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The Effect of Neutral Wettability on Trapped Phase Saturation

by

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Thesis

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The Effect of Neutral Wettability on Trapped Phase Saturation

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Dedication

This work is dedicated to my Lord,

my family,

my friends and K.
Acknowledgements

First, I give all glory and honor to my Almighty Lord and Savior for seeing me through my research. It is all possible because of His grace.

I would like to sincerely acknowledge my supervising professors – Drs. Larry W. Lake and Steven L. Bryant. They were very supportive and helpful through my research, and offered their constant guidance. I would also like to acknowledge Glen Baum for all his help with my experimental work.

Finally, I would like to express my sincere appreciation to my family and friends for constantly encouraging me. They have been patient with me, showing nothing but love and support. I thank you all for being a part of me.
The Effect of Neutral Wettability on Trapped Phase Saturation

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The University of Texas at Austin, 2007

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Wettability is very important when concerned with the flow of fluids in any porous medium. It affects the relative permeability which in turn, determines the ease with which fluids flow during production. It also affects the residual saturation, which determines the amount of fluid that can be recovered economically.

The purpose of this study is to examine the flow behavior of a neutrally wet porous medium. Experiments were carried out to alter the wettability of a porous medium to the neutrally wet state. The contact angles were confirmed using a goniometer. These were followed by absolute permeability and steady-state displacement experiments, observing the trapped phase saturation. These experiments were repeated several times, measuring the differential pressures of the medium at specified flow rates. The hypothesis tested by these experiments was that there is no trapped phase saturation in a neutrally wet porous medium.

Through extensive study, it was discovered that for a neutrally-wet porous medium, there is negligible trapped phase saturation at relatively high velocities. The
various experimental methods and equations used to achieve results are discussed further in this thesis. Also discussed are the indications these results have on the future of fluid recovery in a porous medium.
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1. INTRODUCTION

Wettability is defined as “a tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids.” (Anderson, 1986) There are various methods used in determining reservoir wettability, such as contact angle measurement using reservoir fluids and a pure mineral surface, or imbibition tests on a reservoir core sample.

For a reservoir system, the solid phase may be preferentially oil-wet, preferentially water-wet, or neutrally-wet. Various studies have shown that wettability has a major influence on reservoir fluid recovery. It has also been shown that reservoir wettability depends strongly on the extent to which the organic components are absorbed by the solid phase present (Hamouda and Goumari, 2006). Opinions vary widely on whether the strongly oil-wet (Warren and Calhoun, 1955), strongly water-wet (Mungan, 1966; Owens and Archer, 1971; Morrow, 1990) or neutrally-wet (Richardson et al., 1955; Moore and Slobod, 1956; Tie and Morrow, 2005) state is the optimum wettability state for fluid recovery.

This study focuses on the hypothesis that there is nonzero trapped phase saturation in a neutrally-wet porous medium. To accomplish this objective, first of all, a porous medium’s wettability state was altered to be neutrally-wet. Past literature suggests that a change in the wettability of the fluids for a surface affects the saturation distribution in a reservoir, the reservoir mobilities of the fluids, and the residual phase saturations. We have therefore undertaken an experimental investigation, using steady-state displacement experiments to observe the residual phase saturation at the neutrally-wet state. We have also observed the effect of the flow rate on these results. To evaluate
these experiments, we compared with published data. Stability of the flow regime was
determined by calculating dimensionless numbers such as the mobility ratios, gravity
numbers, and capillary numbers.

The present work is divided into five chapters. Chapter 1 introduces the scope of
the research; Chapter 2 contains a literature review of some concepts and previous works
related to wettability and its effect on relative permeability and trapped phase saturation
in a porous medium. Chapter 3 contains the problem statement, the objective of this work
and how we achieve it. Chapter 4 presents the experimental work with a description of
the equipment, the procedure followed, and the results obtained. Finally, Chapter 5
summarizes the results obtained from this work and gives conclusions and some
recommendations for future work.
2. LITERATURE REVIEW

This project focuses on the effect of neutral wettability on trapped phase saturation. Therefore, the related literature is thoroughly reviewed and discussed in the following sections.

2.1 WETTABILITY

Wettability of a solid surface can be defined in several ways. Anderson (1986) defined wettability as “a tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids.” For example, if a rock is water-wet, there is a tendency for the water to occupy the smaller pores and contact the majority of the solid’s surface.

Numerous studies have been carried out to examine the effect of wettability on relative permeability, trapped phase saturation, capillary pressure, and other parameters that affect fluid flow and fluid recovery in reservoir systems (Okasha et al., 2003; Mitchell et al., 1990; Jadhunadan et al., 1991; Donaldson et al., 1969). According to Johnson and Dettre (1993), to understand wettability, one needs to recognize that it is determined by “the balance between adhesive forces between the liquid and solid and cohesive forces in the liquid. Adhesive forces cause a liquid drop to spread. Cohesive forces cause the drop to ball up” (See Figure 2.1).
2.1.1 Wettability Measurement

Several methods have been proposed to assess the wettability of a solid surface with respect to a fluid system (Honapour, 1986; Cuiec, 1991). Anderson et al. (1986) studied the different methods of wettability measurement: contact angle, the Amott (and Amott-Harvey) method, and the U.S. Bureau of Mines (USBM) method. Their studies also included an analysis on the abilities and limitations of the qualitative methods of measuring wettability: imbibition, microscopic examination, floatation, glass slide, relative permeability curves, capillarimetric method, permeability/saturation relationships, and reservoir logs. The three quantitative methods, which are further discussed below, are most used for laboratory experiments.

2.1.1.1 Contact Angle Method

It has been proposed that the Contact Angle Method is the best to use when working with pure fluids and artificial cores. It is also said to be a superior method when examining the wettability of experimental conditions such as pressure, temperature, and brine chemistry. The most common methods used in the petroleum industry are sessile drop technique, Wilhemy Plate technique, and the Dual-Drop Dual-Crystal (DDDC) technique.

Equation 2.1 helps one understand the relationship between wettability and contact angle. The Young-Dupré equation relates the interfacial tensions by considering horizontal equilibrium acting on the contact line, as shown in Fig. 2.2, to give

\[ \sigma_{A/S} - \sigma_{L/S} = \sigma_{A/L} \cos \theta \]  

(2.1)
For a given value of $\sigma_{A/L}$, the contact angle will increase with a decrease in adhesion between the liquid and solid.

If the free surface energies for the air-solid ($\sigma_{A/S}$) and the liquid-solid ($\sigma_{L/S}$) interfaces are equal, then the left side of equation (2.1) is zero. Since the air-liquid ($\sigma_{A/L}$) interfacial tension is nonzero, $\cos \theta$ must be zero and therefore, the contact angle ($\theta$) is $90^\circ$. Any solid surface with a contact angle of approximately $90^\circ$ is referred to as a neutral or intermediate-wet medium. On the other hand, a large contact angle will mean poor wetting of one of the fluids present. It is possible to obtain zero contact angles but they are always less than $180^\circ$. This indicates zero adhesion.

Certain limitations to this method are listed in past literature such as the fact that the contact angles quoted above refer to smooth surfaces: glass (silica) for sandstones and calcite crystals for carbonate reservoirs. Surface roughness and heterogeneity, however, are known to affect the contact angle and cause contact angle hysteresis. This makes it difficult to obtain reproducible contact angle values with actual reservoir materials.

Another limitation of the contact angle method is that there is no way to measure contact angles under dynamic conditions within a porous medium. However, Slobod and Blum (1952) proposed a method of obtaining the cosine of an “apparent contact angle” using interfacial tension and displacement pressure measurements in natural samples (all measurements taken under static conditions). This proposed method has been criticized in previous literature (Cuiec, 1991) and has not been widely adopted.
2.1.1.2 Amott Method

The Amott method combines spontaneous imbibition and forced displacement of the fluids from a core to measure the average wettability of the solid surface. This method is based on the fact that the wetting fluid will generally imbibe spontaneously into a core, displacing the non-wetting one. Using a centrifuge, the wetting fluid is the forced to imbibe some more into the rock pore space, thereby forcibly displacing the non-wetting fluid. The average wettability of the core is measured in the following five-step process (assuming the fluids are oil and water):

1. The core is centrifuged under brine to obtain residual oil saturation.
2. The same core from step 1 is then immersed in oil for 20 hours. The amount of water displaced by spontaneous imbibition of oil is recorded as $V_{wsp}$.
3. Brine is displaced to irreducible water saturation with oil. The amount of water displaced by forced displacement of oil is recorded as $V_{wt}$.
4. The core is immersed in brine for 20 hours. The volume of oil displaced by spontaneous imbibition of water is recorded as $V_{osp}$.
5. If there is any oil remaining in the core, it is displaced by water to irreducible oil saturation. The total amount of oil displaced by forced displacement is recorded as $V_{ot}$.

The test results for the Amott method are then reported as follows:

- Displacement-by-oil ratio ($\delta_o$): This is the ratio of the water volume displaced by the spontaneous imbibition of oil, to the total water volume displaced by oil imbibition and forced displacement.

\[
\delta_o = \frac{V_{wsp}}{V_{wt}}
\]  

(2.2)
Displacement-by-water ratio ($\delta_w$): The ratio of the oil volume displaced by spontaneous imbibition of water, to the total oil volume displaced by water imbibition and forced displacement.

$$\delta_w = \frac{V_{sop}}{V_{ot}}$$

(2.3)

If the core is preferentially water-wet, we obtain a positive displacement by water ratio and a zero-value displacement by oil ratio. On the other hand, if the core is preferentially oil-wet, we obtain a positive displacement by oil ratio and a zero-value displacement by water ratio. Both ratios have a zero value for neutrally wet cores, indicating the absence of spontaneous imbibition of either oil or brine. However, one of the major problems of this method is that it is insensitive around neutral wettability.

2.1.1.3 USBM Method

This method was developed by Donaldson et al. (1969). Like the Amott test, it measures the average wettability of the core through centrifugal displacement. Wettability is obtained in this case by measuring the area under the curve obtained by plotting the capillary pressure against the water saturation. The ratio of areas under the primary drainage and imbibition capillary pressure curves is then used to calculate the wettability index (see Figure 2.3):

$$WI = \log\left(\frac{A_1}{A_2}\right)$$

(2.4)

where $A_1$ and $A_2$ are the areas under the oil and brine drive curves respectively.
The wettability index is unbounded. Experimentally though, the WI varies from -1 to +1. The core specimen is preferentially oil-wet if WI is less than zero. If the index is greater than zero, it is preferentially water-wet. Compared to the Amott test, this method is particularly sensitive to near neutral wettability. A zero value of the wettability index is usually observed for a neutrally-wet porous medium. A major advantage of this method is that it is sensitive near neutral wettability. Like the Amott method, a major disadvantage is that this method can only be used on plug-size samples, because the samples must be spun in a centrifuge (Donaldson et al., 1969).

2.1.1.4 Combined USBM-Amott Method

This method was developed by Sharma et al. (1985). It occurs in the following 5-step process:

1. The test begins with the core fully saturated in brine. The speed of the centrifuge is increased in steps, while recording the amount of fluid produced from the core at each speed as a function of time. This is done until we reach equilibrium and flow has ceased. The capillary pressure curve can be obtained from the equilibrium saturation and capillary pressure at each speed. Using a centrifuge, crude oil is then used to forcibly displace the brine until residual saturation is reached. The volume of brine collected is recorded as a function of time, at each centrifuge speed.

2. This step is the spontaneous imbibition of brine, whereby the core is kept in a reservoir of brine. The spontaneous expulsion of crude oil from the core is measured and recorded.
3. Using a centrifuge, brine is then used to forcibly displace the crude oil until residual saturation is reached. The volume of crude oil collected is recorded as a function of time, at each centrifuge speed. To ensure more accurate readings, the initial displacement data is recorded with a video camera while subsequent readings are done visually. The core is spun for about 4 hours typically, to ensure equilibrium conditions (i.e. no more flow from core) are met.

4. This step is the spontaneous drainage of brine, whereby the core is kept in a reservoir or crude oil. The spontaneous drainage of brine from the core is measured and recorded.

5. Using a centrifuge, the crude oil is then used to forcefully displace the brine until residual water saturation is reached. Figure 2.4 shows all the steps of this experiment.

At the residual water saturation in Step 5, the core is then aged in crude oil for 20-25 days at room temperature. Steps 2 to 5 are then repeated with the same core, to observe the impact of aging on the wettability of the core, as well as the effect on the capillary desaturation curves.

The wettability changes in the core are measured by calculating Water and Oil USBM and Amott indices. The USBM index is calculated as:

\[ W_{USBM} = \log \frac{A_1}{A_2} \]  

and the Water and Oil-Amott indices are calculated as

\[ W_{Amott} = \frac{\Delta S_w (\text{step} 3)}{\Delta S_w (\text{step} 3 + \text{step} 5)} \]
This combined USBM-Amott Method has two advantages over the standard USBM test: (1) both the USBM index and the Amott ratio can be calculated, and (2) by accounting for the saturation changes at zero capillary pressure, we improve the resolution of the USBM index.

2.1.2 Wettability Alteration

Altering the wettability of a solid surface changes the fluid distribution in the porous medium, thereby affecting the capillary pressure and relative permeabilities of the fluids. Therefore, the ability to alter the wettability of rock surfaces has become very important in the study of enhanced oil recovery. Some studies (Tang and Morrow, 1999; Hamouda et al., 2006) suggest that increasing the temperature is a better and cheaper method of altering the wettability of a rock surface, while other studies suggest that the use of chemical surfactants achieves more reproducible results (Spinler et al., 2000; Morrow and Mason, 2001).

Anderson et al. (1986) conducted extensive studies on the effect of wettability alteration and methods for artificially controlling wettability during laboratory experiments. They found that for a brine/oil/core system, the increased solubility of the wettability altering compounds at high temperatures and pressures in the reservoir causes the system to be more water-wet than at ambient conditions. According to them, the three commonly used methods for artificially controlling the wettability of a system include (1) Treating the core with chemicals such as naphthenic acids and a variety of carboxylic

\[
O_{\text{Amott}} = \frac{\Delta S_w^{(\text{step}4)}}{\Delta S_w^{(\text{step}4 + \text{step}5)}}
\]
acids for carbonate cores; (2) adding surfactants to the reservoir fluids; and (3) using Teflon cores (treated at high temperature and pressure) with pure fluids.

Mattax et al. (1982) studied the behavior of chemical surfactants for enhanced oil recovery in carbonate rocks. They concluded that there is very limited application of surfactants in carbonate reservoirs because they generally have low matrix permeability, salinity, fractures, high hardness, low pore volume, heterogeneity and adsorption. However, Hamouda et al. (2006) found that carbonate reservoirs become more water-wet during thermal recovery. The degree of alteration depends on a combined effect of parameters such as the surface charge, fluid/rock and fluid/fluid interactions. Elevated temperature increases the solubility of the adsorbed materials from surfaces while decreasing the interfacial tension, and could also change the electrokinetic properties of the solid surfaces.
2.2 RELATIVE PERMEABILITY

Relative permeability is a very important factor when considering multiphase flow in a porous medium or a rock. This concept was developed by extending Darcy’s equation to two-phase flow, which takes the following form,

\[ q_1 = \frac{k r_1 k A \Delta P_1}{\mu_1} \]

\[ q_2 = \frac{k r_2 k A \Delta P_2}{\mu_2} \]

where \( q \) is the volumetric flow rate, \( \mu \) is the phase viscosity, \( k \) is the absolute rock permeability, \( k_r \) is the phase relative permeability, \( \Delta P \) is the pressure drop, \( A \) is the cross sectional area perpendicular to flow, and \( L \) is the length in the flow direction. The relative permeability describes the relationship between pressure gradient and the flow rate for each phase at each of the various phase saturations occurring within a permeable medium. It is commonly defined as the ratio of the effective permeability of a specific fluid (oil, water or gas) at a specific saturation, to the absolute permeability of the same fluid at total saturation.

Relative permeability data could be determined from either field data (using the production history of a reservoir and its fluid properties), or experimentally using reservoir core samples. The use of field data is highly uncommon due to the difficulty associated with obtaining accurate production data. Also, the correlation between the relative permeabilities obtained from field data and from laboratory measurements is typically very poor. Therefore, field data is typically avoided in calculating the relative permeability.
The relative permeability of a rock to each fluid phase can be measured by either steady-state (used in this research) or unsteady-state methods. A brief description of these methods is given below.

### 2.2.1 Steady State Methods

In the steady-state method, a fixed ratio of the immiscible fluids is forced through the test sample until there is both saturation and pressure equilibrium. The steady-state methods include:

- **The Penn-State Method**: This method was designed by Morse et al. (1947) and later modified by Osoba et al. (1951), Geffen et al. (1951), and Caudle et al. (1951). In this case, the test core sample is placed between two similar rock samples. This is done to promote mixing of the fluids and to reduce capillary end effects. The sample is then saturated with one fluid phase and the flow rate is adjusted until a predetermined pressure gradient is obtained. The second phase is then injected at a low flow rate and then the flow of the first fluid is reduced slightly to keep a constant pressure difference across the porous medium. Once steady state is reached, the flow rates of both fluids are recorded, as well as the percentage saturation of each fluid within the core sample. After the saturations are determined, the above process is repeated to establish a new steady state equilibrium at a larger flow rate for the second phase, and the fluid saturations are recorded once again. This is done several times at a steady state saturation that is
somewhat higher than the critical saturation until the complete relative permeability curve is established.

- **Single-Sample Dynamic Method**: This method was designed by Richardson et al. (1952), Josendal et al. (1952), and Loomis and Crowell (1962). In this case, the two fluids are injected simultaneously through the test core. Capillary end effects are minimized by using relatively high flow rates, and the saturation gradients are determined by using expressions developed from Darcy’s law.

- **Hassler Method**: This method was developed by Hassler and was later modified by Brownscombe et al. (1950), Josendal et al. (1952), and Gates and Lietz (1950). Semi-permeable membranes, which keep the two fluid phases separated at the inlet and outlet of the core, are installed at each end of the Hassler test assembly. The pressure of each of the fluids is measured separately. The pressure gradients of the fluid phases can then be made equal by adjusting the flow rate of the non-wetting phase.

- **Hafford Method**: This method was developed by Richardson et al. (1952). Here, the non-wetting phase is injected directly into the core sample while the wetting phase is injected through a disc. The center of the disc is used to measure the pressure of the wetting fluid at the inlet of the core sample. This portion is impermeable to the non-wetting phase, and isolated from the rest of the disc by a small metal sleeve. The non-wetting fluid is then injected directly into the sample
and its pressure is measured through a pressure tap. The capillary pressure at the core inlet is simply the pressure difference between the wetting and non-wetting fluid.

- **Stationary Fluid Method**: This method was developed by Leas et al. (1950) and later modified by Osoba et al. (1951). It measures the permeability to gas with the liquid phase held stationary within the core by capillary forces, and the flow rate kept at an extremely small value, so as not to displace any liquid. Osoba et al. (1951) modified the equipment by holding the liquid phase within the core with barriers which were impermeable to the liquid, but permeable to the gas.

- **Dispersed Feed Method**: This method was developed by Richardson et al. (1952). Here, the wetting fluid is introduced to the core sample through a dispersing section of similar material. This section then distributes the wetting fluid through the core inlet in a uniform manner. The non-wetting phase passes through radial grooves through the outlet of the dispersing section, the portion between the dispersing material, and the test sample.
2.2.2 Unsteady-State Method

The theory developed by Buckley and Leverett (1942) and extended by Welge (1952) is used for the measurement of relative permeability under unsteady-state flow. These measurements can be made more rapidly than steady-state measurements and are therefore used for most laboratory measurements of relative permeability.

There are several variations of this method reported in literature (Heaviside, 1991; Dullien, 1992). The fluids are either injected at a constant pressure, constant flow rate or in a pulsed manner.

Welge (1952) developed a method such that when we have high constant flow rates, the relative permeability ratio of non-wetting to wetting fluid can be calculated from the produced fluid ratios. This method was further developed by Johnson et al. (1959) and further improved by Jones and Roszelle (1978). It is commonly referred to as the JBN method. Jones and Roszelle (1978) improved on the initial JBN method by demonstrating a graphical technique that made it easier to use and more accurate. The low constant flow rate methods, however, need capillary pressure data to provide decent approximations of relative permeability (Heaviside, 1991).


2.3 RESIDUAL PHASE SATURATION

The drainage of a porous medium does not completely remove that phase from the pore space. Therefore, the portion of the pore space that still contains this fluid is commonly referred to as the “residual” or “irreducible” phase saturation. Determination of residual phase saturation has been the subject of many experimental and theoretical studies. As this is a very complex problem, the factors that affect residual phase saturation such as wettability, pore structure and saturation history, have been studied extensively.

Stegemeier (1974) observed that residual wetting phase is retained in the finest crevices of the pore constrictions and therefore requires 10 to 100 times the forces used to release the non-wetting phase. Morrow and Mungan (1971) showed that one can achieve minimum irreducible and residual saturation when a porous medium is at or near neutral wettability.

2.3.1 Connection/Disconnection of Fluid Phases in the Pore Space

Past literature (Wardlaw, 1980; Yuan, 1981; Bryant and Johnson, 2003) suggests that for a strongly-wetted pore system, the extent to which the non-wetting phase is trapped depends strongly on the geometric and topologic properties. According to Bryant and Johnson (2003), “a trapped wetting phase can exist as a pendular ring held between two grains in contact; as a liquid bridge held between two grains separated by a small gap; as a lens in a pore throat between two grained pores (each of which drained independently via a different throat); as an island occupying a single pore or several
neighboring pores; or as a more complicated structure formed by connecting any combination of these individual morphologies.” Large pore-throat size ratios and certain types of heterogeneity affect displacement efficiency adversely.

Drainage of a wetting phase from a porous medium does not completely remove that fluid from the pore space. However for a porous medium with intermediate wettability, the displacement efficiency tends to be higher and the pore geometry contributes less to the trapping of fluids (Wardlaw, 1980).

2.3.2 Effect of Wettability on Residual Phase Saturation

Past research (Tie and Morrow, 2005) has shown that the residual phase saturation is lowest when the wettability is nearest to neutral-wet or mixed-wet conditions.

Residual wetting phase saturation occurs as a result of capillary pressure phenomena. As the non-wetting phase is removed from the pore spaces, the wetting phase fills the void areas of the porous medium and is held immobile in the smaller pores by capillary pressure. Studies (Jerauld and Rathmell, 1997; Anderson, 2006) have shown that the non-wetting phase becomes trapped as blobs within the pore because the buoyancy and viscous forces acting on the non-wetting phase cannot overcome the large capillary forces that exist at the small pore throats within the porous medium when the interfacial tension is high.
Figure 2.1 Showing the effect of (a) Adhesive forces, (b) Cohesive forces.
Figure 2.2 Contact angle showing (a) L-wet, (b) neutral, and (c) A-wet systems.
Figure 2.3: This shows the necessary areas for the USBM method, to calculate the wettability index (WI). a) water-wet core where WI > 0; b) oil wet core where WI < 0 (Anderson et al., 1986)
Figure 2.4: Showing the sequence of the experimental steps conducted in the USBM-Amott Method experiments; 1: Primary drainage, 2. Spontaneous imbibition, 3: Primary imbibition, 4: Spontaneous drainage, 5: Secondary drainage. (Chattopadhyay et al., 2002)
3. PROBLEM STATEMENT

The wettability of a permeable medium affects fluid recovery, the relative permeability, capillary pressure and water-flood behavior (Anderson, 1986). Over the years, many wettability studies have been conducted to examine the optimum wettability state for fluid recovery in a hydrocarbon reservoir. Opinions vary widely on whether the strongly oil-wet (Warren and Calhoun, 1955), strongly water-wet (Mungan, 1966; Owens and Archer, 1971; Morrow, 1990) or intermediately-wet (Richardson et al., 1955; Moore and Slobod, 1956; Tie and Morrow, 2005) state is the optimal wettability state for fluid recovery.

The main objective of this study is to demonstrate that there is residual saturation for neutrally wet fluids in permeable media. Similar studies have been conducted previously by Anderson et al. (1986) and many methods have been used to measure wettability. But to accomplish the aforementioned objective in a reproducible experimental procedure, calcite grains are treated using stearic acid dissolved in decane, to achieve a neutrally-wet state. The wettability states are then confirmed by contact angle measurements on flat calcite crystal surfaces after similar treatment with stearic acid and decane.

Displacement experiments are conducted to obtain the relative permeability of the calcite core. The effect of gravity on relative permeabilities and residual phase saturations are observed by conducting both top-down and bottom-up vertical displacement experiments. Also observed is the rate-dependency of the steady-state displacement results.
Based on the results from the displacement experiments, conclusions can then be made concerning whether neutral-wettability is indeed the optimum wettability state for fluid recovery from a typical carbonate reservoir, and what are the implications of this.
4. EXPERIMENTAL WORK

To validate the hypothesis that there is no irreducible phase saturation in a neutrally-wet porous medium, experimental research was required. The ideal data set would consist of residual saturation data as well as capillary pressure data. To simplify the experimental procedure pure fluids and calcite grains were used.

To control the wettability of the permeable medium, we altered the characteristics of the calcite crystals. As an indicator of the wettability, we measured the contact angles using the same fluids as in the displacement experiments on calcite crystals that were treated with the same procedure as the ones used for the calcite grains.

The core holder used was specially designed by Embid Droz (1997) to simultaneously measure the relative permeability and phase pressures. Below we present the different materials and apparatus used and the procedures involved in carrying out these measurements.

4.1 CHARACTERISTICS OF FLUIDS AND SOLID SURFACES

**Fluids**: Air and distilled deionized water were used as the two fluids. All fluid measurements were made at room conditions.

**Porous medium**: The porous medium used in the displacement experiments was formed by calcite grains from blocks provided by Ward’s Natural Science. The size range of the grains is from 0.0025 to 0.0029 inches.

**Solid surfaces**: Calcite crystals were used to measure the contact angles.
**Ceramic rings**: Soilmoisture Equipment Corporation provided the porous ceramic used in the core-holder designed by Embid Droz (1997), a past Doctoral student at The University of Texas. The pore size is of critical importance in the selection of the ceramic because it affects the values of the air entrance pressure and the hydraulic conductivity.

### 4.2 Wettability Alteration

There are numerous methods that could be used to alter the wettability of a surface. Anderson et al. (1986) observed that one of the most common methods is to treat the core with chemicals such as naphthenic acids and a variety of carboxylic acids.

Hamouda et al. (2006) conducted studies on calcite surfaces using saturated and unsaturated fatty acids as well as naphthenic acids to alter the calcite surface. They conducted extensive experimental work on wettability alteration of calcite surfaces due to dissolved carboxylic acids in an oil phase at ambient temperature and different pH. They believed that this would result in a decrease in contact angles on calcite surfaces, noting that temperature has an effect on both oil/water and water/mineral interfaces. By increasing the temperature, the solubility of the adsorbed materials from surfaces is increased, while decreasing the interfacial tension. Elevated temperatures would also change the electrokinetic properties of the solid surface. Other ways to change the wettability of a porous media (Morrow et al., 1973) are by using organosilane compounds or by use of low-energy surfaces such as polytetrafluoroethylene (PTFE).

Originally, calcite has oil-wet characteristics. For the sake of our experiments, the wettability of the calcite crystals and grains were altered using stearic acid (a carboxylic
acid) dissolved in decane and thermal treatment. The technique used is similar to a procedure suggested by Hamouda et al. (2006).

4.2.1 Materials and equipment

**Stearic Acid:** $\text{C}_{18}\text{H}_{36}\text{O}_2$ dissolved in decane was used to alter the wettability of the solid surface used in the contact angle measurements and the calcite grains used as the porous medium in the displacement experiments. The properties of stearic acid are given in Table 4.1

**Solvent:** Decane was used as the solvent in the experiments. The stearic acid was stirred for approximately 30 minutes into the decane at room temperature, to create a 0.02M mixture.

**Vacuum oven:** The surface treatment of the calcite crystals and grains was performed in a vacuum oven at 80ºC. The oven was also used to dry the calcite grain samples.

**Goniometer:** An NRL contact-angle goniometer, Model 100-00 from Rame-Hart Incorporated was used. It included a microsyringe attachment that provided rapid and precise formation of drop specimens. Figure 4.1 shows a photograph of the goniometer.
4.2.2 Calcite Grinding

A manual grinder was used to break the calcite crystals into smaller pieces. These small pieces were crushed even further using a mortar and pestle. The calcite grains were then sorted into the following sieve numbers: 170, 200, and 230, which had opening sizes of 0.0035, 0.0029, and 0.0025 inches respectively. For the purpose of this experiment, the grains that passed through the 200 sieve and remained through the 230 sieve were used. These translate to a mean grain diameter of 0.0027 inches (70 microns).

4.2.3 Surface Treatment

Calcite crystal treatment: To render the wettability of the calcite surface from oil-wet to water-wet, the following procedure was followed:

1) Pre-rinse and dry: The calcite crystal was rinsed twice with isopropyl alcohol. It was then rinsed with distilled water. Following the rinse, it was dried with pure air from the laboratory taps until it was thoroughly dry.

2) Thermal treatment: The crystal was then placed in a beaker of 200 cc of 0.02 M stearic acid dissolved in decane. The beaker was placed in the vacuum oven at 80°C for 24 hours (evaporating the decane).

3) Cooling: The crystal was removed from the beaker after exactly 24 hrs and allowed to cool off at room temperature.

Calcite grains treatment: The treatment of the calcite grains was similar to that of the calcite crystals. The only difference was that the amount of 0.02 M stearic acid used was measured to be directly proportional to the volume of calcite grains.
4.2.4 Wettability tests

Wettability measurements were taken using the Contact Angle method. The calcite crystals were used as a basis to test the surface wettability since they are the same material as the grains used. The primary advantage of using the crystals for the wettability measurements is that they have a smooth flat surface and therefore, their properties can be determined quickly and conveniently using a goniometer. De-ionized water was introduced to the calcite surface using the syringe and the equilibrium left- and right-advancing angles were measured. Also, the stability of the stearic acid treatment was tested through the contact-angle measurements on the treated calcite crystals.

4.3 PERMEABILITY AND CAPILLARY PRESSURE MEASUREMENTS

The experimental setup used to simultaneously measure the permeability and capillary pressure is shown in Figure 4.2. The flow system included a core holder, a displacement pump, five pressure transducers, connection lines and valves.

4.3.1 Apparatus

Core holder: The end plates of the core holder were made of Plexiglas and the body was made of Lexan. Figure 4.3 illustrates the core holder and the dispersing section. One of the essential features of the core holder is that it can measure phase pressures at each ceramic ring. The ceramic rings are oil- and water-wet (shown in Figure 4.4). Although the two phases in this case are water and air, pressure readings were still taken
at the oil-wet rings. The rings were designed such that at the operating pressure, the water-wet rings should be penetrated only by water.

**Pressure transducers:** Validyne variable-reluctance pressure transducers (model DP215) were used to measure pressures during the displacement experiments. The transducers were calibrated at the beginning of each test. The pressure-sensing element is a flat diaphragm of magnetic stainless steel. To select the appropriate diaphragm, the pressures to be measured during the displacement had to lie within the diaphragm range. Diaphragms with pressures up to 10 psig were used during the experiments.

### 4.3.2 Sample Preparation

The acrylic rings had two O-rings that were previously smeared with vacuum grease. The treated calcite grains were dry-packed into the core holder. After assembling the core holder, it was mounted in the flow system and water was injected at 0.50 cc/min until the core was completely saturated.

### 4.3.3 Experimental Procedure

Darcy’s law is the basis for almost all calculations of fluid flow within a reservoir. According to Darcy, the flow rate through a vertical porous medium is described by

\[
q = -\frac{kA \Delta \Phi}{\mu L}
\]

where

\[
\Phi = \text{potential function} = p - \rho gz
\]

\[
q = \text{volumetric flow rate, cc/sec}
\]

\[
k = \text{permeability, darcy}
\]
Steady-state displacement was used to determine the permeability of the core. The displacement pump was calibrated by the traditional time per volume method to measure the flow rate, and the fluid collected was recorded by volume.

After filling the pressure measurement lines, fluid flow through the sample was started. Care had to be taken regarding which differential pressure transducer was used. The range of any of the differential pressure transducers must not be exceeded, since this would cause damage to the delicate diaphragm inside the housing.

The laboratory procedure was begun by saturating the sample with water and measuring the absolute permeability of the porous medium by measuring the flow rate and the pressure drop through the sample at several different upstream pressures. Flow rates were measured with a graduated cylinder and a stopwatch. Better results were obtained when measurements were made over longer time intervals. The permeability was determined by a graphical solution of Darcy’s law, which showed that the permeability is proportional to the slope of a graph of flow rate versus potential difference. For these experiments, the permeability was determined to be 1.298 Darcies (see Figure 4.5 and Appendix).
After the absolute permeability was measured, the water displacement pump was shut-down and the water gauge was closed. The air tap was then opened and moist air was passed through a pressure regulator, to the core, from the top to the bottom. The air was initially pumped through the core at 40 cc/min and we recorded the amount of water produced as a function of time. Once we observed no more water recovery at this rate, the rate was increased to 60 cc/min and then to 80 cc/min to produce the maximum amount of water possible. The saturation of each phase was determined by volumetric balance.

To avoid experimental error in our readings, the treated calcite grain samples in the core were replaced for each experiment.

4.4 SUMMARY OF RESULTS

4.4.1 Wettability Tests

Tables 4.2 and 4.3 summarize the results of the contact angle measured through the water phase, of the untreated and treated calcite crystals respectively. The drops of water used for the contact angle measurements are almost symmetric in all cases, indicating a smooth surface and a reproducible measurement. The size of the drop used was the one appropriate to form a sessile drop. In general, the contact angle did not change with time (see Figure 4.6).

Also, as a side test of neutral wettability, we observed that when water was added to a beaker of treated calcite, under no conditions would the treated calcite mix with the water. The treated calcite remained dry no matter the duration of the mixing. The water
just evaporated from the beaker over a one week period, never saturating the treated calcite sample.

### 4.4.2 Displacement Experiments

As mentioned earlier, the wet air was used to displace the water that was already in the core, from the top down. The rates of air flow were 40, 60 and 80 cc/min. For each rate, we recorded the inlet pressure, along with the pressure at each of the four taps (as shown in Figure 4.4) of the core. P2 and P4 are the pressures in the water-wet rings, while P1 and P3 are the pressures in the oil-wet rings. Although oil was not one of the phases in our experiments, the results at the oil-wet rings were still recorded for the gas flow because we believe they might be some indication of the gas pressure of the core. The experimental results of the displacement experiments are given in Tables 4.4 to 4.7.

To determine the stability of the steady-state displacements, we calculated some dimensionless groups such as the mobility ratio, capillary and gravity numbers (Lake, 1989). The mobility ratio is simply the mobility of the displacing phase over that of the resident phase. Zapata and Lake (1981) have shown that displacement is favorable when the mobility ratio is less than 1, which is the case for the experiments carried out for this research (see Table 4.7). The capillary number measures the effect of viscous forces relative to the surface tension, while the gravity number measures the gravitational stability of the displacement experiments.

The capillary number, $N_c$, is a dimensionless ratio of viscous forces and can be expressed as

$$N_c = \frac{\mu_i u_i}{\sigma}$$
where \( u_i \) is the superficial velocity or Darcy velocity, \( \mu_i \) is the phase viscosity and \( \sigma \) is the water/air surface tension. The subscript \( i \) refers to the flowing fluid phase (oil, gas, or water). The capillary number is used to indicate how strongly trapped residual oil is in a porous medium. During our displacements we used a maximum flow rate of 80 cc/min. The capillary numbers for the treated and untreated calcite experiments ranged from \( 2.5 \times 10^{-7} \) to \( 1.2 \times 10^{-6} \) (see Appendix for sample calculations).

The capillary desaturation curve (CDC) obtained for a water-pure hydrocarbon system in a synthetic permeable medium has a critical capillary number (a knee in the CDC) of approximately \( 10^{-5} \) for the non-wetting phase and \( 10^{-3} \) for the wetting phase (Lake, 1989). The critical capillary number range should increase with a wider pore size distribution for both wetting and non-wetting phases. The calcite grains used in our experiments represent a permeable medium with a narrow pore size distribution. In our case of neutral wettability, we would expect that the capillary number would lie between these two critical numbers but this is not the case. The capillary number is smaller than both critical numbers, falling in the normal range.

The gravity number \( N_g^o \) for a gas-water system can be described as the ratio of gravity to viscous pressure gradients based on the endpoint gas phase permeability (Lake, 1989):

\[
N_g^o = \frac{k_g \Delta \rho g}{\mu_g u}
\]

where

\[
\Delta \rho = \text{density difference} \ (\rho_w - \rho_g), \text{ g/cc}
\]

\[
k_g = \text{gas phase permeability, darcies}
\]
\[ \mu_g = \text{gas viscosity, cp} \]

\[ u = \text{interstitial velocity, cm/s} \]

In our experiments, the gravity numbers for the treated and untreated calcite were $10^{-2}$ and $10^{-1}$ respectively. These numbers are larger than expected but it is believed that the high values are primarily due to the high phase permeability values (see Appendix). The gas phase permeability values especially are expected to have some error because the phase pressures were measured using the oil-wet ceramic rings, based on the initial core design.

Figure 4.7 shows plots of the inlet pressures and the phase pressures as measured during the each displacement experiment. These pressures were measured during the flow of gas and so it was expected that the gas pressures would be very close to zero but this happened only in the untreated calcite. As expected, the inlet pressure is generally the highest pressure observed throughout the flow process. Other than that, there is no particular trend in the pressure readings and therefore we believe the results are neither accurate nor reproducible.

Now focusing on the results for the displacement tests, it can be seen from Figures 4.8 to 4.11 that there is a considerable amount of the water that remains saturated in the core for the untreated calcite, while we have almost complete recovery in the treated calcite. This is just as expected from our initial hypothesis that there is no residual phase saturation in a neutrally-wet porous medium. However, what we found unexpected was the fact that we needed high flow rates to reach almost complete recovery (see Figure 4.11).
As we increase the flow rate, the pressure through the core is increased and we assume the outlet pressure remains constant as atmospheric pressure. The calcite grains used in this experiment are of considerably small grain diameter (0.0027 in) and therefore, the pore spaces are even smaller. The pore space radius was estimated with respect to the grain diameter as $r_{ins} = 0.15R$, where $R$ is the grain radius.

From the pore space radius, we were able to determine the drainage pressure required throughout the porous medium to completely drain the water inside. Drainage pressure is given as

$$P_c = \sigma C_H \cos \theta$$

where $C_H = \frac{2}{r_{ins}}$

The drainage pressure for the untreated calcite turned out to be 4.0 psi which is much larger than the inlet pressure or any of the phase pressures. Therefore, assuming we injected air at a much higher rate during the displacement, translating to a higher pressure, we might be able to fully recover the water saturated in the untreated calcite medium.

For the case of the treated calcite, with contact angles close to 90°, $\cos \theta$ is approximately zero, translating to a drainage pressure close to zero. This explains the ease with which we recovered the water in the treated calcite, but it doesn’t explain the need for the high gas rates needed for water recovery.

Possible sources of experimental errors are damaged diaphragms or O-rings, leaks in the system, uncalibrated pumps and uncalibrated transducers.
### Table 4.1 Fluid Properties

**Fluid system:** Water/air @ 23°C

<table>
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<tr>
<th>Fluid</th>
<th>density [g/cc]</th>
<th>viscosity [cp]</th>
</tr>
</thead>
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<tr>
<td>Water</td>
<td>0.9976</td>
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</tr>
<tr>
<td>Air</td>
<td>0.0012</td>
<td>0.01785</td>
</tr>
</tbody>
</table>

**Stearic Acid:**

IUPAC systematic name is octadecanoic acid

- **Formula:** $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
- **Density:** 0.847 g/cc at 70 °C
- **Molar mass:** 284.47 g/mol
Table 4.2  Water/air contact angle measurements on pure calcite crystals.

<table>
<thead>
<tr>
<th>Reading #</th>
<th>Equilibrium angle</th>
</tr>
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<td></td>
<td>Left (°)</td>
</tr>
<tr>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 4.3  Water/Air contact angle measurements on treated calcite crystals (each reading taken on a different calcite crystal).

<table>
<thead>
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<th>Equilibrium angle</th>
</tr>
</thead>
<tbody>
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<td>88</td>
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<td>9</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>89</td>
</tr>
</tbody>
</table>
Table 4.4  Experimental results for displacement from pure calcite (note: sccm = cc/min)

<table>
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<th>q = 40sccm</th>
<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>t₀</th>
</tr>
</thead>
<tbody>
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<td>0.0</td>
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<td></td>
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<td>P4 = 0.01psi</td>
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<td>P3 = 0.16psi</td>
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<td>P4 = 0.02psi</td>
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</tr>
<tr>
<td>Nc = 1.22E-6</td>
<td>13.8</td>
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<td>2224.7271</td>
</tr>
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</table>

q = 80sccm
### Table 4.5
Experimental results for first displacement from treated calcite.
(note: sccm = cc/min)

<table>
<thead>
<tr>
<th>Q = 60sccm</th>
<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>$t_d$</th>
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<tbody>
<tr>
<td>Pinlet = 1.44psi</td>
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<td></td>
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<tr>
<td>P1 = 0.68psi</td>
<td>1.0</td>
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<td>1.8539</td>
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<tr>
<td>P2 = 0.28psi</td>
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<td>0.0167</td>
<td>3.7079</td>
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<tr>
<td>P3 = 1.86psi</td>
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<td>0.0250</td>
<td>5.5618</td>
</tr>
<tr>
<td>P4 = 0.75psi</td>
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<td>0.0333</td>
<td>7.4158</td>
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<tr>
<td>Nc = 9.74E-7</td>
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<td>0.0417</td>
<td>9.2697</td>
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<td></td>
<td>6.8</td>
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<td>10.8</td>
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<td>10.0000</td>
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Table 4.6  
Experimental results for second displacement from treated calcite.
(note: sccm = cc/min)

<table>
<thead>
<tr>
<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>t₀</th>
<th>P1 = 0.29psi</th>
<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>t₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0000</td>
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<td>Pinlet = 0.81psi</td>
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<td>1.3000</td>
<td>289.2145</td>
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<tr>
<td>2.0</td>
<td>0.0250</td>
<td>3.7079</td>
<td>P1 = 0.74psi</td>
<td>6.6</td>
<td>1.3167</td>
<td>292.9224</td>
</tr>
<tr>
<td>3.0</td>
<td>0.0458</td>
<td>6.7978</td>
<td>P2 = 0.34psi</td>
<td>6.1</td>
<td>1.3667</td>
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<tr>
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<td>0.0583</td>
<td>8.6517</td>
<td>P3 = 0.92psi</td>
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<td>1.4167</td>
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<tr>
<td>3.4</td>
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<td>9.8877</td>
<td>P4 = 0.61psi</td>
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<tr>
<td>Nc = 6.10E-7</td>
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<td>7.0</td>
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<td>348.5406</td>
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<tr>
<td>3.8</td>
<td>0.1167</td>
<td>17.3034</td>
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<tr>
<td>3.9</td>
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<td>P2 = 0.36psi</td>
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<td>2.0000</td>
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</tr>
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<td>P3 = 0.36psi</td>
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<table>
<thead>
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<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>t₀</th>
<th>Pinlet = 2.22psi</th>
<th>Vol (ml)</th>
<th>Time (hrs)</th>
<th>t₀</th>
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<td>11.7500</td>
<td>3485.4058</td>
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<td>P3 = 2.33psi</td>
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<td>11.9167</td>
<td>3534.8442</td>
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<tr>
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<td>15.5000</td>
<td>4597.7693</td>
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<td>3559.5634</td>
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<td>15.8333</td>
<td>4696.6461</td>
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<td>11.5</td>
<td>15.9167</td>
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<td>15.0000</td>
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<td>11.5</td>
<td>18.3333</td>
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Table 4.7  Dimensionless Numbers.

<table>
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<tr>
<th>Experiment</th>
<th>Mo</th>
<th>Ng</th>
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<tr>
<td>Pure Calcite</td>
<td>0.2046</td>
<td>0.1455</td>
</tr>
<tr>
<td>Displacement #1</td>
<td>0.7956</td>
<td>0.0139</td>
</tr>
<tr>
<td>Displacement #2</td>
<td>0.0638</td>
<td>0.0174</td>
</tr>
</tbody>
</table>
Figure 4.1   Photograph of the goniometer (Front and side view, respectively).
Figure 4.2  Setup of the flow system.
Figure 4.3  Dimensions of Core holder.
Figure 4.4: The positions of the ceramic rings in the core holder.
Flow Rate vs. Potential Difference
(Absolute Permeability Determination)

\[ q = (-0.5979)\Delta \Phi - 0.0316 \]

Figure 4.5: Showing the flow rate vs. potential difference (absolute permeability determination) for the calcite core.
Figure 4.6: Showing sessile drop on treated calcite surface.
Figure 4.7: The measured pressures as a function of dimensionless time.
Figure 4.8: Showing the water saturation vs. dimensionless time (top) and cumulative water production vs. time (bottom) for pure calcite.
Figure 4.9: Showing results for the first displacement experiment for treated calcite: water saturation vs. dimensionless time (top) and cumulative water production vs. time (bottom).
Figure 4.10: Showing results for the second displacement experiment for treated calcite: water saturation vs. dimensionless time (top) and cumulative water production vs. time (bottom).
Figure 4.11: Comparing the residual water saturation vs. rate for treated calcite (top) and pure calcite (bottom).
Residual Water Saturation vs. Capillary Number
(Treated Calcite)

Water Saturation vs. Capillary Number
(Pure Calcite)

Figure 4.12: Comparing the residual water saturation vs. capillary number for treated calcite (top) and pure calcite (bottom).

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5. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This work attempted to observe if there is any residual phase saturation in a neutrally-wet medium. To achieve this goal, we conducted steady-state displacement experiments. For the sake of our experiments, calcite grains with controlled wettability were used as the porous medium and we observed the fluid recovery at different gas flow rates.

The following summary, conclusions, and recommendations for future work were derived from this study.

5.1 SUMMARY

1. The wettability of our calcite grain sample was controlled by heating it for 24 hrs at 80°C in 0.02 M stearic acid dissolved in decane. To confirm the neutral-wettability, contact angles were measured using a goniometer. The results did not change within a week, indicating stability with the wettability alteration.

2. Although the core holder used for the experiments was designed to measure the phase permeabilities, the gas phase permeabilities were believed to be inaccurate because they were measured using oil-wet ceramic rings.

5.2 CONCLUSIONS

1. Although the dimensionless numbers derived from the experiments are believed to be inaccurate, due to the flawed phased pressure values, we still believe that the experiments are indeed stable.
2. There is no irreducible phase saturation in the neutrally-wet medium at high velocities.

5.3 RECOMMENDATIONS FOR FUTURE WORK

1. We must develop a method to measure the phase permeability when gas is one of the phases, while simultaneously running the displacement experiments.
2. Investigate the effect of drainage pressure and how this might improve the recovery in a regular carbonate reservoir, without wettability alteration.
3. Examine the effect of temperature on the contact angle and interfacial tension.
4. Investigate the need for high flow rates in a neutrally-wet medium to achieve almost complete recovery.
APPENDIX

SAMPLE CALCULATIONS

- **Calculation of Absolute Permeability**

  From Fig. 4.5, Slope = -0.5979 = \( \frac{q}{\Delta \Phi} = -\frac{kA}{\mu L} \)

  \[ A = 2.71\text{cm}^2, \quad L = 5.88\text{cm}, \quad \mu = 1\text{cp} \]

  Therefore,

  \[ k = \left( \frac{0.5979 \text{cc}}{s - \text{atm}} \right) \left( 1\text{cp} \right) \left( 5.88\text{cm} \right) \left( 2.71\text{cm}^2 \right) = 1.298D \]

- **Calculation of Capillary Number**

  \[ N_c = \frac{\mu_i u_i}{\sigma} \]

  where \( i \) = gas phase

  therefore, at \( q = 40 \text{ cc/min} \)

  \[ u_i = \frac{40 \text{ cc/min}}{(2.71\text{cm}^2)(60 \text{ s/min})} = 0.2462\text{cm/s} \]

  \[ N_c = \left( 0.2462 \frac{\text{cm}}{s} \right) \left( 1.785 \times 10^{-5} \text{Pa} - s \right) \frac{0.01(\text{m/cm})}{72 \times 10^{-3}(\text{Pa} - m)} = 6.10 \times 10^{-7} \]

- **Calculation of gas permeabilities**

  For pure calcite, \( k_g = \frac{q \mu L}{A \Delta \Phi_g} \)

  At initial rate of \( 40 \text{ cc/min} \), \( \Delta P_g = P1 - P3 = (0.75 - 0.15) \text{psi} = 4137 \text{N/m}^2 \)

  \[ \Delta \Phi = \Delta P - \Delta \rho gz \]

  where \( z = 5.88\text{cm} \), \( \Delta \rho = (1000 - 1.275) \text{kg/m}^3 = 998.725 \text{kg/m}^3 \), \( g = 9.81 \text{m/s}^2 \)

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therefore,
\[
\Delta \Phi = 4137 \left( \frac{N}{m^2} \right) - \left( \left( 9.81 \frac{kg}{m^3} \right) \left( 998.725 \frac{g}{m^2} \right) (0.0588 m) \right) = 3561 \left( \frac{N}{m^2} \right) = 0.0352 \text{ atm}
\]

Therefore, \( k_g = \frac{(0.667 \text{ cc} / \text{s})(0.01785 \text{ cp})(5.88 \text{ cm})}{(2.71 \text{ cm}^2)(0.0352 \text{ atm})} = 0.7339 D \)

- **Calculation of water permeabilities**

  For pure calcite, \( k_w = \frac{q \mu L}{A \Delta \Phi_w} \)

  At initial rate of 40 cc/min, \( \Delta P_w = P2 - P4 = 0.19 \text{ psi} = 1310 \text{ N} / m^2 \)

  therefore,
  \[
  \Delta \Phi = 1310 \left( \frac{N}{m^2} \right) - \left( \left( 9.81 \frac{kg}{m^3} \right) \left( 998.725 \frac{g}{m^2} \right) (0.0588 m) \right) = 733 \left( \frac{N}{m^2} \right) = 0.00724 \text{ atm}
  \]

  Therefore, \( k_w = \frac{(0.667 \text{ cc} / \text{s})(1 \text{ cp})(5.88 \text{ cm})}{(2.71 \text{ cm}^2)(0.00724 \text{ atm})} = 119.9 D \)

- **Calculation of Gravity Number**

  \( N_g^o = \frac{k_g \Delta \rho g}{\mu_g u} \)

  For pure calcite,

  \( k_g = 0.7339 D, \quad \mu_g = 0.01785 \text{ cp} \sim 1.785 \times 10^{-5} \text{ Pa-s}, \quad \Delta \rho = 900 \text{ kg/m}^3, \quad g = 9.81 \text{ m/s}^2, \quad u = 0.2462 \text{ cm} / \text{s} \)

  Therefore, \( N_g^o = \frac{(0.7339 D)(9.869 \times 10^{-13} \text{ m}^2 / D)(900 \text{ kg} / \text{m}^3)(9.81 \text{ m/s}^2)}{(1.785 \times 10^{-5} \text{ Pa} - \text{s})(2.462 \times 10^{-3} \text{ m/s})} = 0.1455 \)
- **Calculation of dimensionless time \( t_D \)**

  For \( q = 60 \text{ cc/min} \) and \( t = 600 \text{ min} \)

  \[
  t_D = \frac{qt}{V_p} = \frac{(60\text{cc}/\text{min})(60\text{min})}{(16.18\text{cc})} = 2224.73
  \]

- **Calculation of Mobility Ratio**

  For displacement #1,

  \( k_w = 2.31 \text{D}, \ k_g = 0.033 \text{D}, \ \mu_g = 0.01785 \text{cp and } \mu_w = 1 \text{cp} \)

  therefore,

  \[
  M = \frac{k_w\mu_g}{\mu_wk_g} = \frac{(0.033)(1)}{(0.01785)(2.31)} = 0.7956
  \]

- **Calculation of Drainage Pressure**

  \[
  r_{ins} = 0.15R = (0.15)\left(\frac{0.0027\text{in}}{2}\right)
  \]

  \[
  C_H = \frac{2}{r_{ins}} = 9876.54\text{in}^{-1} = \frac{388,840}{\text{in}} = \frac{388,840}{\text{m}}
  \]

  \[
  P_c = \sigma C_H \cos \theta = 0.072(\text{Pa} - m)\left(\frac{388,840}{\text{m}}\right) = 27997\text{Pa} = 4.06 \text{psi}
  \]


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