Dynamics of Contact Angles and Hemiwicking on Rock Fracture Faces

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Dynamics of Contact Angles and Hemiwicking on Rock Fracture Faces

A Thesis Presented for the Master of Science Degree
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Bohdan Bernhardt Horodecky
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ABSTRACT

The dynamics of contact angles and capillary wicking (hemiwicking) were investigated on rock fracture surfaces from a selection of low-porosity rocks with different mineralogy: Burlington Limestone, Crossville Sandstone, Mancos Shale, Sierra White Granite, Vermilion Bay Granite, and Westerly Granite. Wetting height data for rough fracture faces were acquired in a parallel view using dynamic neutron radiography at the Oak Ridge National Laboratory Neutron Imaging Facility. Hemiwicking rates on the rock fracture surfaces were determined using a high-speed optical setup with a perpendicular viewpoint. Wetting height versus time relationships for both methods were delineated through changepoint analysis. The contact angle of the fracture surface ($\theta_R$) was then quantified based on the maximum wetting height. Statistical significance was assessed at the 95% confidence level. Analysis of variance indicated statistically significant differences in mean $\theta_R$ values between rock types. Regression analyses between $\theta_R$ and the contact angles of polished rock surfaces ($\theta_A$) and the Wenzel Roughness Factor yielded statistically non-significant relationships. Linear regression showed that the median wetting height during hemiwicking behaved linearly with respect to the square root of time. Surface sorptivity was quantified by the proportionality constant between the height of capillary wetting and the square root of time. Analysis of variance indicated statistically significant differences between rock types in mean surface sorptivity values. A statistically significant negative relationship was observed between surface sorptivity and $\theta_A$, while non-significant relationships were observed between surface sorptivity and $\theta_R$, and the Wenzel Roughness Factor. An analysis of variance of the interquartile range (IQR) for wetting height revealed statistically significant dependencies on both rock type and time, with no interaction. Overall, the results point to differences in mineralogy, rather than roughness, as the main control of contact angle and hemiwicking dynamics on rock fracture faces.
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Chapter 1 - Overview of Contact Angles and Hemiwicking

1.1 Introduction

Low-porosity rocks such as cemented sandstones, shales, limestones, and granites, tend to strongly influence fluid transport within the subsurface by acting as impermeable barriers or seals to geological reservoirs. However, fractures in these rocks can act as conduits, greatly increasing hydraulic conductivity and the potential for fluid flow. Given the heterogeneous nature of fracture surfaces, attempts to model the wetting properties of fractured surfaces have been limited in range and applicability. Following the adaptation of fracking technology and horizontal drilling, many researchers have studied the flow of fluids through fractures within unconventional reservoirs under saturated conditions (e.g. Karpyn et al, 2009; Rangel-German and Kovscek, 2002; Javaheri et al., 2017). However, relatively little research has been done to investigate the hydraulic properties of fractured low-porosity rocks under partially-saturated conditions. In this study we investigated the connections between physical properties of rocks found in a traditional geologic sense with the phenomenon of fluid transport over rough surfaces. Specifically, the contact angle was determined to evaluate the wettability of exposed rock fracture surfaces and investigated the relationship it shares with the potential for fluid transport over the rough fracture surface through capillarity (i.e. hemiwicking) for a variety of different low porosity rock types.

1.2 Contact Angle

In order to predict the transport of fluids within fractures under partially-saturated conditions, it is necessary to determine key hydraulic properties of fracture surfaces that define the wetting capabilities inherent to the overall matrix. Solid-liquid contact angles between a wetting fluid and a solid surface are traditionally measured to determine the wettability of a rock. The wettability of a rock represents the tendency or preference for one fluid to adhere to a surface in place of another fluid. As shown in Table 1, wettability is traditionally viewed as a binary concept in geology, with different rocks being designated water-wet if the contact angle is less than roughly 70 degrees or oil-wet if
the contact angle is greater than roughly 115 degrees (Morrow et al. 1990, Zolotukhin and Ursin., 2000; Iglauer et al., 2015). Determining the contact angle provides a key parameter for understanding surface wettability, which is an essential step for modeling multiphase flow of fluids within a porous medium and is a relevant tool for both primary recovery and secondary recovery through waterflooding in the oil and gas industry (Ogunberu, 2005; Kasiri and Bashiri, 2011). Additional applications include estimating enhanced oil and gas recovery in unconventional reservoirs (e.g., Borysenko et al., 2009; Javaheri et al., 2017), decreasing condensate blockage in wellbores (Panga et al., 2006), geologic sequestration of carbon dioxide in subsurface reservoirs (e.g., Wan et al., 2014), the transportation and retention of chemicals in underground waste repositories (e.g., Mohammad and Kibbey, 2005), and evaluating aquifer recharge rates from infiltration in the vadose zone (e.g., Wallach et al., 2013).

Equilibrium contact angles are traditionally measured as the angle of intersection between the gas-liquid-solid interface for a liquid droplet resting on a flat horizontal surface. The magnitude of the equilibrium contact angle of a flat surface ($\theta_s$) is primarily dependent on the adhesive forces between the liquid drop to the solid surface and is determined by the balance of interfacial tensions between the three different phases. This balance has been traditionally described by the Young’s equation (Yuan and Lee, 2013):

$$\cos(\theta_s) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  [1.1]

where $\gamma_{LV}$, $\gamma_{SV}$, and $\gamma_{SL}$ are the interfacial tensions of the liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively (Figure 1a). Ideally, if the liquid has a strong adhesive bond to the solid surface, then the droplet will spread to a greater extent across the surface and reduce the contact angle.

However, Young’s equation is only considered for flat and chemically homogeneous surfaces. Methods used to determine contact angles of a wetting/non-wetting fluid pair on solid surfaces have been reviewed by several authors (e.g., Neumann and Good, 1979; Chau, 2009; Yuan and Lee, 2013). The most commonly used methods for determining the contact angle on rocks are the sessile drop and
captive bubble techniques (Montes Ruiz-Cabello et al., 2011). These methods require ideal, flat polished surfaces, and as such are not particularly well suited to analyzing rock fracture surfaces, which are generally rough and non-ideal.

The characteristics of rough and non-ideal solid surfaces, such as surface roughness and chemically heterogeneities in composition are also thought to affect the magnitude of the contact angle. In a numerical study, Montes Ruiz-Cabello et al. (2011) compared the uncertainties in contact angles resulting from implementing the sessile drop and captive bubble techniques on rough versus smooth surfaces. They found that both advancing and receding contact angles produce different fluctuations in both methods when applied to rough chemically homogeneous surfaces (Montes Ruiz-Cabello et al., 2011). In order to estimate the contact angle for fractured surfaces, modifications to Young’s equation are needed to account for surface roughness and heterogeneous chemical composition. Three primary theoretical models have been used to estimate the contact angle of a rough surface from a flat surface. These models are the Wenzel model (Wenzel, 1936), Cassie model (Cassie, 1948) and the Cassie-Baxter model (Cassie and Baxter, 1944) (Figures 1b – 1d).

Wenzel (1936) estimated the contact angle for a rough chemically homogeneous surface based on the value for an ideal flat surface (Ramón-Torregrossa et al., 2008) with the assumption that the surface features are fully wetted by the fluid. This model is given by (Ambrosia et al., 2018):

\[ \cos \theta_R = r \times \cos \theta_S \]  \hspace{1cm} [1.2]

where \( \theta_R \) is the apparent equilibrium contact angle on a rough surface, representing the angle estimated from the average surface plane of the rough surface, and \( r \) is the roughness factor (Wenzel, 1936):

\[ r = \frac{A_R}{A_S} \]  \hspace{1cm} [1.3]

where \( A_R \) is the projected area of the rough surface relative to the corresponding area of the smooth flat surface, \( A_S \). Ramón-Torregrosa et al. (2008) pointed out the influence of image field of view on the determination of \( r \), and thus on the prediction of \( \theta_R \).
Unlike the Wenzel model, the Cassie model assumes there is no penetration of the fluid into the topographical features of the surface and that the liquid drop rests fully on top of the surface structures and the intervening spaces being filled with a non-wetting fluid (Wang et al., 2018).

\[ \cos \theta_R = f (1 + \cos \theta_S) + f - 1 \quad [1.4] \]

where \( f \) is the fraction of the solid/liquid contact area. The Cassie-Baxter theory assumes there is partial infiltration of the fluid into the rough topographical features of the surface, while small pockets of non-wetting fluid occupy the remaining space (Foster et al., 2012; Wang et al., 2018). Prediction of rough surface contact angles is then achieved through the following equation (Cassie and Baxter, 1944):

\[ \cos \theta_R = r_f f (1 + \cos \theta_S) + f - 1 \quad [1.5] \]

where \( r_f \) is the roughness ratio of the wetted surface area. It should be noted that if \( r_f = 1 \), then the theoretical estimation for the contact angle of an unideal surface by the Cassie-Baxter equation [1.5] is identical to the contact angle estimated for an unideal surface by the Cassie model [1.4].

Figures 1b-d illustrate the differences between the above-mentioned models. For this study, Wenzel roughness factors for each rock type were utilized from Gates et al. (2018). Since this roughness factor was available and there is no present means to measure the solid/liquid contact area ratio for a partially-wetted surface, we utilized the Wenzel model under the common assumption that there is complete wetting between the individual asperities of the rough fracture surface.

Estimations from the Wenzel model (1936) (e.g., Wenzel, 1936; Hazlett, 1990; Onda et al., 1996; Gates et al. 2018) predict that as a flat surface becomes progressively rougher, then the wettability of the surface increases, resulting in a decrease in the contact angle (i.e. increased hydrophilicity). While this model has generally produced good correspondence with experimental results, some researchers have questioned its theoretical veracity (e.g., Wolansky and Marmur, 1999; Gao and McCarthy, 2007). Additionally, experimental results from Kittu et al. (2014) and Rayudu
and Bulut (2014) argue the opposite case, whereby increased roughness on a surface results in an increase in the contact angle (i.e., increased hydrophobicity).

Experimental approaches, such as Meiron et al. (2004) provide a method of measuring the apparent equilibrium contact angle for a liquid droplet on a rough surface. This approach is done by vibrating the surface while taking overhead images of the droplet. The circularity of the drop is monitored, and the contact angle is calculated from the droplet diameter and known volume. The vibrations induce a global energy minimum state, thereby eliminating hysteresis. Thus, the droplet assumes an axisymmetric form that can be analyzed. In addition to determining contact angles on rough surfaces, advancements in 3-d imaging technology and image analysis software have allowed researchers to directly measure contact angles within porous reservoir rocks (Andrew et al. 2014). This approach employed x-ray microtomography to visualize and quantify contact angles in situ within a super-critical CO2–brine–carbonate system.

1.3 Hemiwicking

Hemiwicking refers to the spreading of a liquid by capillary forces along the topographical features of a rough hydrophilic surface. As a liquid drop is put into contact with a rough surface, a film propagates rapidly outward and invades the surface independently to the main liquid body. The spreading of a fluid is further enhanced by the decrease in the liquid-solid contact angle that occurs on rough surfaces (i.e. superhydrophilicity (Bonn et al., 2009; Drelich and Chibowski, 2010). The phenomena of hemiwicking along rough surfaces has been widely studied in various applications such as the fabrication of engineered surfaces (Mikkelsen et al., 2011; Mai et al., 2012) and chromatography of compounds (Spangenberg et al., 2011). Although hemiwicking has been more actively investigated in the fields of material science and engineering, this phenomenon can also be observed on many natural surfaces like rock fracture faces found in geologic reservoirs

The early time dynamic rise of a wetting fluid induced in a vertical tube by capillarity has been widely studied and has been well established to follow the behavior described by Lucas (1918) and Washburn (1921). This behavior predicts that the height
of wetting is proportional to the square root of time and has been labeled by many as the Lucas-Washburn Law:

$$h(t) = \sqrt{Dt}$$  \[1.6\]

$$D = 2 \frac{\gamma \mu x \cos \theta_s}{\eta}$$  \[1.7\]

In these expressions, \(h\) is the wetting height, \(t\) is time, \(x\) is the tube radius, \(\eta\) is the fluid viscosity, and \(D\) is a compound, diffusion-like coefficient, sometimes referred to as sorptivity.

The linear behavior between the wetting height and the square root of time established by the Lucas-Washburn law traditionally holds well for a series of capillary tubes. This behavior is also found to often follow in the case for a porous medium, where a network of interconnected irregularly-shaped pores essentially replicates a bundle of capillary tubes. Here, the structure of pore networks is oversimplified in the assumption that they are considered as an array of capillary tubes (Bico et al., 2002). Although the Lucas-Washburn law and the uptake of water through capillarity (i.e. sorptivity) has been primarily related to capillary tubes and porous media in the past, the same processes can also be applied to heterogeneous rough surfaces.

Heterogeneous rough surfaces, such as geologic material, cannot be defined by a single geometric parameter (Kim et al., 2016), and have been widely documented to be comprised of irregularly-shaped asperities which are heterogeneously distributed over multiple spatial scales (e.g., Power and Tullis, 1991; Boffa et al., 1998; Babadagli and Develi, 2003; Nigon et al., 2017). In engineering fields, the joint roughness coefficient (JRC) is widely used to characterize rock fracture surface roughness (Odling, 1994). While the JRC is a convenient parameter for practical engineering applications, its application is limited to one-dimensional profiles (Develi and Babadagli, 1998). The Wenzel roughness factor, \(r\), as defined by Eq. [1.3], is a 2-dimensional parameter suitable for characterizing the roughness of rock fracture surfaces. When investigating hemiwicking, the quantification of surface roughness from the Wenzel roughness factor
can be related to the equilibrium contact angle of a wetting fluid on an ideal surface through the well-established Wenzel (1936) model, Eq. [1.2]. Currently, however, \( r \) has not been widely used to characterize rock fracture surfaces. Recently, Gates (2018) found that \( r \) provided excellent discrimination between the roughness of fracture surfaces artificially induced in a range of sedimentary and igneous rock types.

Since rock fracture surfaces display many microtopographic channels over multiple scales, they should be good candidates for studying the hemiwicking phenomenon. Many attempts have been made in the past to model hemiwicking over a variety of different rough surfaces. However, many of these approaches predict hemiwicking rates by modeling the transport of a fluid through a wide array of evenly spaced micropillars over a chemically homogenous surface (Bico et al. 2001; Courbin et al. 2007; Ishino et al. 2007). Variations of these models have been defined by their differences in spatial scales. Channel-scale models such as Hay and Dragila (2008) and Hay et al. (2008) model flow between the individual surface asperities or evenly spaced pillar structures. Channel-scale models incorporate detailed descriptions of the complex geometric characteristics of the surface, which includes liquid-solid contact angle, column height, column diameter, and column separation. These models utilize the Navier-Stokes equation for viscous fluids, the Young-Laplace equation for capillary pressure, and geometric characteristics of the surfaces to describe the transport of fluid through each individual surface asperity (Bico et al. 2001; Mai et al. 2012; Wang et al. 2016; and Kim et al. 2016).

In contrast to Channel-scale models, Darcy-scale models predict the transport of fluids over multiple asperities (Tokunaga et al. 2000). Darcy-scale models predict fluid transport by combining steady-state flux and mass balance continuity equations. Despite the differences in these approaches, many of the models conclude that 1) the rate of wetting along the rough surfaces is faster than the bulk matrix. 2) the wetting height is proportional to the square root of time per the Lucas-Wasburn law [1.5].

Unfortunately, the assumptions utilized in these approaches may not be adequate for describing the characteristics of natural surfaces like rock fractures. Many rock fracture surfaces display complex geometric topographies, surface roughness over a variety of scales, and are chemically heterogeneous due to spatial variations in
mineral composition. Consequently, almost no attempts have been made for quantifying the capillary potential (i.e. sorptivity) of fracture surfaces within geologic material. Recently, Brabazon et al. (in press, 2019) investigated rates of spontaneous imbibition in enclosed fractures of rock cores through neutron radiography. In the present study, we used an optical based imaging method to visualize and quantify hemiwicking rates and surface sorptivity of water on exposed rock fracture faces.

Although no relationship has been officially established, hemiwicking can be thought of as type of spontaneous imbibition (SI) over rough surfaces. Spontaneous imbibition is the process in which fluids adsorb into a porous media or fracture system without being driven by any pressure gradient (Morrow and Mason, 2001; Abdallah et al., 2007; Schmid et al., 2012). Spontaneous imbibition is a phenomenon widely studied in both geosciences and petroleum engineering and is an important factor to consider in many practical applications like enhanced oil and gas recovery estimates for conventional and unconventional reservoirs (Rangel-German and Kovscek, 2002), retention of fracturing fluid in unconventional reservoirs (Ghanbari and Dehghanpour, 2016; Dehghanpour et al., 2013), and evaluating the integrity of underground waste reservoirs (Gaurina-Medimurec et al., 2017), and the weathering of engineered structures (Hanžič et al., 2003; Hall and Hoff, 2007). As spontaneous imbibition occurs within rock fracture systems, roughness elements or surface asperities lead to the uptake of fluids through hemiwicking. This process of capillary driven transport has the potential to cause films of fluid to propagate over fracture surfaces at a much quicker rate than main fluid reservoir (Bico et al., 2002). These films can have a dramatic influence on the rate of transport over a surface. Given this relationship, investigating the process of surface hemiwicking on fracture surfaces for low-porosity rocks can provide us with greater insight into the capillary forces inherent on fracture surfaces within geological materials relative to the matrix.

During spontaneous imbibition, a wetting fluid enters a porous medium through capillary action (Morrow and Mason, 2001; Schmid et al., 2012). The rate of infiltration into the porous medium (i.e. sorptivity), is simply quantified by the proportionality constant between wetting height and time depicted in Equation [1.5], which represents the sorptivity of the medium. Sorptivity is a measurement that defines the capacity or
potential for a medium to absorb or desorb a liquid through capillarity (Philip, 1957). This common linear relationship established between the wetting height and the square root of time is synonymous to the Lucas-Washburn law (Lucas, 1918; Washburn 1921).

Experimental studies that have investigated hemiwick ing have employed methods to identify the height of wetting with respect to time. This has been done by measuring the visually-observable contrast between the wet and dry areas of a rough surface since rough surfaces appear darker when wet as a result of reflecting less light (Twomey et al., 1986; Lekner and Dorf, 1988; Mall and da Vitoria Lobo, 1995). Early studies measured the maximum, average, and minimum heights of the wetting front by hand with a ruler and later through film-based photography (Tokunaga et al. 2000; and Ketterson, 1995). Following the rise of digital imaging technology, high speed cameras have become the ubiquitous approach for capturing time series of digital images in order to show the dynamic movement of wetting fronts. Budziak and Neumann (1990) introduced this technique for contact angle measurement. Modern digital camera systems are now routinely employed to measure the dynamics of hemiwick ing (e.g., Vorobyev and Guo, 2009, 2010; Mai et al., 2012; Wang et al., 2016; Kim et al., 2016). The digital images can be readily analyzed to extract the mean height of wetting versus time.

1.4 Relevance to Industry etc.

It is important to understand the hydraulic properties of fractured low-porosity rocks and their influence on spontaneous imbibition rates for various industrial applications. This phenomenon has been shown to play a role in enhanced oil and gas extraction (Dehghanpour et al., 2013; Morrow et al., 2001; Bikkina et al. 2016), hydraulic fracturing leak-off (Ghanbari and Dehghanpour., 2016), retention of potentially hazardous wastes within deep geologic reservoirs and aquifers (Roychaudhuri et al., 2013; Gaurina-Medimurec et al., 2017), and the wetting of building materials and other engineered structures (Hanžič et al., 2003; Hall and Hoff, 2007; Gagné et al., 2011; Bao et al., 2017). Further details of these applications are discussed below.
1.4.1 Enhanced Oil and Gas Recovery

Understanding both the wettability and capillary potential of geologic reservoirs has been widely considered an important factor when extracting oil and gas in conventional reservoirs (Rangel-German and Kovscek, 2002). Many conventional reservoirs undergo a process of secondary hydrocarbon recovery known as waterflooding. Waterflooding is a commonly used secondary method of recovery in which water is injected into the reservoir to displace any residual oil left over (Anderson, 1987). This process is conducted until a non-ideal water-oil ratio is produced after breakthrough. It has been widely recognized under waterflooding procedures that reservoirs with a high wettability (i.e. water-wet) are generally more efficient at hydrocarbon production than reservoirs with low wettability (i.e. oil-wet) (Anderson, 1987). Generally, the forces of capillarity, gravity, and viscosity govern the migration of fluids within geologic formations (Karpyn et al, 2009). The production of hydrocarbons from secondary recovery methods is largely tied to the imbibition of water through the reservoir, which is driven by the relationship between wettability and relative permeability (Anderson 1987; Bikkina et al. 2016). Additionally, introducing different chemical compounds to geologic reservoirs can be used to significantly alter the wetting conditions as determined by the contact angle (Anderson 1987), as well as reduce the likelihood of water blockage occurring near the wellbore area (Panga et al., 2006). After secondary recovery, most of the remaining hydrocarbons are held within the reservoir by capillary forces (Bondor et al., 1992; Bikkina et al., 2016). In order to further produce from these reservoirs, the capillary number is used to evaluate the ratio of viscous drag versus surface tension, and thus, contact angles are needed (Bondor et al., 1992; Ayirala and Rao, 2004; Kasiri and Bashiri, 2011).

While enhanced oil recovery and other secondary recovery methods discussed above focused primarily on the porous matrix of conventional reservoirs, furthering our understanding of the hydraulic properties of fracture systems within low-porosity rock may prove beneficial to the rapidly growing sector of unconventional reservoirs. Following the introduction of hydraulic fracturing and horizontal drilling, unconventional reservoirs, such as tight gas shales and sandstones have become increasingly relevant and economically viable in the current energy industry (Borysenko et al., 2009; Reinicke
Hydraulic fracturing (i.e. fracking) is a process by which mixtures of water, surfactants, proppants (typically sand), and other chemical additives are injected at high pressures to artificially fracture the reservoir, change the reservoir’s wettability, and increase the overall permeability of the system (Babadagli et al., 2005; Rivard et al., 2014; Osiptsov, 2017; Osman et al., 2018). The resulting interconnected fracture networks facilitate higher rates of fluid transport within the reservoirs, allowing for more efficient hydrocarbon recovery. Thus, further understanding the influence of fracture surfaces on wettability, capillary wicking, and the differences these surfaces have relative to the matrix, may aid in future efforts in enhanced oil and gas recovery.

1.4.2 Hydraulic Fracturing Fluid Retention and Aquifer Contamination

As discussed above, hydraulic fracturing has become a widely employed method for enhancing the recovery potential of both conventional and unconventional oil and gas reservoirs. The process of fracturing unconventional reservoirs commonly requires large volumes of water, as well as a variety of chemicals used to alter reservoir conditions like wettability. These chemicals include surfactants, friction reducers, biocides, stabilizers, and proppants (Roychaudhuri et al., 2013; Rivard et al., 2014; Osiptsov, 2017; Osman et al., 2018). After this process, it is common to recover only a small fraction of the injected fluids, with most of the fluid remaining within the formation (Cheng, et al., 2012; Roychaudhuri et al., 2013; Ghanbari et al., 2016). The retention of these fluids within a fractured reservoir is largely attributed to capillarity driven spontaneous imbibition into the existing matrix that encompasses the fractures (Roychaudhuri et al., 2013; Dehghanpour et al., 2013; Ghanbari and Dehghanpour, 2016). The eventual fate of this loss of recoverable fracturing fluid (i.e. leakoff) through either the matrix or fractures may pose significant environmental effects towards the water quality of other adjacent aquifer systems (Myers, 2012).

Unfortunately, these concerns are not only limited to the transport of hydraulic fracturing fluids. Many contaminants such as dense nonaqueous phase liquids (DNAPLS) and other organic compounds are a common product in many industrial applications. These wastes have proven to be an extensive issue at many contaminated
sites around the world, as they are immiscible in water and can reside or travel in aquifers for very long intervals of time (Mohammad and Kibbey, 2005). Typically, many wastes are stored in underground storage containers. However, over time many of these containers can be compromised, which can lead to the leakage and transport of the waste into surrounding aquifers. Studies such as Powers et al. (1995) and Mohammad and Kibbey (2005) suggest that the transport of nonaqueous phase contaminants can be influenced by the capillary potential and wettability of the existing aquifer systems. This concern for the retention of contaminants in fractured reservoirs as well as the transport of DNAPL’s within aquifer systems addresses the need for further measurement and modeling of hydraulic properties that control fluid transport within fractured systems.

1.4.3 Geologic Waste Repositories

Considering the growing concerns for climate change and global warming, the sequestration of carbon dioxide in deep saline aquifers has been considered a viable means for controlling greenhouse gas emissions into the atmosphere (IPCC, 2005). During this process, carbon dioxide is injected into deep geological waste repositories, which typically consist of saline aquifers (porous, brine-filled geological reservoirs) that are constrained by natural barriers or low-permeability caprock seals (Ellis and Bazylak, 2013; Gaurina-Medimurec et al., 2017). Once injected, the trapping and immobilization of the CO$_2$ with minimal leakage within the reservoir is the primary goal. The primary trapping mechanisms for CO$_2$ within the reservoir are structural trapping, capillary (i.e. residual) trapping, local capillary trapping, solubility trapping, and mineral trapping. In the case for capillary trapping mechanisms, estimating the storage capacity and preventing leakage from capillary failure of CO$_2$ is done by determining the capillary pressure and subsequent change in reservoir wettability after injection (Ellis and Bazylak, 2013; Saraji et al., 2013, Wan et al., 2014; Dalton et al., 2018). In addition to leakage of CO$_2$ facilitated by capillary failure, the presence of fractures and potential migration pathways within the overlaying structural trap or “caprock” of deep geological repositories is an important factor to consider when containing the sequestered waste (Kaldi et al., 2013; Gaurina-Medimurec et al., 2017). The integrity of the caprock, as
well as the hydraulic properties of the reservoir are all key parameters required for developing accurate risk assessments of deep waste repositories (IPCC, 2005; Saraji et al., 2013).

Similar concerns for the potential transport of waste through fracture networks can be applied to the subsurface storage of nuclear waste. Instead of storing waste directly into the reservoir, isolation of nuclear waste is provided through a combination of engineered structures and natural barriers (e.g. granite bedrock, salt, or clay) (Suzuki et al., 2018; World Nuclear Association, 2018). Prominent examples of these efforts have been conducted at Yucca Mountain in Nevada, Waste Isolation Pilot Plant in New Mexico, Stripa Site in Sweden, and the Opalinus Clay in Switzerland (World Nuclear Association, 2018; WIPP, 1991; Bossart et al., 2004). Engineered containers typically consisting of steel, bentonite clay, and concrete are typically used to isolate nuclear waste within low-permeability reservoirs (Kim et al., 2011). Despite these efforts, storage containers for nuclear waste can become compromised over time. This can allow for leakage of waste into surrounding aquifers by preexisting fractures or fractures created during excavation. Given these concerns, further understanding the hydraulic properties of low-porosity rock materials and the dynamics of capillary fluid transport over fracture surfaces within them may help mitigate potential contamination of valuable water and atmospheric resources, as well as improve the criteria for selecting suitable formations for deep waste storage.

1.4.4 Wetting of Engineered Surfaces

Repeated wetting through spontaneous imbibition and hemiwicking have been shown to be the primary cause of degradation for many building materials and other engineered structures (Hanžič et al., 2003). Much research has focused on understanding the influence surface wettability has on the integrity of many building materials. Factors such as surface absorption of concretes and mortar bond strength are considered important indicators for the long-term integrity of many building materials as they are repeatedly exposed to water (Hall et al., 1989; Taha et al., 2001). In addition, some research has sought to control the phenomena of hemiwicking on engineered surfaces by altering surface geometries of nanotubes and sensors.
(Mikkelsen et al., 2011). Further investigation into the wetting potential of a variety of different rock materials may help in evaluating ideal materials for construction and improving their integrity over time.

1.5 Goals, Objectives, and Hypotheses

This study focuses on the factors controlling unsaturated flow along fracture surfaces in low-porosity rocks. There are two primary goals. 1) Develop and test a new method to facilitate direct measurements of apparent equilibrium contact angles on exposed rock fracture faces using neutron radiography. 2) Develop and test a new optical method to facilitate direct measurements of hemiwicking rates over exposed rock fracture faces. The specific objectives of this study are:

1) Contact angles
   a. Visualize and quantify the water meniscus uptake along exposed rock fracture faces using neutron radiography and high-speed optical imaging
   b. Quantify apparent equilibrium contact angle of rock fracture faces on a suite of low-porosity sedimentary and igneous rocks
   c. Compare apparent contact angle of rock fracture faces to intrinsic contact angles determined by the sessile drop method on polished surfaces of the same rock types
   d. Develop and test a theoretical model for the dynamics of menisci movement on a fracture surface and compare to existing theoretical models

2) Hemiwicking
   a. Visualize and quantify hemiwicking of water along exposed rock fracture surfaces using high speed optical imagery
   b. Estimate surface sorptivity through quantifying the rate of hemiwicking of rock fracture surface
   c. Test for statistical relationships between fracture surface sorptivity, fracture surface contact angle, and other physicochemical rock properties

The hypotheses to be tested include:
Contact angles:
1. Equilibrium apparent contact angle will differ among mineralogical compositions between sedimentary and igneous rocks
2. Contact angles estimated for fracture surfaces will be less than contact angles estimated for polished surfaces, due to surface roughness

Hemiwicking:
1. Transport of water along fracture surfaces through hemiwickiing will behave linearly with respect to the square root of time
2. Rates of hemiwickiing (i.e. sorptivity) will differ among different mineralogical compositions between sedimentary and igneous rock types
3. Rock fractures with high surface sorptivity parameters will have a strong negative correlation to contact angle measurements
Chapter 2 – Transient Analysis of Contact Angle Dynamics on Rock Fracture Faces

2.1 Introduction

The wettability of rocks and rock fracture faces plays a crucial role in understanding the transport and retention of fluids within geologic reservoirs. Wettability defines the relative adhesion of two fluids to a solid surface (Donaldson and Alam, 2008) and provides a measurement of preference for one fluid to adhere to a surface in the presence of another fluid. Surface wettability is quantitatively represented by the contact angle. The contact angle is the equilibrium angle between the solid surface, wetting fluid, and non-wetting fluid. The equilibrium contact angle \( \theta_s \) can be determined under both unsaturated conditions (e.g. water, air, and rock), or saturated conditions (e.g. oil, brine, and rock). The magnitude of \( \theta_s \) represents the mechanical equilibrium between the three previously describes phases. The equilibrium contact angle is defined by Young’s equation (Yuan and Lee, 2013):

\[
\cos(\theta_s) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]  

[2.1]

where \( \theta_s \) is the contact angle for a flat surface. \( \gamma_{LV}, \gamma_{SV}, \) and \( \gamma_{SL} \) are the interfacial tensions of the liquid-vapor, solid-vapor, and solid-liquid interfaces respectively (Figure 1a). Young’s equation represents the contact angles determined for chemically homogeneous flat surfaces and assumes there is no contact angle hysteresis. These assumptions reduce the applicability of Young’s equation to natural surfaces like rock fracture faces (Yuan and Lee, 2013). Contact angle hysteresis is typically defined as the difference between the advancing and receding contact angles observed as a wetting fluid moves across a surface (Andrieu et al., 1994; Kamusewitz et al., 1999). Hysteresis can be propelled and enhanced by common features of rock fractures such as heterogeneity in the geochemical composition of a surface, as well as different degrees of roughness of the surface (Good et al., 1993). While equilibrium contact angles have
been estimated for soil particles (Bachmann and McHale, 2009) and polished rock surfaces (Gates et al., 2018), to date similar measurements do not seem to have been run on to rough rock fracture surfaces.

Past studies have shown that contact angles defined by the Young’s equation, Equation [2.1], for natural and engineered surfaces can deviate from their flat surface counterparts due to the introduction of chemical heterogeneity and surface roughness (Hazlett, 1990, Onda et al., 1996; Montes Ruiz-Cabello et al. 2011; Kubiack et al., 2011; Rayudu and Bulut, 2014). Currently there are few methods available for measuring contact angles on non-ideal rough surfaces or rock fracture surfaces. Attempts to estimate the thermodynamic equilibrium contact angles of rough, chemically heterogeneous surfaces have traditionally employed the Wenzel (Wenzel, 1936), the Cassie (Cassie, 1948) and the Cassie-Baxter (Cassie and Baxter, 1944) models.

The Wenzel model assumes that as a wetting fluid comes into contact with a rough surface, the fluid fully penetrates and travels within the rough topographical features of the surface (Figure 1b). Prediction of the rough apparent contact angle is based on the equilibrium contact angle for a polished surface of the same material, i.e., (Wenzel, 1936):

$$\cos \theta_R = r \times \cos \theta_S$$ [2.2]

where $\theta_R$ is the apparent contact angles on a rough surface and $r$ is the roughness factor (Wenzel, 1936):

$$r = \frac{A_R}{A_S}$$ [2.3]

where $A_R$ is the projected area of the rough surface relative to the corresponding area of the smooth flat surface, $A_S$. Ramón-Torregrosa et al. (2008) pointed out the influence of image field of view on the determination of $r$, and thus on the prediction of $\theta_R$.

Unlike the Wenzel model, the Cassie model assumes there is no penetration of the fluid into the topographical features of the surface and that the liquid drop rests on
fully on top of the surface structures with the valleys filled with non-wetting fluid (Cassie, 1948; Wang et al., 2018).

\[
\cos \theta_R = f(1 + \cos \theta_S) + f - 1 \tag{2.4}
\]

where \( f \) is the fraction of the solid/liquid contact area (Figure 1c). The Cassie-Baxter model (Figure 1d) assumes that as a liquid meets a rough surface, the liquid does not fully penetrate inside the rough topographical features, but instead lies on top of the features over a small film of non-wetting fluid (Foster et al., 2012). Prediction of rough surface contact angles by the Cassie-Baxter model is achieved with the following equation (Cassie and Baxter, 1944):

\[
\cos \theta_R = r_f f(1 + \cos \theta_S) + f - 1 \tag{2.5}
\]

Where \( r_f \) is the roughness factor of the wetted surface area. It should be noted that in Equation [2.5], if \( r_f = 1 \), then the theoretical estimation for the contact angle of an unideal surface by the Cassie-Baxter equation [2.5] is identical to the contact angle estimated for an unideal surface by the Cassie model [2.4].

Figure 1 illustrates the differences between the above-mentioned models. For the present study, Wenzel roughness factors for each rock type studied were available from Gates et al. (2018). Since the roughness factor was already measured and there are no known methods to independently acquire solid/liquid contact area ratios, we utilized the Wenzel model, Equation [2.2], under the common assumption that there is complete wetting between the individual asperities of the rough fracture surface.

Theoretical models based on the Wenzel and Cassie-Baxter approach (Hazlett et al., 1990; Onda et al., 1996; Gates et al., 2018) predict that \( \theta_R \) decreases as surface roughness increases. Despite these findings, this area is in a state of contention with some researchers questioning the validity of the Wenzel model (Wolansky and Marmur, 1999; Rao et al., 2003; Gao and McCarthy, 2007). Additionally, experimental results from other studies that tested the use of progressively finer polishing grits on initially rough rock surfaces (Kittu et al., 2014; Rayudu and Bulut, 2014) indicate the opposite
trend, where by increased surface roughness shows an increase in contact angle (i.e. increased hydrophobicity).

As previously mentioned, the contact angle is primarily dependent on the level of adhesive forces between the solid surface and the wetting fluid (Esfahani and Haghighi, 2004; Donaldson and Alam, 2008). As shown in Table 1, the relationship between wettability and contact angle can range from water-wet (hydrophilic) to oil/air wet (hydrophobic) (Zolotukhin and Ursin., 2000; Iglauer et al., 2015). The magnitude of the contact angle and thus, the degree of wettability for geological materials can change depending on variations in pressure, temperature, and mineralogical composition (Ogunberu and Muhammad, 2005; Hamouda et al., 2006). Other investigations suggest that the wettability of a material may be influenced by the saturation history i.e. hysteresis (Kasiri and Bashiri, 2011). In this case, pore surfaces that have been initially in contact with oil or air may display more hydrophobic tendencies.

Determining the contact angle for different geologic materials is an essential step in multiphase flow modeling for estimating the relative permeability and capillary pressure-saturation functions of different porous media (Kasiri and Bashiri, 2011). These functions are of particular relevance to many applications like enhanced oil and gas recovery for both conventional and non-conventional reservoirs (Morrow et al., 1990; Borysenko et al., 2009), secondary recovery through waterflooding of reservoirs (Anderson, 1986), decreasing condensate blockage in wellbores (Panga et al., 2006), geological sequestration of carbon dioxide within brine saturated aquifers (Wan et al., 2014), retention of fracking fluids and other chemicals in subsurface reservoirs (Mohammad and Kibbey, 2005), and groundwater recharge through infiltration (Wallach et al., 2013).

Many methods have been used in the past to estimate the contact angle of wetting fluids on natural materials (Shang et al., 2008). The most commonly used method is the sessile drop method, where the contact angle is estimated after a liquid drop is deposited on an ideal flat surface. Some rocks, such as shales can be suitable for direct contact angle measurements through sessile drop techniques due to their ability to be fractured along distinct bedding planes (Borysenko et al., 2009). Direct contact angle measurements, using both the sessile drop and captive bubble
techniques, have also been reported for freshly exposed cleavage surfaces of Muscovite mica (e.g., Wan et al., 2014 and Mugele et al., 2015). However, this approach is dependent on the orientation of the bedding planes relative to coring. Recently, Gates et al. (2018) showed that measurement of contact angles on a variety of polished rock surfaces is achievable through sessile drop techniques. While this may be acceptable for a limited amount of geologic material, estimating the contact angle of polished surfaces is not adequate for most materials that exhibit roughness over multiple length scales such as rock fracture surfaces (Boffa et al., 1998; Babadagli and Develi, 2003). Artificially reducing the roughness of a surface through polishing raises the concern of whether or not contact angles estimated on polished rock surfaces are truly representative for natural fracture surfaces. Thus, the ability to estimate contact angles directly from rock fracture surfaces may provide more information on the influence surface roughness has on wetting potential.

Another widely used method is the Wilhelmy plate method, where an ideal flat surface is introduced into a liquid reservoir. By measuring the equilibrium height of wetting by capillary rise, it is possible to estimate the contact angle of a vertical flat surface using the following equation (Neuman and Good, 1979):

\[
sin(\theta_S) = 1 - \frac{\Delta \rho g h_E^2}{2\sigma}
\]

where \(\Delta \rho\) is the difference in density between the wetting and non-wetting fluids, \(g\) is gravitational acceleration, \(h_E\) is the maximum equilibrium wetting height measured along the plate, and \(\sigma\) is the surface tension between the wetting and non-wetting fluid pair. The assumptions associated with Equation [2.6] are the surface is infinitely wide, flat, and chemically-homogeneous. Experimental results from this approach show that surfaces that are \(\geq 2\) cm wide produce acceptable contact angle estimates (Neumann and Good, 1979), are highly reproducible, and can be easily adapted for digital image acquisition and analysis (Budziak and Neumann, 1990).

The theoretical implications of this approach have been further explored by Neumann and Good (1972) and Gaydos and Neumann (1994) to determine contact angles on chemically heterogeneous vertical surfaces. Additional studies by Cain et al.
(1983) and Kwok et al. (1995) have employed capillary rise techniques on vertical surfaces to evaluate the difference between smooth and rough surfaces for a variety of different materials. However, there is no evidence that this method has been applied to rock fracture surfaces.

Bracke et al. (1989) attempted to modify Eq. [2.6] to account for the dynamics of capillary rise of silicon oils on a vertical platinum plate. Bracke et al. (1989) assumed that at $t$ was equal to 0, and that $\theta_D$, the dynamic contact angle is $90^\circ$. Then for the expression $\theta_D = f(t)$, $\theta_D$ asymptotically approaches $\theta_S$ as described by Equation [2.6] with increasing time. In comparison, other studies have argued that the shape of the water meniscus is constant (Keller and Miksis, 1983; Clanet and Quéré 2002) during capillary rise on a vertical surface (i.e., $\theta_D = \theta_S \neq f(t)$), so that Equation [2.6] only holds at equilibrium or the maximum wetting height. From the theoretical model derived by Clanet and Quéré (2002), the equilibrium height of capillary rise, $h$, at a vertical surface is given by:

$$ h \approx \kappa \left( \frac{\sigma t^2}{\rho} \right)^{\frac{1}{3}}, \quad t < t_E \quad [2.7a] $$

$$ h = h_E, \quad t \geq t_E \quad [2.7b] $$

where $\kappa$ is a constant related to meniscus shape, $\rho$ is the density of the wetting fluid, and $t_E$ is the characteristic time for the capillary rise.

In addition to estimating contact angles of surfaces based on vertical capillary rise, other studies have shown the Wilhelmy plate method can be used to indirectly estimate contact angles of vertical flat surfaces by evaluating the force balance between both the surface and the liquid reservoir (Al-Shareef et al., 2013; Wang et al., 2017; Karim and Kavehpour, 2018).

Other approaches, such as Meiron et al. (2004) provide a method of measuring the apparent equilibrium contact angle for a liquid droplet on a rough surface. This approach is done by vibrating the surface while taking top-view images of the droplet. The circularity of the drop is monitored, and the contact angle is calculated from the droplet diameter and known volume. The vibrations induce a global energy minimum state, thereby eliminating hysteresis. Thus, the droplet assumes an axisymmetric form.
that can be analyzed. The method was successfully tested on a series of rough wax surfaces with Wenzel roughness factors ranging from 1.01 to 1.25.

In addition to determining contact angles on rough surfaces, advancements in 3D imaging technology and image analysis software have allowed researchers to directly measure contact angles within porous reservoir rocks. Andrew et al. (2014) employed x-ray microtomography to visualize and quantify contact angles in situ within a supercritical CO₂–brine–carbonate system. The measurements resulted in a distribution of contact angles ranging from 35° to 55°. This distribution was attributed to contact angle hysteresis and surface heterogeneity. Al Ratrou et al. (2017) and Scanziani et al. (2017) have recently reported advances in the algorithms used to automatically compute contact angles from the segmented x-ray tomograms. Currently, there seems to be no evidence to indicate that these approaches have been applied to rock fracture surfaces.

Many of the studies discussed above emphasize the lack of research for wetting phenomena associated with natural surfaces and more specifically, rock fracture surfaces. The objectives of this research was to visualize and quantify the dynamic behavior of the contact angle for water under unsaturated conditions on exposed fracture surfaces for a variety of different rock types. Apparent equilibrium contact angles estimated for vertically oriented fracture surfaces will then be compared to intrinsic contact angles determined by the sessile drop approach for polished surfaces of the same rock types. A theoretical model describing the dynamics of menisci movement will be applied to contact angle movement on rock fracture surfaces. The hypotheses to be tested included: 1) the equilibrium apparent contact angle will differ among the mineralogical compositions between sedimentary and igneous rocks, and 2) due to surface roughness, the equilibrium apparent contact angle of the rough fracture surfaces will be less than the intrinsic contact angles determined for polished surface counterparts.
2.2 Materials and Methods

2.2.1 Rock Cores

A selection of low-porosity rock cores was acquired through a commercial vendor, Kocurek Industries Inc. located in Caldwell, TX. The cores consist of both sedimentary and igneous rock obtained from unknown surface outcrops. The sedimentary cores include the Burlington Limestone, Crossville Sandstone, and Mancos Shale (cored both parallel and perpendicular to bedding). The igneous cores consist of a selection of granites designated Vermilion Bay Granite A (Morning Rose), Vermilion Bay Granite B (North American Pink), Sierra White Granite, and Westerly Granite. The dimensions of the cylindrical cores are a length of 5.08 cm and a diameter of 2.54 cm.

The Crossville sandstone (also known as “Crab Orchard Sandstone”) is a fine-grained, light-gray fine-to-medium grained sandstone deposited during the Pennsylvanian period within the Kentucky and Tennessee region of the United States. The Crossville sandstone commonly displays red, yellow, brown, and gray bands due to iron oxidation (Wanless, 1946). The permeability of the Crossville sandstone ranges between $3 \times 10^{-18}$ and $3 \times 10^{-17} \text{ m}^2$ (Gehne and Benson, 2017). The Burlington Limestone (also known as “Carthage Marble”) is a fine-grained light-gray crystalline limestone. Permeability of the Burlington Limestone is described by Kocurek Industries Inc. to range from $4 \times 10^{-18}$ and $7 \times 10^{-18} \text{ m}^2$.

The Mancos Shale is an interbedded shale and siltstone reservoir located in the United States throughout Colorado, New Mexico, Wyoming, and Utah. Deposited during the Late Cretaceous, the Mancos shale is a well-known unconventional reservoir and has an estimated volumetric gas reserve of 595 billion cubic meters as described by McLennan et al. (1983). Permeability of the Mancos Shale ranges from $3 \times 10^{-17}$ and $9 \times 10^{-19} \text{ m}^2$ (Mokhtari and Tutuncu, 2015). Core samples of the Mancos shale were provided with bedding planes oriented perpendicular to the coring and parallel to the coring.

Vermilion Bay Granite A and Vermilion Granite B (also known as “Morning Rose” Granite and “North American Pink” Granite, respectively) are pink to light-red alkali granites ranging from Northern Minnesota, US, to Western Ontario, Canada. The Sierra
White Granite is a granodiorite that was emplaced between the Permian and Tertiary periods (Jennings et al., 1977). The permeability of the Sierra White Granite is approximately $8 \times 10^{-19} \text{ m}^2$ (Ye and Ghassemi, 2018). The Westerly Granite is a brownish-gray to light-gray granite established in Rhode Island during the Pennsylvanian period (Quinn et al., 1971). The permeability of the Westerly Granite is approximately $6 \times 10^{-20} \text{ m}^2$ (Brace et al., 1968).

Physicochemical properties such as bulk density, solid phase density, and porosity of each respective rock cores were measured by Andrew Vial (personal communication in August, 2017) through methods presented by Donnelly et al. (2016). Core volume was computed from the dimensions of the cylindrical cores. Recently, intrinsic contact angles for deionized-water were measured by a sessile drop method on flat polished surfaces of each rock type (Gates et al., 2018). Additionally, Wenzel model-based roughness factors were estimated by Gates (2018) using a Phenom Pho X SEM (Phenom-World B.V., Eindhoven, Netherlands).

2.2.2 Core Preparation and Fracture Replication

All rock cores were oven dried at 105°C for roughly twenty-four hours to ensure each core has an initial moisture content of zero. The cores were then wrapped in Kapton® Tape and fractured through the widely used Brazilian method. The Brazilian method (Figure 2) induces a mode-1 tensile fracture to the core by applying stress between two parallel loading plates until the tensile strength of the core is exceeded, resulting in a brittle fracture (Hathaway et al, 2009; Li et al., 2013, Cheng et al., 2015). Typically, fracture surfaces for geologic material are produced under laboratory conditions and are used as a proxy for in situ fracture geometries (Vogler et al. 2017; Faoro et al. 2012; Li et al. 2013). Fracturing of the rock cores was done manually using a Model M Carver Laboratory Press with a 25 Ton Hydraulic Unit (Model No. 3925). Once fractured the Kapton® Tape was removed from the cores and the two halves were split apart along the fracture plane. This provided us with two exposed fracture surfaces for testing per rock core. In between testing, the fractured core halves were kept in climate-sealed containers to minimize any changes in moisture content over time.
2.2.3 Dynamic Neutron Radiography

The wetting height of a water meniscus on the fracture surface was obtained in a cross sectional view as a function of time for each rock-type using neutron radiography. Neutron radiography provides a unique way to quantitatively delineate the wetting height for different rock types through high-resolution image sequences at rapid frame rates. Neutron radiography has been utilized in the past for visualizing fluid transport within a variety of different porous geologic material and concrete (Hanžič et al. 2003, Kanematsu et al., 2009; Hall et al., 2013; Kang et al., 2013; Perfect et al., 2014).

Neutron imaging was conducted at the Neutron Imaging Facility (beam line CG-1D, HFIR) at Oak Ridge National Laboratory (ORNL). Data were collected during July 2018. The beam line used a sCMOS detector, which has a spatial resolution of 100 µm and field of view of 66 x 56 mm². Pixel size measured during testing was 20 µm. The detector was set at a constant frame rate of 33 frames per second during data collection.

For the imaging, the oven-dried core halves were placed individually in front of the neutron detector with their exposed fracture surfaces aligned parallel to the neutron beam-line (Figure 3). Relative to a perpendicular orientation, this alignment produced a sufficiently thick layer of water that could be measured by the neutron detector. The cores were imaged through time while the base was brought into contact with a liquid reservoir filled with deionized water. Once contact is made the resulting wetting of the liquid meniscus along the fracture surface was visualized and recorded as a series of time-stamped grayscale images. Cores that presented sufficient image quality and a distinct water meniscus were then used for wetting height determination.

Image stacks for each rock core were analyzed to delineate the change in wetting height of the meniscus with respect to time. Images were first normalized through ImageJ (Schneider, 2012) to more clearly visualize the extent of wetting of the meniscus along the fracture surface (Figure 4). The normalization of the image divides the pixel values of each image in the stack by a selected image before contact was made between the base of the core and the water reservoir.

Pixel gray-scale values were then averaged over a transect that was applied over a portion of the meniscus in contact with the exposed fracture surface. Average
gray-scale values for each pixel length were determined in each transect. Change point analysis was then employed to determine the wetting height of the meniscus along the fracture surface through time for each normalized image (Figure 5). Change point analysis is a tool developed in R that can identify when a series of observations experience a significant shift in statistical properties (Eckley et al., 2011). Change point analysis has been previously utilized in climatology and finances (Beaulieu et al., 2012; Reeves et al., 2007; Erdman and Emerson, 2008; Zeileis et al., 2010). Recently, Brabazon et al. (2018) utilized change point analysis to measure rates of spontaneous imbibition in enclosed fractured cores. This approach was adopted by applying a single change point model to each image series transect in the image series to determine the exact point where the average gray-scale pixel values experience significant shifts in both the mean and variance (Brabazon et al., 2018). The resulting changepoint determined for each time-stamped image provides an approach to automatically measure the distance the meniscus has traveled up along the exposed fracture surface of the rock core through time. The pixel length of the wetting height was then converted to millimeters by initially measuring the pixel length an object of known dimension through the neutron beamline, in this case, a metal cylinder with a diameter of 38.08 millimeters, which produced a pixel size of 20 μm.

### 2.2.4 Contact Angle Estimation

Due to the rapid nature of spontaneous imbibition of water along the fracture surfaces relative to the frame rate inherent to the sCMOS detector, roughly ten counts of dynamic wetting height could be measured before equilibrium height is reached for each core. Apparent contact angles for the rough surfaces (θ<sub>R</sub>), were then estimated from the equilibrium wetting heights extracted from each core via the change point analysis. This was accomplished by utilizing Equations [2.6] and [2.7] where contact angles can be estimated based on the maximum wetting height of liquid by capillarity on a vertically flat plate. In this case, we substitute <i>h<sub>E</sub></i> with our own equilibrium wetting height, while θ<sub>S</sub>, Δρ, g, and σ are known constants. A segmented non-linear regression model was developed in SAS based on Equations [2.7a] and [2.7b] to test whether the dynamics of the wetting height observed on the fracture surface followed the predictions.
from Clanet and Quéré (2002). Figure 6 shows the typical fit of the model for a Crossville Sandstone sample. Further statistical analyses conducted on the contact angle estimates are described in the section below.

2.2.5 **Statistical Analyses**

An analysis of variance or “ANOVA” was performed on the estimated apparent contact angles of the fracture surfaces (θᵣ) to statistically evaluate the influence of rock type. Additionally, a Tukey Honestly Significance Difference (HSD) test was added to the ANOVA for pairwise comparisons of mean contact angle values between all rock types. A statistical relationship between θᵣ and the measured sessile drop contact angle of polished rock surfaces (θₐ) (Gates et al. 2018) was evaluated through linear regression. It should be noted that θₐ was not measured for the Mancos Shale cores with parallel bedding due to the inability to obtain finely polished surfaces with these samples. As a result, only shale cores with perpendicular bedding planes were used in the linear regression analysis. Statistical significance was assessed at the p < 0.05 level. The statistical analyses were performed through a combination of the R software environment (R Core Team, 2016) and SAS (SAS Institute Inc., 2012).

2.3 **Results**

Of the fifty-two cores used in this study, twenty-four cores were used for time-series analysis. Rock cores that lacked measurable menisci rise were excluded from time series analysis. A segmented non-linear regression model based on the model by Clanet and Quéré (2002) resulted in twenty-two of the twenty-four cores having a coefficient of determination that was greater than 0.90. The resulting equilibrium wetting heights and the time taken to reach equilibrium for the water menisci along the fracture surfaces are given in Table 3. Minimum and maximum equilibrium wetting heights along the fracture surfaces were 0.6 mm and 2.44 mm respectively. The minimum and maximum equilibrium time for each fracture surface is 0.165 seconds and 0.990 seconds respectively.
The distributions of $\theta_R$ among different rock types are shown in Figure 7. The residuals of the contact angle were tested for normality. The Shapiro-Wilk test had a p-value of 0.3754, which indicated that the null hypothesis that contact angles were normally distributed could not be rejected. The analysis of variance performed on the contact angles indicated significant differences among the different rock types tested (at $p < 0.05$). Among all the different rock types, the mean contact angle ranged from 42.34° to 71.58° degrees (Table 4). Contact angles for the Burlington Limestone were unable to be estimated due to no measurable rise of the meniscus along the fracture surface. Statistical comparisons through the Tukey HSD test indicate three distinct groups with statistically different mean contact angles among the rock types (Table 4).

A comparative analysis was also conducted between the apparent contact angle of the rough fracture faces ($\theta_R$) and the sessile drop measured intrinsic contact angles of polished surfaces ($\theta_A$). Linear regression conducted on $\theta_R$ and $\theta_A$ indicated a positive relationship that was not statistically significant (at $p < 0.05$) (Figure 8). Comparisons of the standard errors between $\theta_R$ and $\theta_A$ show a larger standard deviation observed over rough rock fracture faces ($\theta_R$). Linear regression conducted on $\theta_R$ and the Wenzel Roughness factor of each rock type indicate a positive relationship that is also not statistically significant (at $p < 0.05$) (Figure 9).

2.4 Discussion and Conclusions

From Table 3, the sandstone and shale rocks generally had higher equilibrium wetting heights than the granites. Wetting heights of the sandstone and shale rocks ranged from 1.48 mm to 2.44 mm. After fitting the segmented model based on equations [2.6] and [2.7], we showed that almost all the cores listed in Table 3 produced a coefficient of determination that is above 0.90. This implies that the dynamic rise of the water meniscus along the fracture surface before it reaches equilibrium tends to follow a $t^{2/3}$ behavior, thus, supporting the conclusions established by the Clanet and Quéré (2002) model.

As can be seen in Table 4 and Figure 7, the sedimentary rocks generally produced lower contact angles, with arithmetic means ranging from 42.34 to 71.58
degrees. Among the sedimentary rocks, the Mancos shale with perpendicular bedding yielded the lowest contact angle, followed by the Mancos shale with parallel bedding, and the Crab Orchard sandstone, with arithmetic means of 42.34, 46.93, and 49.01 degrees, respectively. The low contact angles estimated from these rocks imply that the fracture surfaces of the sedimentary cores tend to possess higher surface wettability, are more hydrophilic, and had a greater extent of wetting along the vertical fracture surfaces. In comparison, the igneous rock samples produced relatively high contact angles ranging from 64.32 to 71.58 degrees. The Sierra White granite produced the highest average contact angle, followed by the Westerly granite, and finally the Vermilion Bay Granite, with arithmetic means of 71.58, 65.28, and 64.32 degrees respectively. The high contact angles associated with the fracture surfaces of the igneous cores indicate low surface wettability, more hydrophobicity, and a much lower extent of wetting along the vertical fracture surface. It should be noted that the most hydrophobic rock was the Burlington Limestone. Contact angles for the Burlington Limestone were not able to be estimated due to no measurable rise of the water meniscus along the fracture surfaces in the neutron radiographs.

Based on the contact angle as described by the Young’s Equation [1], the primary reason for the difference in contact angles among the different rock types is largely attributed to variations in mineralogical composition and or the roughness of the surface. Variations in a rock’s primary mineralogical composition may alter the interfacial potential between the water reservoir and the rock core. In this case, sand and silt grains derived from quartz may have a greater adhesive potential to water than the feldspar dominated crystals of the granite cores, which causes the difference in contact angle.

Figure 8 shows the linear regression performed between $\theta_R$ and $\theta_A$. The p-value concludes that the regression between the two variables is not statistically significant. Despite this shortcoming, the general positive trend observed between $\theta_R$ and $\theta_A$ implies that the difference in the underlying adhesion forces that drive the value of the contact angle between the different rock types are still present. From Figure 8 we see an overprediction in the contact angle for the rough fracture surface ($\theta_R$) compared to the contact angle associated with the polished rock surfaces ($\theta_A$). This leads us to
believe the rough features of the fracture surfaces decreases the overall wetting capabilities of the different rock types. This is at odds with the theoretical predictions of the Wenzel and Cassie-Baxter models, which predict a decrease in the equilibrium contact angle (i.e. increasing hydrophilicity) when the roughness of the surface increases. Additionally, comparison between the standardized errors of $\theta_R$ and $\theta_A$ in Figure 8 show the same magnitude for the two methods. From Figure 9 we see a positive trend between $\theta_R$ and the Wenzel Roughness Factor of each rock type. Although this relationship was not statistically significant, the positive trend observed between surface roughness and the contact angle imply that the contact angle increases with increasing roughness. However, the results shown in Figures 8 and 9 may also imply that the introduction of roughness may confound the forces of adhesion that drive the wetting fluid up along these geological surfaces. Furthermore, increasing the sample size and rock type diversity in future investigations may reveal whether these relationships are truly non-significant.

As previously discussed in the introduction to this chapter, the effect of introducing roughness to a surface on the contact angle is still in contention. The Wenzel based model established in Wenzel (1936) shows that applying a roughness factor to contact angles on a polished surface leads to a reduction in contact angle prediction. In contrast, studies like Kittu et al. (2014) and Rayudu and Bulut (2014) present experimental data that shows the opposite case, where comparing an initially rough surface to progressively smoother variants showed an increase in wetting capability. The results of this study side with the argument where an increase in surface roughness reduces the wetting capability (increased hydrophobicity) of the fracture surface.

Based on the results of this study, it seems that the wetting capabilities of rock fracture surfaces are largely influenced by the mineralogical composition of the rocks, with only a partial influence being attributed to the surface roughness. For the Modified Wilhelmy Plate method used in this study, further testing using polished core surface may provide better comparative analysis of contact angles relative to the sessile drop technique conducted by Gates et al., (2018). Additionally, two different approaches were utilized for estimating contact angles from both studies. In Gates et al. (2018)
contact angles of polished surfaces were directly measured, while contact angles of rough rock fracture surfaces were estimated using a theoretical approach, Equation [2.5], in this study. Further investigations into these phenomena should include a greater number and diversity of rock types to ensure more statistical evaluations. Finally, enhancing the spatial resolution capabilities of the neutron detection system would benefit this approach by ensuring a more accurate imaging data set on which to apply the change point analysis.
3.1 Introduction & Literature Review

Hemiwicking is a capillary-driven flow process, where wetting fluids (e.g., water, brine) displace preexisting non-wetting fluids (e.g., air, oil, or natural gas) in channels on rough hydrophilic surfaces (Bico et al., 2001; Quéré, 2008). The term hemiwicking is largely associated with various branches of material sciences or engineering, with common applications concerned with nanofabrication of hydrophobic surfaces (Mikkelsen et al., 2011) and thin layer chromatography (Spangenberg et al., 2011). Previous investigations have produced many analytical and numerical approaches to model hemiwicking over rough surfaces. Invariably, these approaches are concerned with artificial materials, such as nano-engineered textured surfaces (Ishino et al., 2007; Xiao and Wang, 2011; Mai et al., 2012; Lai et al., 2013; Kim et al., 2016), acid-etched intermetallic substrates (Liu et al., 2011), hierarchical Zinc Oxide based nano-structures (Wang et al., 2016), carbon nanotubes on zircaloy (Ahn et al., 2012), laser-etched or abraded metals and glass (Vorobyev and Guo, 2009, 2010; Tokunaga et al., 2000), and even human skin (Dussaud et al., 2003). Many of the materials tested have homogeneous chemical compositions and known geometries to their surfaces (i.e. ideal surfaces). In comparison, many natural surfaces, such as fractures in geologic material are considered unideal surfaces. Such surfaces display bulk chemical heterogeneities and surface roughness over multiple scales, which can greatly influence fluid transport.

Hemiwicking can be viewed as an extension of spontaneous imbibition (SI), although no definitive theoretical relationship has been established. Spontaneous imbibition is the process of absorption of a fluid into a porous media or fracture system without being driven by a pressure gradient (Morrow and Mason, 2001; Schmid et al., 2012). Spontaneous imbibition is a phenomenon widely studied in both geosciences and petroleum engineering and is an important factor to consider in many practical applications like enhanced oil and gas recovery estimates for conventional and unconventional reservoirs (Rangel-German and Kovscek, 2002), retention of fracturing fluid in unconventional reservoirs (Ghanbari et al., 2016; Dehganpour et al., 2013), and
evaluating the quality of underground waste reservoirs (Gaurina-Medimurec et al., 2017). As spontaneous imbibition occurs within rock fracture systems, roughness elements or surface asperities can lead to the uptake of fluids through hemiwicking. This process of capillary driven transport has the potential to cause films of fluid to propagate over fracture surfaces at a much quicker rate than within the main fluid reservoir (Bico et al., 2002). It should be noted that throughout this process, capillary forces act as the driving force for the invasion of a fluid into a porous medium while the viscous forces of the fluid resist. Given this relationship, investigating the process of hemiwicking on fracture surfaces of low-porosity rocks can provide us with greater insight into the capillary forces inherent in fracture networks within geological materials relative to the overall matrix.

The phenomenon of hemiwicking of water and other wetting fluids on rock fracture surfaces most likely occurs in nature above the water table, in the variably-saturated or vadose zone. Within the vadose zone, fractures drain more readily than the surrounding matrix. As a result, there are frequently many air-filled fractures whose rough surfaces can facilitate the transport of water by hemiwicking when a free water source is introduced (e.g. precipitation, a rise in the water table, or from anthropogenic leaks and spills). Thus, hemiwicking contributes to hydrologic fluxes within the vadose zone, as well as the transport and dispersion of dissolved chemicals and colloids. Furthermore, from a civil engineering perspective, the hemiwicking of water on rock fracture surfaces likely contributes to weathering-induced damage of building materials, foundations, road cuts, and tunnels (Hanžič et al., 2003; Hall et al., 1989; Hall and Hoff, 2007; Taha et al., 2001).

Theoretical models for hemiwicking over rough surfaces can be broadly divided between two approaches based on different spatial scales (i.e. Channel-scale and Darcy-scale). Channel-scale models (Hay and Dragila, 2008; Hay et al. 2008) model flow between individual surface asperities, which consist of evenly-spaced cylindrical posts superimposed on a flat surface. In order to model fluid transport through individual surface asperities, these approaches include explicit descriptions of the geometric characteristics of a surface for which the flow is occurring over. The models proposed by Hay and Dragila (2008) and Hay et al. (2008) describe flow over these rough surfaces by combining the Navier-Stokes equation for viscous fluids, the Young-Laplace equation for
capillary pressure, and detailed descriptions of the surface geometry. This approach predicts the dynamics of wetting height based on the contact angle and spacing between the rough cylindrical structures on the surface. Other channel-scale models include those developed by Bico et al. (2001), Mai et al. (2012), Wang et al. (2016), and Kim et al. (2016) based on slightly different geometric shapes for the surfaces asperities.

Darcy-scale models, such as Tokunaga et al. (2000), evaluate transient film flow of rough surfaces over multiple asperities. This is done by combining steady-state flux and mass balance continuity equations based on the assumption of a step function approximation for the wetting profile. Despite the differences in the two approaches, one common conclusion among these studies is that the wetting front advances linearly with respect to the square root of time. Additionally, it is observed that the rate of wetting along the surface is much higher than within the matrix.

During the process of spontaneous imbibition, a wetting fluid enters a porous medium through capillary action (Morrow and Mason, 2001; Schmid et al., 2012). The rate of infiltration can be characterized by the proportionality constant (known as the sorptivity) between wetting height and the square root of time. This common linear relationship established between the wetting height and the square root of time is synonymous to the Lucas-Washburn law (Lucas, 1918; Washburn 1921). Sorptivity is a measurement that defines the capacity or potential of a porous medium to absorb or desorb a liquid through capillarity (Philip, 1957).

Although many investigations of wetting phenomena have been conducted on a variety of different surfaces, almost no attempts have been made at quantifying the sorptivity of fracture surfaces on geologic materials. Recently, Brabazon et al. (2019) investigated rates of spontaneous imbibition in enclosed fractures of rock cores through neutron radiography. In this study, the main objective was to visualize the capillary rise of water on exposed rock fracture surfaces due to hemiwickling. The surface sorptivity was quantified between the central tendency of the wetting height and the square root of time. Linear regression analysis was then used to determine any significant statistical relationships between fracture surface sorptivity, the apparent fracture surface contact angle, the intrinsic contact angle for a polished surface, and the surface roughness. The hypotheses tested included: 1) transport of water along the fracture surfaces through
hemiwicking will behave linearly with respect to the square root of time, 2) the rate of hemiwicking (i.e. sorptivity) will differ among the different rocks types due to bulk mineralogical compositions, and 3) rock fracture surfaces with high surface sorptivity values will have a strong negative relationship to contact angle estimates.

3.1.1 Theory

For a vertically oriented flat surface, the equilibrium height of capillary rise, \( h_E \), is described by (Neumann and Good, 1979):

\[
h_E = \sqrt{\frac{2\sigma(1-\sin(\theta_S))}{\Delta \rho g}} \quad [3.1]
\]

where \( \theta_S \) is the equilibrium contact angle for a flat plate, \( \Delta \rho \) is the difference in density between the wetting and non-wetting fluids, \( g \) is gravitational acceleration, and \( \sigma \) is the surface tension between the wetting and non-wetting fluids. As previously described in Chapter 2, the contact angle estimated for rough surfaces is altered according to the Wenzel (1936) equation:

\[
\cos \theta_R = r \times \cos \theta_S \quad [3.2]
\]

where \( \theta_R \) is the theoretical apparent contact angle of the fluid pair for a rough surface, and \( r \) is the Wenzel roughness factor which is defined as (Wenzel, 1936):

\[
r = \frac{A_R}{A_S} \quad [3.3]
\]

where \( A_R \) = the projected area of the rough surface relative to the corresponding area of the smooth flat surface, \( A_S \). Rearranging Equation [3.2] and substituting into Equation [3.1] results in the following expression for a meniscus contacting a rough surface:

\[
(h_E)_R = \sqrt{\frac{2\sigma(1-\sqrt{1-\left(\frac{\cos(\theta_S)}{r^2}\right)}}{\Delta \rho g}} \quad [3.4]
\]
where \((h_E)_R\) is the equilibrium height of rise on the rough surface. Thus, the distance traveled by the wetting front, due to hemiwicking, \(z\), is defined as:

\[
z = h_T - (h_E)_R
\]  

[3.5]

where \(h_T\) is the total height of the wetting front. Since rough surfaces produce variations in the height of the wetting front (Cain et al., 1983; Kwok et al. 1995), we evaluate the height of the wetting front along the spatial extent of the rock fracture face. Thus, we rewrite Equation [3.5] as:

\[
\langle z \rangle = \langle h_T \rangle - \langle (h_E)_R \rangle
\]  

[3.6]

where the angle brackets signify a measure of the central tendency. The time required for the meniscus to reach equilibrium, \(t_E\), is assumed to be negligibly short compared to the time scale, \(t\), of the hemiwicking process, i.e.

\[
t = t_T - t_E \approx t_T
\]  

[3.7]

where \(t_T\) is the total time elapsed since the wetting fluid contacted the rough surface. As described above, Darcy-scale and channel-scale models (Hay and Dragila, 2008; and Hay et al., 2008; Tokunaga et al., 2000) predict a square root of time dependency per the Lucas-Washburn law for the macroscopic distance travelled by the wetting front. The resulting proportionality constant, for which we here coin the term the surface sorptivity, \(S_S\), provides an integrated measure of the impact of the roughness elements on surficial capillary action. Based on Equations [3.6], [3.7], and the models reviewed previously, we write the following general expression for the early-time dynamics of hemiwicking:

\[
\langle z \rangle = S_S \sqrt{t}
\]  

[3.8]
al., 2017). For many engineering applications, the joint roughness coefficient (JRC) is widely used to characterize rock fracture surface roughness (Odling, 1994). Barton (1973) developed 10 typical profiles exhibiting different degrees of roughness and assigned JRC values ranging from 2 to 20 to describe them. These standard profiles were later adopted by the International Society for Rock Mechanics and Rock Engineering (ISRM, 1978; Develi and Babadagli, 1998). While the JRC is a convenient parameter for practical engineering applications, its application is limited to one-dimensional profiles (Develi and Babadagli, 1998).

The Wenzel roughness factor, $r$, as defined by Eq. [3.3], is a 2-dimensional parameter suitable for characterizing the roughness of rock fracture surfaces. For investigating hemiwickung, the Wenzel roughness factor is particularly applicable to the quantification of roughness since it can be related to the equilibrium contact angle of a wetting fluid on an ideal surface through the well-established Wenzel (1936) model, Equation [3.2]. Currently, however, $r$ has not been widely used to characterize rock fracture surfaces. Bizjak (2010) employed this parameter to quantify the roughness of ten tuff samples using the Advanced Topometric Sensor (ATOS I) system. This system combines photogrammetry and fringe projection and can yield high density three-dimensional point clouds for images of surfaces. The resulting values of $r$ ranged from 1.02, for a plane joint, up to 1.38 for a very rough surface. More recently, Gates (2018) found that $r$ provided excellent discrimination between the roughness of fracture surfaces artificially induced in a range of sedimentary and igneous rock types.

Most experimental studies of hemiwickung have employed optical methods to identify the height of wetting with respect to time. This is done by measuring the visually-observable contrast between the wet and dry areas of a rough surface since rough surfaces appear darker when wet. This is a result of the rough surface reflecting less light when wet (Twomey et al., 1986; Lekner and Dorf, 1988; Mall and da Vitoria Lobo, 1995). For this approach, the rough surface is positioned to directly face the viewer. Early studies such as Tokunaga et al. (2000) measured the maximum, average, and minimum heights of the wetting front by hand with a ruler. Tokunaga et al. (2000) and Ketterson (1995) used film-based photography to capture a series of images at different time intervals. Following the introduction of digital imaging technology, high speed
cameras have become the ubiquitous approach for capturing time series of digital images in order to show the dynamic movement of wetting fronts. Budziak and Neumann (1990) introduced this technique for contact angle measurement. However, while their system provided excellent spatial resolution for accurate measurement of the equilibrium height of wetting, it was not able to capture the dynamics of the capillary rise process. Modern digital camera systems are now routinely employed to measure the dynamics of hemiwicking, with typical frame rates ranging from 5 to 500 fps (e.g., Vorobyev and Guo, 2009, 201; Mai et al., 2012; Wang et al., 2016; Kim et al., 2016). The digital image stack that is acquired can be readily analyzed to extract the mean height of wetting versus time using standard image processing software combined with change point detection analysis (Brabazon et al., 2019).

Since rock fracture surfaces display many microtopographic channels over multiple scales, they should be good candidates for studying the phenomenon of hemiwicking. However, to this day only a handful of studies have investigated hemiwicking on rock fracture surfaces. Tokunaga et al., 2000 measured water spreading on glass casts of rock fracture surfaces, while Cheng et al. (2015) presented a photograph (see their Fig. 6) showing the greater extent of wetting on a rock fracture surface, due to hemiwicking, as compared to spontaneous imbibition within the porous matrix. However, only Tokunaga and Wan (2001) have previously quantified the dynamics of liquid spreading on actual rock fracture surfaces. These authors measured spontaneous imbibition of water on natural fracture surfaces of welded tuff and rhyolite samples. They showed that the wetting front advanced linearly with the square root of time, and that the slope of this relationship (i.e. surface sorptivity) was much higher for the fracture zone than for the matrix. However, none of these studies related the degree of hemiwicking to any independently-measured surface roughness parameters.

As discussed above, previous theoretical models suggest that the median height of wetting will scale linearly with respect to the square root of time (i.e. Lucas Washburn law). The main objective of this research is to visualize and quantify the dynamics of hemiwicking of water along exposed fracture surfaces for a selection of sedimentary and igneous rocks. An optical high-speed camera was used to determine median wetting height and the interquartile range (IQR) of the wetting front as functions of time.
Fracture surface sorptivity was quantified based on the slope of the median wetting height and the square root of time and tested for linear behavior. We also investigated the time dependency of the IQR. Statistical relationships were examined between the extent of hemiwicking and physicochemical properties of the fracture faces, such as equilibrium contact angle and surface roughness.

3.2 Materials and Methods

Prior to imaging, all rock cores were oven dried at 105°C for approximately twenty-four hours to ensure each core had an initial moisture content of zero. The cores were then wrapped in Kapton® Tape and fractured through the widely used Brazilian method. The Brazilian method (Figure 2a) induces a mode-1 tensile fracture through the core by applying stress between two parallel loading plates until the tensile strength of the core is exceeded, resulting in a brittle fracture (Hathaway et al., 2009; Li et al., 2013, Cheng et al., 2015). Typically, fracture surfaces for geologic material are produced under laboratory conditions and are used as a proxy for in situ fracture geometries (Vogler et al. 2017; Faoro et al. 2012; Li et al. 2013). Fracturing of the rock cores was done manually using a Model M Carver Laboratory Press with a 25 Ton Hydraulic Unit (Model No. 3925). Once fractured the Kapton® Tape was removed from the core and it was separated into two halves along the fracture plane. The two separate samples were then used as replicates with exposed fracture faces (Figure 2b). A list of the different rock types used in this study is given in Table 2. In this study, core samples with highly brittle and flaky edges were excluded from testing to minimize any edge effects on the rate of wetting along the fracture surfaces.

An optical system was developed to observe the uptake of water along the exposed fracture face (Figure 10). The optical system consists of a Basler Ace acA1920-155um high speed camera. Images produced by the camera had a measured pixel size of approximately 15.5 µm length. The camera was positioned to look through a MDA4 Spectrum Illumination Diffused Axial light source to ensure even lighting throughout the fracture surface. In this system we introduced a water reservoir to the base of a suspended rock core using an adjustable height platform. Just before initial contact has been made between the base of the core and the water reservoir the high-
speed camera is used to acquire high resolution, time-stamped 2D grayscale images to observe the uptake of the wetting front along the fracture surface (Figure 11). The camera was run at a constant frame rate of 10 frames per second. Total recording time for each core was approximately 10 seconds, which began just before contact was made between the base of the core and the water reservoir. As the water travels along the rock fracture surface, the optical and chromatic change in surface color is recorded. The images are first normalized in ImageJ (Schneider, 2012) to more easily distinguish the transition between the wet and dry phases of the fracture surface (Figure 12). The normalization of the image divides the pixel values of each image in the stack by a selected image before contact was made between the base of the core and the water reservoir. Conversion of image pixels to millimeters was achieved by measuring the dimensions of the core through ImageJ (Schneider, 2012) and assuming the diameter of the cores to be exactly 25.4 mm as indicated by the commercial vendor. The image stacks were then cropped to remove any interference caused by the water meniscus and isolate the zone where hemiwicking occurs (Figure 12). Determining the maximum wetting height of the water meniscus on the core was done by measuring the maximum height along each edge of the core. The average between the two heights was used as the starting point for measuring wetting height of capillary hemiwicking along the fracture surface (Figure 12). Finally, the images were converted to a sequence of matrices for every time stamp recorded. The matrices consist of the normalized pixel values for every point in the image for each time stamp.

Change point (CP) analysis (Eckley et al., 2011) is applied to the pixel value matrices of each matrix in order to determine the wetting height along the entire wetting front of the rock core. Change point is a tool developed in R that can identify when a sequence of observations experiences an abrupt shift in its statistical properties. A single change point model was applied to detect statistical shifts in both the mean and variance of the gray-scale pixel values in every pixel column of each image acquired from the optical system. Recently, Brabazon et al. (2019) utilized CP analysis to extract wetting height of water imbibition in enclosed rock fractures. A similar approach was adopted and utilized for this project to apply change point analysis along the entire wetting interface of the exposed fracture surfaces. The resulting change point profile for
each image in the time series provides us with a mathematical representation of the
distance the water has traveled over the entire width of the exposed fracture face
(Figure 13). From the change point profiles, basic summary statistics, such as median
wetting height and the interquartile range (IQR) were extracted for further statistical
analysis. A description of the statistical analyses employed in this study is given below.

3.3 Statistical Analyses

Distributions of the wetting heights extracted by the CP analysis are not normally
distributed and required nonparametric statistical analysis. For nonparametric analyses
we extracted the median wetting height for each CP profile time stamp. As mentioned
above, studies of hemiwicking over a variety of surface asperities (Hay et al., 2008 and
Tokunaga et al., 2000) share a common conclusion that the wetting height behaves
linearly to the square root of time. For this study we tested the hypothesis that the
median height of wetting across the fracture surface follows the linear trend described
by the well-established Lucas-Washburn law.

A square root transformation was applied to the time scale for each image stack
collected. Next, a series of linear regressions was performed on the median wetting
height and square root of time between each rock sample tested. The intercept of the
linear regression was set at zero to establish a point of reference for where the change
in wetting height begins with respect to time. Statistical testing of the residuals was also
conducted to test for autocorrelation, homoscedasticity, and normality. Once completed
we extracted the proportionality constant or slope of the regression equation to
determine the surface sorptivity of each fracture face. An analysis of variance (ANOVA)
and a Tukey Honestly Significance Difference (HSD) test were conducted on the
surface sorptivity parameter to see if there were any significant differences in the
wetting capabilities of the different rock types. Correlation analysis was then performed
between the surface sorptivities, and the equilibrium contact angles and Wenzel
roughness factors for the different rock fracture faces.

In addition to analyzing the central tendency of hemiwicking along the fracture
surface, we also investigated the IQR for any time dependencies. The IQR was
employed as a measure of wetting front width, with larger values indicative of fingering.
The IQR’s determined for each rock type were not normally distributed. Therefore, a log transformation was applied to the IQR to normalize the data. An analysis of variance (ANOVA) was conducted on the log-transformed values to evaluate if there were any significant contributions of rock type and/or time effects to changes in the IQR. Additionally, we tested if there was any significant interaction between rock type and time. After the log transformation was applied to the IQR, the residuals were tested for normality, where we were unable to reject the null hypothesis. Finally, the ANOVA was expanded by adding a statistical comparison of means test, the Tukey (HSD) test, for the log-transformed IQR with respect to both rock type and time.

3.4 Results and Discussion

Surface sorptivity parameters were quantified from the slopes of the regression lines fitted to the median wetting height versus the square root of time data acquired from the optical imaging measurements. Although the regressions produced from this study were all statistically significant, one underlying issue was the presence of trends within the residuals. Typically, trends within residuals indicate underlying issues or the need for improvement with modeling procedures. Average trends in the residuals are presented in Figure 14. It can be clearly seen that both over prediction and under prediction occurred along the timescale of analysis. An important observation made in Figure 14 is that the trends of the residuals are not consistent among all the rock types tested in this study. So, overall the model fitted the data reasonably well, without any systematic deviations when consider over all the rock types.

Statistical analysis on the pooled individual residuals was also performed to test for homoscedasticity, autocorrelation, and normality. A statistical specification with a p-value of less than 0.05 determined that the residuals were overall heteroscedastic. A Durbin-Watson test with a p-value less than 0.05 indicated that the residuals from the regressions showed positive autocorrelation. Finally, a Kolmogorov-Smirnov test for normality indicated that the residuals were not normally distributed. These results indicate that the residuals lack some of the key statistical modeling requirements and that further improvements to the model should be explored and implemented.
Sorptivity values for each rock tested and their corresponding coefficient of determination for the regressions are given in Table 5. The distributions and average sorptivity values divided up between each rock type are shown in Figure 15. Average sorptivity values and Tukey grouping are listed in Table 6. From the distributions of surface sorptivity we see two general groups, with the sedimentary rocks (sandstone & shales) possessing relatively high surface sorptivity values averaging between 1.08 mm·sec$^{-0.5}$ to 1.37 mm·sec$^{-0.5}$. In contrast, we see the selection of igneous rocks (granites) have lower average surface sorptivity values between 0.39 mm·sec$^{-0.5}$ to 0.80 mm·sec$^{-0.5}$. Surface sorptivity of the Burlington Limestone was unable to be estimated due to no measurable capillary rise of water on the fracture surface.

The ANOVA indicated significant differences (at p < 0.05) in the average sorptivity values between the different rock types. From the Tukey HSD test in Figure 15 we see a significant statistical difference between the Mancos Shales with parallel bedding and the Vermilion Bay Granite B. The rest of the rock types share the statistical grouping B; however, we see that each of the remaining sedimentary and igneous rock types are statistically similar to either the Mancos Shale parallel bedding or Vermilion Bay Granite B, which are the maximum and minimum respectively.

In addition to comparing the surface sorptivity among different rock types, linear regression analyses were applied between surface sorptivity and both the equilibrium contact angles collected on polished samples of the same rock types (data from Gates et al. 2018) and the contact angles estimated from the rough fracture surfaces of this research. As previously discussed, the contact angle is the angle between the liquid-gas-solid interface along a surface and provides us with an estimate of surface wettability. Surface wettability represents the ease to which and adhesive bond can be formed between a solid surface and a wetting fluid. From Figure 16 we see a statistically significant regression between surface sorptivity and the equilibrium contact angle of the polished rock surfaces. This negative relationship implies that hydrophilic surfaces with a higher surface wettability (lower contact angle) produce faster rates of wetting by hemiwick over the fracture surface. In the absence of surface roughness it is likely being driven by differences in mineralogical composition among the different rock types. A linear regression between surface sorptivity and apparent contact angles
of rough fractured surfaces was also conducted and produced a relationship that was not statistically significant (at p < 0.05). This result was surprising, as it is assumed that the hemiwicking of fluid is driven by rough asperities along a surface. In this case it seems the introduction of roughness to the different rock surfaces is masking the surface wettability of the surface as shown by the pronounced linear trend in Figure 16. This speculation is furthered by a statistically non-significant negative relationship between the fracture surface sorptivity and $\theta_R$ (Figure 17).

Finally, regression analysis was also performed between surface sorptivity and Wenzel based roughness factors that were measured for the same rock types used in this study from Gates et al. 2018. In Figure 18 we see a negative relationship between surface sorptivity and the Wenzel-based roughness factor that is not statistically significant (at p < 0.05). This result contradicts our initial views, where we expected to see higher surface sorptivity values for rock types that displayed higher degrees of surface roughness. Instead it appears that differences in wettability due to differences in mineralogical composition may play a dominant role.

It should be noted that the rise of wetting along many of these fracture surfaces (particularly the granites) was susceptible to preferential flow paths or fingering movement as hemiwicking occurs. The presence of preferential flow paths can dramatically enhance the rate of wetting along specific portions of the fracture surface (Figure 19), which as a result may increase the average sorptivity estimates of less hydrophilic rocks (granites). The cause of this preferential flow, whether it be the presence of microfractures beneath the fracture surface, the presence of certain topographical features, or other factors that may aid in this process are currently unknown and warrants further research.

In an effort to quantify the width of the wetting front observed on the rock fracture surfaces, we investigated the difference between the upper 75th and lower 25th percentile values in wetting height (i.e., the IQR) for any rock type and/or time dependency. An ANOVA determined a significant contribution (at p < 0.05) was given to the log of the IQR independently by both rock type and time, while no significant interaction effect between rock type and time was found. From the box plots in Figure 20 we see significant differences in the average values of the log of the IQR among the
different rock types tested in the study. The sedimentary rocks (sandstone and shales) show smaller average values of the log IQR, while the igneous rocks (granites) show consistently larger average values of the log IQR. These results imply that the igneous rocks exhibited wider wetting fronts, likely due to preferential flow behavior or fingered transport along their fracture surfaces.

In addition to rock type, the ANOVA indicated significant differences in the log of the IQR with respect to the time scale associated with the images acquired by the optical system. From the boxplots in Figure 21 we see higher average values for the log of the IQR at late times as compared to early times. This trend shows that as a wetting fluid proceeds along the fracture surface there is an overall increase in the IQR of the wetting front with elapsed time. This implies that the more time the hemiwicking process has to proceed, the more susceptible the transport is to preferential flow or fingered transport, i.e. the greater the spread of high and low values of wetting around the median value over time.

3.5 Conclusions

This study evaluated the time evolution of a wetting fluid interface along exposed rock fracture surfaces. Regression analysis between the median wetting height and the square root of time showed a linear relationship that is consistent with the Lucas-Washburn law. Surface sorptivity for the highly hydrophobic Burlington Limestone was not able to be estimated since there was no measurable capillary rise of the water meniscus along the fracture surfaces. Mean surface sorptivity values for the other rock types ranged from $0.386 \text{ mm} \cdot \text{sec}^{-0.5}$ to $1.38 \text{ mm} \cdot \text{sec}^{-0.5}$ (Table 1), with statistical differences being established by the Tukey HSD test (Figure 15). The magnitudes of these values for natural rough surfaces are comparable to rates of capillary wetting observed previously on the rough surfaces of various engineered materials (Tokunaga et al., 2000; Liu et al., 2011; Ahn et al., 2016; Kim et al., 2016; Wang et al., 2016).

A significant negative relationship was observed between surface sorptivity and equilibrium contact angle for a smooth surface (Figure 16). This relationship means that as the water is transported more readily along the fracture surfaces that possess higher degrees of surface wettability (water-wet rock types). In contrast, a negative relationship
observed between surface sorptivity and contact angles estimated for the rough fracture surfaces was non-significant. Finally, a non-significant negative relationship was observed between surface sorptivity and the Wenzel roughness factor for each rock type. Overall, these results imply that the rate of hemiwicking is less dependent on the degree of surface roughness, and more largely attributed to variations in mineralogical composition, and the influence on the potential adhesive bonds between a wetting fluid and rock fracture surfaces (i.e. surface wettability) described by the equilibrium contact angle for a polished surface. This conclusion is consistent with the results shown in Figure 7 and Table 3, where higher surface sorptivity values are paired with the sedimentary rocks, which display lower contact angles as compared to the igneous rocks.

One challenge of this investigation is the clear presence of trends within the residuals of the linear regression models. The trends in the residuals were not consistent among all the rock types tested (Figure 14). Further testing showed that a collection of all the residuals displayed positive autocorrelation, heteroscedasticity, and a non-normal distribution. These shortcomings suggest that the regression model associated with the central tendency of wetting versus the square root of time is not fully acceptable from a purely statistical point of view but remains a reliable method for evaluating surface wetting potential and predicting early-time hemiwicking on rock fracture faces.

Further studies adopting these methods may benefit by developing a more reliable means to reduce reflective interference in the optical setup, and by establishing a more accurate point of transition between hemiwicking and transport of the main liquid body as it contacts the fracture surface (i.e. the water meniscus). Although the relationship between roughness and surface sorptivity was found to be insignificant, additional research in evaluating roughness of rock fracture surfaces on a variety of scales may be of benefit. As discussed in Morgan et al. (2013) and Vogler et al. (2017), fracture formation mechanisms influence roughness differently at small scales than they do at larger scales. This is thought to be the result of intragranular dominated fractures being produced from laboratory induced fractures. Thus, future studies may produce more statistically significant relationships between fracture surface roughness and
fracture surface sorptivity over a series of larger scales. Additionally, further investigations would benefit from a greater sampling size of diverse rock types for a more extensive statistical analysis of surface sorptivity and physicochemical properties of rocks.

For the analysis of the upper and lower wetting boundaries, results of the Tukey HSD test indicate statistical differences in the log of the IQR among different rock types. The larger range of IQR observed for the granite cores in Figure 20 suggests that the igneous rocks are typically more susceptible to preferential flow behavior, while the sedimentary rocks seem to display more uniformed transport across the fracture surface. Despite these results, it should be reiterated that the primary cause of this behavior over the rock fracture surfaces is currently unknown.

The results of the Tukey HSD test with respect to time (Figure 21) indicate that regardless of the rock type, the IQR of wetting tends to increase over time. This behavior implies that as time increases, fluid transport by hemiwickling tends to naturally gravitate towards greater spreading of the wetting front and more preferential flow patterns. Gruener et al. (2009) observed a time-dependent widening of the wetting front within nanoporous Vycor glass. Finally, it should be noted that our results are based on an early time transient analysis, with testing intervals of approximately ten seconds and have yet to be validated over larger time scales.
Chapter 4 - Conclusions and Suggestions for Future Research

4.1 Conclusions

The overall goal of this study was to investigate the dynamics of fluid transport along rock fracture surfaces and the interconnections this process shares with similar phenomena in material sciences. Here we developed two different methodologies to measure and model fracture surface contact angle and fracture surface sorptivity. Cores from eight rock types were analyzed: Crossville Sandstone, Mancos Shale (with bedding planes both perpendicular and parallel to coring), Burlington Limestone, Vermilion Bay Granites (A and B variants), Sierra White Granite, and Westerly Granite. Cores were fractured using a hydraulic press following the Brazilian method. Each rock core half had a length of approximately 5.08 cm and a diameter of 2.54 cm. These rocks were chosen as examples of low-porosity rock types that traditionally serve as barriers within geological settings. Additionally, these rocks types are similar to those commonly used in a variety of different industrial applications such as enhanced oil and gas recovery, hydraulic fracturing of unconventional reservoirs, subterranean waste storage, and aquifer integrity. Thus, furthering our understanding of the hydraulic properties inherent to fracture surfaces within these different rock types can have many benefits.

The first method employed in this study allowed us to evaluate the wettability of rock fracture surfaces based on the contact angle. Contact angles of water along rough rock fracture surfaces were visualized and calculated on a total of 55 rock cores. Data representing the dynamic movement of the water meniscus on the fracture surface was acquired through neutron radiography, which produced neutron radiographs that allowed us to quantitatively measure and model maximum wetting heights. A theoretical model representing the change in wetting height of the water meniscus was modified from Clanet and Quéré (2002) and applied to the data for each rock type. The model was validated on 24 of the rock cores (Table 4). Contact angle estimations were produced through a modification of Neuman and Good’s (1979) model for estimating contact angles on a vertically flat surface. Contact angles ranged from 42.34 to 71.58 degrees (Table 3). In general, sedimentary rocks (sandstone and shale) tended to have
lower contact angles (i.e. high wettability) as a result of greater maximum wetting heights. In contrast, the igneous rocks all produced relatively high contact angles (i.e. low wettability) and displayed low maximum wetting heights. Over prediction of contact angles for rough fracture surfaces was observed when compared to contact angles measured on polished surfaces of the same rock types using the sessile drop method. This implies that the wetting capabilities of rock surfaces decreased when different degrees of roughness are introduced to the surface, or that the two methods inherently produce different results.

The second method employed in this study allowed us to evaluate the sorptivity of rock fracture surfaces through the rate of hemiwicking. Surface sorptivity of rock fracture surfaces was determined on a total of 90 rock cores. Data representing the rate of wetting was acquired through an optical system, which produced gray scale images that allowed us to quantify wetting height with respect to time along the entire length of the fracture surface. A linear relationship was observed between the median wetting height and the square root of time, indicating that the behavior of wetting on rock fracture surfaces is consistent with behavior observed on other rough engineered surfaces (i.e. Lucas-Washburn Law). Surface sorptivity is represented by the proportionality constant between wetting height and square root of time in each linear regression. Surface sorptivity values ranged from 0.35 to 1.33 mm·sec$^{-0.5}$.

Sedimentary rocks (sandstone and shale) produce higher surface sorptivity estimates, while the igneous rocks (granites) produced comparatively lower surface sorptivity estimates. A statistically significant negative relationship was found between surface sorptivity and intrinsic contact angles of polished rock surfaces (Figure 16). This indicates that a fracture surface with a low contact angle (high surface wettability) tends to display higher rates of surface wetting through capillary action or hemiwicking. A non-significant relationship was found between surface sorptivity and the rough surface contact angles measured from the modified Wilhelmy Plate method. From this, it seems the roughness of the fracture surface masks the underlying adhesion force between the surface and the fluid. In addition, a statistically non-significant relationship was observed between surface sorptivity and the Wenzel Roughness Factor (Figure 18). These results imply that, while roughness is a requirement for hemiwicking, the differences in rate of
hemiwicking along a fracture are not primarily driven by the degree of topographical roughness, but is largely influenced by mineralogical composition, which in turn controls the adhesion force between the surface and the liquid reservoir.

Analysis of the interquartile range (IQR) of the wetting front was performed in an effort to quantify the occurrence of preferential flow paths observed over some of the rock fracture surfaces. Analysis of variance for the IQR of wetting height along the fracture surface revealed a significant dependence on both rock type and time independently with no significant interaction effect. In general, the IQR produced by each igneous rock (granite) was greater in magnitude than the IQR produced from each sedimentary rock (sandstone and shale). These results lead us to believe that the fracture surfaces of the granite cores are more susceptible to preferential flow than the sandstone and shale cores. However, whether or not this behavior is primarily influenced by variations in chemical composition or the presence of microfractures is currently unknown. Finally, the IQR was shown to increase with respect to time regardless of rock type, implying that as time progresses, transport of water along fracture surfaces via capillary action naturally gravitates towards a widening of the wetting front. A similar observation was made by Gruener et al. (2009) with respect to anomalous widening of the wetting front in nanoporous Vycor glass.

4.2 Suggestions for Future Research

This study provided measurements of both rough fracture surface contact angles and capillary wicking rates along rough fractured surfaces for low-porosity rocks under unsaturated conditions. Further investigation of the dynamic hydraulic properties of rock fracture surfaces should begin by expanding on fracture sample size. This can be done by analyzing the hydraulic properties of fractures along larger cores. For this study, each core used had relatively small dimensions, with a diameter of 25.4 mm and a length of 50.8 mm. As suggested in Morgan et al. (2013) and Vogler et al. (2017), degrees of roughness on rock fracture surfaces at larger scales tend to be smoother, while roughness measured on small scale cores tends to be greater. This is thought to be the result of an increase in intragranular cracks along the zone of high tensile stress. This results in fracture geometries that do not follow typical grain boundaries observed
in rocks under in situ conditions. Thus, performing the Brazilian method on cores with greater dimensions may result in inducing fracture surfaces that are more representative or comparable to natural fracture systems observed in geologic material. In addition, increasing the area of the fracture surface may benefit both methods by reducing any edge effects and undesired influences caused by rock flaking or microfractures present around the edges of the core. Future work on fracture surface wettability may also seek to investigate the change in contact angle in relation to variations in temperature and pressure. All of the measurements conducted in this study, as well as a majority of other research determine contact angles at atmospheric conditions, which may not be representative of those under in-situ conditions for geologic reservoirs.

Contact angles of rough rock fracture surfaces were estimated with data acquired through neutron radiography. One limiting factor in the neutron radiography system was the resolution of the neutron detector. The neutron detector used in this study yielded a 100 μm or 0.1 mm resolution. The pixel size was determined to be 0.02 mm at the time of data collection. Given that the maximum extent of the water meniscus observed along the rock fracture faces is roughly 2 mm in height, enhancing the spatial resolution capabilities of the detector during neutron radiography may reduce noise shown in the neutron radiographs and provide more accurate datasets to perform change point analysis on. However, increasing the spatial resolution may result in the necessity of decreasing the temporal resolution. This is an undesirable option considering the rapid nature of the movement of the water meniscus on the fracture surface once the reservoir contacts the base of the core. Finally, most of the data in this investigation were acquired within relatively short time scales. Future work investigating the wetting properties of natural fracture surfaces should implement larger time series for data collection to ensure the conclusions made in this study are consistent throughout greater time scales.

Contact angles were estimated using an approach by Neumann and Good (1979), which predicts the contact angle based on the maximum wetting height for a vertically flat plate. Future theoretical models for predicting contact angles on rough fracture surfaces will have to undergo additional modifications to implement both
roughness and chemical heterogeneity to ensure greater accuracy. Furthermore, future comparative analysis between contact angles for rough fracture surfaces and contact angles for polished rock surfaces should be conducted using the same capillary rise technique. In this study, data for estimating contact angles for rough fracture surfaces was acquired through a Wilhelmy Plate approach, while contact angles estimated from polished rocks were acquired from a sessile drop technique. Future data collection using a Wilhelmy plate approach should also include measurements of polished rock cores to ensure a more accurate comparison.

Wetting rates along rock fracture surfaces due to capillary action were measured and modeled using data acquired through an optical approach. One limitation facing this approach is the need to reduce unwanted reflection of light along the curvature of the water meniscus as it imbibes up the fracture surface. Reflectance of light along the water meniscus was most notable in rock types with a darker colored matrix (e.g. shales). Future studies utilizing optical systems may reduce noise by better control of ambient lighting conditions to prevent the reflection of light back into the camera or through minor adjustments in image normalization during data acquisition. Improvements to this aspect of the study may enable an additional means for estimating contact angles of rock fracture surfaces by visualizing the water meniscus from a parallel perspective.

Previous studies that modeled hemiwicking over rough surfaces indicate a linear relationship between wetting height and the square root of time. Linear regressions between median wetting height and the square root of time were evaluated and yielded linear trends sufficient enough for the scope of this study. However, trends observed within the residuals of the regressions indicate further improvements must be made in order to be statistically acceptable. Future studies seeking to develop more validated statistical analysis should also look to establish a more reliable or accurate means to determine the transition between the cessation of the water meniscus movement and the start to capillary hemiwicking transport along the fracture surface. As depicted in Figure 12, the maximum extent of the water meniscus along the core was estimated by hand and averaged between both edges of the core. This point marked the starting point of hemiwicking for which wetting height measurements were taken from. The
ability to accurately determine the exact point to which hemiwicking begins along rough fracture faces may provide data sets that may better follow the square root of time relationships discussed above. Several of the statistical relationships presented in this research were based on mean values, and as a result included only a limited number of data points (i.e., n = 5). Because of this it was difficult to establish any significant relationships between the physical and hydraulic properties of each rock type used in this study. Future studies should investigate a wider range of rock types, as well as a greater number of replicates, to facilitate the establishment of relationships that are more statistically significant.
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Appendix
Appendix 1 - Tables
Table 1: Classifications of rock wettability based on contact angle (Zolotukhin and Ursin, 2000).

<table>
<thead>
<tr>
<th>Wettability State</th>
<th>Contact angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete wetting</td>
<td>0</td>
</tr>
<tr>
<td>Water-wet</td>
<td>0 - 70</td>
</tr>
<tr>
<td>Neutral wet</td>
<td>70 - 110</td>
</tr>
<tr>
<td>Non-wetting to water</td>
<td>110 - 180</td>
</tr>
<tr>
<td>Complete non-wetting to water</td>
<td>180</td>
</tr>
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</table>
Table 2: Physical rock properties of the sample rock types used in this study. Mean of measured values and standard errors are shown. Abbreviations of rock types are listed below rock name. Note only physical properties of Mancos Shale with perpendicular bedding were measured.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Bulk Density (g cm⁻³)†</th>
<th>Solid Phase Density (g cm⁻³) †</th>
<th>Porosity (%)†</th>
<th>θₛ - Equilibrium Contact Angle (°)‡</th>
<th>Wenzel Roughness Factor‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crossville Sandstone</td>
<td>2.50 ± &lt;0.01</td>
<td>2.65 ± &lt;0.01</td>
<td>5.85 ± 0.27</td>
<td>42.6 ± 4.3</td>
<td>1.62 ± 0.09</td>
</tr>
<tr>
<td>(CS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mancos Shale</td>
<td>2.50 ± &lt;0.01</td>
<td>2.64 ± &lt;0.01</td>
<td>5.59 ± 0.39</td>
<td>38.4 ± 4.9</td>
<td>1.76 ± 0.09</td>
</tr>
<tr>
<td>(MS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burlington Limestone</td>
<td>2.66 ± &lt;0.01</td>
<td>2.70 ± &lt;0.01</td>
<td>1.77 ± 0.09</td>
<td>76.4 ± 3.3</td>
<td>1.63 ± 0.09</td>
</tr>
<tr>
<td>(BL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vermilion Bay Granite A (VBA)</td>
<td>2.61 ± &lt;0.01</td>
<td>2.63 ± &lt;0.01</td>
<td>0.69 ± 0.15</td>
<td>58.8 ± 4.1</td>
<td>1.88 ± 0.11</td>
</tr>
<tr>
<td>Vermilion Bay Granite B (VBB)</td>
<td>2.61 ± &lt;0.01</td>
<td>2.70 ± &lt;0.01</td>
<td>0.81 ± 0.10</td>
<td>55.9 ± 2.9</td>
<td>1.82 ± 0.16</td>
</tr>
<tr>
<td>Sierra White Granite</td>
<td>2.63 ± &lt;0.01</td>
<td>2.67 ± &lt;0.01</td>
<td>1.49 ± 0.13</td>
<td>46.2 ± 2.6</td>
<td>1.84 ± 0.13</td>
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<tr>
<td>(SW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Westerly Granite</td>
<td>2.63 ± &lt;0.01</td>
<td>2.63 ± &lt;0.01</td>
<td>0.89 ± 0.10</td>
<td>52.5 ± 2.1</td>
<td>1.70 ± 0.16</td>
</tr>
<tr>
<td>(WG)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

† Values measured using the method of Donnelly et al. (2016) by Andrew Vial
‡ Values reported in previous study by Gates (2018)
Table 3: Equilibrium time and height listed for each rock core used in this study. Corresponding apparent contact angle of fracture surfaces is shown based on equation by Neuman and Good (1979). Goodness of fit is shown by coefficient of determination. Apparent contact angle estimated from equilibrium height using Eq. \[3.1\]. CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), VBA – Vermilion Bay Granite A (Morning Rose), SW – Sierra White Granite, WG – Westerly Granite.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Replicate</th>
<th>Equilibrium Time (sec)</th>
<th>Equilibrium Height (mm)</th>
<th>R²</th>
<th>Apparent Contact Angle of Fracture Surface (°)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.64</td>
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<tr>
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</tr>
<tr>
<td>CS</td>
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</tr>
<tr>
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<tr>
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Table 4: Mean apparent contact angle and standard error between each rock type. Tukey groupings and number of cores tested are included.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Mean Apparent Contact Angle of Fracture Surfaces (°)</th>
<th>Tukey Grouping</th>
<th>Number of Cores</th>
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<tbody>
<tr>
<td>Crossville Sandstone</td>
<td>49.01 ± 2.9</td>
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<td>Mancos Shale (perpendicular)</td>
<td>42.34 ± 2.1</td>
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<td>Mancos Shale (parallel)</td>
<td>46.93 ± 3.9</td>
<td>AB</td>
<td>5</td>
</tr>
<tr>
<td>Vermilion Bay Granite A</td>
<td>64.32 ± 4.9</td>
<td>BC</td>
<td>4</td>
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<tr>
<td>Sierra White</td>
<td>71.58 ± 2.3</td>
<td>C</td>
<td>4</td>
</tr>
<tr>
<td>Westerly Granite</td>
<td>65.28 ± 1.5</td>
<td>C</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 5: Surface sorptivity listed for each rock core used in this study. Goodness of fit for linear regression is shown by coefficient of determination. CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), VBA – Vermilion Bay Granite A (Morning Rose), VBB – Vermilion Bay Granite B (North American Pink), SW – Sierra White Granite, WG – Westerly Granite.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Replicate</th>
<th>Surface Sorptivity (mm sec$^{-0.5}$)</th>
<th>$R^2$</th>
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<tbody>
<tr>
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<tr>
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Table 5 Continued

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Replicate</th>
<th>Surface Sorptivity (mm sec$^{-0.5}$)</th>
<th>$R^2$</th>
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<tbody>
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<td>0.796</td>
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<td>0.747</td>
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Table 6: Mean surface sorptivity and standard error between each rock type. Tukey groupings and number of cores tested are included.

<table>
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<tr>
<th>Rock Type</th>
<th>Mean Surface Sorptivity (mm sec(^{-0.5}))</th>
<th>Tukey Grouping</th>
<th>Number of Fracture Faces</th>
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<tr>
<td>Mancos Shale (parallel)</td>
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<td>1.046 ± 0.12</td>
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<tr>
<td>Vermilion Bay Granite A</td>
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<tr>
<td>Vermilion Bay Granite B</td>
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<td>Sierra White</td>
<td>0.789 ± 0.10</td>
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<tr>
<td>Westerly Granite</td>
<td>0.616 ± 0.16</td>
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Appendix 2 - Figures
Figure 1: (a) Schematic diagram of Young’s model, Eq. [1.1]. (b) Schematic diagram of Wenzel model Eq. [1.2]. (c) Schematic diagram of Cassie model Eq. [1.4]. (d) Schematic diagram of Cassie-Baxter model Eq. [1.5]. (Wang et al., 2018)
Figure 2: (a) Rock core placed between flat horizontal plates of hydraulic press. Rock cores were compressed to induce Mode I fractures into the cores (Brazilian Method). (b) Individual rock fracture replicates were separated after being fractured and tested.
Figure 3: Neutron radiography imaging set-up with the SCMOS detector at Oak Ridge National Laboratory. The base of the half rock core is brought in contact with a water reservoir (aluminum container) in front of the beam-line while the detector images as neutrons are attenuated by the water.
Figure 4: (A) Neutron radiograph produced by the SCMOS detector of a Crossville Sandstone sample. The fracture face of the core is oriented parallel to the beam line. Note the water reservoir and water meniscus (black) along the fracture surface. (B) Normalized image of water meniscus along fracture surface of Crossville Sandstone Image normalization was performed by dividing pixel values of the image stack by the frame where initial contact is made between the base of the core and the water reservoir.
Figure 5: (A) Normalized neutron radiograph with an applied transect (red). Pixel values of each row are averaged out and used for changepoint analysis. (B) Plot showing average normalized pixel values (x-axis) versus vertical height of fracture in pixels (y-axis). Change point analysis applied to plot indicates point of change (blue dashed line). The green lines represent the mean pixel values between water meniscus (low pixel values) and dry fracture surface (high pixel values).
Figure 6: Typical fit of the segmented non-linear regression model to Eq. [2.7] for Crossville sandstone. The coefficient of determination $R^2$ is shown for each rock type in Table 3. x-axis represents the square root of time and y-axis represents the wetting height in mm.
Figure 7: Boxplots of estimated rough contact angle for each rock type with Tukey letter groupings shown. Y-axis is apparent contact angle for rough fracture surface (degrees). The arithmetic average of each distribution is shown as a maroon diamond. Hinges of boxplot represent the 25th and 75th percentiles of the distribution. Rock types that share the same Tukey letter are not significantly different from one another. CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), VBA – Vermilion Bay Granite A (Morning Rose), SW – Sierra White Granite, WG – Westerly Granite.
Figure 8: Linear regression relationship between average sessile drop contact angle values for polished rock surfaces (x-axis) and average contact angle values of rough fracture surface for each rock type. Sessile drop contact angles were measured by Gates (2018). 1:1 line (black) shown for comparison. CS – Crossville Sandstone, MSB – Mancos Shale (parallel bedding), VBA – Vermilion Bay Granite A (Morning Rose), SW – Sierra White Granite, WG – Westerly Granite. NS indicates not statistically significant (at p < 0.05).
Figure 9: Linear regression relationship between rough contact angles ($\theta_R$) and Wenzel Roughness Factor for all rock types. Coefficient of determination ($R^2$) is included. Wenzel Roughness measurements were measured by Gates et al. (2018). Wenzel roughness error bars were not included to improve clarity but are shown in Table 4. NS indicates not statistically significant (at p < 0.05).
Figure 10: Optical imaging system. A water reservoir (plastic container) is brought into contact with the base of the suspended half rock core. At the same time the high-speed camera records the water uptake along the fracture face from a perpendicular viewpoint.
Figure 11: Standard 2D grayscale image of Crossville Sandstone acquired from the optical system. Dark pixels represent wetted phase of core fracture face.
Figure 12: Normalized image of Crossville Sandstone created from grayscale image stack acquired from optical system. Image normalization was performed by dividing pixel values of the image stack by the frame where initial contact is made between the base of the core and the water reservoir. Dark pixels represent wetted phase of core fracture face. Note the zone below the dashed line, which represents the water meniscus rise along the core. The dashed line marks the zero point where hemiwicking wetting height begins and wetting height is measured.
Figure 13: Change point profile of Crossville Sandstone generated from change point analysis applied to each pixel column. A profile is generated for every frame collected from each rock type tested. Summary statistics extracted from each time stamped profile include median pixel height, upper 75th percentile, and lower 25th percentile.
Figure 14: Line diagram showing average trends of residuals for each rock type throughout the time series. Lines determined through geom_smooth function of ggplot2 in R (Wickham et al. 2016). CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), SW – Sierra White Granite, VBA – Vermilion Bay Granite A (Morning Rose), VBB – Vermilion Bay Granite B (North American Pink), WG – Westerly Granite.
Figure 15: Boxplots of surface sorptivity for each rock type with Tukey letter groupings shown. Y-axis is surface sorptivity in \( \text{mm} \cdot \text{sec}^{-0.5} \). X-axis are each rock typed tested in this study. The median value of each distribution is shown as a black bold horizontal line. The arithmetic average of each distribution is shown as a maroon diamond. Hinges of boxplot represent the 25\(^{th}\) and 75\(^{th}\) percentiles of the distribution. Rock types that share the same Tukey letter are not significantly different from one another. CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), VBA – Vermilion Bay Granite A (Morning Rose), VBB – Vermilion Bay Granite B (North American Pink), SW – Sierra White Granite, WG – Westerly Granite.
Figure 16: Linear regression relationship between measured surface sorptivity values and sessile drop contact angles for polished surfaces ($\theta_A$) of all rock types. Statistical p value ($p$) and coefficient of determination ($R^2$) are included. Contact angle measurements were measured by Gates et al. (2018).
Figure 17: Linear regression relationship between measured surface sorptivity values and rough surface contact angles for fractured surfaces ($\theta_r$) of all rock types. Statistical p value ($p$) and coefficient of determination ($R^2$) are included. NS indicates not statistically significant (at $p < 0.05$).
Figure 18: Linear regression relationship between measured surface sorptivity values and Wenzel Roughness Factor for all rock types. Statistical p value (p) and coefficient of determination ($R^2$) are included. Wenzel Roughness measurements were measured by Gates et al. (2018). Wenzel roughness error bars were not included to improve clarity but are shown in Table 6. NS indicates not statistically significant (at p < 0.05).
Figure 19: Normalized image of Westerly Granite created from grayscale image stack acquired from optical system. Image used to display preferential flow patterns on the right half of the fracture face.
Figure 20: Boxplots of IQR for each rock type with Tukey letter groupings shown. Y-axis is the log of the IQR (mm). X-axis are each rock typed tested in this study. The median value of each distribution is shown as a black bold horizontal line. The arithmetic average of each distribution is shown as a maroon diamond. Hinges of the colored boxplots represent the 25th and 75th percentiles of the distributions. Rock types with the same Tukey letter grouping do not show a significant statistical difference from each other. CS – Crossville Sandstone, MSA – Mancos Shale (perpendicular bedding), MSB – Mancos Shale (parallel bedding), SW – Sierra White Granite, VBA – Vermilion Bay Granite A (Morning Rose), VBB – Vermilion Bay Granite B (North American Pink), WG – Westerly Granite.
Figure 21: Boxplots of IQR with respect to recording time intervals. Y-axis is the log of the IQR (mm). X-axis is time segmented into one second intervals. The median value of each distribution is shown as a black bold horizontal line. The arithmetic average of each distribution is shown as a maroon diamond. Hinges of the colored boxplots represent the 25th and 75th percentiles of the distributions. Time intervals with the same Tukey letter grouping do not show a significant statistical difference from each other.
Vita

Bohdan (Dan) Horodecky was born in Los Angeles, California to Vanessa and Bob Horodecky; he has a younger sister, Kalyna. Dan attended high school at Klein Oak in Spring, TX graduating in 2011. Dan then attended the University of Texas at Austin where he graduated with his B.S. in Geology in Spring 2016. From Spring 2016 to Fall 2017, Dan worked as a staff geologist for an environmental consulting firm located in San Antonio, TX. In the Fall of 2017 Dan entered the graduate program in the Department of Earth and Planetary Sciences at the University of Tennessee in Knoxville, Tennessee. Dan graduated with a Master of Science Degree in Geology in Spring 2019.