95°C and time of aging at 5.5 weeks.
4. Optimization results for restoring wettability using USBM method provided an optimum brine salinity of 115,000 ppm, temperature of aging at 99°C and aging time for 6.2 weeks.
5. Optimal solution for restoration using SEM-MLA method is under process and the final results will be presented later.

6. Response surface models and 2-D contour plots were successfully developed for analyzing the interaction between the three input parameters on contact angle measurement. The results for Berea were in strong agreement with proven results

3.5 References

1. Alotaibi, M.B., Azmy, R., & Nasr-El-Din, H.A., 2010. Wettability Challenges in Carbonate Reservoirs. Paper SPE-129972, Presented at the SPE Improved Oil Recovery Symposium. Tulsa, Oklahoma, USA, 24-28 April.
2. Anderson, W.G., 1986, Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *Journal of Petroleum Technology*, 38(10), 1125-1144.
3. Begum, M., Reza Yassin, M., Dehghanpour, H., & Dunn, L., 2017. Rock-Fluid Interactions in the Duvernay Formation: Measurement of Wettability and Imbibition Oil Recovery. Paper SPE-185065, Presented at the SPE Unconventional resources conference, Calgary, Alberta, Canada, 15-16 February.
4. Hirasaki, G. J., Rohan, J. A., Dubey, S.T., & Niko, H., 1990. Wettability Evaluation During Restored-State Core Analysis. Paper SPE-20506, Presented at the SPE Annual Technical Conferences and Exhibition, New Orleans, Louisisana, USA, 23-26 September.
5. Jadhunandan, P.P., & Morrow, N.R. 1995, Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems. *SPE Reservoir Engineering*, 10(1) 40-46.
6. Karimi, S., Kazemi, H., & Simpson, G. A., 2017. Capillary Pressure, Fluid Distribution, and Oil Recovery in Preserved Middle Bakken Cores. Paper SPE-185095, Presented at the SPE Oklahoma City Oil and Gas Symposium, Oklahoma city, Oklahoma, USA, 27-31 March.
7. Kumar, M., Fogden, A., Senden, T., & Knackstedt, M. A., 2012. Investigation of Pore-Scale Mixed Wettability. Paper SPE -129974, *SPE Journal*, 17(01), 20-30.
8. Luo, P., & Li, S. (2017, February 15). Simultaneous Capillary Pressure and Wettability Determination for Tight Bakken Cores Using an Ultra-High-Speed Centrifuge. Paper

SPE-185067, Presented at the SPE Unconventional Resources Conference, Calgary, Alberta, Canada, 15-16 February.

9. Robin, M., Combes, R., Degreve, F., & Cuiec, L., 1997: Wettability of Porous Media from Environmental Scanning Electron Microscopy: From Model to Reservoir Rocks, Paper SPE-37235, Presented at the International Symposium on oilfield Chemistry, Houston, Texas, USA, 18-21 February.
10. Robin, M., Combes, R., & Cuiec, L., 1998. Two SEM Techniques To Investigate Reservoir-Rock Wettability. *Journal of Petroleum Technology*, 50(11), 77-79.
11. Schmatz, J., Klaver, J., Jiang, M., & Urai, J. L., 2017. Nanoscale Morphology of Brine/Oil/Mineral Contacts in Connected Pores of Carbonate Reservoirs: Insights on Wettability From Cryo-BIB-SEM. *SPE Journal*, 22(05), 1374 -1384.
12. Sripal, E.A., James, L.A., 2016, Application of an optimization method for restoration of Core samples for SCAL experiments, Presented at the Annual Symposium of the Society of Core Analysts, Snowmass, Colorado, USA, 22-26 August.
13. Tang. G.Q, and N.R. Morrow, 1999, Influence of Brine composition and Fines Migration on Crude Oil/Brine/Rock Interactions and oil recovery. *Journal of Petroleum Science and Engineering*. 24 (2-4), 99-111.
14. Vijapurapu, C.S., & Rao, D.N., 2003, Effect of Brine Dilution and Surfactant Concentration on Spreading and Wettability. Paper SPE-80273, Presented at the International Symposium on oilfield Chemistry, Houston, Texas, USA, 18-21 February.
15. Zhou, X., Morrow, N.R., & Ma, S. (2000). Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding. *SPE Journal*, 05 (02), 199-207.

3.6 Appendix

Table 3-8: C30+ oil Composition

Component	Boiling point	MW	C30+ Composition		
	(°C)	(g/mol)	mass frac	mole frac	vol frac
Carbon Dioxide	-79	44.01	0.0000	0.0000	0.0000
Nitrogen	-196	28.01	0.0000	0.0000	0.0000
Methane	-162	16.04	0.0000	0.0000	0.0000
Ethane	-89	30.07	0.0000	0.0000	0.0000
Propane	-42	44.10	0.0002	0.0009	0.0003
Iso-Butane	-12	58.12	0.0003	0.0012	0.0005
n-Butane	0	58.12	0.0018	0.0070	0.0026
Iso-Pentane	28	72.15	0.0028	0.0086	0.0040
n-Pentane	36	72.15	0.0054	0.0165	0.0075
Hexanes	37-69	84.00	0.0163	0.0427	0.0206
Methylcyclopentane	70	84.16	0.0050	0.0131	0.0058
Benzene	80	78.11	0.0028	0.0079	0.0028
Cyclohexane	81	84.16	0.0046	0.0121	0.0052
Heptanes	70-98	96.00	0.0227	0.0522	0.0273
Methylcyclohexane	101	98.19	0.0096	0.0215	0.0108
Toluene	111	92.14	0.0077	0.0184	0.0077
Octanes	99-126	107.00	0.0304	0.0628	0.0355
Ethylbenzene	136	106.17	0.0028	0.0059	0.0028
m&p-Xylene	139	106.17	0.0065	0.0135	0.0065
o-Xylene	144	106.17	0.0036	0.0076	0.0036
Nonanes	127-151	121.00	0.0298	0.0543	0.0338
Decanes	152-174	134.00	0.0419	0.0691	0.0467
Tetradecanes	237-253	190.00	0.0333	0.0387	0.0352
Pentadecanes	254-271	206.00	0.0370	0.0397	0.0386
Hexadecanes	272-287	222.00	0.0316	0.0314	0.0327
Heptadecanes	288-302	237.00	0.0301	0.0280	0.0308
Octadecanes	303-317	251.00	0.0311	0.0273	0.0317
Nonadecanes	318-331	263.00	0.0292	0.0245	0.0296
Eicosanes	332-343	275.00	0.0261	0.0209	0.0262
Heneicosanes	344-357	291.00	0.0244	0.0185	0.0244
Docosanes	358-369	305.00	0.0228	0.0165	0.0227
Triacosanes	370-380	318.00	0.0220	0.0153	0.0218
Tetracosanes	381-391	331.00	0.0209	0.0140	0.0206
Pentacosanes	392-402	345.00	0.0216	0.0138	0.0212
Hexacosanes	403-412	359.00	0.0177	0.0109	0.0173
Heptacosanes	413-422	374.00	0.0190	0.0112	0.0184
Octacosanes	423-432	388.00	0.0190	0.0108	0.0184
Nonacosanes	433-441	402.00	0.0185	0.0101	0.0178
Triacontanes+	442-449+	634.37	0.2917	0.1015	0.2494
MW g/mol				220.80	

4 CHAPTER FOUR

Application of an SEM Imaging and MLA Mapping method as a tool for Wettability restoration in Reservoir Core samples SCAL Experiments (Paper 2, Published)

This chapter is an edited version of the article published by **Journal of Minerals**: Sripal, Edison., Grant, David., L.A.James., "Application of SEM Imaging and MLA Mapping Method as a tool for Wettability Restoration in Reservoir Sample for SCAL Experiments". Journal of Minerals 2018.

Abstract

In reservoir engineering, special core analysis experiments (SCAL) are performed in the lab to evaluate the production capabilities of an oil reservoir. A critical component of SCAL experiments is core wettability restoration to its original wettability, i.e., oil wet condition. Typically, aging is performed by saturating the core with oil and aging at reservoir temperature where time is the variable in question dictating whether the resulting restored core is strongly or weakly oil-wet. In the lab, core wettability is often experimentally validated using contact angle measurements or USBM (United States Bureau of Mines) wettability tests, which are often time consuming, expensive and prone to error. In this study we developed a novel method by using Scanning Electron Microscope (SEM) and mineral liberation analysis (MLA) imaging (at low vacuum conditions) to determine the wettability of rocks saturated with reservoir fluids such as oil and brine. For this work a systematic approach was applied with comparing the SEM-MLA method against conventional methods to quantify the degree of uncertainty linked to a) wettability estimation and b) the aging time. We have used a comprehensive suite of core samples such as Berea, Silurian Dolomite and Chalk to represent the bulk of oil reservoirs in the world.

Keywords: SEM-MLA, Special Core Analysis (SCAL), Wettability, USBM

4.1 Introduction

Special core analysis (SCAL) data are important for reservoir characterization and secondary and tertiary production optimization or enhanced oil recovery (EOR). An important consideration for ensuring quality and reliability in SCAL experiments is the restoration of core wettability. Incomplete core sample restoration may lead to unrealistic estimates of residual oil saturation, and inaccurate capillary pressure and relative permeability measurements key parameters in simulating the reservoir productivity. Reservoir rock is generally considered to be oil-wet and can be achieved either from native or from restored states [1]. Obtaining native state core samples is challenging both economically and operationally. It requires suspending production, protecting the sample from drilling fluids, and preventing any evaporation or contamination [2]. Hence, laboratory experiments are routinely performed on core samples that have been cleaned of drilling and remaining reservoir fluids and then restored. Restoration typically involves cleaning the core sample with various solvents, rendering it water wet. The cleaned samples are then saturated with brine at reservoir conditions (to establish connate water saturation) and crude oil to capillary pressure. The oil/brine saturated cores are aged at reservoir conditions. Literature is replete with various aging strategies, but the conundrum is the lack of a commonly accepted wettability restoration period for either sandstones or carbonates.

Wettability is the tendency of one fluid to spread on the solid surface in the presence of another immiscible fluid. Wettability is of paramount importance in oil recovery from low permeability chalk to high permeability sandstones as they control the flow and distribution of fluids [1]. In the past, numerous studies have indicated multiple factors influencing wettability including oil composition, rock mineralogy, fluid saturation, brine composition, temperature and aging time [2]. Although carbonate reservoirs tend to be intermediate to strongly oil wet, laboratory investigations on core restoration has many uncertainties [3,4].

Aging time and temperature are generally accepted to be the two most important factors contributing to the aging process. Anderson (1986) [2] indicated that 1000 h (40 days) of aging at reservoir temperature is sufficient for wettability equilibrium. Additionally, during the aging process it is important to saturate the core with brine prior to oil to ensure the wettability effects due to brine chemistry are not ignored [5]. Numerous studies have demonstrated the effect of increased brine salinity on rendering the sample water wet and ultimately increasing the oil recovery on carbonate rocks [4,6]. Alternately, it has also been widely demonstrated that brine composition containing mainly sulfate ions to have a positive impact in recovering oil from carbonate reservoirs by altering the surface charge on the rocks and making it water wet [6–8].

Wettability is generally quantified by contact angle measurements or United States Bureau of Mines (USBM) method or both. For a reservoir rock to be deemed oil-wet, the contact angle in an oil–brine–rock system that should be >105° [2] or wettability index to be −1. USBM wettability index is calculated from the drainage and imbibition capillary pressure curves and Robin (2001) [8] demonstrated a qualitative differentiation between oil-wet to water-wet capillary pressure curves. Lately, USBM wettability methods are increasingly applied to understand shale formation wettability in unconventional oil reservoirs [9–11]. In addition to the above two methods, digital imaging methods like SEM analysis are increasingly applied for wettability characterization. CRYO SEM (cryogenic scanning electron microscopy) and ESEM (environmental scanning electron microscopy) methods [9–12] were initially used to analyze wettability in rocks and packed glass beads that were saturated with reservoir fluids. However, these analyses were not accurate as it often compromised the sample integrity due to extreme changes in the physical state because of cooling and polishing. In a seminal method, we applied the SEM-MLA (scanning electron microscopy-mineral liberation analysis) method by testing the sample without any changes to its physical state.

In this paper we try to determine the threshold duration beyond which the aging does not change the wetting state of Berea sandstone, Silurian dolomite and outcrop chalk. After aging the cores at high temperature for varying periods of time, wettability determination was performed using contact angle measurements, the USBM method, and compared against SEM-MLA analysis. Specifically, the study was carried out on outcrop chalk and Berea samples as laboratory core flooding and SCAL experiments are routinely performed on core samples from restored state [1]. A common SCAL program can last for months if not for years. A significant portion of this time is spent on aging the reservoir cores and validating the wettability. Any significant reduction time in wettability validation will contribute immensely to reducing cost and concentrated effort on characterizing the reservoir. We aim to achieve this by applying this low vacuum SEM-MLA method to validate the state of wettability.

4.2 Materials and Methods

Porous media: The porous media used for this work was outcrop chalk from Kansas, which is a low permeable (2 mD) high porosity rock. The Berea samples came from Cleveland Quarries (Ohio, USA) and had a porosity in the range of 18–21% and gas permeability of 350 mD. The Silurian dolomite was obtained from Kocurec Industries, Texas, USA. Porosity of the dolomites varied from 13 to 14% and the gas permeability was measured to be 120 mD. The petrophysical characteristics of the core samples are listed in Table 4-1. Core samples were cut to 1.5” diameter by about 2” length. The core samples were initially sonicated to remove any fines and dried at 90 °C for two days before being subject to saturation. Porosity was determined by the saturation test. Air and brine permeability were measured by conventional methods (permeameter).

Table 4-1: Experimental measurement of wettability by contact angle, SEM-(MLA) and United States Bureau of Mines (USBM) method for Berea, chalk and dolomite samples at different aging times.

Berea Sample	Sample ID	Porosity (%)	Time (weeks)	Contact Angle (°)	SEM-MLA Oil %	Wettability Index (USBM)	Wettability State
Berea1	B1	18.43	0.5	70	0	0.262	Water wet
Berea2	B2	18.17	2	82	7.42	0.414	Water wet
Berea3	B3	19.01	4	95	22.43	-0.014	Intermediate
Berea4	B4	20.29	6	103	37.53	0.033	Oil wet
Berea5	B5	18.42	8	112	73.47	0.768	Oil wet
Chalk 1	C1	38.57	1	65	6	0.368	Water wet
Chalk 2	C2	38.49	2	66	10	0.510	Water wet
Chalk 3	C3	37.76	3	78	14	0.005	intermediate
Chalk 4	C4	36.93	4	85	24	-0.018	Oil wet
Chalk 5	C5	38.04	5	102	36	-0.165	Oil wet
Dolomite1	D1	38.06	0.5	65	0	-0.165	Water wet
Dolomite 2	D2	37.63	4	95	36.78	0.364	Intermediate

Fluids: The first part of the experiment involved saturation test to determine porosity. Only one type of brine was used for all experiments. The physical properties of brine used in this work are presented in Table 4-2. After saturation all the core samples were aged at constant temperature of 90 °C and the aging period was varied. Conventional dead crude oil with 6 cP viscosity and 858 kg/m^3 density was used as the non-wetting phase. The composition of the crude oil used for this work is presented in Table 4-3. The oil was filtered and degassed by vacuuming it for 48 h to prevent any gas production during the drainage. During the aging process the core samples were circulated with few pore volumes of oil at constant intervals.

Table 4-2: Composition and properties of brine

Brine Salinity (NaCl) (ppm)	Density (kg/m^3)	Viscosity (cP)	IFT with Oil (mNm)
64,000	1060	1.05	70.8

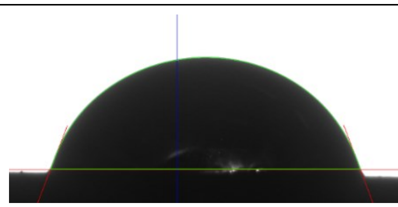
Table 4-3: Composition of crude oil

Composition of Hibernia Crude Oil			
Component	Mass fraction	Mole fraction	Volume fraction
CO_2	0.0000	0.0000	0.0000
N_2	0.0000	0.0000	0.0000
C1	0.0000	0.0000	0.0000
C2	0.0000	0.0000	0.0000
C3	0.0002	0.0009	0.0003
i-C4	0.0003	0.0012	0.0005
n-C4	0.0018	0.0070	0.0026
i-C5	0.0028	0.0086	0.0040
n-C5	0.0054	0.0165	0.0075
C6	0.0163	0.0427	0.0206
C7+	0.9732	0.9231	0.9646

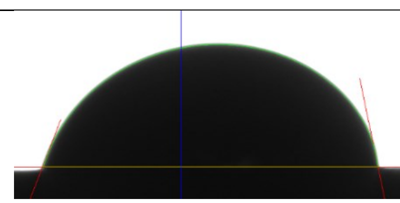
The core samples for testing were initially cut to 2” length with two 5 mm sections cut from top and bottom of the core. The idea was to use the core sample for capillary pressure measurement (USBM wettability measurement) and the thin section being used for the contact angle measurement and SEM-MLA analysis. The samples were then sonicated for 20 min and dried in an oven for 24 h before being saturated with the representative brine as outlined in the experimental plan.

In the first stage of experiment, the core samples were brought to connate water condition and oil saturation. The brine saturated samples (core + thin section) were loaded in to a coreholder with an overburden pressure of 6900 kPa (1000 psi) and centrifuged in drainage mode. A Rotosilenta 630RS refrigerated centrifuge from Vinci technologies (Nanterre, France) was used for this purpose. The drainage test with oil displacing brine was carried out in 7 centrifugation steps starting from 500 rpm to a maximum of 3500 rpm with 3 h of equilibration time per rpm step at 25° C.

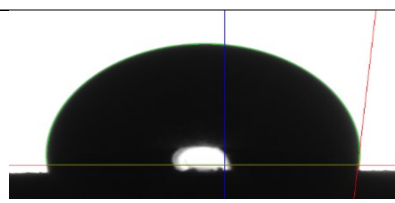
After centrifuging, the coreholders were disassembled to inspect the oil saturation in the core samples. The samples were again loaded in the core holder and the overburden pressure was adjusted prior to placing them in the oven for aging. Once aging was completed, the top (thin) section of the core sample was loaded in a Vinci IFT 700 instrument (Vinci Technologies, Nanterre, France) to measure the contact angle by the sessile drop method using brine as the drop fluid. The measured contact angles for the aged core samples are listed in Table 4-1. Figure 4-1 shows representative contact angles for the brine sessile drop in the presence of air for all the core samples. Figure 4-1a–e are the contact angle measurements for Chalk 1 through Chalk 5 that were aged at increasing time of 1 to 5 weeks. Figure 4-1f–j are the contact angle measurements of Berea 1 through Berea 5 that were aged at increasing time of 0.5 to 8 weeks. Figure 4-1 ((k) and (l) are the contact angle measurement for clean and 4 weeks aged Silurian dolomite.



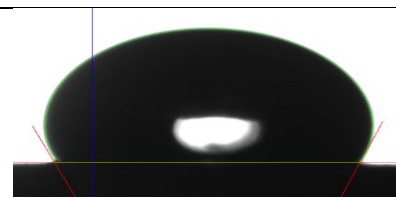
(a) Chalk 1 (θ = 65°) Age time: 1 week



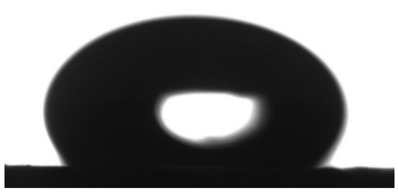
Chalk 2 (θ = 66°) Age time: 2 weeks



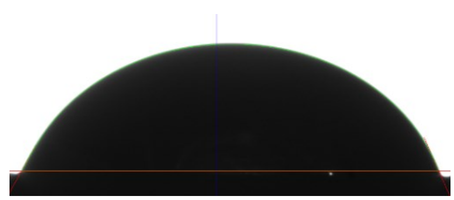
Chalk 3 (θ = 78°) Age time: 3 weeks



Chalk 4 (θ = 85°) Age time: 4 weeks



Chalk 5 (θ = 102°) Age time: 6 weeks



Berea 1 (θ = 70°). Age time: 1 week

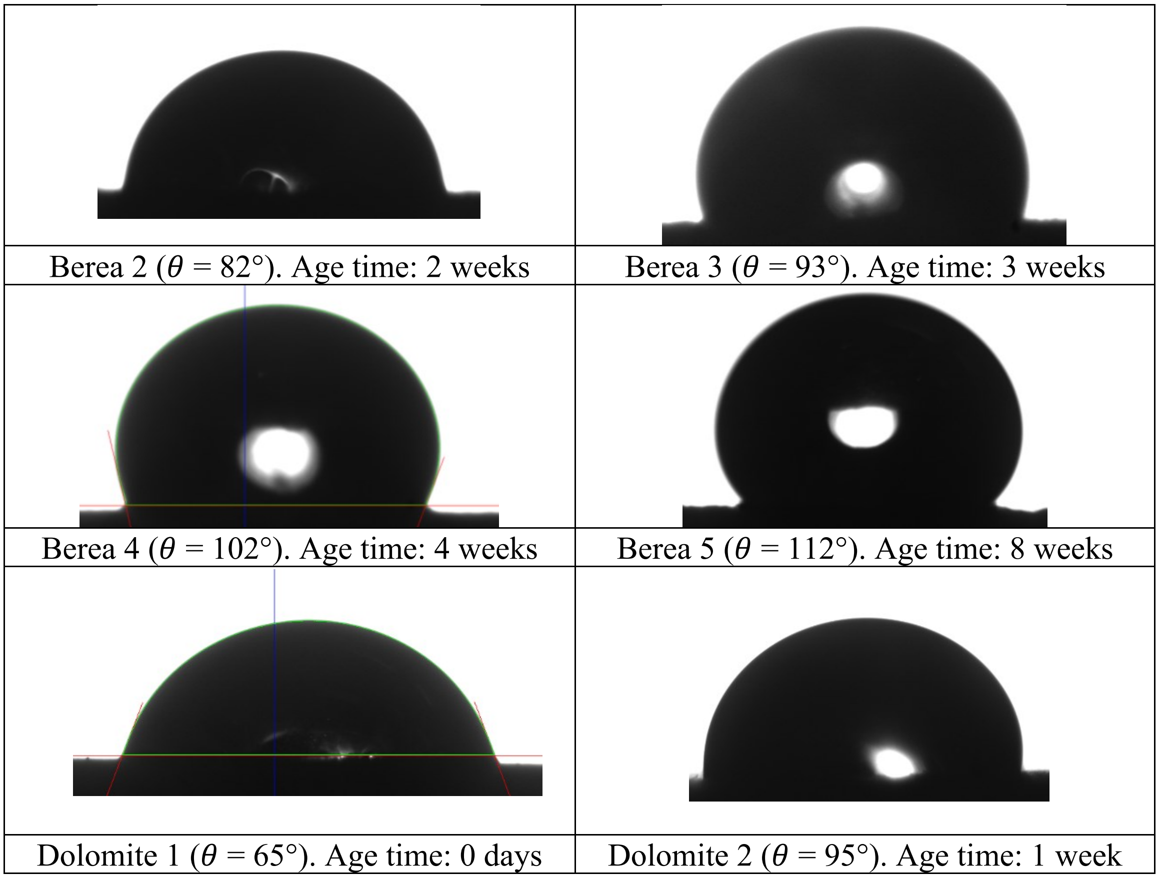
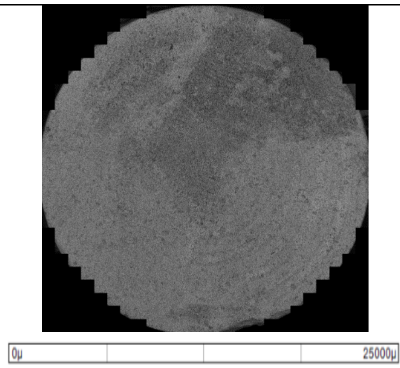
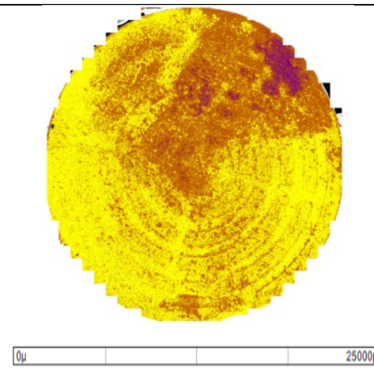


Figure 4-1: Brine droplet of size 5 × 10−4 mL placed onto the aged top end piece. (a) Chalk 1 (θ = 65°); (b) Chalk 2 (θ = 66°); (c) Chalk 3 (θ = 78°); (d) Chalk 4 (θ = 85°); (e) Chalk 5 (θ = 102°); (f) Berea 1 (θ = 70°); (g) Berea 2 (θ = 82°); (h) Berea 3 (θ = 93°); (i) Berea 4 (θ = 102°); (j) Berea 5 (θ = 112°); (k) Silurian dolomite 1 (θ = 65°); (l) Silurian dolomite 2 (θ = 95°).

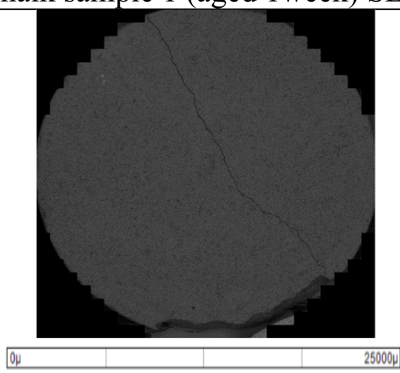
In the second stage, the bottom (thin) section of the aged core sample was carefully removed and secured in a glass container to ensure no oil gets vaporized from the pores due to exposure and was utilised for SEM-MLA analysis. FEI Quanta 650 FEG (Brno, Czech Republic) scanning electron microscope, equipped with Bruker high throughput energy dispersive x-ray (EDX) system (Bruker, Billerica, Massachusetts, USA) and backscattered electron detectors was used for this purpose. Imaging on the flat sample surfaces was carried out at very low vacuum conditions (79 Pa) to prevent evaporation of fluids. Additionally, the samples were not subject to any metallic or carbon coating on the surface, except for the liquid graphite coating on the sample holder. Instrument conditions and parameters include a high voltage of 25 kV, spot size of 5.75, working distance of 13.5 mm, 10 nA beam current, 16 µs BSE dwell time, 10 pixel minimum size (400 pixel frame resolution for 1 mm HFW) and 12 ms spectrum dwell for EDX. Each of these MLA acquisitions was completed using version 3.1.4.683 MLA™ software and took between 3 and 4 h per sample. Minerals and fluids in the core sample were calculated through a custom classification script that accounted for porosity and minerals. The mineralogy was determined using GXMAP measurement mode within FEI Mineral Liberation AnalyzerTM software, (version 3.1.4.683) equipped on a FEI Quanta 650 Field Emission Gun (FEG) SEM (Brno, Czech Republic). Each mineral identified must be within an 80% match to a known standard x-ray. For the determination of porosity, the "Pores" were determined using a custom classification, in which material that had a greyscale of certain range was scripted to be "Pores" instead of background material. This darker material of "Pores" was not matched to any x-ray standard. The results for individual samples were acquired as digital map of the minerals and a data table listing their mineral composition. Figure 4-2 is an example of mineral map and BSEM image of a core samples aged for varying time periods at 90 °C. Figure 4-2a–c are the SEM image of Chalk 1, Chalk 3 and Chalk 5 respectively and Figure 2g–i are the corresponding MLA images. Figure 4-2d,e are the SEM images of Berea 1 and Berea 5 with Figure 2i,j representing the corresponding MLA images. Figure 4-2f is the SEM image of Silurian dolomite 2 and Figure 4-2l is the corresponding MLA image. The minerals identified from the mineral map for chalk samples are listed in Table 4-4. Wettability assessment was based on the organic (oil) content of the sample in direct comparison to brine and mineral composition prior to saturation. The organic content for each sample is listed in Table 4-1 as SEM-MLA oil%.



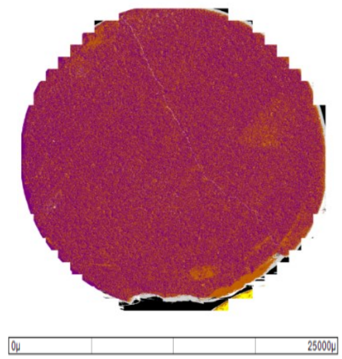
Chalk sample 1 (aged 1week) SEM



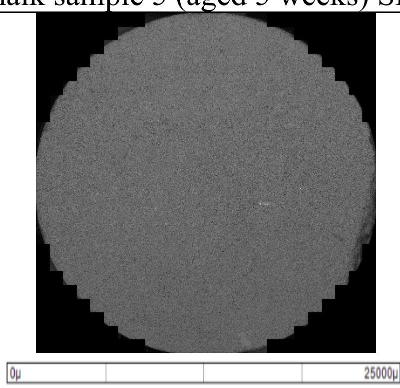
Chalk sample 1(aged 1week) MLA



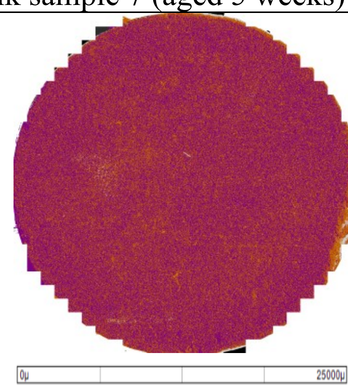
Chalk sample 5 (aged 5 weeks) SEM



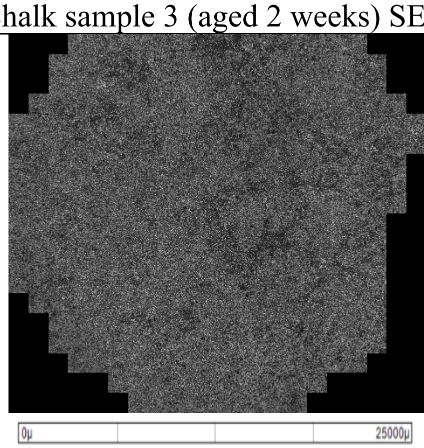
Chalk sample 7 (aged 5 weeks) MLA



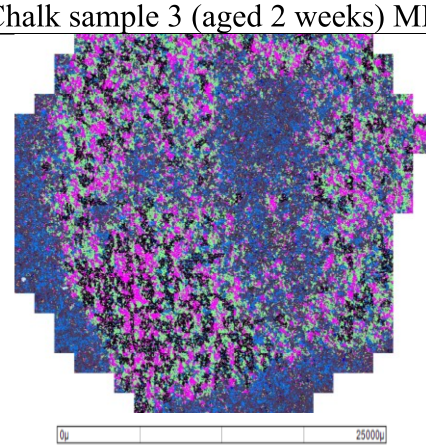
Chalk sample 3 (aged 2 weeks) SEM



Chalk sample 3 (aged 2 weeks) MLA



Berea sample 1 (aged 2 weeks) SEM



Berea 1 (aged 2 weeks) MLA

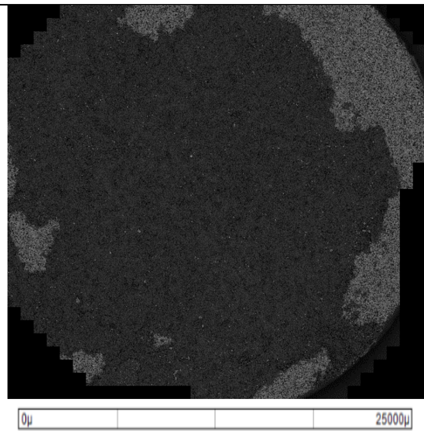
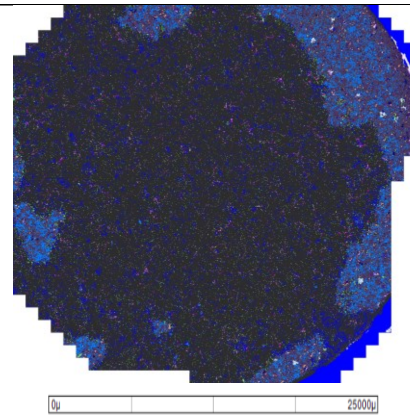
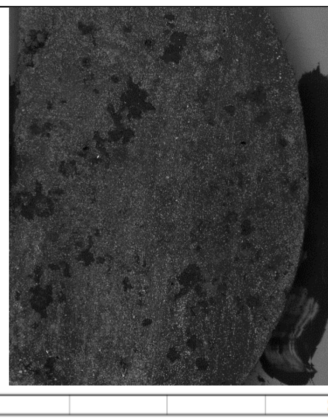
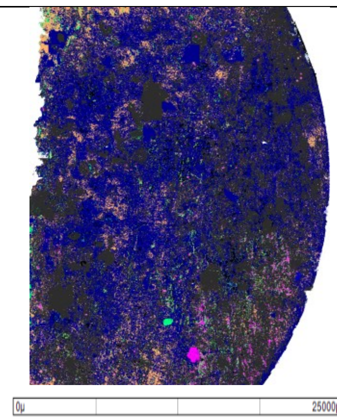
	
Berea sample 5 (aged 6 weeks) SEM	Berea sample 5 (aged 6 weeks) MLA
	
Silurian Dolomite 2 (aged 4 weeks) SEM	Silurian Dolomite 2 (aged 4 weeks) MLA

Figure 4-2: (a–f) SEM images of Chalk 1, Chalk 3, Chalk 5, Berea 1, Berea 5 and Silurian dolomite 2 respectively. (g–l) are the MLA images of Chalk 1, Chalk 3, Chalk 5, Berea 1, Berea 5 and Silurian dolomite 2 respectively

Table 4-4: Mineral list from the SEM-MLA analysis for chalk samples

Color	Mineral	No. 1 (Area %)	No. 2 (Area %)	No. 3 (Area %)	No. 4 (Area %)	No. 5 (Area %)
	Carbonate	83	81	80	35	38
	Halite	7	9	1	27	24
	Oil	6	10	14	24	36
	Others	4	0	5	14	2

After the primary drainage test was completed, the imbibition step was started to force brine into the aged core sample to displace oil. The core samples were loaded in the core holder (in imbibition mode) with overburden pressure of 6900 kPa (1000 psi). The receiving tubes were filled with the representative brine for each sample and the samples were centrifuged from 500 to 3500 rpm in seven steps of 3 h duration in each step. At the end of the imbibition test, the secondary drainage step was carried out by forcing oil through the brine saturated samples. The secondary drainage process was also carried out in seven steps. The secondary drainage data and the imbibition data were analyzed and the area under each curve was calculated. Figures 4-3 and 4-4 are the capillary pressure curves generated for samples saturated with oil at different brine concentration (drainage (D)) and displacement of oil under different brine concentrations (imbibition (I)). The USBM wettability index was calculated based on the area under the curve for both secondary drainage (A_1) and primary imbibition (A_2) using the formula $W = \log(A_1/A_2)$. The trapezoidal method was used to estimate the area under the curves using the capillary pressure points as the basis for each sample. A sample calculation for area under the capillary pressure curves for dolomite sample is presented in Figure 4-A1 and Table 4-A1 (Appendix A). Typically, the wettability index ranges from >0 for water wet, to <0 for oil wet and 0 for neutrally wet. In comparison with the contact angle measurement, the USBM method provides a macroscopic average of the core plugs used in this study [13,14]. The wettability index calculated via the USBM method for all the core samples are listed in Table 4-1.

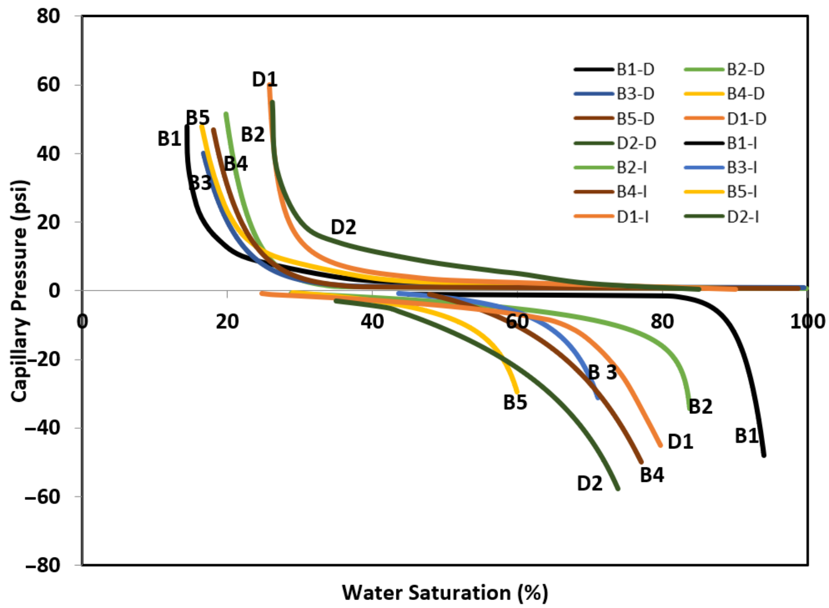


Figure 4-3: Capillary pressure curves for Berea and Silurian dolomite samples

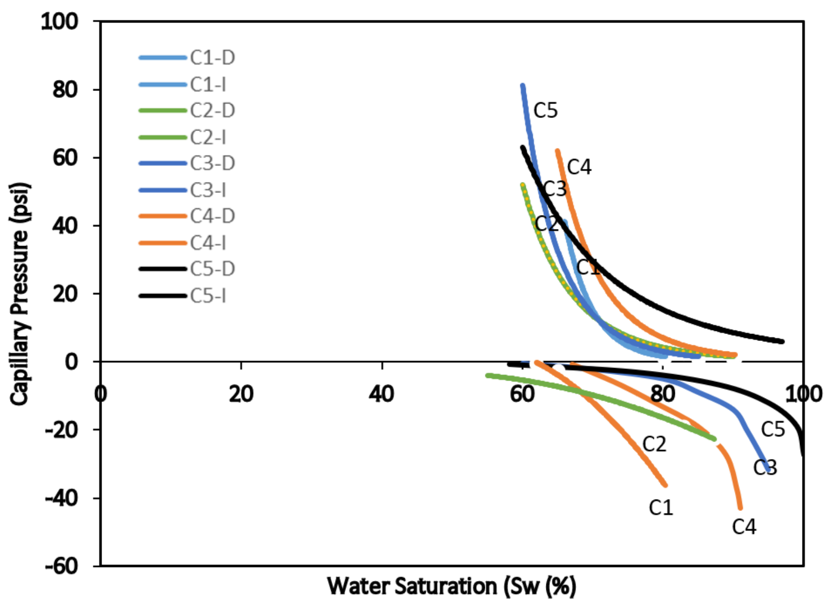


Figure 4-4: Capillary pressure curves for Chalk samples

4.3 Results

The premise of this work is to establish an alternative method to determine wettability in sandstone and carbonates. Wettability was altered by aging the samples with brine and crude oil at constant temperature. The tests were initiated by bringing the core samples to residual water and initial oil saturation using the centrifugal method. The oil saturated core samples with crude oil and connate water were aged for the different times and further analysis was carried out Contact angle measurements were first measured to determine wettability and were carried out on thin slices from aged core samples. The sessile drop method was applied with brine as the drop fluid on the aged core sample. For samples that were aged for few days less than a week, a stable drop could not be attained as it started spreading. Hence, the contact angle was considerably less and it was below 70°. Figure 4-1 is a display of all the contact angle images obtained from the samples used for this work. For samples that were aged more than a week, a more stable drop was formed and the contact angle increased to almost 80. Further, the difference in contact angle for samples of increasing aging time is indicated in Figure 4-1. As the aging time was increased to more than 4 weeks, more oil wet characteristics were observed with contact angle reaching more than 100. However, typical oil wet characteristics was displayed for samples that were aged above 6 weeks as the contact angle was more than 105. Increasing contact angle was also evident from the Figures 4-5 and 4-6 where a direct comparison of contact angle against SEM-MLA data was plotted for Berea and chalk

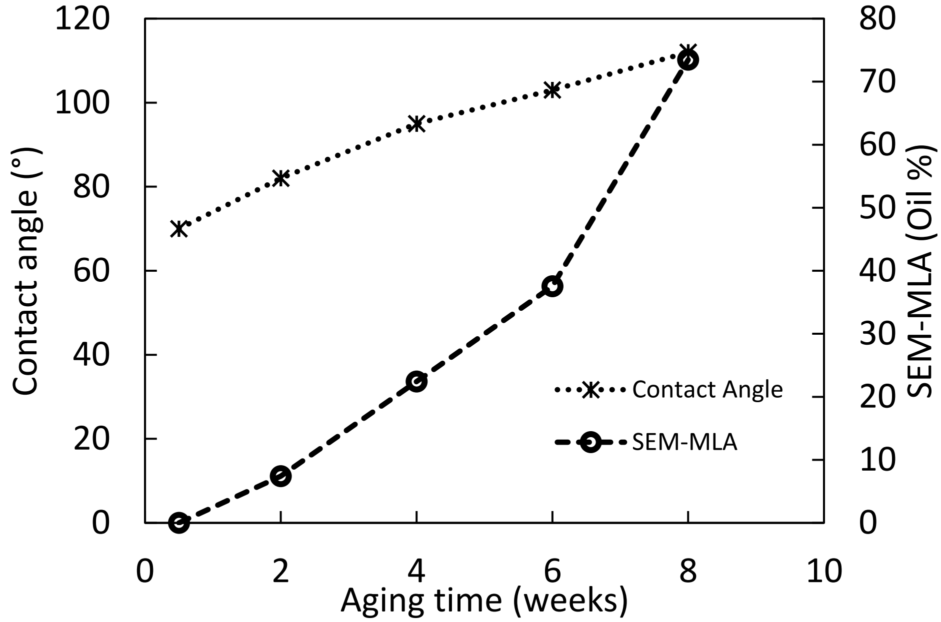


Figure 4-5: Comparison of contact angle data and SEM-MLA data for Berea

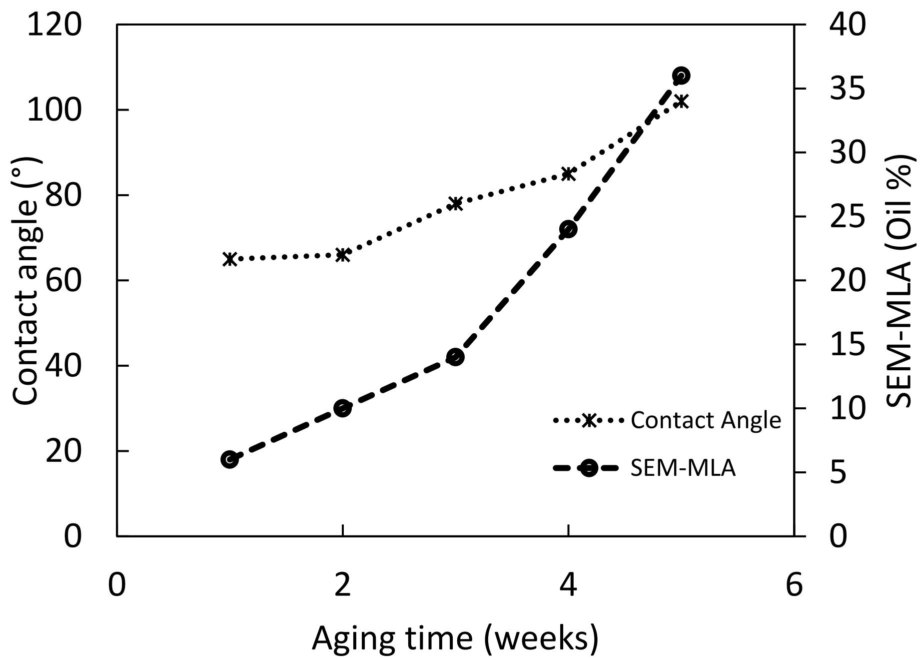


Figure 4-6: Comparison of contact angle data and SEM-MLA for chalk

The wettability index from the USBM method was analyzed using the area under the secondary drainage curve and the imbibition curve using the formula I = log (A1/A2). After the samples were aged, primary imbibition test was carried out followed by secondary drainage. Beside the uncertainty with confining pressure, the sample length impacted the extent of saturation in the chalk samples. The sample sizes were reduced to almost 1" to produce reasonable oil saturation, production and secondary drainage. As it can be seen from Table 4-1 and Figure 4-7, the wettability index did not follow a trend that was observed in contact angle measurement and SEM-MLA analysis. This is largely due to the inconsistency with data acquisition through laborious experimental process of bringing the core sample to ambient condition before changing from drainage to imbibition coreholders and vice versa.

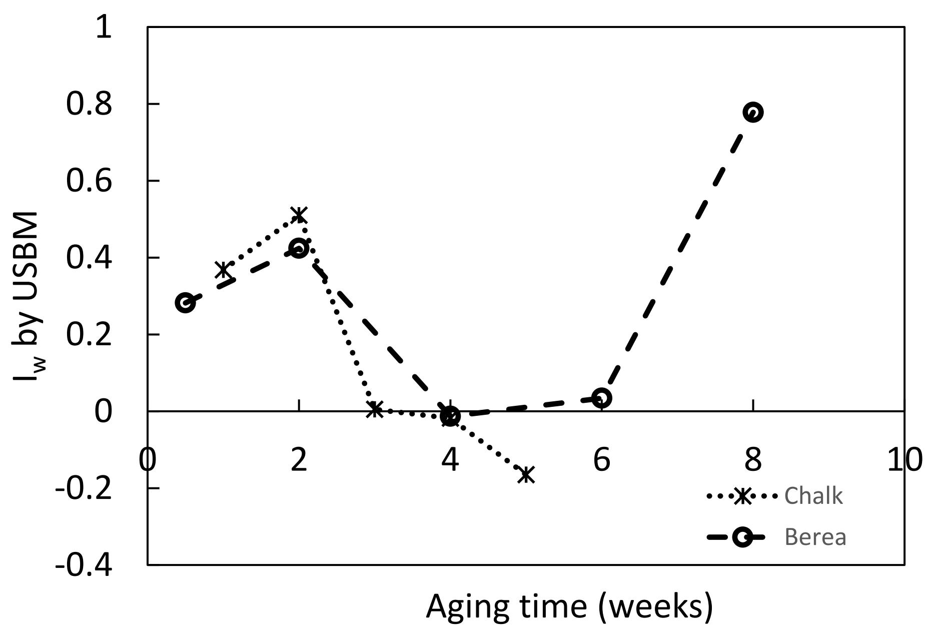


Figure 4-7: Comparison of USBM wettability index data between Berea and Chalk

4.4 Discussion

It was evident that the breakthrough pressure for chalk was significantly higher than Berea and Silurian dolomite because of its low permeability. Additionally, the pore size distribution is quite narrow in the range of 50 μm. In spite of the variations in the USBM results, we are able to demonstrate oil-wet characteristics for the chalk sample that were aged more than 3 weeks. Contrarily, Berea samples showed oil-wet characteristics when aged more than 4 weeks. The wettability index measured from USBM method was in close agreement with other published results [14,15] in predicting optimal time of 4 weeks for chalk, 6 weeks for Berea and more than 4 weeks for dolomite to render reservoir rocks oil-wet [1].

The last method to validate wettability was using SEM-MLA analysis where the samples were analyzed to provide an estimate of oil present. Initial tests on thin slices aged core samples provided inconclusive results as the saturation at the lower part of the core sample was not uniform. Thin slices from top of the core were later imaged and the corresponding mineral composition for a sample is shown in Table 4-3. As the chalk mineral composition was mainly carbonate and the brine composition was made of only NaCl, the MLA analysis straight forward compared to Berea and Silurian dolomite, which has more quartz and calcite respectively. A clean sample of each type of rock with crude oil and one with brine saturation were initially analyzed to detect the corresponding oil/brine signature and saved in the SEM database to match aged core samples. This was more effective in mineral liberation analysis and resulted in each sample yielding the corresponding oil residue values. The individual estimates for oil present in the aged core samples are tabulated in Table 4-1. Figures 4-5 and 4-6 were a direct comparison of the SEM-MLA data against the contact angle measurement. It is evident SEM-MLA method showed increasing oil residue in core sample with aging time corroborating the results from contact angle measurement.

4.5 Conclusions

1. A suite of Berea, dolomite and outcrop chalk cores were prepared and aged at increasing duration at constant temperature. Wettability was validated using three diverse methods, i.e., contact angle, USBM wettability index and oil content using SEM-MLA analysis
2. With increasing aging time, the core samples indicated increasing oil-wet characteristics. Contact angle measurements indicated agreed strongly oil-wet characteristics for increased aging time. Contact angle values varied from 60 (water-wet) to 120° (oil-wet). Above aging time of 4 weeks the contact angle measurements were stable with a contact angle value around 110°.
3. A new method to estimate wettability was tested using SEM-MLA analysis, which provided more direct and convincing results. Oil presence in core samples is quantified via MLA analysis and the strategy to change wettability with increasing aging time was validated. Interestingly MLA analysis on chalk and Berea samples were straightforward with a simplified mineral list with increasing oil residue for increased aging time.
4. A comprehensive estimate of more than 5 weeks for chalk and 6 weeks for Berea was commonly agreed between three different wettability measurements to ensure core samples are oil wet.
5. The test on Silurian dolomite can further be strengthened by increasing the number of test samples with aging time to provide a similar estimate as Berea and chalk

4.6 Appendix

Table 4-5: Area under the curve calculation using trapezoidal rule for dolomite 2.

P_c (psi)	S_w (%)	Area
26.20	78.03	1157.11
28.40	35.64	454.83
30.20	20.12	190.91
35.60	14.32	215.47
46.50	9.07	152.80
56.50	6.10	63.04
60.50	5.02	182.53
70.20	2.23	125.26
79.30	0.55	
Area under drainage curve (A_1)		2541.96
Area under imbibition curve (A_2)		5862.43
Wettability Index (USBM)	$Log(A_1/A_2)$	−0.363

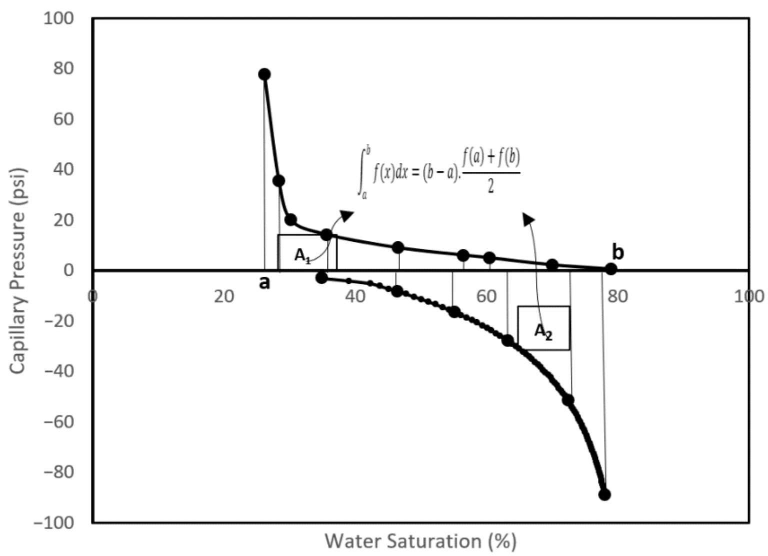


Figure 4-8: USBM wettability index from capillary pressure curves of dolomite 2.

4.7 References

1. Hirasaki, G.J., Rohan, J.A., Dubey, S.T., Niko, H. Wettability evaluation during restored-state core analysis. Paper SPE-20506, Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, LA, USA, 23–26 September 1990.
2. Anderson, W.G. Wettability Literature Survey-Part 1: Rock/Oil/Brine interactions and the effects of core handling on wettability. J. Pet. Technol. 1986, 38 (10), 1125–1144. https://doi.org/10.2118/13932-pa.

3. Alotaibi, M.B., Azmy, R., Nasr-El-Din, H.A. Wettability challenges in carbonate reservoirs. Paper SPE-129972, Presented at the SPE Improved Oil Recovery Symposium. Tulsa, OK, USA, 24–28 April 2010.
4. Zangiabadi, B., Korsnes, R.I., Madland, M.V., Hildebrand-Habel, T., Hiorth, A., Kristiansen, T.G. Mechanical properties of high and lower porosity outcrop chalk at various wetting states. Presented at the 43rd US Rock Mechanics Symposium and 4th US-Canada Rock Mechanics, Asheville, NC, USA, 28 June 2009.
5. Vijapurapu, C.S. Rao, D.N. Effect of brine dilution and surfactant concentration on spreading and wettability. Paper SPE-80273, Presented at the International Symposium on oilfield Chemistry, Houston, TX, USA, 18–21 February 2003.
6. Zhou, X.-M.; Torsaeter, O.; Xie, X.; Morrow, N. R. The effect of crude-oil aging time and temperature on the rate of water imbibition and long-term recovery by imbibition. SPE Form. Evaluation 1995, 10 (4), 259–266. https://doi.org/10.2118/26674-pa.
7. Jadhunandan, P., Morrow, N. Effect of wettability on waterflood recovery for Crude-Oil/Brine/Rock systems. SPE Reserv. Eng. 1995, 10 (1), 40–46. https://doi.org/10.2118/22597-pa.
8. Zhang, P., T. Austad. The relative effects of acid number and temperature on chalk wettability. Paper presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, TX, 2 February 2005. https://doi.org/10.2118/92999-MS.
9. Robin, M., Combes, R., Degreve, F., Cuiec, L., Wettability of porous media from environmental scanning electron microscopy: from model to reservoir rocks. Paper SPE-37235, Presented at the International Symposium on oilfield Chemistry, Houston, TX, USA, 18–21 February 1997.
10. Robin, M.; Combes, R.; Cuiec, L. Two SEM techniques to investigate reservoir-rock wettability. J. Pet. Technol. 1998, 50 (11), 77–79. https://doi.org/10.2118/1198-0077-jpt.
11. Schmatz, J.; Klaver, J.; Jiang, M.; Urai, J. L. Nanoscale morphology of brine/oil/mineral contacts in connected pores of carbonate reservoirs: insights on wettability from Cryo-BIB-SEM. SPE J. 2017, 22 (5), 1374–1384. https://doi.org/10.2118/180049-pa.

12. Kumar, M.; Fogden, A.; Senden, T.; Knackstedt, M.A. Investigation of pore-scale mixed wettability. SPE J. 2012, 17 (1), 20–30. https://doi.org/10.2118/129974-pa.
13. Yassin, M. R.; Dehghanpour, H.; Begum, M.; Dunn, L. Evaluation of Imbibition Oil Recovery in the Duvernay Formation. SPE Reserv. Evaluation Eng. 2018, 21 (2), 257–272. https://doi.org/10.2118/185065-pa.
14. Graue, A.; Viksund, B. G.; Baldwin, B. A. Reproducible wettability alteration of low-permeable outcrop chalk. SPE Reserv. Evaluation Eng. 1999, 2 (2), 134–140. https://doi.org/10.2118/55904-pa.
15. Zhou, X., Morrow, N.R., Ma, S. Interrelationship of wettability, initial water saturation, aging time, and oil recovery by spontaneous imbibition and waterflooding. SPE J. 2000, 5 (2), 199–207. https:// doi.org/10.2118/62507-pa

5 CHAPTER FIVE

An Experimental Approach In Evaluating Ordering Criteria For Composite Core Arrangement in Special Core Analysis

(Paper 3, Published)

This chapter is an edited version of the article published in **Global Journal of Science and Engineering**: Sripal, Edison., Sofla Jafari, Saeed., L. A. James., "An Experimental Analysis in Evaluating Ordering Criteria For Composite Core Arrangement in Special Core Analysis". Global Journal of Science and Engineering, Vol. 05 (2022) 14-18

Abstract

Composite cores of core plugs from different heights of an exploration well core are often used for routine and special core analysis to evaluate an oil reservoir. The question is whether or not the order of the core plugs in the composite core makes a difference to the absolute and relative permeability measurements? The seminal work by Huppler (1969), proposed ordering individual core samples harmonically in a composite core to match the overall permeability [1]. Langaas (1998) proposed ordering the core samples in decreasing permeability for effective relative permeability measurements, based on theoretical framework of North Sea sandstones [2]. In this paper we tested the methods proposed by Huppler [1] and Langaas [2] experimentally. Core samples with permeability ranging from 50 mD to 2 Darcy were used for this work. The orientation of the core samples was tested for permeability and relative permeability and compared with the theoretical model developed by Langaas [2]. In addition to the experimental work, simulations were performed with the three different composite cores and the representative recovery factor was compared to provide the appropriate composite core arrangement

KEYWORDS: Enhanced Oil Recovery, Coreflooding, Composite core, Relative permeability

5.1 Introduction

The development of appropriate geological and reservoir simulation models relies significantly on routine and specialized core analysis (SCAL) data. SCAL tests include wettability, capillary pressure, relative permeability measurements, and coreflooding tests, which often take several months to conduct to represent actual flow conditions exhibited in the field. In order to produce quality SCAL data, it is important to select the representative cores from each stratum level of the reservoir. Laboratory measurement of oil-water relative permeability is one of the essential elements in designing a water flood project. The success of a water-flooding project depends on many factors such as proper well location and pattern, and injection and production rates. But prior to that, the response of the reservoir rock to water flooding must be evaluated as unfavorable wettability may reduce the ultimate oil recovery by water injection. Siddiqui et al. [3] proposed a comprehensive protocol to select representative core plug samples for SCAL experiments based on a combination of reservoir zonation, heterogeneity analysis and application of RQI (Reservoir Quality Index) techniques [3]. Normally, to determine oil-water relative permeability data in the laboratory, cores from the same reservoir are used. Since reservoir cores are relatively short in length (4 – 8 cm), then employing these cores to obtain the relative permeabilities for any given reservoir will often result in significant errors. These errors are due to both the capillary end effects and errors associated with inaccuracies in volume measurements becoming significant for small cores. These set of stringent requirements are generally compromised as the bedding planes being along the small dimension of the whole core so that only short core samples are available for laboratory experiments. Short cores of few inches long result in poor material balance accuracy wherein experimental results are often subject to infrequent flaws in the core and a greater influence of undesired end effects. To overcome all the mentioned shortcomings, composite cores are constructed by series arrangement of small core plugs (~1.5 - 2”) drilled parallel to the bedding plane [3]. It often involves having capillary bridges between samples to overcome capillary end effects under triaxial compression to increase the relative accuracy of volume measurements [4].

An important aspect of using composite core samples for lab scale experiments is to determine the relative permeability which determine the recovery of fluids from reservoir simulated through coreflooding experiments. Relative permeability experiments are preferentially performed at steady state conditions. The rigorous, time consuming steady state method can be circumvented by performing unsteady state relative permeability measurements. Unsteady state relative permeability measurements are favoured as steady state experiments do not explicitly depict reservoir flow mechanism of one fluid displacing another [4]. Despite these advantages, unsteady state experiments are difficult to process as data is limited to a smaller range of saturations and/or fluid flow conditions making extrapolation (relative permeability models) over the entire saturation range uncertain. Most of the experimental methods do not include capillary pressure gradient effects which are often overcome by performing the experiments at higher flow rates resulting in non-uniform sweep and limited saturation range. Using a semi analytical approach, Civan and Donaldson [5] have overcome the requirement of running unsteady state experiments at high flow rates by accounting for capillary pressure effects. The semi analytical approach is also hindered by the errors arising from numerical differentiation and integration [6].

The complexities involved in experimental and interpretation methods led to the use of empirical relative permeability models *viz a viz* history matching core scale simulations as a tool to determine and tune the continuous relative permeability function [7]. The limited experimental data range is extrapolated and fit over the entire saturation range by choosing a relative permeability model and history matching coreflooding and simulation production data [8]. The resulting relative permeability curves based on the choice of parametric functions fulfils the data for the complete saturation range [9].

Laboratory relative permeability experiments are carried out on composite cores made up by stacking a series of smaller core plugs of length ~1.5 - 2 inches. The resulting composite core is considered as a single core with average physical properties. In industry, composite cores are regularly used to perform coreflooding experiments to determine recovery factors and residual oil saturations after flooding [2]. There is no consensus on the orientation of the composite core and the industry is divided in choosing the order of the smaller core plugs in the composite core.

An introductory work on this subject was developed by Huppler [1] based on permeability of individual cores. Imposing a harmonic averaging method that composite core be created using a harmonic averaging of permeability of consecutive cores. The criterion is that the sequence of ordering the cores is such that the average permeability between two adjacent cores is close to the harmonic average of the overall permeability. For example, a composite core will be ordered as 100, 40, 80, and 60 mD with a combined harmonic average of ~62 mD. It is important to understand that Huppler neglected capillary effects and considered equal relative permeability and porosity for all the core plugs in the composite core.

Alternately Langaas et al. [2] proposed ordering the cores in decreasing permeability in the composite core. This was based on numerical study on sandstone samples from North Sea. The permeability of the cores ranged from 400 to 1000 mD with the assumption that porosity and relative permeability are the same for all core plugs. Considering capillary effects with a water to oil ratio of 0.4:2.4 and an injection rate of 2.53 ml/min, three different sequence types were studied i.e ascending, descending, and the Huppler criteria. Unsteady state core flooding experiments were simulated, and relative permeability was calculated using the JBN (Johnson, Bossler & Naumann) method. Eventually, Langaas et al. proposed that for coreflooding experiments that provide the best estimate for residual oil saturation, the best ordering of a composite core is samples with decreasing permeability along the flow direction i.e., the sample at the inlet at the highest permeability and the sample at the outlet has the lowest permeability. Langaas also tried varying the water viscosity from .4 to 14 cP and found no real change in the shape of the relative permeability curves and as expected, oil recovery increased (decreasing Sor) with increasing water viscosity.

Following the Langaas numerical study, experimental studies were conducted by Zekri et al. [4] and Mohammadi et al. [10]. Zekri et al. performed unsteady state relative permeability experiments on a suite of carbonates cores from the United Arab Emirates (UAE) with permeability ranging from 0.55 to 30 mD. The composite core order was compared based on recovery factor. Decreasing permeability order resulted in the highest recovery factor when the water to oil viscosity ratio was 1:15. In a similar approach Mohammadi et al. [10] proposed ordering cores with increasing permeability along the flow direction to produce a high recovery factor for a waterflood experiment on carbonate cores. It should be noted ordering the composite cores to achieve the highest recovery factor is an artificial criterion and on the contrary the criterion should be more realistically based on injection and production well placement and reservoir drainage strategies.

The important question is what ordering of cores in a composite is appropriate for coreflooding experiments. Huppler's criteria of harmonic average of the permeability is often considered the industry norm for composite core preparation. But there is no consensus on choosing either an increasing permeability or decreasing permeability along the flow direction. Often experiments are performed with composite cores increasing in permeability along the flow direction to supposedly reduce experimental time and cost with the objective being maximum oil recovery. This is, in fact, debatable because the additional time it takes to do coreflooding in a marginally higher vs lower permeability is insignificant compared to the time to prepare the experiment, fluids, and post experiment analysis. Further, we are no more certain using one average relative permeability curve compared to another. Conclusions for one arrangement versus another based on higher recovery and time savings alone are not significant. Preferred composite core arrangements that reduce uncertainty between unsteady state and steady state results have more valuable information.

In this work we attempt to experimentally demonstrate the outcome of different composite core arrangements on the coreflooding results such as relative permeability, recovery factor, and fractional flow. From comparative analysis of the results from these composite core arrangements we attempt to provide a recommendation that is suitable for depicting reservoir flooding mechanism in the lab that could aid field scale simulations.

5.2 Mathematical Formulation

One dimensional linear flow for oil and water is represented by the following form of Darcy's law [11],

$$q_o = -\frac{kk_{ro}(Sw)}{\mu_o}\left(\frac{\partial P_o}{\partial x} - g\Delta\rho\ Sin\theta\right) \tag{1}$$

where k is the absolute permeability, Kro is the relative permeability of oil. Sw is the water saturation, qo is the flow rate of oil, μ_o is the oil viscosity, and Po is the pressure of oil phase. A similar expression can be written for water, qw. By combining the flow equations for water and oil and including the capillary pressure gradient in the direction of flow, the equations combine to give

$$\Delta\rho = \rho_w - \rho_o \tag{2}$$

The fractional flow of water at any point can be further written as;

$$f_w = \frac{1 + \frac{k k_{ro} A}{q_t \mu_o}\left(\frac{\partial P_c}{\partial x} - g\Delta\rho\, Sin\theta\right)}{1 + \frac{k_o}{k_w}, \frac{\mu_w}{\mu_o}} \tag{3}$$

When there is significant fluid density differences coreflooding tests are carried out under gravity stable conditions where the coreholder is set up vertically where a denser fluid (water) is injected from the bottom and a lighter fluid is injected from the top. In most cases, relative permeability tests involving high water-oil mobility ratios are performed at high flow rates to avoid capillary end effects [12]. Hence it is important to consider the capillary end effect when cores are arranged in sequence of increasing permeability along the flow direction

5.3 Experimental Methods

5.3.1 Porous Medium

The porous media used for this work are consolidated sandstone core plugs from Hibernia B-16 offshore Newfoundland containing 95% quartz. The physical properties of the core samples are listed in Table 5-1. Core plugs of 3.8 cm diameter (1.5") were taken between 3962 and 4037 m from half of a 4" exploration well core.

Table 5-1: Physical properties of core plugs

Core No.	Sat. porosity (%)	Air Permeability (mD)	MIP Permeability (mD)
1	18.95	134	114
2	18.28	315	247
3	19.95	525	550
4	20.28	924	870
5	20.39	2800	1488

5.3.2 Fluids

The physical properties of the 90,000 ppm brine (*NaCl 84.38%; $CaCl_2$*$2H_2O$ 12.32%; $MgCl_2$*$6H_2O$ 2.57%; KCl 0.4%; Na_2SO_4 0.32%)* used to determine the saturation porosity, brine-permeability, and for initial saturation are presented in Table 5-2 Offshore Newfoundland dead crude oil with 6 cP viscosity and 878 Kg/m^3 density was used as the non-wetting phase. The total acid number (TAN) of the crude oil was analyzed and found to be 0 mg KOH/g indicatin no acid components in the oil. The oil mixture was filtered (5 μm filter paper) and degassed by vacuuming for 48 hours to prevent gas production during the drainage. The physical properties of the offshore NL crude oil are tabulated in Table 5-3. The composition of the oil mixture was analyzed using an *Agilent 7890A Gas Chromatograph with Simulated Distillation* (SIMDIS) system (see Table 5-4), density was measured using Anton Parr DMA 50 and viscosity was measured with PVT Viscometer.

Table 5-2: Physical properties of brine

Brine Salinity (ppm)	Density (kg/m^3)	Viscosity (cP)	IFT with oil (Nm/m)
64,284	1060	1.05	70.8

Table 5-3: Physical properties of oil

Color	Density (kg/m^3)	Viscosity (cP)
Light brown	858	6

Table 5-4: Composition of crude oil

Component	Mass fraction	Mole fraction	Volume fraction
CO_2	0.0000	0.0000	0.0000
N_2	0.0000	0.0000	0.0000
C1	0.0000	0.0000	0.0000
C2	0.0000	0.0000	0.0000
C3	0.0002	0.0009	0.0003
i-C4	0.0003	0.0012	0.0005
n-C4	0.0018	0.0070	0.0026
i-C5	0.0028	0.0086	0.0040
n-C5	0.0054	0.0165	0.0075
C6	0.0163	0.0427	0.0206
C7+	0.9732	0.9231	0.9646

5.3.3 Mercury Porosimetry

Additionally (five) dried sample of diameter 38.1 mm and 4-5 mm length (4.5 - 5.7 cm^3 volume) was analyzed using a *Micromeretrics Autopore IV 9500* instrument. The sample was subjected to mercury intrusion from 0.1 MPa (15 psi) to 228 MPa (33000 psi) to estimate porosity, density, tortuosity, and pore/mineral surface areas. Intrusion and extrusion data were used to estimate capillary pressure curves and the pore size distribution. Figure 5-1 is a plot of the capillary pressure for the 5 core samples selected for this work.

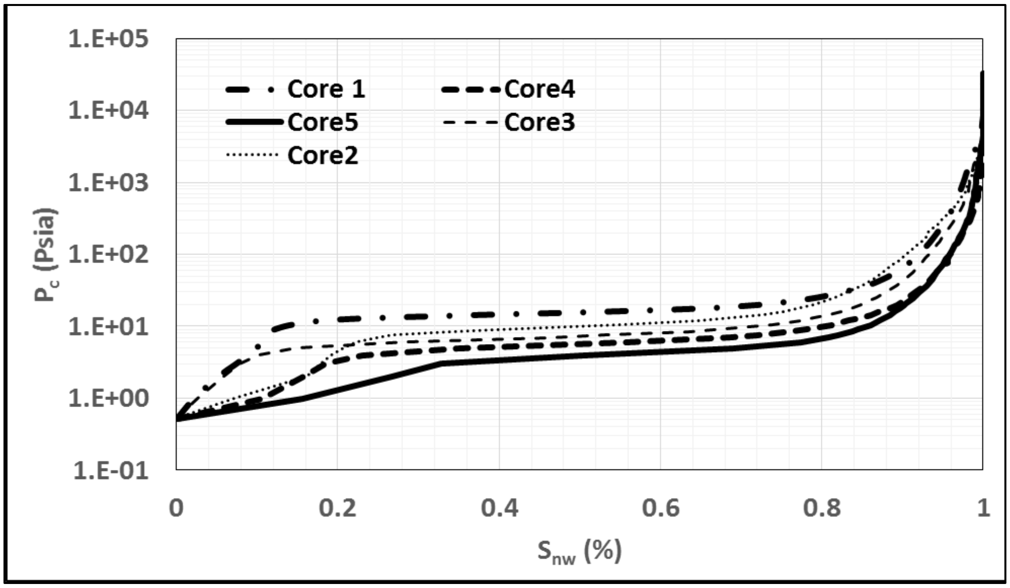


Figure 5-1: Drainage Capillary pressure for the 5 core plugs (Mercury porosimetry)

5.3.4 Coreflooding Experiments

Figure 5-2 is a schematic of the coreflooding experiment used in this study. The custom made experimental set up is capable of measuring steady state / unsteady state relative permeability for oil-water at pressure up to 69 MPa (10,000 psi) and temperature up to 200° C. The core samples were loaded into Vinci triaxial coreholder and a Whatman© Grade 1 filter paper was placed between individual core samples to ensure uniform saturation. Two high pressure accumulators were used for storing oil and water and injection was carried out using two high pressure dual cylinder continuous injection pumps (Quizix 20K). A Vinci back pressure regulator was installed at the outlet of the coreholder to simulate in situ conditions and the pressure drop across the coreholder was measured using a Keller PRD33X high precision differential pressure transducer with a pressure range of 0 – 40 bar and an accuracy of ± 0,05 %FS.

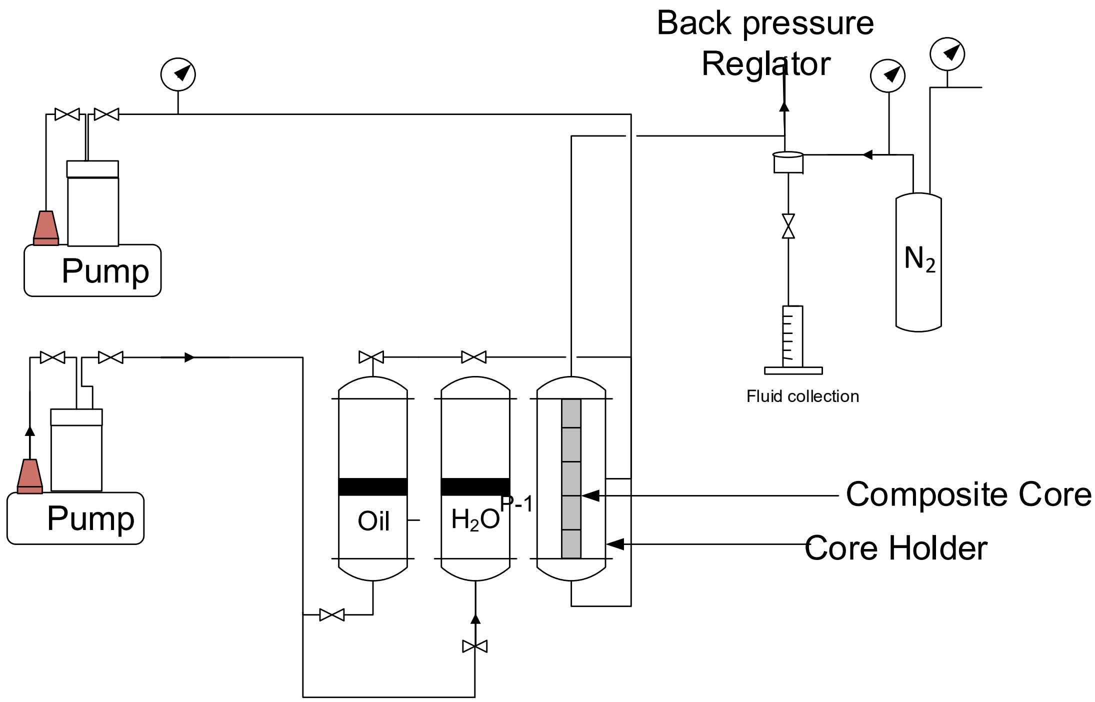


Figure 5-2: Schematic experimental set-up for coreflooding.

Prior to loading the core sample in the coreholder, the core plugs were cleaned in a soxhlet (toluene & iso propyl alcohol) for 24 hours to remove fluids and salt. A small section of 3mm thickness was cut from the core plugs to analyse capillary pressure by Mercury Intrusion Porosimetry. The cleaned cores were dried overnight at 90^o C. The cleaned core plugs were first tested for air permeability then vacuum saturated with brine to determine the porosity.

The 5 brine saturated cores were mounted into the core holders of the *Rotosilenta 630RS* centrifuge from Vinci Technologies. An overburden/confining pressure of 13.7 MPa (2000 psi) was used, and the centrifuge was operated in drainage mode to displace the brine with oil to irreducible water saturation. Drainage was performed in 7 steps from 500 to 3500 rpm in increments of 500 rpm with 3 hours of equilibration time for each step. The capillary pressure was calculated at any position, r, along the core length using the Hassler-Brunner equation [14]:

$$P_c(r) = \frac{1}{2}\Delta\rho\omega^2(r_1^2 - r^2) \tag{4}$$

where $\Delta\rho = \rho_{out} - \rho_{in}$ is the density difference between the fluid expelled from the core (ρ_{out}) and the fluid entering the core (ρ_{in}), ω is the angular rotation speed of the centrifuge and r (varying from 0 to 5 cm) are the distances from the rotational axis to the outlet face and any point along the core length.

After reaching an equilibrium between the oil/water saturation and capillary pressure, hence when no more brine is being produced, the brine expelled from the core was measured and the average water saturation for each rotation speed was obtained. This water saturation (%) was plotted against the capillary pressure estimated from equation (1) to produce the capillary pressure curve. The raw data points are fitted with a Forbes spline model to get the final capillary pressure curves. This is the suggested approach as raw data only provides average saturation and the fitted model provides the local saturation at every pressure points. Figure 5-3 is the capillary pressure curve for the 5 core plugs selected for this work.

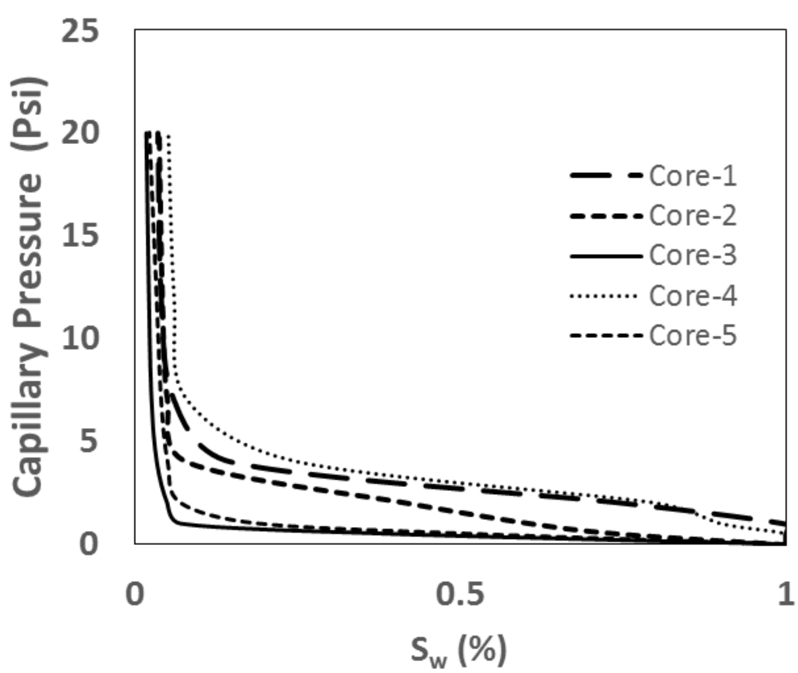


Figure 5-3: Drainage capillary pressure of the 5 core plugs (Centrifuge).

The capillary pressure data from the centrifuge experiment is used to determine the relative permeability of individual core plugs using Hagoort method [15] which is a modification of Buckley Leverett method [16]. The water volume for each step in the centrifuge experiment is plotted against the rotational speed to determine the capillary pressure vs. water saturation. The experimental capillary pressure curve was fitted with Pc-LET model to form the simulated capillary pressure curve. Finally, optimization was carried out on the model capillary pressure curve and fitted with a modified Corey model [17] to produce the relative permeability curve for each core plug. The process of producing the individual relative permeability curves from centrifuge experiment was carried out using Cydar© software. Figure 5-4 is a representation of relative permeability of the five core samples used in this work. This particular process is very cumbersome involving numerous iterations to produce the end results. The relative permeability data along with other pertrophysical properties for core plugs are used as input data to simulate composite coreflooding in Eclipse 100 simulator.

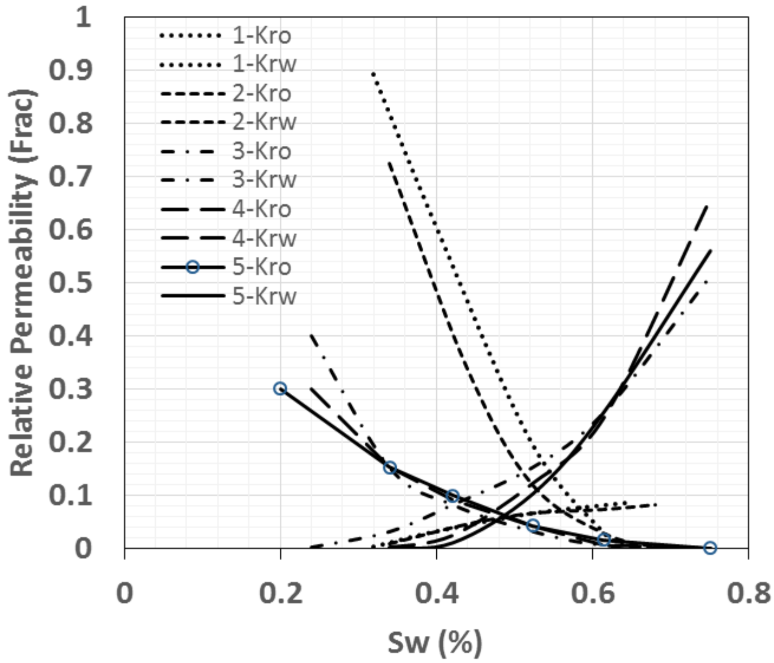


Figure 5-4: Relative permeability of 5 core plugs.

After performing the centrifuge drainage test, the confining pressure was reduced to 100 psi and the core holders, with cores and end pieces inside, were placed in the oven to age at 90°C for 10 days. The typical aging time is around 40 days, but due to lack to time and extent of experimentation, aging time was restricted to 10 days.

The aged core plugs were arranged as per the desired orientation by stacking one top of another with a Whatman© Grade 1 filter paper was placed between individual core samples in between acting as a contact. The arranged core plugs were wrapped with a Teflon tape and tin sheet and loaded into a Viton sleeve. The prepared composite core was then loaded into the Vinci triaxial coreholder and a confining pressure of 3.5 MPa (500 psi) was applied. Oil was injected for 3 – 5 pore volumes. Temperature was maintained at 25°C. Initial effective permeability to live crude oil was measured to estimate the initial permeability endpoint value for relative permeability calculations. Once sufficient oil was injected, irreducible water saturation is considered to be reached. Water injection was initiated at a constant rate of 40 cm^3/hr. The back pressure regulator (BPR) at the outlet of the coreholder ensured constant flow across the sample and differential pressure and fluid production was observed for every step of the process (Figure 5-2). Additionally, a number of endpoint water permeabilites at higher rate to ensure the endpoint water permeability for data analysis is included. At the end of the waterflood, the set up was brought to ambient condition and the samples were extracted from the coreholder and subject to Soxhlet to measure residual fluid saturation and complete the material balance. The same procedure of waterflood was repeated for the other two composite core arrangements which was created by changing the sequential arrangement of the core plugs.

5.3.5 Simulation

The coreflooding simulation for this work was carried out using Eclipse 100©. The model grid was created incorporating physical parameters such as porosity, permeability, and relative permeability from experimental results of individual cores samples. The total dimensions of the model were 3.5 cm x 3.5 cm x 25 cm with 5 grids in X and Y dimensions and 50 grids in Z. The dimensions of the model core were selected based on the experimental core dimensions. To mimic 5 different cores, the model is equally divided in 5 blocks in Z direction and the physical properties of each bock is adjusted based on the experimental measurements.

Figure 5-5 is the graphical depiction of the gird model depicting flow at different composite core arrangement. This resulted in each core sample physically measuring 3.5 cm x 3.5 cm in are perpendicular to flow and 5 cm in length in the model. Figure 5-5 depicts the 3-D model flow simulation for the different composite core orientations with 1:6 fluid viscosity ratio after 18 minutes of water injection. As illustrated in the figure, core arrangement can have significant effect on the oil saturation distribution in the core, its breakthrough time, and oil recovery factor. 18 min after injection, breakthrough is already happened in the Huppler and Random models, but it is not the case in the decreasing and increasing models. Among all these models, decreasing model shows more piston like displacement procedure. The main purpose of the simulation is to calculate the recovery factor for waterflooding experiment when composite core was arranged with increasing or decreasing permeability along the flow direction. Additionally, recovery factor on composite core according to Huppler criteria and random orientation was also simulated using this model.

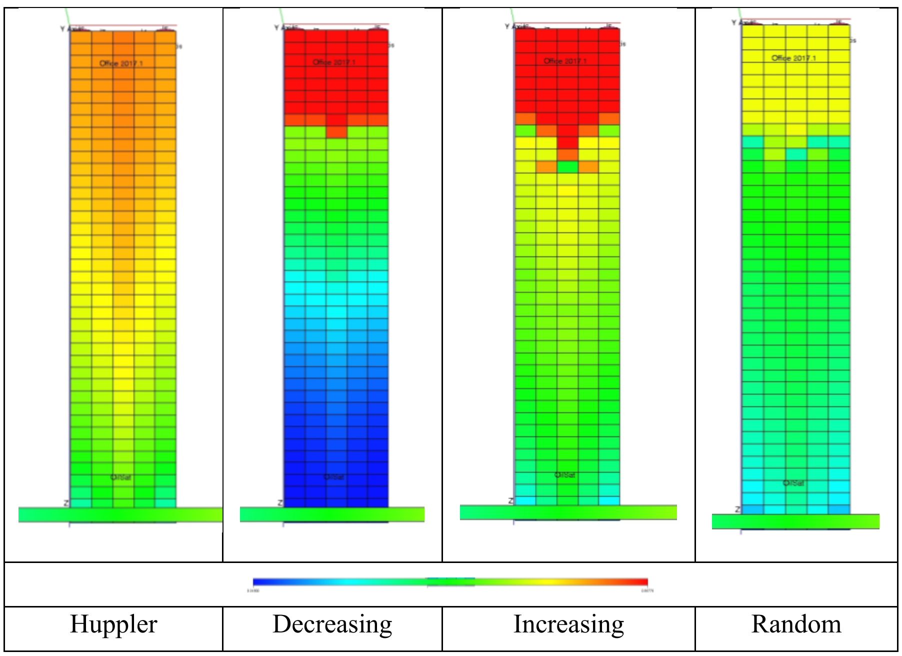


Figure 5-5: 1D 2-phase flow model with grids in Eclipse 100 ©.

5.4 Results and Discussion

The first step was to determine the physical properties of core plugs selected to sequence it in the composite core. The samples were then saturated with brine and the capillary pressures were determined from the primary drainage centrifuge experiments. Capillary pressure was also produced from Mercury Intrusion Porosimetry (Figure 5-1) to show the closeness of breakthrough pressure and demonstrate the low saturation jump between the cores. The capillary pressure data from centrifuge experiment (Figure 3) was used to determine the relative permeability for individual core plugs using the Hagoort method [15] using the Cydar© software. Figure 5-4 show the relative permeability of core plugs whose permeability range from 100 to 2800 mD. It is evident from the Figure 5-4 that the samples were initially water wet as highest relative permeability of water is close to 0.2 S_w and the K_{ro} and K_{rw} curves intersect at around 0.5% Sw. Additionally the capillary pressure curves from Mercury porosimetry indicate the difference in the breakthrough pressure for each core plug and the insignificant capillary pressure required for saturation jump from one plug to another in the composite. The raw data including the fluid volume and the time was input into the Cydar © software to produce the saturation and capillary pressure and fitted to a model using the JBN method [18]. The produced relative permeability curve was further simulated using spline fit and optimised with a Corey model to produce the final relative permeability curves.

5.4.1 Case 1 – Increasing permeability

In this arrangement the core with the highest permeability was placed at the coreholder outlet and the least permeable sample was placed next to the inlet of the coreholder. Figure 5-6 shows the orientation of this arrangement in each experiment. Figures 5-7 and 5-8 show the relative permeability and fractional flow curve for this arrangement. It is evident from the relative permeability curve that this arrangement produced less oil compared to the decreasing permeability arrangement and Huppler arrangement. The S_{or} value was the highest among the three arrangements. Although this is the most favoured arrangement of cores for coreflooding as it expedites the experimentation time, it provides not so favourable oil recovery compared to decreasing permeability arrangement. This is also evident from the experimental recovery factor comparison in Figure 10 and recovery factor from simulation in Figure 11.

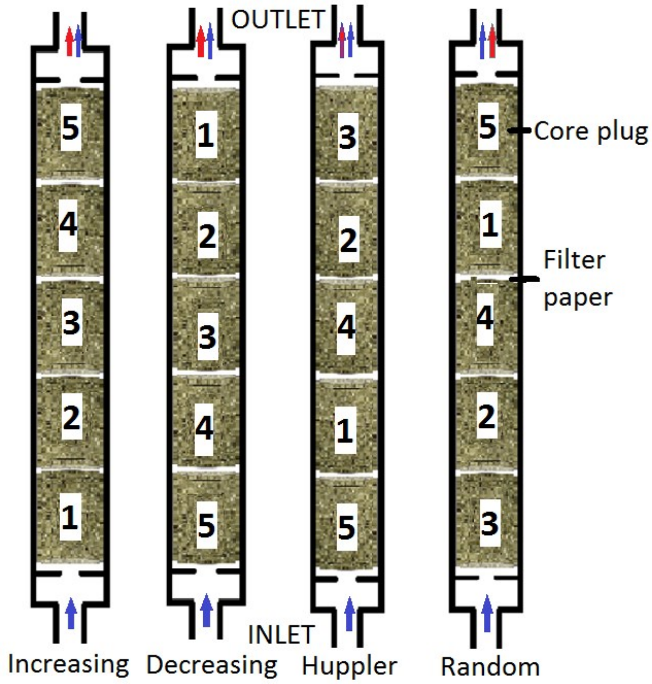


Figure 5-6: Composite core plug arrangements (Random arrangement is only simulated, no experimental data).

A comparison plot of relative permeability between the three arrangements is presented in Figure 5-7. Figure 5-8 is a comparison plot of fractional flow curves**.**

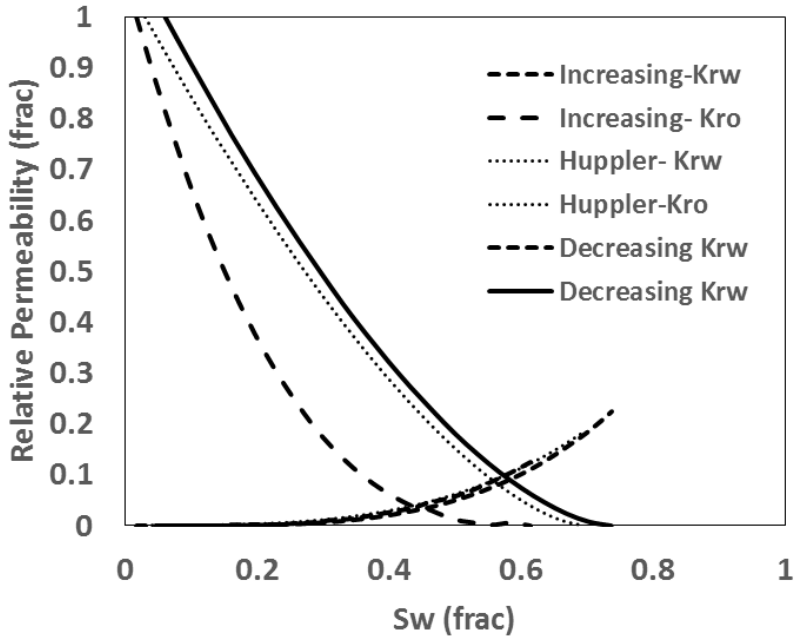


Figure 5-7: Experimental relative permeability curves for three composite arrangements.

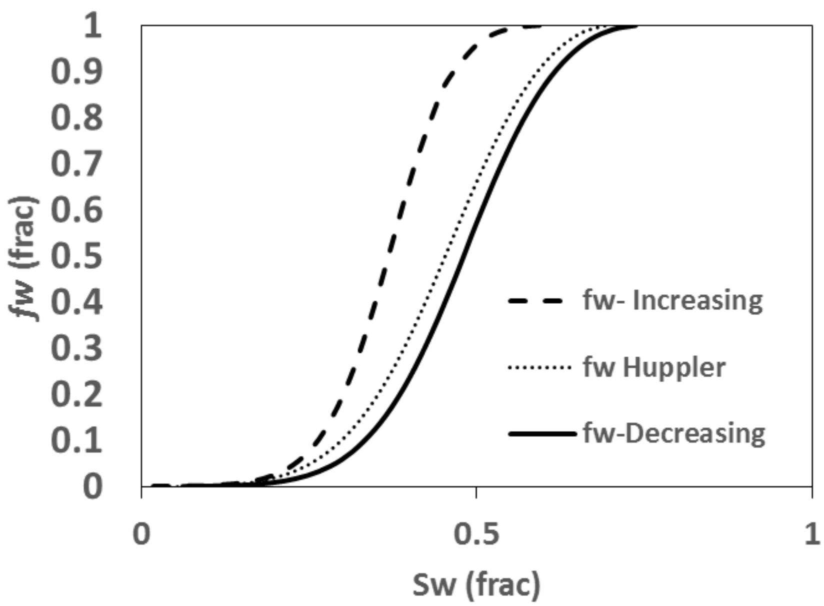


Figure 5-8: Comparison of experimental fractional flow curves for three composite core arrangements

5.4.2 Case 2 Huppler arrangement

Huppler proposed that the harmonic average between two adjacent plugs should be close to the overall average of the composite core [1] (e.g. 1000mD, 400mD, 800mD, 600mD). Figures

5-7 and 5-8 are the relative permeability and fractional flow curve for this arrangement shown in dotted line. It is evident that this arrangement resulted in comparatively more oil recovery than the increasing permeability set-up. The S_{or} value is produced from the relative permeability curves is between increasing and decreasing permeability arrangement. The recovery factor results from experiment and simulation (Figure 5-10 & 5-11) indicated that Huppler's arrangement provided more recovery than increasing permeability arrangement but less than decreasing permeability arrangement. We also performed a simulation on a composite core that was a reverse of Huppler criteria. This was to demonstrate the random orientation of core plugs in a composite core and see if the oil recovery improves. Unfortunately, this arrangement provided less oil recovery than all the other arrangements.

5.4.3 Case 3 Decreasing Permeability

In this arrangement the core plugs were arranged in decreasing order of permeability along the fluid flow. Figures 5-7 and 5-8 are the relative permeability and fractional flow curves produced from this experiment. The S_{or} is comparatively high for this arrangement as the water relative permeability end point is underestimated. From the fractional flow curve when the tangent is extrapolated to f_w =1 it can be observed that the average water saturation is reduced because the low permeability core at the outlet of the coreholder has low water saturation which results in increasing the total relative permeability. In general, in the high water saturation region of the relative permeability curves, the oil relative permeability is the critical component and therefor S_{or} become important for analysing recovery. Coreflooding experiments are designed with an emphasis on exerting highest oil recovery possible [23]. Based on these criteria of Sor and recovery factor, the declining permeability arrangement provides the favourable option for coreflooding experiments. This is supported by the simulation runs on the different arrangements where the declining permeability arrangement shows high recovery factor. Additionally, the comparison of the differential pressure plot against the time of the experiment indicates the same trend which is shown in Figure 5-9. Additionally, the effect of viscosity ratio on the recovery factor was also simulated. Figure 5-12 shows the comparison of increasing and decreasing permeability models and the effect of increasing viscosity ratio of water to oil. There was no effect of viscosity in the case of increasing permeability, but it did decrease the recovery in decreasing permeability condition.

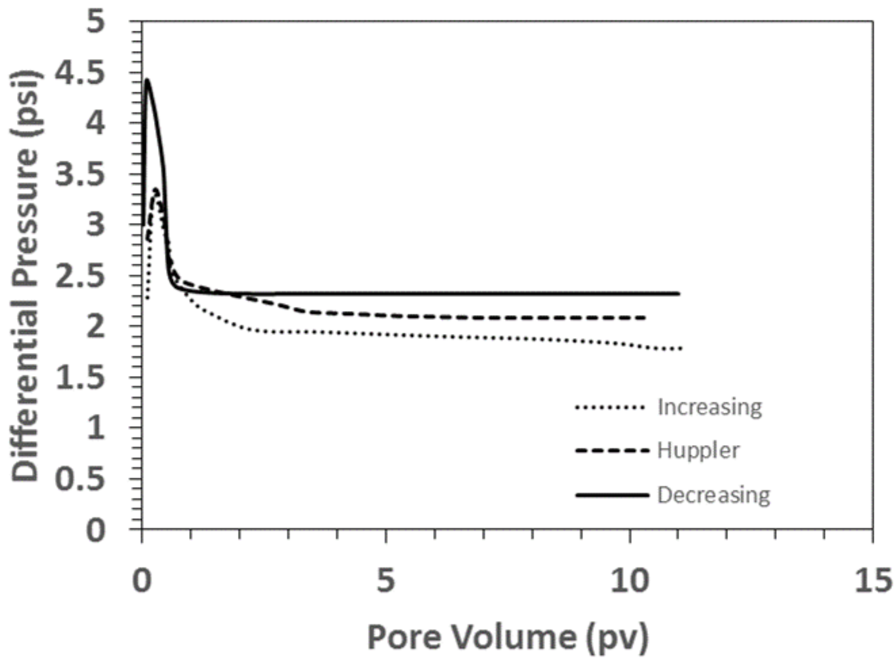


Figure 5-9: Comparison of differential pressure vs time.

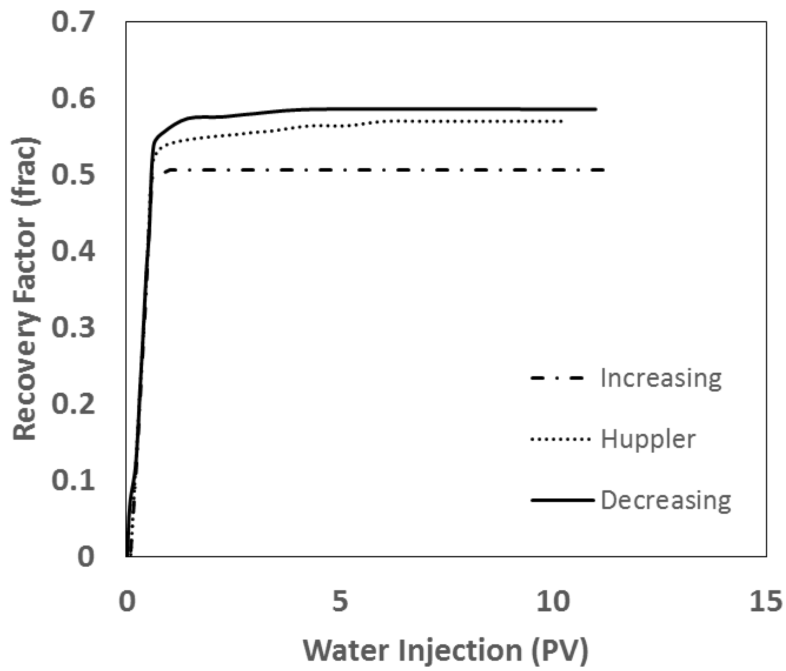
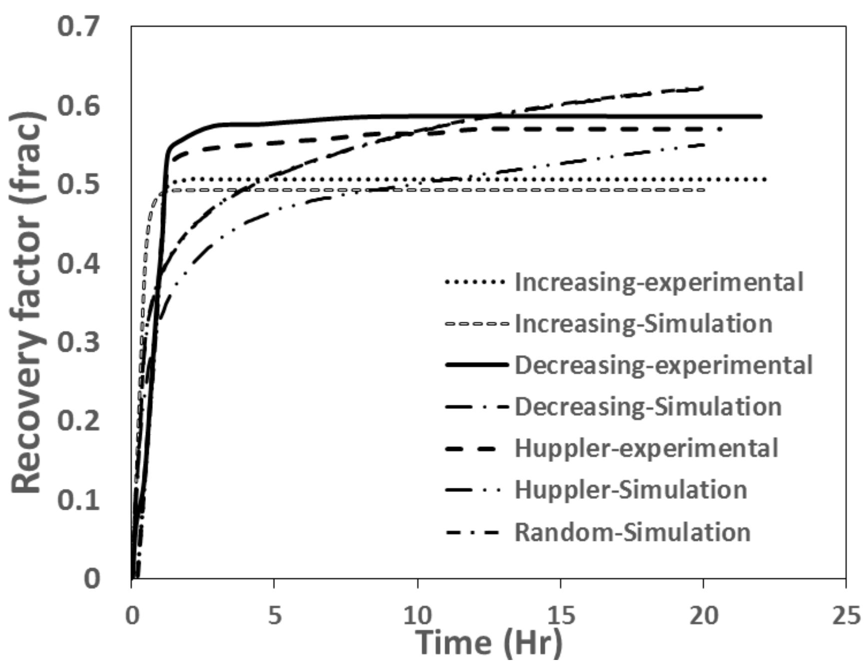


Figure 5-10: Comparison of experimental oil recovery for the three composite core arrangements.



Is

Figure 5-11: Comparison of oil recovery factor for the three composite core arrangement exp vs simulation longer run.

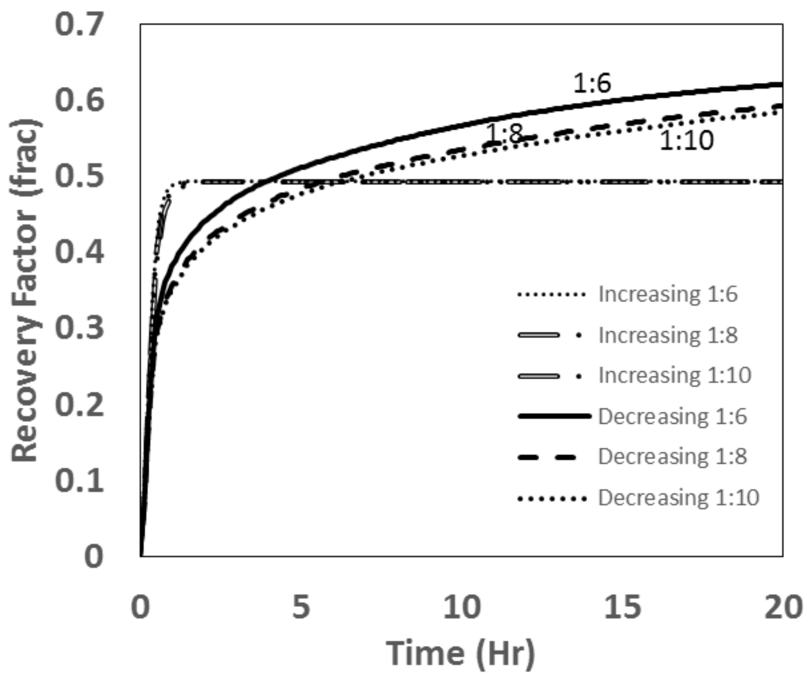


Figure 5-12: Comparison of viscosity ratio on increasing and decreasing permeability arrangement.

5.5 Conclusions

Relative permeability on composite core samples were examined for different orientation of individual cores. Both experimental and simulation work were performed on the composite cores when the individual cores were arranged according to increasing, decreasing permeability, random orientation and Huppler's arrangement. The lab scale experiments involved saturating the composite core and performing a waterflood with relative permeability computed from volume of fluids produced and the differential pressure across the sample. Additionally, recovery factory was compared for each case. Eclipse 100 was used to perform waterflood simulation on the different arrangement of composite core. A comparative study provided the following output;

1. The best arrangement for the coreflooding experiment is the decreasing permeability along the fluid flow where the highest permeability is at the inlet and the lowest

permeability is at the outlet. This result is in agreement with the Langaas et.al [2] simulation results but contrary to single core experiments by Zekri et al. [4].

2. The relative permeabilties of the three different arrangements indicated higher relative permeability for the decreasing permeability set up and the increasing permeability arrangement showed the lowest relative permeability, with Huppler's criteria of composite core arrangement coming in between.
3. The fractional flow curves and the differential pressure drops also demonstrated the same behaviour observed in relative permeability comparison.
4. In addition to experimental study, a simulation approach was tested for the different arrangement of the composite core. Recovery factors was compared and the declining permeability arrangement was found to support waterflood with high recovery factor.
5. The sum of squared errors between the experimental and simulated recover data was the least for increasing permeability set up (0.099), Huppler criteria yielded 0.12 and decreasing permeability produced 0.34.

5.6 Nomenclature

1. K = absolute permeability, Darcy
2. K_r = relative permeability
3. k_{ro} = oil relative permeability
4. k_{rw} = water relative permeability
5. P = pressure, atm
6. P_c = capillary pressure, psi
7. q = volumetric flow rate, cm3/s
8. S = saturation, fraction
9. S_{or} = residual oil saturation, fraction
10. S_{wr} = residual water saturation, fraction
11. f_w = fractional flow

5.7 References

1. Huppler, J., 1969. Waterflood relative permeabilities in composite cores. J. Pet.Technol.(United States) 21
2. Langaas, K., Ekrann, S., Ebeltoft, E., 1998. A criterion for ordering individuals in a composite core. J. Pet. Sci. Eng. 19 (1), 21–32. https://doi.org/10.1016/S0920-4105(97)00032-6.
3. Siddiqui, S., Okasha, T. M., Funk, J. J., & Al-Harbi, A. M. (2006, December 1). Improvements in the Selection Criteria for the Representative Special Core Analysis Samples. Society of Petroleum Engineers. doi:10.2118/84302-PA
4. Zekri, A.Y., Almehaideb, R.A., 2006. Relative permeability measurements of composite cores—an experimental approach. Pet. Sci. Technol. 24 (6), 717–736 https://doi.org/10.2118/77939-MS
5. Civan, F., Donaldson, E., 1989. Relative permeability from unsteady-state displacements with capillary pressure included. SPE. Form. Eval. 4 (2), 189 –193. https://doi.org/10.2118/16200-PA
6. Hussain, F., Cinar, Y., Bedrikovetsky, P.G., 2010. Comparison of methods for drainage relative permeability estimation from displacement tests. In: SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers
7. Aziz, K., Settari, A., 1979. Petroleum Reservoir Simulation. Applied Science Publ. Ltd., London, UK.
8. Brooks, R.H., Corey, A.T., 1964. Hydraulic properties of porous media and their relation to drainage design. Trans. ASAE 7 (1), 26 – 0028. https://doi.org/10.13031/2013.40684
9. Ghazanfari, M., Khodabakhsh, M., Kharrat, R., Rashtchian, D., Vossoughi, S., 2006.Unsteady state relative permeability and capillary pressure estimation of porousmedia. In: XVI International CMWR Conf., Denmark
10. Watson, A., Richmond, P., Kerig, P., Tao, T., 1988. A regression-based method for estimating relative permeabilities from displacement experiments. SPE. Res. Eng. 3 (03), 953–958. https://doi.org/10.2118/15064-PA
11. Alamooti A.M., Ghazanfari. M., Masihi. M., investigating the relative permeability behaviour in presence of capillary effect in composite core systems. Journal of Petroleum Science and Engineering 160 (2018) 341 – 350 350.

12. Tarek, A., 2007. Reservoir Engineering Handbook. Elsevier
13. Honarpour, M., Koederitz, F., Herbert, A., 1986. Relative Permeability of Petroleum Reservoirs. CRC Press, Boca Raton, Fl.
14. Hassler, G.L., & Brunner, E. "Measurement of capillary pressures in small core samples," Trans. AIME, (1945) 160, 114-123
15. Hagoort, J.: "Oil Recovery by Gravity Drainage", SPEJ, June 1980, p 139-150
16. Buckley, S.E., Leverett, M., 1942. Mechanism of fluid displacement in sands. Trans. AIME 146 (01), 107 –116.https://doi.org/10.2118/942107-G
17. Corey, A.T., 1954. The interrelation between gas and oil relative permeabilities. Prod. Mon. 19 (1), 38–41
18. Johnson, E., Bossler, D., Naumann, V., 1959. Calculation of relative permeability from displacement experiments. Trans. AIME 216, 370 –372
19. Jones, S., Roszelle, W., 1978. Graphical techniques for determining relative permeability from displacement experiments. J. Pet. Technol. 30 (05), 807 –817. https://doi.org/10.2118/6045-PA
20. Li, K., Shen, P., Qing, T., 1994. A new method for calculating oil-water relative permeabilities with consideration of capillary pressure. Mech. Pract. 16 (2), 46–52
21. Richmond, P., Watson, A., 1990. Estimation of multiphase flow functions from displacement experiments. SPE. Res. Eng. 5 (1), 121 – 127. https://doi.org/10.2118/18569-PA
22. Toth, J., Bodi, T., Szucs, P., Civan, F., 1998. Practical method for analysis of immiscible displacement in laboratory core tests. Transp. Porous. Media. 31 (3), 347 – 363. https://doi.org/10.1023/A:1006570117639
23. McPhee C., Reed, J., & Zubizarreta, I., Core Analysis: A Best Practice Guide, Elsevier, Amsterdam, Netherlands, (2015), 64, 313-345.

5.8 Appendix

Table 5-5 – Coreflood data for the increasing permeability composite core arrangement

Water Injection	Oil Production (frac)	Oil Prod fract (OIP)	Pressure drop
0.098	0.098	1	1.28
0.223	0.215	0.219	2.28
0.447	0.437	0.445	1.92
0.542	0.532	0.542	1.8
0.585	0.585	0.595	1.54
1.008	0.597	0.608	1.25
1.37	0.597	0.608	1.13
2.268	0.597	0.608	0.96
3.69	0.597	0.608	0.94
5.956	0.597	0.608	0.9
8.164	0.597	0.608	0.87
9.697	0.597	0.608	0.83
10.549	0.597	0.608	0.78
11.188	0.597	0.608	0.78

Table 5-6 Relative permeability data for the increasing permeability composite core arrangement

Water sat	Water rel perm Krw	Oil Rel perm Kro	Rel Perm Ratio	Water	Oil
0.018	0	1	0	0	1
0.048	0.0001	0.8691	13518	0.0004	0.9996
0.078	0.0002	0.7497	4916	0.001	0.999
0.107	0.0003	0.6413	2064	0.0023	0.9977
0.137	0.0006	0.5435	901	0.0053	0.9947
0.167	0.0011	0.4558	410	0.0116	0.9884
0.197	0.0019	0.3777	196	0.0241	0.9759
0.227	0.0032	0.3088	97	0.0471	0.9529
0.257	0.0049	0.2485	50.53	0.0874	0.9126
0.286	0.0073	0.1963	26.72	0.1533	0.8468
0.316	0.0106	0.1518	14.35	0.2522	0.7478
0.346	0.0148	0.1143	7.74	0.3848	0.6152
0.376	0.0201	0.0834	4.15	0.5383	0.4617
0.406	0.0267	0.0584	2.191	0.6884	0.3116
0.436	0.0347	0.0389	1.121	0.812	0.188
0.466	0.0445	0.0343	0.545	0.8988	0.1012
0.496	0.0561	0.0138	0.245	0.9518	0.0482
0.525	0.0697	0.0068	0.098	0.9802	0.0198
0.555	0.0856	0.0027	0.032	0.9934	0.066
0.585	0.1041	0.008	0.007	0.9985	0.0015
0.615	0.1252	0	0	1	0

Table 5-7 Coreflood data for the decreasing permeability composite core arrangement

Water Injection	Oil Production (frac)	Oil Prod frac (OIP)	Pressure drop
0.102	0.093	0.96	1.86
0.248	0.24	0.248	2.34
0.394	0.38	0.392	2.16
0.481	0.474	0.489	1.92
0.549	0.547	0.565	1.6
0.574	0.574	0.592	1.65
0.865	0.607	0.627	1.43
2.779	0.634	0.654	1.21
3.374	0.647	0.668	1.14
4.314	0.654	0.675	1.12
5.159	0.654	0.675	1.1
6.066	0.66	0.682	1.09
7.163	0.66	0.682	1.08
7.626	0.66	0.682	1.08

Table 5-8 Relative permeability data for the decreasing permeability composite core arrangement

Water sat	Water rel perm Krw	Oil Rel perm Kro	Rel Perm Ratio	Water	Oil
0.031	0	1	0	0	1
0.064	0.0001	0.9245	9046	0.0005	0.9996
0.097	0.0003	0.851	2901	0.0017	0.998
0.13	0.0007	0.7797	1137	0.0043	0.9958
0.164	0.0014	0.7106	506	0.00953	0.9905
0.197	0.0026	0.6438	249	0.0196	0.981
0.23	0.0044	0.5793	133	0.0352	0.9649
0.263	0.0069	0.5172	75.17	0.0605	0.9395
0.296	0.01039	0.4576	44.41	0.0982	0.9018
0.329	0.01483	0.4006	27.1	0.1515	0.8485
0.362	0.02056	0.3462	16.91	0.2225	0.7775
0.395	0.0275	0.2947	10.7	0.3114	0.6886
0.428	0.0362	0.2462	6.81	0.4154	0.5846
0.461	0.0465	0.2008	4.321	0.5283	0.4717
0.494	0.0587	0.1586	2.703	0.6417	0.3583
0.527	0.073	0.1201	1.646	0.7462	0.2583
0.56	0.08951	0.0855	0.955	0.8352	0.1648
0.593	0.1084	0.0552	0.509	0.9049	0.0951
0.626	0.1299	0.0298	0.229	0.9548	0.0452
0.659	0.1541	0.0104	0.068	0.9862	0.0138
0.692	0.1816	0	0	1	0

Table 5-9 Coreflood data for the Huppler's criteria of composite core arrangement

Water Injection	Oil Production (frac)	Oil Prod fract (OIP)		Pressure drop
0.018	0.002	0.002	5.58	0.106
0.075	0.068	0.072	6.15	0.245
0.215	0.212	0.226	6.76	0.401
0.327	0.321	0.341	5.94	0.455
0.425	0.423	0.451	4.57	0.55
0.465	0.465	0.495	3.21	0.605
0.531	0.519	0.553	2.58	0.815
0.631	0.628	0.668	2.42	2.65
0.871	0.646	0.688	2.36	3.35
1.437	0.664	0.707	2.33	4.15
2.221	0.664	0.707	2.32	5.55
2.953	0.67	0.713	2.32	6.25
4.422	0.676	0.72	2.32	7.45
6.123	0.676	0.72	2.32	10.5

Table 5-10 Relative permeability data for the Huppler's criteria of composite core arrangement

Water sat	Water rel perm Krw	Oil Rel perm Kro	Rel Perm Ratio	Water	Oil
0.061	0	1	0	0	1
0.095	0.0001	0.9198	7855	0.0006	0.9994
0.129	0.0003	0.8422	2913	0.0017	0.9983
0.162	0.0006	0.7673	1254	0.0038	0.9963
0.196	0.0012	0.6951	574	0.0084	0.9917
0.23	0.0022	0.6257	279	0.017	0.984
0.264	0.0039	0.5592	144	0.0324	0.9679
0.298	0.00632	0.4956	78.92	0.0578	0.94229
0.331	0.0097	0.4351	44.86	0.0974	0.9026
0.365	0.0143	0.3776	26.33	0.1553	0.8448
0.399	0.0206	0.3234	15.81	0.2343	0.7658
0.433	0.0288	0.2724	9.63	0.3345	0.6655
0.467	0.0381	0.225	5.9	0.4505	0.5495
0.5	0.0503	0.1811	3.607	0.573	0.427
0.534	0.0647	0.141	2.173	0.6901	0.3099
0.568	0.0824	0.1049	1.273	0.7918	0.2082
0.602	0.1031	0.0731	0.708	0.8724	0.12762
0.636	0.1274	0.0459	0.36	0.9308	0.0698
0.669	0.1556	0.0239	0.154	0.9693	0.0366
0.703	0.1871	0.0078	0.042	0.9913	0.0085
0.737	0.2252	0	0	1	0

Table 5-11 Differential pressure data for increasing permeability experiment

Water Injection	Oil Production (frac)	Oil Prod fract (OIP)	Delta Pressure (psi)
0.098	0.098	1	1.28
0.223	0.215	0.219	2.28
0.447	0.437	0.445	1.92
0.542	0.532	0.542	1.8
0.585	0.585	0.595	1.54
1.008	0.597	0.608	1.25
1.37	0.597	0.608	1.13
2.268	0.597	0.608	0.96
3.69	0.597	0.608	0.94
5.956	0.597	0.608	0.9
8.164	0.597	0.608	0.87
9.697	0.597	0.608	0.83
10.549	0.597	0.608	0.78
11.188	0.597	0.608	0.78

Table 5-12 Differential pressure data for decreasing permeability experiment

Water Injection	Oil Production (frac)	Oil Prod fract (OIP)	Pressure drop
0.102	0.093	0.96	1.86
0.248	0.24	0.248	2.34
0.394	0.38	0.392	2.16
0.481	0.474	0.489	1.92
0.549	0.547	0.565	1.6
0.574	0.574	0.592	1.65
0.865	0.607	0.627	1.43
2.779	0.634	0.654	1.21
3.374	0.647	0.668	1.14
4.314	0.654	0.675	1.12
5.159	0.654	0.675	1.1
6.066	0.66	0.682	1.09
7.163	0.66	0.682	1.08
7.626	0.66	0.682	1.08

Table 5-13 Differential pressure data for Huppler arrangement experiment

Water Injection	Oil Production (frac)	Oil Prod fract (OIP)	Pressure drop
0.102	0.093	0.96	1.86
0.248	0.24	0.248	2.34
0.394	0.38	0.392	2.16
0.481	0.474	0.489	1.92
0.549	0.547	0.565	1.6
0.574	0.574	0.592	1.65
0.865	0.607	0.627	1.43
2.779	0.634	0.654	1.21
3.374	0.647	0.668	1.14
4.314	0.654	0.675	1.12
5.159	0.654	0.675	1.1
6.066	0.66	0.682	1.09
7.163	0.66	0.682	1.08
7.626	0.66	0.682	1.08

Table 5-14 Coreflooding data for different composite arrangements using Eclipse© Simulation

Increasing Permeability			Decreasing Permeability			Huppler Arrangement		
Time (hr)	PV inj	RF (frac)	Time (hr)	PV inj	RF (frac)	Time (hr)	PV inj	RF (frac)
0	0	0	0	0	0	0	0	0
0.02	0.017391	0.040713	0.1	0.086957	0.139601	0.02	0.017391	0.020313
0.04	0.034783	0.066224	0.2	0.173913	0.253264	0.04	0.034783	0.025814
0.06	0.052174	0.091722	0.3	0.26087	0.339189	0.06	0.052174	0.031344
0.08	0.069565	0.11722	0.4	0.347826	0.393102	0.08	0.069565	0.036952
0.1	0.086957	0.142716	0.5	0.434783	0.427192	0.1	0.086957	0.042617
0.12	0.104348	0.168208	0.6	0.521739	0.447614	0.12	0.104348	0.048329
0.14	0.121739	0.193685	0.7	0.608696	0.45939	0.14	0.121739	0.054077
0.16	0.13913	0.219124	0.8	0.695652	0.466648	0.16	0.13913	0.059855
0.18	0.156522	0.244465	0.9	0.782609	0.471261	0.18	0.156522	0.065659
0.2	0.173913	0.269585	1	0.869565	0.474131	0.2	0.173913	0.071483
0.22	0.191304	0.294242	1.1	0.956522	0.47586	0.22	0.191304	0.077325
0.24	0.208696	0.318022	1.2	1.043478	0.47687	0.24	0.208696	0.083183
0.26	0.226087	0.340327	1.3	1.130435	0.477445	0.26	0.226087	0.089055
0.28	0.243478	0.360481	1.4	1.217391	0.477767	0.28	0.243478	0.09494
0.3	0.26087	0.37797	1.5	1.304348	0.477945	0.3	0.26087	0.100838
0.32	0.278261	0.392743	1.6	1.391304	0.478043	0.32	0.278261	0.106745
0.34	0.295652	0.405185	1.7	1.478261	0.478097	0.34	0.295652	0.112665
0.36	0.313043	0.41581	1.8	1.565217	0.478128	0.36	0.313043	0.11902
0.38	0.330435	0.424972	1.9	1.652174	0.478145	0.38	0.330435	0.125544
0.4	0.347826	0.432836	2	1.73913	0.478154	0.4	0.347826	0.132145
0.42	0.365217	0.439519	2.1	1.826087	0.478159	0.42	0.365217	0.138801

0.44	0.382609	0.445124	2.2	1.913043	0.478162	0.44	0.382609	0.145496
0.46	0.4	0.449776	2.3	2	0.478164	0.46	0.4	0.152222
0.48	0.417391	0.453648	2.4	2.086957	0.478165	0.48	0.417391	0.158974
0.5	0.434783	0.456881	2.5	2.173913	0.478166	0.5	0.434783	0.165746
0.52	0.452174	0.459617	2.6	2.260869	0.478166	0.52	0.452174	0.172535
0.54	0.469565	0.46197	2.7	2.347826	0.478166	0.54	0.469565	0.179338
0.56	0.486957	0.464018	2.8	2.434783	0.478166	0.56	0.486957	0.186153
0.58	0.504348	0.465817	2.9	2.521739	0.478166	0.58	0.504348	0.192978
0.6	0.521739	0.467403	3	2.608696	0.478166	0.6	0.521739	0.199814
0.62	0.53913	0.468804	3.1	2.695652	0.478166	0.62	0.53913	0.206659
0.64	0.556522	0.470043	3.2	2.782609	0.478166	0.64	0.556522	0.213512
0.66	0.573913	0.471139	3.3	2.869565	0.478166	0.66	0.573913	0.220372
0.68	0.591304	0.472106	3.4	2.956522	0.478166	0.68	0.591304	0.227291
0.7	0.608696	0.472954	3.5	3.043478	0.478166	0.7	0.608696	0.234347
0.72	0.626087	0.473698	3.6	3.130435	0.478166	0.72	0.626087	0.241454
0.74	0.643478	0.47435	3.7	3.217391	0.478166	0.74	0.643478	0.248591
0.76	0.66087	0.474918	3.8	3.304348	0.478166	0.76	0.66087	0.255748
0.78	0.678261	0.475412	3.9	3.391304	0.478166	0.78	0.678261	0.262921
0.8	0.695652	0.47584	4	3.478261	0.478166	0.8	0.695652	0.2701
0.82	0.713043	0.47621	4.1	3.565217	0.478166	0.82	0.713043	0.277291
0.84	0.730435	0.47653	4.2	3.652174	0.478166	0.84	0.730435	0.284491
0.86	0.747826	0.476805	4.3	3.739131	0.478166	0.86	0.747826	0.291699
0.88	0.765217	0.477043	4.4	3.826087	0.478166	0.88	0.765217	0.298913
0.9	0.782609	0.477246	4.5	3.913043	0.478166	0.9	0.782609	0.306134
0.92	0.8	0.477421	4.6	4	0.478166	0.92	0.8	0.313361
0.94	0.817391	0.477571	4.7	4.086956	0.478166	0.94	0.817391	0.320593
0.96	0.834783	0.477699	4.8	4.173913	0.478166	0.96	0.834783	0.327829
0.98	0.852174	0.477809	4.9	4.26087	0.478166	0.98	0.852174	0.335069
1	0.869565	0.477903	5	4.347826	0.478166	1	0.869565	0.342314
1.02	0.886957	0.477984	5.1	4.434783	0.478166	1.02	0.886957	0.349674
1.04	0.904348	0.478052	5.2	4.521739	0.478166	1.04	0.904348	0.357136
1.06	0.921739	0.478111	5.3	4.608696	0.478166	1.06	0.921739	0.36464
1.08	0.93913	0.478162	5.4	4.695652	0.478166	1.08	0.93913	0.372167
1.1	0.956522	0.478205	5.5	4.782609	0.478166	1.1	0.956522	0.37971
1.12	0.973913	0.478242	5.6	4.869565	0.478166	1.12	0.973913	0.387261
1.14	0.991304	0.478274	5.7	4.956522	0.478166	1.14	0.991304	0.394824
1.16	1.008696	0.478301	5.8	5.043478	0.478166	1.16	1.008696	0.402397
1.18	1.026087	0.478324	5.9	5.130435	0.478166	1.18	1.026087	0.409975
1.2	1.043478	0.478345	6	5.217391	0.478166	1.2	1.043478	0.417558
1.22	1.06087	0.478362	6.1	5.304348	0.478166	1.22	1.06087	0.425148
1.24	1.078261	0.478377	6.2	5.391304	0.478166	1.24	1.078261	0.432742
1.26	1.095652	0.47839	6.3	5.478261	0.478166	1.26	1.095652	0.44034
1.28	1.113043	0.478401	6.4	5.565217	0.478166	1.28	1.113043	0.447944

1.3	1.130435	0.47841	6.5	5.652174	0.478166	1.3	1.130435	0.455551
1.32	1.147826	0.478419	6.6	5.73913	0.478166	1.32	1.147826	0.463163
1.34	1.165217	0.478426	6.7	5.826087	0.478166	1.34	1.165217	0.470773
1.36	1.182609	0.478432	6.8	5.913044	0.478166	1.36	1.182609	0.477941
1.38	1.2	0.478437	6.9	6	0.478166	1.38	1.2	0.484936
1.4	1.217391	0.478442	7	6.086957	0.478166	1.4	1.217391	0.491847
1.42	1.234783	0.478446	7.1	6.173913	0.478166	1.42	1.234783	0.498707
1.44	1.252174	0.478449	7.2	6.260869	0.478166	1.44	1.252174	0.505533
1.46	1.269565	0.478452	7.3	6.347826	0.478166	1.46	1.269565	0.512334
1.48	1.286957	0.478455	7.4	6.434783	0.478166	1.48	1.286957	0.519117
1.5	1.304348	0.478457	7.5	6.521739	0.478166	1.5	1.304348	0.525886
1.52	1.321739	0.478459	7.6	6.608696	0.478166	1.52	1.321739	0.532645
1.54	1.33913	0.47846	7.7	6.695652	0.478166	1.54	1.33913	0.539395
1.56	1.356522	0.478462	7.8	6.782609	0.478166	1.56	1.356522	0.546138
1.58	1.373913	0.478463	7.9	6.869565	0.478166	1.58	1.373913	0.552875
1.6	1.391304	0.478464	8	6.956522	0.478166	1.6	1.391304	0.559606
1.62	1.408696	0.478465	8.1	7.043479	0.478166	1.62	1.408696	0.566331
1.64	1.426087	0.478466	8.2	7.130435	0.478166	1.64	1.426087	0.57305
1.66	1.443478	0.478466	8.3	7.217391	0.478166	1.66	1.443478	0.579764
1.68	1.460869	0.478467	8.4	7.304347	0.478166	1.68	1.460869	0.585724
1.7	1.478261	0.478468	8.5	7.391304	0.478166	1.7	1.478261	0.589242
1.72	1.495652	0.478468	8.6	7.478261	0.478166	1.72	1.495652	0.591965
1.74	1.513043	0.478468	8.7	7.565217	0.478166	1.74	1.513043	0.594307
1.76	1.530435	0.478469	8.8	7.652174	0.478166	1.76	1.530435	0.596422
1.78	1.547826	0.478469	8.9	7.73913	0.478166	1.78	1.547826	0.598379
1.8	1.565217	0.478469	9	7.826087	0.478166	1.8	1.565217	0.600216
1.82	1.582609	0.478469	9.1	7.913044	0.478166	1.82	1.582609	0.601956
1.84	1.6	0.47847	9.2	8	0.478166	1.84	1.6	0.603612
1.86	1.617391	0.47847	9.3	8.086957	0.478166	1.86	1.617391	0.605195
1.88	1.634783	0.47847	9.4	8.173913	0.478166	1.88	1.634783	0.60671
1.9	1.652174	0.47847	9.5	8.26087	0.478166	1.9	1.652174	0.608163
1.92	1.669565	0.47847	9.6	8.347826	0.478166	1.92	1.669565	0.609559
1.94	1.686957	0.47847	9.7	8.434782	0.478166	1.94	1.686957	0.610902
1.96	1.704348	0.47847	9.8	8.521739	0.478166	1.96	1.704348	0.612193
1.98	1.721739	0.47847	9.9	8.608695	0.478166	1.98	1.721739	0.613436
2	1.73913	0.47847	10	8.695652	0.478166	2	1.73913	0.614633
2.02	1.756522	0.478471	10.1	8.782609	0.478166	2.02	1.756522	0.615786
2.04	1.773913	0.478471	10.2	8.869565	0.478166	2.04	1.773913	0.616897
2.06	1.791304	0.478471	10.3	8.956522	0.478166	2.06	1.791304	0.617967
2.08	1.808696	0.478471	10.4	9.043478	0.478166	2.08	1.808696	0.618998
2.1	1.826087	0.478471	10.5	9.130435	0.478166	2.1	1.826087	0.619991
2.12	1.843478	0.478471	10.6	9.217391	0.478166	2.12	1.843478	0.620947
2.14	1.86087	0.478471	10.7	9.304348	0.478166	2.14	1.86087	0.621869

2.16	1.878261	0.478471	10.8	9.391304	0.478166	2.16	1.878261	0.622756
2.18	1.895652	0.478471	10.9	9.478261	0.478166	2.18	1.895652	0.62361
2.2	1.913043	0.478471	11	9.565217	0.478166	2.2	1.913043	0.624431
2.22	1.930435	0.478471	11.1	9.652174	0.478166	2.22	1.930435	0.625222
2.24	1.947826	0.478471	11.2	9.73913	0.478166	2.24	1.947826	0.625982
2.26	1.965217	0.478471	11.3	9.826087	0.478166	2.26	1.965217	0.626712
2.28	1.982609	0.478471	11.4	9.913043	0.478166	2.28	1.982609	0.627413
2.3	2	0.478471	11.5	10	0.478166	2.3	2	0.628087
2.32	2.017391	0.478471	11.6	10.08696	0.478166	2.32	2.017391	0.628733
2.34	2.034783	0.478471	11.7	10.17391	0.478166	2.34	2.034783	0.629352
2.36	2.052174	0.478471	11.8	10.26087	0.478166	2.36	2.052174	0.629945
2.38	2.069565	0.478471	11.9	10.34783	0.478166	2.38	2.069565	0.630513
2.4	2.086957	0.478471	12	10.43478	0.478166	2.4	2.086957	0.631056
2.42	2.104348	0.478471	12.1	10.52174	0.478166	2.42	2.104348	0.631576
2.44	2.121739	0.478471	12.2	10.6087	0.478166	2.44	2.121739	0.632072
2.46	2.13913	0.478471	12.3	10.69565	0.478166	2.46	2.13913	0.632544
2.48	2.156522	0.478471	12.4	10.78261	0.478166	2.48	2.156522	0.632995
2.5	2.173913	0.478471	12.5	10.86957	0.478166	2.5	2.173913	0.633424
2.52	2.191304	0.478471	12.6	10.95652	0.478166	2.52	2.191304	0.633832
2.54	2.208696	0.478471	12.7	11.04348	0.478166	2.54	2.208696	0.63422
2.56	2.226087	0.478471	12.8	11.13043	0.478166	2.56	2.226087	0.634587
2.58	2.243478	0.478471	12.9	11.21739	0.478166	2.58	2.243478	0.634936
2.6	2.260869	0.478471	13	11.30435	0.478166	2.6	2.260869	0.635265
2.62	2.278261	0.478471	13.1	11.3913	0.478166	2.62	2.278261	0.635576
2.64	2.295652	0.478471	13.2	11.47826	0.478166	2.64	2.295652	0.63587
2.66	2.313044	0.478471	13.3	11.56522	0.478166	2.66	2.313044	0.636146
2.68	2.330435	0.478471	13.4	11.65217	0.478166	2.68	2.330435	0.636406
2.7	2.347826	0.478471	13.5	11.73913	0.478166	2.7	2.347826	0.636649
2.72	2.365217	0.478471	13.6	11.82609	0.478166	2.72	2.365217	0.636877
2.74	2.382609	0.478471	13.7	11.91304	0.478166	2.74	2.382609	0.637091
2.76	2.4	0.478471	13.8	12	0.478166	2.76	2.4	0.63729
2.78	2.417391	0.478471	13.9	12.08696	0.478166	2.78	2.417391	0.637475
2.8	2.434783	0.478471	14	12.17391	0.478166	2.8	2.434783	0.637647
2.82	2.452174	0.478471	14.1	12.26087	0.478166	2.82	2.452174	0.637806
2.84	2.469565	0.478471	14.2	12.34783	0.478166	2.84	2.469565	0.637953
2.86	2.486956	0.478471	14.3	12.43478	0.478166	2.86	2.486956	0.638089
2.88	2.504348	0.478471	14.4	12.52174	0.478166	2.88	2.504348	0.638214
2.9	2.521739	0.478471	14.5	12.6087	0.478166	2.9	2.521739	0.638328
2.92	2.539131	0.478471	14.6	12.69565	0.478166	2.92	2.539131	0.638433
2.94	2.556522	0.478471	14.7	12.78261	0.478166	2.94	2.556522	0.638528
2.96	2.573913	0.478471	14.8	12.86957	0.478166	2.96	2.573913	0.638615
2.98	2.591304	0.478471	14.9	12.95652	0.478166	2.98	2.591304	0.638693
3	2.608696	0.478471	15	13.04348	0.478166	3	2.608696	0.638764

3.02	2.626087	0.478471	15.1	13.13043	0.478166	3.02	2.626087	0.638828
3.04	2.643478	0.478471	15.2	13.21739	0.478166	3.04	2.643478	0.638885
3.06	2.660869	0.478471	15.3	13.30435	0.478166	3.06	2.660869	0.638936
3.08	2.678261	0.478471	15.4	13.3913	0.478166	3.08	2.678261	0.638981
3.1	2.695652	0.478471	15.5	13.47826	0.478166	3.1	2.695652	0.639021
3.12	2.713043	0.478471	15.6	13.56522	0.478166	3.12	2.713043	0.639057
3.14	2.730435	0.478471	15.7	13.65217	0.478166	3.14	2.730435	0.639088
3.16	2.747826	0.478471	15.8	13.73913	0.478166	3.16	2.747826	0.639116
3.18	2.765217	0.478471	15.9	13.82609	0.478166	3.18	2.765217	0.639139
3.2	2.782609	0.478471	16	13.91304	0.478166	3.2	2.782609	0.63916
3.22	2.8	0.478471	16.1	14	0.478166	3.22	2.8	0.639178
3.24	2.817391	0.478471	16.2	14.08696	0.478166	3.24	2.817391	0.639194
3.26	2.834783	0.478471	16.3	14.17391	0.478166	3.26	2.834783	0.639207
3.28	2.852174	0.478471	16.4	14.26087	0.478166	3.28	2.852174	0.639218
3.3	2.869565	0.478471	16.5	14.34783	0.478166	3.3	2.869565	0.639228
3.32	2.886956	0.478471	16.6	14.43478	0.478166	3.32	2.886956	0.639236
3.34	2.904348	0.478471	16.7	14.52174	0.478166	3.34	2.904348	0.639243
3.36	2.921739	0.478471	16.8	14.60869	0.478166	3.36	2.921739	0.639249
3.38	2.939131	0.478471	16.9	14.69565	0.478166	3.38	2.939131	0.639254
3.4	2.956522	0.478471	17	14.78261	0.478166	3.4	2.956522	0.639258
3.42	2.973913	0.478471	17.1	14.86957	0.478166	3.42	2.973913	0.639261
3.44	2.991304	0.478471	17.2	14.95652	0.478166	3.44	2.991304	0.639264
3.46	3.008696	0.478471	17.3	15.04348	0.478166	3.46	3.008696	0.639267
3.48	3.026087	0.478471	17.4	15.13043	0.478166	3.48	3.026087	0.639269
3.5	3.043478	0.478471	17.5	15.21739	0.478166	3.5	3.043478	0.63927
3.52	3.06087	0.478471	17.6	15.30435	0.478166	3.52	3.06087	0.639272
3.54	3.078261	0.478471	17.7	15.39131	0.478166	3.54	3.078261	0.639273
3.56	3.095652	0.478471	17.8	15.47826	0.478166	3.56	3.095652	0.639274
3.58	3.113043	0.478471	17.9	15.56522	0.478166	3.58	3.113043	0.639275
3.6	3.130435	0.478471	18	15.65217	0.478166	3.6	3.130435	0.639275
3.62	3.147826	0.478471	18.1	15.73913	0.478166	3.62	3.147826	0.639276
3.64	3.165217	0.478471	18.2	15.82609	0.478166	3.64	3.165217	0.639276
3.66	3.182609	0.478471	18.3	15.91304	0.478166	3.66	3.182609	0.639277
3.68	3.2	0.478471	18.4	16	0.478166	3.68	3.2	0.639277
3.7	3.217391	0.478471	18.5	16.08696	0.478166	3.7	3.217391	0.639278
3.72	3.234783	0.478471	18.6	16.17391	0.478166	3.72	3.234783	0.639278
3.74	3.252174	0.478471	18.7	16.26087	0.478166	3.74	3.252174	0.639278
3.76	3.269565	0.478471	18.8	16.34783	0.478166	3.76	3.269565	0.639278
3.78	3.286957	0.478471	18.9	16.43478	0.478166	3.78	3.286957	0.639279
3.8	3.304348	0.478471	19	16.52174	0.478166	3.8	3.304348	0.639279
3.82	3.321739	0.478471	19.1	16.6087	0.478166	3.82	3.321739	0.639279
3.84	3.33913	0.478471	19.2	16.69565	0.478166	3.84	3.33913	0.639279
3.86	3.356522	0.478471	19.3	16.78261	0.478166	3.86	3.356522	0.63928

3.88	3.373913	0.478471	19.4	16.86957	0.478166	3.88	3.373913	0.63928
3.9	3.391304	0.478471	19.5	16.95652	0.478166	3.9	3.391304	0.63928
3.92	3.408696	0.478471	19.6	17.04348	0.478166	3.92	3.408696	0.63928
3.94	3.426087	0.478471	19.7	17.13044	0.478166	3.94	3.426087	0.639281
3.96	3.443478	0.478471	19.8	17.21739	0.478166	3.96	3.443478	0.639281
3.98	3.46087	0.478471	19.9	17.30435	0.478166	3.98	3.46087	0.639281
4	3.478261	0.478471	20	17.3913	0.478166	4	3.478261	0.639281

6 CHAPTER SIX

Conclusions and Recommendations

Wettability as a rock-fluid interaction parameter is paramount as it dictates the flow of fluids in multi-phase systems that are generally encountered in reservoir engineering. Wettability of cores plays an important factor as impacts the waterflood flood behavior thereby the relative permeability. The oil relative permeability and water relative permeability tend to increase or decrease when the porous medium is either fractional wet or mixed wet. Hence, native state cores or restored state cores where reservoir wettability is preserved or restored are suggested for relative permeability measurement. Wettability is measured in the lab following standard procedures and are generally represented as contact angle or wettability index. Like every other Special Core Analysis experiment, wettability tests are expensive and time-consuming resulting in limiting the number of plugs for testing thereby lack of proper wettability definition of the reservoir.

6.1 Wettability Restoration

Response Surface Modelling (RSM) using three factor Box Behnken Design was successfully applied to study and optimise brine salinity, temperature of aging and aging time for wettability restoration in core samples.

1. Applying the optimization methodology, the optimum value of input parameters for restoring oil-wet conditions using contact angle measurement was calculated as brine salinity at 104,257 ppm, temperature at 95°C and time of aging at 5.5 weeks.
2. Optimization results for restoring wettability using USBM method provided an optimum brine salinity of 115,000 ppm, temperature of aging at 99°C and aging time for 6.2 weeks.
3. Response surface models and 2-D contour plots were successfully developed for analyzing the interaction between the three input parameters on contact angle measurement. From this comprehensive experimental work, our recommendation for wettability restoration in Berea sandstone is 6 weeks at 95°C using 115,000 ppm brine and a light crude oil. The results for Berea were in strong agreement with proven results.

6.2 SEM as tool for wettability restoration

1. A new method to estimate wettability was tested using SEM-MLA analysis, which provided more direct and convincing results. Oil presence in core samples was quantified via MLA analysis and the strategy to change wettability with increasing aging time was validated. MLA analysis on chalk and Berea samples were straightforward with a simplified mineral list with increasing oil residue for increased aging time
2. A comprehensive estimate of more than five weeks for chalk and six weeks for Berea was commonly agreed between three different wettability measurements to ensure core samples are oil wet.

6.3 Composite Core Arrangement

1. The best arrangement for the coreflooding experiment is decreasing permeability in the direction of fluid flow where the highest permeability is at the inlet and the lowest permeability is at the outlet. This result is in agreement with Langaas et.al [2] simulation results but contrary to single core experiments by Zekri. [3].
2. The relative permeabilties of the three different arrangements indicated a higher relative permeability for the decreasing permeability set up. The increasing permeability arrangement showed the lowest relative permeability, with Huppler's criteria of composite core arrangement coming in between.
3. The fractional flow curves and differential pressure drops demonstrated the same behaviour as observed in the relative permeability comparison.
4. In addition to the experimental study, a simulation approach was tested for the different arrangements of the composite core. Recovery factors were compared and the decreasing permeability arrangement was found to support waterflood with a high recovery factor.

5. The sum of squared errors between the experimental and simulated recovery data was the least for the increasing permeability set up (0.099), Huppler criteria yielded 0.12 and decreasing permeability produced 0.34.

Based on the comprehensive experiment and simulation analysis, the best arrangement for coreflooding is not the composite arrangement giving the highest recovery. Rather it is the arrangement that can best be simulated and results in piston like displacement. Hence, our recommendation for coreflooding is a composite core with the decreasing permeability arrangement as it proved to be the best arrangement for recovery besides agreeing with the results of Langaas [2] et al.

6.4 Recommendations for Future work

Based on the literature review and results obtained in this thesis, the following are recommended for potential future work.

1. **Consider the effect of optimal wettability and simplified (restricted) models.** Applying the optimization methodology, the optimum value of input parameter for restoring oil-wet conditions in Berea samples were successfully calculated as brine salinity at 99,165 ppm, temperature at 80ºC and time of aging at 5.7 weeks. Optimization results for restoring intermediate oil wettability in Silurian dolomite provided an optimum brine salinity of 103,000 ppm, temperature of aging at 88ºC and aging time for 5.8 days. The range of input parameters used for wettability restoration for both the samples were wide. In order get a more substantiable optimal values, the range could be modified to fit narrow the optimal values.
2. **Extend the work on the SEM-MLA method for wettability determination**. The newly developed SEM-MLA method for oil/brine chalk surface determination

provided a direct observation of the chemical composition of the end-pieces. An increasing amount of oil present on the samples was measured using MLA analysis. It was found that the oil fraction increased steadily from 10% to 46% when aging time was increased from 6 to 30 days. The SEM-MLA methods can be further tested by comparing the results from other reservoir rocks against chalk samples which was straight forward as the mineral list was limited.

3. **Consider the effect of oil composition** The effect of different types of oil was not considered in this study. Oil with a greater amount of aromatic and resin components is considered to render the rock surface more oil-wet. The composition of oil, with varying quantities of aromatic and resins, could be statistically analyzed in the same way the temperature and time was studied.

4. **Consider different rock types.** Rock samples with a higher quartz content were also observed to increase the oil-wetness**.** A statistical methodology can be applied for different rock types and extend the range of reservoir rock types that could be rendered oil wet.

5. **Extend the parameters for aging**. The experimental results were analyzed statistically using a regression model and analysis of variance (ANOVA). The ANOVA results for both Berea and Silurian dolomite showed high coefficient of determination values, ensuring a satisfactory fit of the developed mathematical model with the experimental data. The input parameters can now be brought closer to the optimal value and experiments carried out in the smaller range and tested with an appropriate statistical model.

6. **Composite core**. Both experimental and simulation work were performed on the composite cores where the permeability varied from 100 mD to 2000 mD. Future work could develop more rigorous simulations on composite core arrangements with higher permeability (2000 mD) and less standard deviation and compared with experimental results.
7. Composite Core Experiments – More experiments on cores are to be performed to do relative permeability studies to see how these vary. Further, sensitivity analysis on the relative permeability data as to be carried out evaluate the tuning parameters

6.5 References

1. Huppler, J., 1969. Waterflood relative permeabilities in composite cores. J. Pet.Technol.(United States) 21
2. Langaas, K., Ekrann, S., Ebeltoft, E., 1998. A criterion for ordering individuals in a composite core. J. Pet. Sci. Eng. 19 (1), 21–32. https://doi.org/10.1016/S0920-4105(97)00032-6.
3. Zekri, A.Y., Almehaideb, R.A., 2006. Relative permeability measurements of composite cores—an experimental approach. Pet. Sci. Technol. 24 (6), 717–736 https://doi.org/10.2118/77939-MS