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Doctor of Philosophy

In

The Gordon A. and Mary Cain Department of Chemical Engineering

By
Pradeep Bhattad
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ABSTRACT

Imbibition in porous media is governed by the complex interplay between viscous and capillary forces, pore structure and fluid properties. Understanding and predicting imbibition is important in many natural and engineered applications; it affects the efficiency of oil production operations, the moisture and contaminant transport in soil science, and the formation of defects in certain types of composite materials. Majority of the studies published on the transient imbibition behavior in a porous medium were conducted in the simplified 2D transparent micromodels or the 2D projection visualization (X-ray or visible light) of the 3D porous medium. However, the pore level transient imbibition studies have not been reported on real three dimensional porous medium. The main challenge arises from the slowness of the present 3D imaging techniques in comparison with the speed of the pore filling events.

To overcome these difficulties, we have developed a novel experimental technique using UV-induced polymerization, which allows the fluid phase distributions to be frozen in place during transient imbibition. Pore-scale structure of the front can then be examined in the 3D microscopic details using the X-ray Computed micro-Tomography (XCT). We have also developed a suite of advanced image segmentation programs to segment the grayscale XCT data. Image-based physically representative pore network generation techniques were unitized to quantify the geometry and topology of pore, wetting and nonwetting phase structure. Using UV initiated polymerization technique and image-based quantitative analysis tools; we have studied the effects of capillary number, pore structure and surface roughness on the structure of the transient imbibition front.
CHAPTER 1 INTRODUCTION

Imbibition is the process by which the wetting fluid displaces the nonwetting fluid from a porous medium. Understanding and predicting imbibition is important in many natural and engineered applications; it affects the ability of dry soils to take up water during rainfall or flooding (Crestana et al. 1985), the efficiency of oil production operations (Dullien 1979, 1998), and the formation of defects in reinforced polymer composite materials (Ruiz et al. 2006; Simacek and Advani 2007).

Imbibition is relatively well understood mechanistically. Experimental studies have uncovered fundamental phenomenological behavior, such as the role of the pore geometry in dictating the non-equilibrium dynamics during pore-filling events (Lenormand and Zarcone 1984; Lenormand 1986), the role of roughness and wetting films for providing wetting phase connectivity (Lenormand and Zarcone 1984), the role of bypassing and snap-off in trapping nonwetting phase (Rose and Witherspoon 1956; Chatzis and Dullien 1983), and the significant hysteresis between primary and secondary imbibition due to conductivity in wetting films (Haines 1930; Morrow 1975). Most of these and other conclusions have come from three classes of experiments:

1. Equilibrium tomography experiments (Al-Raoush and Willson 2005; Seright et al. 2006): X-ray Computed micro-Tomography (XCT) can provide quantitative information about pore-scale structure (including phase distributions at the pore scale). However, because tomography scans are slow compared to the time-scales for most imbibition processes, the results from these experiments only provide details on the equilibrium conditions, not the pore-level displacement dynamics.

2. Micromodel experiments (Wardlaw 1980; Chatzis et al. 1983; Lenormand and Zarcone 1984;
Lenormand and Zarcone 1985; Lenormand 1990): These experiments allow one to observe pore-scale dynamics. However, micro-models provide a simplistic view of the pore structure, both because of their pore-scale geometry and because they are two-dimensional. 2D versus 3D effects are less important for certain phenomena such as solute dispersion or viscous fingering. However, the differences can be significant for immiscible fluid behavior because 2D geometries do not allow for the existence of bi-continuous phase, except in a simple parallel topology.

3. Projection visualizations (Baldwin et al. 1996; Akin and Kovscek 1999; Chen et al. 2003) (x-ray or visible light): Here, visible light or X-rays are projected from the side of a column during imbibition. These experiments allow one to observe the dynamic behavior of the imbibition front (i.e., fraction of pore space invaded with respect to time), but only in an average sense over cross section through which the light passes through, and the pore level details of the pore filling cannot be inferred from these experiments.

To our knowledge, there have been no studies that have been able to quantitatively capture the 3D pore-level transient imbibition front. The approach that will be used here is to combine a novel technique that can freeze a multiphase interface and then image that interface using high-resolution XCT.

The noninvasive and nondestructive nature of XCT, the high spatial and energy (synchrotron X-ray source) resolution, and increased availability of XCT imaging facilities have made this a primary 3D imaging technique to study natural and artificial porous media and the fluids present within the pore space. However, XCT imaging of the transient displacement events (in multiphase flow) in a real 3D porous medium is difficult due to the slow acquisition of the X-ray projections compared to the velocities of pore filling events. For example, a pore level imbibition
event may take place within the order of 1-100 seconds, while the acquisition time for a 3D data
using XCT is of the order of 5-30 minutes, depending on system configuration and settings. Moreover, any movements or shifting within the system (e.g., fluid-fluid interface in motion within the pore space) during acquisition results in blurring in the reconstructed images and a degradation of the details. 2D glass micro-model experiments, on the other hand, provide visual details of transient imbibition and can be easily visualized; however, they do not capture the 3D complexity of the pore space in real porous media, nor the bi-continuous phase distribution in an immiscible displacement.

1.1 Objective

Understanding the structure of the transient imbibition front and the influence of the pore structure and flow parameters (e.g., capillary number, wettability, viscosity etc.) on the pore-level displacement events is important in order to model imbibition phenomenon accurately. In current pore scale computational models for imbibition, the physics of the film flow ahead of the bulk front and its effects on the displacement dynamics are either not incorporated or are based on simplified rule-based models derived from simplified 2D micro-model experiments, which do not capture the underlying physics of imbibition processes that occur in a natural 3D porous medium.

In order to study pore-level imbibition in a real 3D porous medium, we describe a novel experimental technique that allows the fluid phase distributions to be frozen in place during primary imbibition, such that the 3D XCT imaging is possible. We use UV-induced polymerizable liquid as the wetting phase, which upon exposure to UV light, quickly (i.e., at time scales smaller than those of the pore filling events) undergoes a phase change from liquid to solid phase. The pore-scale structure of the front can then be imaged in 3D using XCT and then
analyzed using advanced image-based characterization tools. The experimental techniques used to study the transient imbibition are described in Chapter 3. Questions answered using this novel experimental technique are:

- During primary imbibition, are wetting films able to advance ahead of the bulk imbibition front; and if so, what factors most strongly influence this effect?
- What is the pore-scale structure of wetting phase that has advanced ahead of the bulk imbibition front?
- Does wetting phase, advanced ahead of the bulk front, play a similar role as the residual wetting phase already present in the pore space, during secondary imbibition?
- Is trapping of the nonwetting phase during primary imbibition associated more with pore-scale snap-off events (e.g., where wetting films have advanced) or by the bypassing of pores by the bulk imbibition front?

1.2 Dissertation Outline

An outline of research work carried out is shown in Figure 2-1. The dissertation is divided into seven independent chapters and each chapter focuses on the important aspect of this research. The novel experimental technique to arrest the progress of wetting front using UV initiated polymerization, experimental setup and 3D imaging of the transient imbibition experiments are covered in Chapter 3. Chapter 4 & 5 describe the image segmentation and pore structure characterization techniques respectively. Analysis of the transient wetting front and the effect of capillary number and pore structure are given in Chapter 6. The final chapter discusses the overall conclusion and proposes ideas for the future research.
Introduction and research objectives (Chapter 1)

Background (Chapter 2)

UV initiated Polymerization (Chapter 3 and Appendix I)

Transient Imbibition Experiments (Chapter 3)

3D imaging using XCT (Chapter 3 and Appendix II)

Noise removal and three phase image segmentation (Chapter 4)

Voxel-based pore structure evaluation from segmented 3D images (Chapter 5)

Evaluation of the wetting phase configuration at the wetting front (Chapter 6)

Summary and Future Research (Chapter 7)

Figure 1-1: Flowchart illustrating overview of the current thesis work
CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

2.1 Terminology

The terms commonly used in the literature dealing with the study of multiphase flow in porous medium are summarized in this section.

2.1.1 Wettability

The terms wetting or nonwetting are often used to describe the extent of spreading of a liquid on a surface, which arises from the adhesive forces between the molecules in the liquid phase to the molecules on the surface of the solid. The contact angle ($\theta$) is the most commonly used parameter for quantifying wettability. A liquid is termed completely wetting to the solid if $\theta$ is less than $90^\circ$ and the fluid spreads onto the solid. In practice $\theta$ less than $30^\circ$ is considered completely wetting and $\theta$ greater than $90^\circ$ the fluid is nonwetting, as shown in the Figure 2-1.

![Figure 2-1: Schematic showing effect of wettability on the shape of a liquid drop resting on the surface of a solid. (a) Wetting fluid and (b) Nonwetting fluid.](image)

2.1.2 Interfacial Tension

Interfacial tension ($\sigma$) is a force that arises at an interface from the cohesive forces between the molecules of two immiscible fluid phases. Interfacial tension works to minimize the interfacial area between the fluids. When an interface is formed between liquid and gases (e.g., water and air), the interfacial tension is often termed surface tension.
2.1.3 Capillarity

Capillary forces arise as a result of the cohesive forces (i.e., attraction of similar molecules) and adhesive forces (i.e., attraction of dissimilar molecules) across the fluid interface (Adamson 1997). Capillarity or capillary action occupies a place in general thermodynamics in the context of macroscopic behavior, such as an equilibrium shape of a fluid-fluid interface (e.g., meniscus, liquid drop shape, and films) rather than the details of molecular structure. For example, when a thin glass tube is contacted with water, the water rises above the bulk interface wherever it is in contact with the glass (Figure 2-2).

![Diagram of capillarity phenomena](image)

Figure 2-2: Capillarity phenomena in a tube (a) the wetting fluid rises above the bulk fluid surface (b) the nonwetting fluid show a dip below the bulk surface.

An adhesive force causes the water molecules to be attracted toward the glass surface and can be seen as the force resulting in wetting of the solid. If this is the only force, then the water will continue to rise on the surface of glass. However, an opposing cohesive force between the water molecules minimizes the interfacial area. Balance of adhesive and cohesive forces results in an equilibrium shape of an interface. Cohesive forces can also be viewed as an interfacial tension force. Wettability and interfacial tension are the most commonly measured parameters to determine capillary force (Equation 2-1).
2.1.4 Capillary Pressure

Capillary pressure arises from the balance between adhesive and cohesive forces and is the most basic parameter governing the multiphase flow behavior in a porous medium. It is defined as the difference between nonwetting phase pressure and wetting phase pressure across an interface. The Laplace equation relates the capillary pressure ($P_c$) to the surface tension ($\sigma$), contact angle ($\theta$), and the mean curvature of the interface ($1/R$) in a capillary (Equation 2-1).

$$P_c = P_{nw} - P_w = \frac{2\sigma \cos \theta}{R}$$ (2-1)

2.2 Multiphase Flow in Porous Media

Flow in a porous medium occurs in many engineering applications, such as oil recovery from reservoirs, flow in packed bed reactors, membrane separations, and subsurface solute transport. Multiphase flow in porous media involves immiscible displacement in the pore space due to a combination of capillary action, pressure gradient, and/or gravity (e.g., displacement of petroleum oil from the reservoir rocks using water as the displacing fluid). The displacement phenomenon is classified into two main categories: (1) drainage, and (2) imbibition based on the wettability of the invading and displaced fluids.

2.3 Drainage

Drainage is a process by which the nonwetting fluid displaces the wetting fluid from a porous medium. For drainage to occur in a given pore, the pressure in the nonwetting phase must exceed the pore capillary pressure. Hence spontaneous capillary displacement of the wetting phase is not possible and drainage always occurs under an externally applied pressure or gravity. During drainage, the nonwetting phase enters a pore when the applied pressure gradient exceeds the critical capillary pressure of the pore (pore-throat). Hence, accessible pores (lower capillary pressure in the large pore) larger than the critical size will drain. For further displacement of a
wetting phase from the smaller pores, the pressure gradient must be increased. This quasi-static displacement approach is utilized in the drainage simulation (Fatt 1956; Blunt et al. 2002) and mercury porosimetry to determine the pore size distribution (Brooks and Corey 1964; van Genuchten 1980).

2.4 Imbibition

Imbibition is a process by which the wetting fluid displaces the nonwetting fluid from a porous medium. Unlike the drainage, imbibition is a decreasing function of capillary pressure (wetting phase invades a pores when the local pressure across the interface is smaller than the capillary pressure). Hence, the wetting fluid can spontaneously moves into the pore space without any externally applied pressure or gravity. Washburn (1921) studied the relation between the height of capillary rise ($L$) and time ($t$) to reach equilibrium during free spontaneous capillary rise in a porous medium. The height is inversely proportional to the square root of time (Equation 2-2).

\[ t = \frac{2L^2 \mu}{r \sigma \cos \theta} \]  

(2-2)

When an interface rises into the porous medium under the influence of an externally applied pressure gradient or gravity, it is termed the forced imbibition. If the applied pressure gradient is much larger in magnitude than the capillary forces, imbibition takes place due to the viscous forces and rise of the interface can be predicted by Poiseuille's equation. On the other hand, if the applied pressure gradient is in the opposite direction so as to retard the imbibition displacement, the flow occurs only due to capillary forces and the phenomenon is termed controlled spontaneous imbibition. The controlled spontaneous imbibition effect can also be observed by controlling the supply of the imbibing fluid to the porous medium.

Another classification of imbibition is based on the saturation history of the porous medium.
Primary imbibition occurs when the pore space is completely occupied with a nonwetting phase and a wetting phase is absent from pore space prior to imbibition. Secondary imbibition occurs when the pore space contains wetting phase along with nonwetting phase prior to imbibition. The secondary imbibition is often observed in the reservoir rocks containing connate water or an irreducible wetting phase saturation at the end of drainage.

2.5 Imbibition Mechanism

Imbibition occurs when the capillary pressure decreases and saturation in the pore space increases. Hence, the capillary pressure vs. saturation curve decreases monotonously at the core or larger scales. However, at the pore scale, the relationship is not a monotonically decreasing function, as illustrated by an example of imbibition into a cubic pore in Figure 2-3. As the saturation in the pore increases, the curvature of the fluid-fluid interface in the corners of the square cross section increases and capillary pressure subsequently decreases. However the after certain point, any further saturation increase would lead to a decrease in the curvature and the interface can no longer maintain a three-phase contact line with the solid surface. This instability results in the collapse of the interfaces and the pore is completely filled. This phenomenon was first observed by Haines (1925) and is termed the Haines Jump. Thermodynamic stability limits of a fluid-fluid interface in simple geometries, such as fluid between two spherical particles or between sphere and a flat plat (Melrose 1966; Melrose and Wallick 1967; Erle et al. 1971; Orr et al. 1975) were carried out. However, theoretical calculations are not possible for complex pore geometries found in a porous medium.

Based on the advancement of the fluid-fluid interface through the pore space, the imbibition displacement mechanism can be divided in two main categories, (1) Frontal displacement and (2) Snap-off displacement.
Figure 2-3: Schematic depicting the Haines jump in a cubic pore.

2.5.1 Frontal Displacement

During frontal displacement, the wetting fluid completely occupies the center of the flow channel (pore or throat) with the front moving forward by displacing nonwetting fluid in piston-type fashion. Several variations of the frontal displacement mechanism are reported based on simplified pore geometries, connectivity of the pore, and the number of wetting phase filled throats connected to the pores (Lenormand and Zarcone 1984; Lenormand 1990; Blunt and Scher 1995). For a regular lattice of coordination number ($z$), there are $z$ possible numbers of imbibition mechanisms, $I_0$ to $I_{z-1}$. The subscript denotes the number of nonwetting phase filled throat connected to a given pore (Figure 2-4). The requisite capillary pressures for these mechanisms are ranked as $P_c(I_0) > P_c(I_1) > \cdots > P_c(I_{z-1})$. The $I_0$ mechanism is possible only for the compressible nonwetting phase case.
Figure 2-4: Schematics of various types of frontal displacement in the pore with coordination number of $z = 4$ (Blunt and Scher 1995). (a) Throat filling. (b) $I_0$ for compressible nonwetting fluid. (c) $I_1$ one throat through with nonwetting fluid can leave the pore. (d) $I_2$, nonwetting fluid leave from adjacent throats. (e) $I_2$, nonwetting fluid can leave through two opposite throats and (f) $I_3$, three throats filled with nonwetting fluid.

2.5.2 Snap-off Displacement

The snap-off displacement mechanism involves the movement of the interface in the form of films along the solid surface; thus, the front does not completely occupy the pore or throat. The wetting films move ahead of the bulk front through corners or along rough surfaces of the pore walls due to higher capillary pressure, sometimes called microcapillarity. Tzimas et al. (1997) observed punctuated motion of wetting films in the corners of a 2D glass micromodel. The films move rapidly to a few pore lengths ahead of the bulk front, and then stops to equilibrate with the bulk front. Once stationary, the pressure in the wetting films increase to equilibrate with the bulk front, thus gradually growing thicker (i.e., saturation increases). The column of the nonwetting phase becomes unstable and collapse thus filling the channel. Critical capillary pressure for the snap-off to occur is always lower than any frontal displacement mechanisms ($I_0 \ldots I_{z-1}$). Hence, snap-off occurs only when frontal advance is not possible (Lenormand and Zarcone 1984; Lenormand 1990; Vizika et al. 1994; Blunt and Scher 1995).
2.5.3 Effect of Capillary Number on Imbibition

Capillary number, the ratio of viscous to capillary forces \((Ca = \mu v / \sigma \cos \theta)\), is the most important parameter for determining the governing mechanisms during imbibition. Macroscopically, the saturation in a porous medium may vary from a step change across the interface (piston type front) in a viscous dominant flow regime to a more gradual change (dendritic front growth, Lenormand and Zarcone 1984) in a capillary dominant flow regime. It has been widely reported that the residual oil saturation decreases with increases in capillary number (Lake 1989; Tzimas et al. 1997; Nguyen et al. 2006), leading to increase in the sweep efficiency of the waterflooding method of oil recovery. The imbibition mechanism in viscous flow regimes \((Ca > 10^{-4})\) is dominated by frontal displacement. In this flow regime, the wetting fluid occupies the pores and throats behind the interface, and the saturation change across the interface is sharp. In capillary driven flow regime, the interface is diffused and the saturation changes gradually across the interface. During imbibition at low capillary numbers, \((Ca < 10^{-6})\), the meniscus advances slowly through the porous media due to low capillary pressure. In the presence of the wetting phase in the form of surface films or corner flow, snap-off can occur and can lead to the trapping of nonwetting fluid, thus decreasing the displacement efficiency.

2.6 Effect of Wettability on Imbibition

Wettability affects the mechanism of the displacement significantly. Tzimas et al(1997) show that, for the small contact angle\((\theta < 10^\circ)\), extensive microfingering is observed at low flow rates in 2D glass micromodels and the residual saturation of oil increases. With increases in the contact angle, the extent of micro-fingering, as well as the residual nonwetting phase saturation, is also reduced (Wardlaw 1980). Snap-off is possible only when the invading fluid completely wets the solid. Yu and Wardlaw (1986) show that snap-off does not occur at \(\theta > 70^\circ\).
2.7 Effect of Viscosity Ratio on Imbibition

\[ \text{Viscosity ratio} = \kappa = \frac{\mu_{nw}}{\mu_w} \]  

(2-3)

The viscosity ratio between the nonwetting and wetting phase fluids is also an important parameter to determine the trapping of nonwetting phase during imbibition. In the viscous-dominant flow regime, the displacement efficiency increases for favorable viscosity ratios \((\kappa < 1)\) (Equation 2-3). Under unfavorable conditions \((\kappa > 1)\), viscous fingering takes place, whereby fingers of wetting phase penetrate the viscous nonwetting phase (Homsy 1987). Vizika et al. (1994), using experiments in 2D micromodels, show the effect of viscosity ratio at low capillary numbers. The height of the films in a capillary dominant flow regime varies from 2-3 pore diameters under favorable viscosity ratio and increases to 10-15 pore lengths under unfavorable viscosity ratio. At low capillary numbers, where the viscous effects are small, the viscosity ratio has a local effect in the form of micro-finger formation, which they attribute to a local increase in the velocity in the narrow channels (Vizika et al. 1994).

2.8 Effect of Pore Structure on Imbibition

A real porous medium consists of a complex 3D network of pores and pore-throats. The pore structure has a significant effect on imbibition because it affects the pore filling mechanism and leads to trapping of nonwetting fluid. The parameters affecting imbibition in porous medium are listed below.

2.8.1 Pore Size Distribution

From the petroleum literature, the amount of trapped nonwetting phase in sandstones with narrow pore size distribution is lower than that in the carbonate rocks (Stegemeier 1974; Wardlaw 1980; Lake 1989) with wide pore size distribution. Packing heterogeneity leading to a wider pore size distribution is also reported as primary cause of air entrapment in the
manufacture of composites, such as fiber reinforced plastics (Michaud and Mortensen 2001; Alms and Advani 2007).

The pore doublet model (Rose and Witherspoon 1956, 1958) is often used to explain the effect of heterogeneity in pore-size and its effect on the trapping of nonwetting fluid in the wide pores. The model consists of two capillaries of different diameter connected at both the ends (Figure 2-5). The heterogeneity factor $\beta = R_2/R_1$ is the ratio of the large to small capillary radius. The length of both capillaries is much larger than the radius of the large capillary, hence well-developed Poiseulle flow can be assumed. The driving force across each path is equal and is the sum of the applied pressure difference and capillary pressure determined by the radius of the capillary. The ratio of the velocities in each of the capillaries is given by equations (2-4) and (2-5).

From equation (2-4), the limit of negligible capillary forces (i.e., large $Ca$) as is the case in drainage, the velocity in each path is proportional to the square of its radius. Hence, the interface in the large capillary will reach the end before the smaller capillary and the fluid wetting phase will be trapped in the small capillary. Then if viscous forces are negligible (i.e., small $Ca$), as in the case in spontaneous imbibition, then the smaller radii will imbibe faster and the nonwetting fluid in the large capillary will be trapped.

![Figure 2-5: Schematic of a typical pore doublet model (Lake 1989).](image-url)
Chatzis and Dullien (1983) conducted experiments to study the trapping of nonwetting fluid in a pore doublet model during primary and secondary imbibition and show that no trapping of nonwetting phase occurs during primary imbibition. As predicted by the pore doublet model, the interface in the smaller capillary moves, however the interface in the larger capillary does not move until the interface in the smaller capillary comes to rest at the other end of the pore doublet. Both the interfaces meet towards the exit of the pore doublet exits the pore doublet. Hence, trapping of nonwetting was not observed during primary imbibition. Similar experiments conducted on the pore doublets models connected in series also do not show trapping of nonwetting phase during primary imbibition.

\[
\frac{v_2}{v_1} = \frac{4N_c + \left(\frac{1}{\beta} - 1\right)}{\frac{4N_c}{\beta^2} + \beta^2 \left(\frac{1}{\beta} - 1\right)} \quad (2-4)
\]

\[
N_c = \frac{\mu L q}{\pi R_1^3 \sigma \cos \theta} \quad (2-5)
\]

2.8.2 Surface Roughness

Surface roughness is observed in many natural reservoir rocks and can vary from smooth crystalline surface of dolomite to pitted or clay coated surfaces of sandstone. Surface roughness can pin the three phase contact line and causes difference in advancing and receding contact angles, modifies wettability of the surfaces thus affecting multiphase flow in a porous medium. Dullien et. al. (1989) conducted spontaneous imbibition experiments using smooth and etched glass beads packing. At equilibrium the height of the wetting fluid was higher in etched glass beads compared to the smooth beads. The difference in capillary rise is due to the capillarity of the microchannels on the roughened surface of spheres. The film flow due to the surface capillarity and flow along the corners of porous media were simulated on 2D micromodels and
show that the microcapillary effect can lead to the film flow and snap off ahead of the bulk front (Lenormand and Zarcone 1984; Blunt et al. 1992; Blunt and Scher 1995).

2.8.3 Pore/Throat Aspect Ratio

The ratio of diameter of the pore to the diameter of pore-throat is an important pore-structural parameter affecting the flow pattern during imbibition since it determines the relative importance of snap-off versus frontal displacement mechanism in a given pore throat. In certain rocks with vuggy type pore spaces, the porosity is high but the displacement efficiencies are still low. This effect is attributed to the increase in the pore to throat aspect ratio (Stegemeier 1974; Wardlaw 1980). In porous media with high aspect ratio, the snap-off is dominant displacement mechanism (Jerauld and Salter 1990; Nguyen et al. 2004).

2.8.4 Pore Coordination Number

Pore coordination number is a measure of connectivity of the pores and is defined as average number of throats connecting a given pore. In porous medium with large coordination number, the number of paths nonwetting and wetting phase can invade also increase resulting in overall increase in the displacement efficiency. Wardlaw (1980) studied 92 carbonate rock samples and correlated decreases in the porosity to decreases of the displacement efficiency. It is generally known that the decrease in porosity results in the decrease of coordination number (Dullien 1979). As discussed in the frontal displacement (Section 2.5.1), probability of the frontal displacement events also increases with increase in the coordination number. Critical capillary pressure for the pore filling also increases result in reduced trapping of nonwetting phase.

2.9 Effect of Initial Saturation on Imbibition

Initial saturation is often present in the pore space prior to invasion in many present in natural oil bearing rocks in the form of thin films, pendular rings and interconnected networks of small
pore filled with the wetting phase. This process can occur in cases where the porous medium has previously drained, leaving a residual saturation behind. It can also occur in situations where the initial wetting-phase saturation formed from a different mechanism, such as capillary condensation of water vapor in the proton exchange membrane of fuel cell (Koido et al. 2008) or from diagenetic or thermodynamic processes in oil and gas reservoirs (Lombard et al. 2000). In any of these cases, the presence of this initial wetting phase can have a significant impact on imbibition because as the saturation increases, the films, collars, pendular rings, etc., swell and can connect with each other to form hydraulically conductive paths. Hence, the wetting phase can propagate more quickly through the porous media, and a larger amount of non-wetting phase can end up becoming disconnected and trapped.

Chatzis and Dullien (1983) conducted imbibition experiments to study the effect of initial saturation on trapping of nonwetting fluid, in micromodel of pore doublets and triplets connected in series. No trapping of wetting phase was observed in the case of the primary imbibition of n-Decane against air which is consistent with the single pore doublet experiment explained in the section 2.9.1. However, trapping of oil in the pores was observed during the secondary imbibition displacement in the presence of connate water. The phenomenon of trapping of the nonwetting phase in the pores can be explained by the swelling of the connate water films (residual wetting phase) and subsequent snap-off of the wetting phase films ahead of the displacement front leads to trapping of the nonwetting.

Barci et al. (1985) performed secondary imbibition experiments to study the brine imbibition (displacing oil) in sandstone using an acoustic probe. They found hyper-dispersion at low initial saturation and as the saturation increased in the pore space the displacement transitioned towards hypo-dispersion. (Hyper-dispersion: no distinguishable wetting front is observed and the
saturation profile is uniform along the length of the column. Hypo-dispersion: classic frontal displacement where the profile undergoes a step change in saturation across the wetting front.) Melean et al. (2003) showed the simultaneous saturation increase throughout the length of the sand packing in the presence of initial saturation at low capillary numbers and moving toward classic piston-type displacement as the capillary number increases.

2.10 Imbibition Pattern

Conditions such as capillary number, contact angle, wettability, pore space topology, saturation history and viscosity ratio between the invading and the displaced fluid pair give rise to varied pore filling patterns in the porous media, which are categorized into five flow regimes (Blunt and Scher 1995; Hughes and Blunt 2000). The results of these imbibition patterns in a 2D micromodel are shown in the Figure 2-6.

1. Bond percolation (Low Ca, Low \( \theta \), High \( S_{ui} \)): The initial saturation present in the form of films and pendular rings starts to swell and the saturation increases uniformly along the entire height of the porous medium. Trapped nonwetting phase saturation can be more than 50% in 2D glass micromodels.

2. Frontal advance (High Ca, Moderate to high \( \theta \), None to low \( S_{ui} \)): The wetting front moves thought the column in piston type fashion and saturation undergoes a sharp transition across the wetting front. The width of the wetting front is less than 10 pores. Viscous fingering and wider pore size distribution can lead to an increase in the width of the front. However, at the pore scale the front remains flat and the bypassed pores can be filled due to cooperative pore filling. Little or no trapping of the nonwetting phase is observed.

3. Compact cluster growth (Low Ca, High \( \theta \), Low \( S_{ui} \)): High contact angle suppresses snap-off. However, at small capillary number flow, snap-off can still occur in small pores. The pores
filled due to the snap-off can lead to frontal advance in the connected pores, thus creating compact clusters of saturated pores along the flow path in the porous medium.

Figure 2-6: Filling pattern (Hughes and Blunt 2000). (a) Bond percolation, (b) Frontal displacement, (c) Cluster growth, (d) Ramified cluster growth and (e) Dendritic frontal advance.

4. Ramified cluster growth (Low $Ca$, Moderate to high $\theta$, High $S_w$): Cluster growth is similar to compact cluster growth; however, the high initial saturation provides sites for cluster growth throughout the height of the porous medium.

5. Dendritic frontal advance (High $Ca$, Moderate to high $\theta$, High $S_w$): Due to high capillary number, frontal advance dominates the snap-off event to fill the pores. However, with the presence of the wetting phase ahead of the advancing front and moderate to high contact angles, the wetting fluid bypasses nonwetting phase that is present in the large pores and can lead to the trapping of the nonwetting fluid. The width of the wetting front is about 10 pores or more.

2.11 2D vs. 3D Experiments

Much of the experimental work on wetting front propagation has been conducted in simplified 2D pore geometries. These have provided important mechanistic understanding, but it is important to understand their limitations. Pore geometry is simplified in micromodel systems: pores and pore throats are generally better defined, and geometry may be affected by the construction method (e.g., eye-shaped cross-sections for traditional glass-fused micromodels, which are highly effective at conducting wetting fluid along the corners). Surfaces are generally
more uniform than what can be found inside many natural porous media, where surface vary from molecularly smooth crystalline surfaces to rough clay-covered surfaces. Connectivity and spatially heterogeneity may be limited in a 2D lattice pattern.

The most important limitation in micromodels is the fundamental limitations on topology in 2D versus 3D domains. In real materials, the two phases can form intertwined bicontinuous networks. In 2D geometries, the two fluids can coexist (and flow) only on a parallel geometry or if one of the fluids moves as a discontinuous phase (i.e., a bubbling flow). Chatzis and Dullien (1977) reported that breakthrough conditions for multiphase flow depend on the interconnectivity and dimensionality of the network and that 3D pore networks differ substantially from 2D networks for immiscible displacement.
CHAPTER 3 TRANSIENT IMBIBITION EXPERIMENTS

3.1 Experiments on Transient Imbibition in 3D Porous Media

The experimental study of the imbibition in a real 3D porous media has been difficult due to the speed of the pore filling events and the time taken to acquire a 3D image data. For example, the pore level events take place in the order of 1-100 seconds, while the acquisition time for 3D data using X-ray CT is of the order of 10-30 minutes. Moreover the 3D reconstruction of a tomography projection data in which the liquid interfaces are in motion is not possible with current techniques. For this reason, many results have been published in which dynamic primary and secondary imbibition have been studied by tracking the average wetting front using 2D radiograph projection of 3D images. This approach is fast (on the order of fraction of second per projection) but does not provide details such as film and pendular rings, and other pore level structures that are necessary to answer the questions addressed in this work.

In order to overcome this limitation for 3D XCT imaging of a dynamic wetting front, we developed a novel experimental technique that arrests the progress of the wetting front in porous media such that 3D image acquisition is possible. The idea is to use a wetting phase that has chemical formulation that allows for a phase change from liquid to solid without disturbing the flow characteristics (i.e., an external stimulus is used to bring about the phase change). In order to achieve this, the wetting phase should satisfy following criteria:

1. The fluid should exhibit good wettability with respect to the packing materials.
2. The phase conversion from liquid to solid phase should be faster than the characteristic time for pore filling.
3. The volume change (shrinkage) should be minimal, such that it does not affect the position and pore-scale structure of the imbibition front.
4. The solidified wetting front should be stable during transportation to the imaging facility and during the imaging.

3.2 Polymerizable Mixture

A number of different formulations were proposed and/or tested in the process of developing this technique (see Appendix II). The following formulation was chosen as the most effective, and was used for the results presented later (Chapter 6). The wetting fluid used in this study consisted of a mixture of 85 wt% 1,6-Hexanediol diacrylate (Polysciences Inc.), 10 wt% 2,3 Dibromopropyl acrylate (Tokyo Kasei Kogyo Co. Ltd., Japan) and 5 wt% Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide / 2-hydroxy-2-methylpropiopehnone 50/50 (Sigma Aldrich).

Upon exposure to UV radiation, the initiator molecules break down to release free radicals (Equation (3-1) and (3-2)) that initiate the chain reaction.

\[
\begin{align*}
\text{UV light} & \quad \text{ initiator molecules} \\
\text{initiator molecules} & \quad \rightarrow \quad \text{free radicals}
\end{align*}
\]

The polymerization process consists of crosslinking of monomer species with the acrylic functional groups to form a polymer. The cross-linked polymer is solid and the phase transition from liquid to solid occurs in 2-3 seconds, which is faster than the quickest pore filling time at the highest capillary number flow chosen to study the transient imbibition (i.e., purely from volumetric flow point of view and not accounting for non-equilibrium events such as Haines hump). Various acrylic monomers were tested for this criteria and 1,6-Hexanediol diacrylate
showed conversions of greater than 90% in two seconds in our experiments with 5mm diameter columns containing the polymerizable mixture. The polymerization tests were also carried out in the presence of packing materials (described below) and complete phase transition throughout the column was confirmed visually after cutting open the polymerized packed columns. Further details of the photoiniated polymerization are given in Appendix I.

Low viscosity and surface tension also make the 1,6-Hexanediol diacrylate (Sp gravity = 1.01, Vapor pressure < 0.01 mmHg, surface tension = 9 dynes/cm, viscosity = 35.7 cP) ideal for the transient imbibition experiments.

**3.3 Packing Materials**

In order to study the effect of pore structure and surface roughness on transient imbibition, four types of packing materials were chosen: (i) Smooth spherical polystyrene beads (250-300 μm, Norstone Inc.), (ii) Rough spherical polystyrene beads (250-300 μm), (iii) Sand particles (210-300 μm, Unimin Corp.), and (iv) Cylinders (diameter 90-100 μm and aspect ratio 10-20, Mo-Sci Speciality Products LLC.). Roughened spherical polystyrene beads and naturally rough
sand particles were chosen to study the effect of surface roughness (see Figure 3-2b&c). The rough spherical polystyrene beads were created from the smooth polystyrene beads by sanding the surface of the particles with sandpaper (3M, Wet/Dry 320 grit silicon carbide paper). The sand particles are irregular in shape, which leads to closer packings with lower porosity compared to the random sphere packings. High aspect ratio cylindrical particles were created by cutting 1-2 mm length segments from long glass fibers. The high-aspect-ratio cylindrical particles create high porosity packings when placed randomly in the column.

Table 3-1: List of column materials tested to create unconsolidated packing for the transient imbibition experiments.

<table>
<thead>
<tr>
<th>Column Material</th>
<th>Capillary Rise (mm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic</td>
<td>5</td>
<td>High Wettability, Transparent to UV, Column becomes rigid and breaks upon interaction with acrylic monomers</td>
</tr>
<tr>
<td>PVC</td>
<td>2.5</td>
<td>Low wettability, Blocks UV, Mechanically Stable</td>
</tr>
<tr>
<td>Butyrate</td>
<td>3</td>
<td>Low wettability, Transparent to UV, Mechanically Stable</td>
</tr>
<tr>
<td>Glass</td>
<td>5</td>
<td>Wetting, Transparent to UV, Difficult to thread and attach flow valves, Fragile</td>
</tr>
</tbody>
</table>

The random packings were created by adding the packing media into plastic columns (Column material Butyrate, ID = 3.175 mm, OD = 6.35 mm, Length = 50 mm, McMaster-Carr Corp., GA, USA), and then shaking the columns using a vortex mixer to help remove macroscopic heterogeneity (the goal being to obtain microscopically heterogeneous but macroscopically uniform packings as shown in Figure 3-3). The butyrate columns were chosen because butyrate was not as wetting to the polymerizable mixture as other materials and because of its ability to allow UV light to pass through (see Table 3-1). Large spheres of diameter 0.9–1.0 mm were added near the end region of the column to serve as flow distributors. The column was fitted with three-way micro-fluidic valves and connected to a syringe pump using Teflon tubing (OD = 1.59 mm and ID = 0.79 mm).
Figure 3-2: SEM images of the packing materials used in the experiments. Left column: Low resolution and Right Column: High resolution. (a) Smooth polystyrene spheres, (b) Rough polystyrene spheres, (c) Sand and, (d) Smooth glass cylinders.
Figure 3-3: Segmented XCT image showing random packing of various packing materials. (a) Smooth spherical particles, (b) Irregular sand particles, and (c) High aspect ratio cylinders.

3.4 Spontaneous Imbibition

Spontaneous capillary rise experiments were performed to determine the limits of flow regimes (viscous dominant, capillary dominant and transition from viscous to capillary dominant) for each of the packing materials. In each of these experiments, the packed column was brought in contact with a reservoir of wetting fluid and rise of the wetting front was recorded as a function of time (Figure 3-4a). The wetting fluid used in this experiments was a mixture of 1,6-Hexanediol diacrylate (90 wt%) and Dibromopropyl acrylate (10 wt%). A small amount of Oil Red O dye (Sigma) was added to visualize the rise of wetting interface in the packed column. The initiator was not added to this experiment to avoid polymerization, which might result from exposure to the natural light. The flow rate was calculated from the spontaneous capillary rise experiments and shown in Figure 3-4b and capillary numbers are
reported in Table 3-2 using the porosity of the each column calculated from the segmented images. Three flow rates were chosen from this experiment, which represent the initial viscous-driven flow rate (high), an intermediate flow rate in the transition regime and a final low flow rate, which is capillary dominated.

Figure 3-4: Spontaneous Capillary rise experiments (Top) Capillary rise, (Bottom) Flow rate.
Table 3-2: Capillary number calculations for the transient imbibition experiments

<table>
<thead>
<tr>
<th>Packing Material</th>
<th>Porosity</th>
<th>Effective Area (m$^2$)</th>
<th>Flow Rate (m$^3$/hr)</th>
<th>Flow Rate (m$^3$/s)</th>
<th>Effective Velocity (m/s)</th>
<th>$Ca = \frac{\mu V}{\sigma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth Sphere</td>
<td>0.3319</td>
<td>2.63E-06</td>
<td>1.000</td>
<td>2.78E-10</td>
<td>1.06E-04</td>
<td>2.66E-06</td>
</tr>
<tr>
<td></td>
<td>0.3558</td>
<td>2.82E-06</td>
<td>0.100</td>
<td>2.78E-11</td>
<td>9.86E-06</td>
<td>2.49E-06</td>
</tr>
<tr>
<td></td>
<td>0.3268</td>
<td>2.59E-06</td>
<td>0.005</td>
<td>1.39E-12</td>
<td>5.37E-07</td>
<td>1.35E-07</td>
</tr>
<tr>
<td>Rough Sphere</td>
<td>0.3747</td>
<td>2.97E-06</td>
<td>1.000</td>
<td>2.78E-10</td>
<td>9.36E-05</td>
<td>2.36E-05</td>
</tr>
<tr>
<td></td>
<td>0.3786</td>
<td>3.00E-06</td>
<td>0.100</td>
<td>2.78E-11</td>
<td>9.27E-05</td>
<td>2.34E-06</td>
</tr>
<tr>
<td></td>
<td>0.3761</td>
<td>2.98E-06</td>
<td>0.005</td>
<td>1.39E-12</td>
<td>4.66E-06</td>
<td>1.18E-07</td>
</tr>
<tr>
<td>Sand</td>
<td>0.3382</td>
<td>2.68E-06</td>
<td>1.5</td>
<td>4.17E-10</td>
<td>1.56E-04</td>
<td>2.08E-04</td>
</tr>
<tr>
<td></td>
<td>0.3470</td>
<td>2.75E-06</td>
<td>0.1</td>
<td>2.78E-11</td>
<td>1.01E-05</td>
<td>1.35E-05</td>
</tr>
<tr>
<td></td>
<td>0.3404</td>
<td>2.70E-06</td>
<td>0.005</td>
<td>1.39E-12</td>
<td>5.15E-07</td>
<td>1.30E-07</td>
</tr>
<tr>
<td>Cylinder</td>
<td>0.6962</td>
<td>5.51E-06</td>
<td>1.000</td>
<td>2.78E-10</td>
<td>5.04E-05</td>
<td>1.27E-05</td>
</tr>
<tr>
<td></td>
<td>0.7717</td>
<td>6.11E-06</td>
<td>0.100</td>
<td>2.78E-11</td>
<td>4.55E-06</td>
<td>1.15E-06</td>
</tr>
<tr>
<td></td>
<td>0.7011</td>
<td>5.55E-06</td>
<td>0.005</td>
<td>1.39E-12</td>
<td>2.5E-07</td>
<td>6.31E-08</td>
</tr>
</tbody>
</table>

3.5 Transient Imbibition

A syringe pump (Harvard Apparatus #33) was used to provide the flow of polymerizable mixture at a constant flow rate to the column. The experimental setup to freeze the transient imbibition front is show in Figure 3-5. The experiments were carried out in a UV chamber (Uvitron Intelliray 600) with uniform light intensity of 200 mW/cm$^2$ (UVA 320-390 nm). The wetting phase was introduced into the packed column at constant flow rate (see Table 3-2).
When the wetting front reached a predetermined height, (away from the entrance region to avoid end effects) the syringe pump was stopped and simultaneously the column was exposed to the UV light for the period of 10 seconds.

3.6 Absorption Edge Imaging

Absorption edge imaging was performed on the solidified columns using synchrotron XCT at the GSECARS 13-BMD beamline at Argonne National Laboratory, Argonne, IL. The energies used were above and below the Bromine edge at 13.524 keV and 13.424 keV respectively. The noise in the image was removed using anisotropic diffusion (Frangakis and Hegerl 2001) and segmentation was performed using an indicator kriging algorithm similar to that described by Oh and Lindquist (1999). Both the images (above and below the Bromine absorption edge) were used to obtain the final three phase segmented images (Bhattad et al. 2010).

Details of image three phase image segmentation algorithms can be found in Chapter 4 and the X-ray imaging setup and absorption edge imaging are given in Appendix II.
CHAPTER 4 IMAGE PROCESSING

4.1 Introduction

X-Ray Computed Tomography (XCT) is an important tool to study porous media microstructure and fluids present within the void space in microscopic detail. The X-ray attenuation coefficients of the chemical species present in the phase and the density of the phase dictate the X-ray absorption and result in an intensity value mapping in the final grayscale absorption image. Solids present in the natural porous media typically contain minerals with high X-ray attenuation resulting in a grayscale image with good contrast between the solid and void phases. For systems where more than one fluid phase is present in the porous media with similar X-ray absorption values, small amounts of chemicals with high attenuation coefficients are usually added to one of the fluid phases to increase the contrast in the resulting absorption image (grayscale image), and the intensity levels of each phase is identified with its peak in the histogram. When the X-ray beam is not monochromatic, it is not possible to selectively illuminate one of the phases and the result is a single image containing three phases. The segmentation of three (or more) phase imaged has not been well studied in the image processing literature.

For quantitative analysis of the pore structure (e.g., properties such as porosity, permeability, anisotropy and fluid phase characteristics such as distribution of wetting and non-wetting phase interfacial area and curvature), the grayscale image needs to be segmented. In addition to aiding in quantifying these properties, the resulting segmented image can also be used for image based modeling techniques, such as pore network modeling, finite element, and Lattice Boltzmann simulations to calculate relative permeability, trapping, and distribution of the wetting and non-wetting phases.
The segmentation of an image is performed to partition the image into regions with similar predefined criteria such as similarity of the intensity values, connected components or bounding edges. Once segmented, a porous media image typically contains connected sets of voxels with similar properties, and the image can then be used for the analysis of the structural properties of the material. There are many segmentation techniques available in the literature; they can be classified into edge-based and threshold-based segmentation. These techniques require well-defined edges to segment the image into regions bounded by the edges and are used in applications such as counting the number of objects present in the image. The edge-based techniques include level set, active contour, and watershed techniques (Vincent and Soille 1991; Sheppard et al. 2004). The techniques have also been developed to overcome the isolated noise present in the image, which can lead to breakup of larger region. On the other hand histogram based techniques such as simple and multiple thresholding, clustering and Indicator Kriging, operate based on the discontinuity or abrupt change in the intensity values in the histogram. The chosen threshold value serves as the guideline, and every voxel in the image is then classified into respective regions based on the similarity in the grayscale intensity. Histogram-based techniques are best suited for the segmentation of phases in XCT images and two or more phases can be segmented by choosing an appropriate number of threshold values. The threshold values can be chosen manually or automatically (e.g., based on the entropy maximization techniques (Kapur et al. 1985; Kesavan and Kapur 1989)). The accuracy of threshold-based segmentation techniques is affected by the noise present in the image.

Noise in XCT images can arise from various sources. Examples include scattered X-ray photons impinging on the detector to create speckle noise with very high intensity, imperfections in the detector causing ring artifacts or error and approximation in the reconstruction adding to noise and blurring (Herman 1980). Impurities in natural samples can also cause noise, and
attenuation values close to each other can lead to blurring and merging of the phase intensities and merging of two or more peaks in the image histogram. Accurate segmentation of an image into separate phases or components requires the removal of most or all of the noise in the image.

From an image processing perspective, the noise in the XCT image can be characterized as random voxels with the intensity higher or lower than the surrounding neighborhood voxels and which can statistically can be treated as outliers. The main challenge for any noise removal algorithm is to be able to distinguish the phase edges and small features in the image and selectively alter only the noisy voxels. The literature contains many methods ranging from simple low pass averaging filters to process-based filters such as anisotropic diffusion and wavelet transform. Averaging filters such as the Gaussian filter, the median filter and the Sobel filter rely on a weighted stencil which is convoluted with the voxel neighborhood, and the intensity value of the each voxel in the image is replaced with the linear weighted average of its neighborhood voxels. However, these filters do not preserve the small features and cause blurring around the edges. Process-based filters that adapt to the local features have been used with promising results on XCT images. Process-based noise removal filters such as non-linear anisotropic diffusion and wavelet transform have been successfully used with 3D XCT images.

In this chapter we use nonlinear anisotropic diffusion for de-noising of the image, and threshold indicator kriging for segmentation of the image into respective phases. In the next sections, we discuss the development of nonlinear anisotropic diffusion, the edge stopping parameter, stopping criteria for the iterative diffusion process, and adoption of indicator kriging for three phase XCT images.

4.2 Anisotropic Diffusion
The diffusion process equilibrates fluctuations in a property to its neighborhood. In image
processing, the noise in the grayscale image can be visualized as the fluctuations in the grayscale values. The diffusion equation (4-1) is applied to the grayscale (intensity) values \( I(x, y, z) \) to equilibrate the noise to its surrounding neighborhood. With a constant diffusion coefficient, the diffusion equation takes the form of linear isotropic diffusion (Equation 4-3). The solution of this equation is the most commonly used Gaussian filter. The Gaussian filter, similar to other averaging filters causes blurring near the edges and the loss of small features in the image. Perona and Malik (1990) proposed a nonlinear isotropic diffusion approach with a modification of the diffusion coefficient that takes into account the local image intensity by constructing the diffusion coefficient as an inverse function of the local image gradient (Equation 4-5). This approach causes the diffusive flux to be minimized across the edges since these are regions where there is a maximum in the image gradient. However, this approach is unsatisfactory as the noise around the object edges does not get removed due to the low flux, and the small component of the flux normal to the edges can still cause blurring as the number of iteration increases. In order to overcome this problem, nonlinear anisotropic diffusion (Equation 4-4) is used, in which the diffusion coefficient is a tensor. The anisotropy causes the tangential component of the diffusion coefficient tensor to remove noise around the object edges, while minimizing the diffusion normal to the object boundaries.

\[
\frac{\partial I}{\partial t} = \nabla(C \cdot \nabla I) \quad (4-1)
\]

\[
I(x, t = 0) = I_0 \quad (4-2)
\]

\[
\frac{\partial I}{\partial t} = c \nabla^2 I \quad (4-3)
\]

\[
\frac{\partial I}{\partial t} = \text{div}(c(|\nabla I|) \cdot \nabla I) \quad (4-4)
\]
The diffusion tensor calculation takes into account local features, such as the gradient in the grayscale values and directionality of the gradients in the form of eigen values and eigen vectors. These local features are calculated using the structural tensor smoothed using the Gaussian filter of width $\sigma$. The eigen vector $e_{i,j}$ orients the co-ordinates along the local image structure and the relative magnitude of the eigen values $\lambda_i$ can be used to identify the nature of the feature in the image, such as corners, edges, planes, and isolated noise voxels. Refer to Spies et al. (2002; 2005) for more details on the eigen value analysis.

Here, we will review three diffusion coefficient schemes for de-noising XCT images: Edge Enhancing Diffusion (EED), Coherence Enhancing Diffusion (CED); and a hybrid of the EED and CED (HYB).

The EED scheme was proposed by Perona and Malik (1990), in which the magnitude of the diffusion coefficient is monotonically decreasing function of the image gradient (Equation (4-5)). This allows the diffusion flux to be minimized across the phase edges (large image gradient), while smoothing the noise present in the homogenous regions of the image.

$$c(|\nabla I|) = \frac{1}{(1 + (|\nabla I|/K)^2)} \quad \text{(4-5)}$$

$$C_{ij} = e_{ij} \begin{bmatrix} c(\lambda_1) & 0 & 0 \\ 0 & c(\lambda_2) & 0 \\ 0 & 0 & c(\lambda_3) \end{bmatrix} e_{ji} \quad \text{(4-6)}$$

$$J_\sigma = G_\sigma * (\nabla I \nabla I^T) \quad \text{(4-7)}$$

The edge stopping parameter $K$ differentiates the edges and homogenous region in the image and is a user defined parameter.
The CED scheme was proposed by Wickret and Scharr (2002) to improve the continuity of the thin line-like structures in the presence of noise in an image.

Here, $\alpha$ and $M$ are user defined parameters and $\alpha$ is typically a small number; with $\alpha = 1$, the filtering becomes a Gaussian filter. The $(\lambda_1 - \lambda_3)$ term is large for line-like structure.

The Hybrid Scheme (HYB) put forward by Frangkis and Hagerl (2001) combines the EED to remove noise from the homogenous regions of the image and CED which can enhance thin line-like features in the image. The EED filter is used when the $(\lambda_1 - \lambda_3)$ term is smaller than a chosen threshold value; otherwise, the CED filter is used.

$$c(\lambda_1) = c(\lambda_2) = \alpha \text{ and } c(\lambda_3) = \alpha + (1 - \alpha)\exp(-M/(\lambda_1 - \lambda_3)^2)$$

(4-9)

The non-linear anisotropic diffusion algorithm is implemented using the explicit finite volume method so that the mean gray scale value of the original image is conserved. No flux boundary conditions are applied at all the image boundaries. For stability, a small fixed time step of order 0.1 is used and solution is achieved by an iterative process. By conserving the mean grayscale value of the image we also ensure that the mean value of each phase remains close to that of original image. The removal of noise from homogenous regions reduces the variance of grayscale values in each of the phases, leading to narrowing of the peaks and improved peak separation in the image intensity histogram.

The two main issues associated with implementation of the anisotropic diffusion algorithm are the user specified edge stopping parameter ($K$) and the absence of a stopping criterion. The edge stopping parameter is used to distinguish the noise present in the homogenous region of the image from the edges. This information is difficult to obtain by visual observation of the image histogram. Eigen value analysis shows that the smallest eigen value is a good measure of the
uncorrelated noise in the image (Spies et al. 2002). In our algorithm, we use the smallest eigenvalues averaged over the whole image as the edge stopping parameter. The results of the choice of threshold values are shown in the Figure 4-2. Since equation (4-4) is solved iteratively and there is no definite measure of the enhancement of the image, a pre-defined stopping criterion does not exist for the diffusion application on an image. Here, we use the initial measure of the image noise as the starting point and the iterative process is stopped when the confidence level (Equation 4-10) reaches the pre-specified value of 0.75 (Scharr and Spies 2005).

\[
\text{Confidence} = \omega = \begin{cases} 
0 & \text{if } \lambda_3 \geq K \\
\left(\frac{K - \lambda_3}{K}\right)^2 & \text{else}
\end{cases} \quad (4-10)
\]

4.3 Indicator Kriging

Kriging (Rossi et al. 1994) is a commonly used geo-statistics technique to estimate a value at an un-sampled location based on measured values in the neighborhood locations. However from an image segmentation point of view, the probability of the unknown having a value larger than the threshold is more useful. Indicator kriging provides the probability of a value at an un-sampled location being above the pre-defined threshold using linear-weighted combinations of the measured values in the neighborhood. Oh and Lindquist (1999) describe an indicator kriging technique for image thresholding in conjunction with the two point spatial covariance. The algorithm is implemented in two steps: (1) The thresholding step (Equation 4-11) involves a-priori assignment of a portion of the image voxels into two populations; and (2) the kriging step (Equation 4-12 to 4-17) where the kriging weights are calculated from the two point spatial covariance relation calculated using smoothed indicators. The linear combinations of weights and indicators are then used to calculate the probability of the unknown voxel belonging to either population.
As described in Oh and Lindquist (1999), in the thresholding step the threshold values can be chosen manually or by using entropy maximization algorithms. In the kriging step the indicators are smoothed to reduce the severity of the order relation errors. The two set of weights are calculated from the globally average covariance relations for each assigned population and hence the weights are globally averaged and need to be calculated only once. The same weights are used for all unknown voxels. Information on balancing of the negative weights and how to treat the voxels near the image boundaries can be found in the original paper by Oh and Lindquist (1999). Their algorithm also use two passes of a majority filter to remove the isolated voxels in the a-priori assigned population. In our implementation, we do not follow this approach since we have found that it introduces artifacts such as joining of separated particles and loss of thin features from the segmented image.

\[
Z(x) = \begin{cases} 
\Pi_0 & \text{if } z(x) \leq T_1 \\
\Pi_1 & \text{if } z(x) \geq T_2 \\
\text{Unassigned} & \text{Otherwise}
\end{cases}
\]  

(4-11)

\[
i(T_i; x) = \begin{cases} 
1 & \text{if } z(x) < T_i - S_i^l \\
0 & \text{if } z(x) > T_i + S_i^r \\
\frac{F(T_i + S_i^r) - F(z(x))}{F(T_i + S_i^r) - F(T_i - S_i^l)} & \text{Otherwise}
\end{cases}
\]

\[i = 0, 1\]  

(4-12)

\[S_0^l = S_1^r = 0 \text{ and } S_1^l = S_0^r = (\sigma_0 T_1 + \sigma_1 T_0)/(T_0 + T_1)\]  

(4-13)

\[
\sum_{j=1}^{n} \lambda_j C(x_k - x_j) + \mu = C(x_k - x_0) \quad k = 1, \ldots, n
\]  

(4-14)

\[
\sum_{j=1}^{n} \lambda_j = 1
\]  

(4-15)
\[
P(T_i; x_0 | n) = \sum_{j=1}^{n} \lambda_j(T_i; x_0) \hat{i}(T_i; x_j), \quad i = 0, 1
\] (4-16)

\[
Z(x_0) \in \begin{cases} 
\Pi_0 & \text{if } P(T_0; x_0 | n) > 1 - P(T_1; x_0 | n) \\
\Pi_1 & \text{otherwise}
\end{cases}
\] (4-17)

4.4 Results and Discussion

Here, we will demonstrate our methods on a three phase image of the size 350*350*350 (voxels) that contains quartz sand, a chlorinated solvent (tetrachloroethylene), and water that was doped with 8% KI. The imaging was performed at the GSECARS 13-BMD tomography beamline at the Advanced Photon Source at two X-ray energies: 33.07 keV (below the iodine absorption k-edge) and 33.27 keV (above the iodine absorption k-edge). The voxel resolution of the resulting images (Figure 4-1a&b) is 9.92 μm. Visual observation of the below edge image (Figure 4-1a) show three distinct phases. However, in the image histogram, the peaks for the oil and water phases are merged due to the large variance in the phase gray scale values. This makes the below edge image ideal for our study. The below edge image containing all three phases is primarily used in examples while the above edge image will be used for comparison of the final segmentation results.

The image was first subjected to the nonlinear anisotropic diffusion process to remove noise from the image and to separate the peaks in the image histogram. The effect of edge stopping parameter (K) on the images following application of the EED filter is demonstrated in Figure 4-2. We can see from visual inspection of the images that there is over smoothing of the image at higher user specified values of K (Figure 4-2c), resulting in blurring and loss of features, while lower values of K (Figure 4-2b) results in lower diffusive flux and require higher numbers of iterations to achieve satisfactory noise removal. The selection of the appropriate K values (faster
noise removal while still preserving the features) is an important consideration. Figure 4-2d shows the filtered image following the use of the automatic K selection and stopping criteria.

![Image of filtered images](image)

Figure 4-1: Section of the image acquired at two energies above and below the Iodine absorption K edge. (a) Below edge image at energy 33.07keV, (b) Above edge image at energy 33.27keV, (c) Histogram of the below edge image and (d) Histogram of the above edge image.

The smallest eigen values averaged over all the voxels from the original image is used as K and the confidence level of 0.75 is used as the stopping criteria. Figure 4-3 shows filtered images produced using the three diffusion functions described earlier in this study, all with automatic K selection and stopping criteria of a confidence level equal to 0.75. Visual observation of the resulting noise free images show that each diffusion filter tested removes noise from the image effectively without over smoothing the edges. The enhanced peak separation and emergence of the oil phase peak (which was initially merged with the water phase peak) following application
of the three filters is shown in Figure 4-4. Equilibration of grayscale values in each of the phases is also visible with a reduction in the variance of each peak. In addition, the smoothness of the histograms ensures that entropy maximization algorithms find the true global minima if automatic threshold selection algorithms were to be used.

Figure 4-2: Section of the image showing the effect of edge stopping parameter (K) using EED filter: (a)Original below edge image, (b) K=10 after 10 iterations, (c) K=50 after 10 iterations, and (d) K selected automatically using the average of the lowest eigen value, and stopping criteria 0.75 was also applied. Results achieved in 3 iterations. All images are of size 350*350*350, resolution 9.92μm/voxel.

Once the original image (Figure 4-5a) was processed with the anisotropic diffusion program, most of the isolated noise voxels in the homogenous regions of the image were smoothed to the
neighborhood grayscale values (Figure 4-5b) and the image could now be segmented using
threshold-based techniques. Figure 4-5c and Figure 4-5d show the images after application of
simple thresholding to segment solids from the below edge image. The image thresholded
following anisotropic diffusion shows a significantly lower number of noise voxels compared to
the segmented image, thus negating the need to employ post-segmentation noise removal
schemes such as the majority filter.

Figure 4-3: Section of image showing the results of noise smoothing with nonlinear anisotropic
diffusion using three diffusion filters: (a) Original below edge image, (b) Edge Enhancing
Diffusion, (c) Coherence Enhancing diffusion, and (d) Hybrid Filter. All images are of size
350*350*350, resolution 9.92µm/voxel.
Figure 4-4: Histogram showing the use of three diffusion filters and peak separation.

From the histogram of the filtered image (Figure 4-6b), there are a range of values between two peaks, and in the filtered image these values lie mostly at the phase boundaries. Hence a single threshold value cannot be used for the segmentation of phases. Here, we use an indicator kriging-based algorithm, which uses two threshold values for the partial segmentation of the image into two phases and grayscale values between the two thresholds are assigned to either of the phases using the kriging statistics. The threshold values are manually chosen from the image histogram and visual observation. Indicator kriging is designed mainly for data with two univariate peaks (e.g., two phases in a grayscale image). In our segmentation scheme for the three phase image, we choose firstly to segment the phase that results in a smaller standard deviation on either side of the chosen threshold values. For example, thresholding the solid phase (the right peak in Figure 4-6b) results in a standard deviation of 11.98 on the left of the lower threshold value in the histogram; the segmentation of the oil phase (left peak) results in a standard deviation of 16.78 on the right of the higher threshold value in the histogram. Hence we choose the one with the lower standard deviation to be segmented first, which in this example
represents the solid phase (Figure 4-6d). In the second pass, the segmented image is subtracted from the clean gray scale image so that the range of grayscale values in the image represents only the two fluid phases (Figure 4-6e). The segmented solid phase in the image is not used to calculate the two point covariance correlation, and during the probability calculation, the segmented part is treated as the boundary with an indicator value of 0.5. The resulting segmented image (Figure 4-6f) contains all three phases: oil, water, and solids.

Figure 4-5: Section of the image showing the results of simple thresholding test (a) Original below edge image (b) clean below edge image (EED) (c) Simple threshold results showing misclassified voxels in the original image (d) simple threshold results showing the smoothing of noise voxels using anisotropic diffusion. All images are of size 350*350*350, resolution 9.92μm/voxel
Figure 4-6: Section of the image showing the Indicator Kriging segmentation for 3 phase image. (a) Noise free below edge image processed using EED) (b) Image histogram showing threshold values selected for the solid phase (c) Partially threshold image: White-solid, Black-Rest of the image containing Oil and Water, Gray-Unassigned voxels (d) Segmented image showing solid (White) and rest of the image (Black) (e) Solid subtracted from the clean grayscale image (f) Fully segmented three phase image: White-Solid, Gray-Water and Black-Oil phase All images are of size 350*350*350, resolution 9.92μm/voxel
To compare the results of peak separation obtained in the below edge image using anisotropic diffusion and our scheme of three phase segmentation using Indicator kriging, we can compare the image to that obtained using both above- and below-edge images. The above-edge image is also subjected to anisotropic diffusion using EED (automatic selection of K and stopping criteria 0.75) and the indicator kriging program is used for segmentation of the oil phase from the rest of the image. The solid phase is segmented from the filtered below-edge image using indicator kriging and the resulting images are combined to obtain the segmented three phase image. The comparison shows the effectiveness of our scheme to segment the three phases from the low contrast three phase image (Figure 4-7).

![Figure 4-7: Section of the image showing the comparison with the segmentation using the above edge image](image)

(a) Segmentation result from below edge only (Solid 57.508%, Water 35.436% and Oil 7.056% of image)
(b) Segmentation results using the both above and below edge image (Solid 57.508%, Water 39.395% and Oil 7.097% of image). All images are of size 350*350*350, resolution 9.92μm/voxel

4.5 Conclusion

Nonlinear anisotropic diffusion effectively removes noise from porous media images and preserves the local structure in the data. All the filters tested have shown effective noise removal without blurring the edges when used with an appropriate edge stopping parameter and stopping
criteria. Manual selection of an edge stopping parameter is difficult in the low contrast multi-
phase images, but automatic selection by eigen value analysis provides effective noise removal.
The peak separation and reduction in the grayscale variance of each peak increases the accuracy
of the image segmentation. Indicator kriging designed for two-phase image segmentation can be
adapted for the segmentation of three-phase images. A comparison with above- and below-edge
images show that this segmentation approach is effective and should prove useful for separating
phases in XCT images where absorption edge imaging is not an option.
CHAPTER 5 IMAGE BASED PORE NETWORK GENERATION

5.1 Introduction

Flow in porous media occurs in engineering applications such as oil recovery, flow in packed bed reactors, membrane separations, and subsurface solute transport. While Darcy’s law or similar approaches can be used for modeling flow at the continuum scale, the accuracy of such simulations requires correct estimation of one or more parameters such as porosity, heterogeneity, relative permeability, capillary pressure relationships, etc. These parameters are typically measured experimentally. However, microscale simulations are becoming increasingly viable methods for obtaining this information. The most fundamental approach is direct solution of the equations of motion in the pore space using an approach such as the finite element, finite volume, or lattice Boltzmann method. If performed on a sufficiently large domain, then information such as fluid flowrates, pressure gradients, or solute distributions can be used to determine relevant macroscopic parameters. The large computational cost associated with these methods can reduce the effectiveness of these techniques because of time and/or size limitations.

Network modeling is an alternative technique for pore-scale flow modeling, which is less rigorous than the aforementioned methods but is dramatically more efficient computationally. In network modeling, the pore space is discretized into pores and connecting pore-throats. A mass balance is imposed at each pore, and flow through the pore throats is approximated by one-dimensional Poiseuille-type equations. The consequence of this coarsening of the pore space is that sub-pore phenomena cannot be simulated directly; however, network modeling allows flow to be modeled over orders-of-magnitude larger physical domains. Network model simulations have been used to study processes such as imbibition (Fenwick and Blunt 1998; Gladkikh and Bryant 2005), drainage (Blunt et al. 1992; Fenwick and Blunt 1998), single phase and relative permeability computation (Bryant and Blunt 1992; Oren and Bakke 2002), the effects of pore
structure on relative permeability (Bryant and Johnson 2003; Al-Kharusi and Blunt 2008), capillary pressure behavior (Fatt 1956; Silin and Patzek 2006; Al-Kharusi and Blunt 2008), residence time distributions (Thompson and Fogler 1997), dispersion (Sahimi et al. 1986), measurement of interfacial area and fluid phase distribution (Dalla et al. 2002), relationships between non-wetting phase distributions and pore geometry (Hilpert et al. 2000), non-Newtonian flow in packed beds (Balhoff and Thompson 2004), and with continuum models in a multiscale framework (Balhoff et al. 2007; Balhoff et al. 2008).

The predictive capability of network models depends on the process being modeled, the assumptions made in approximating the fluid mechanics, and how well the network structure depicts the actual geometry and topology of the real porous media. With the widespread use of non-destructive 3D imaging and the development of image-based modeling techniques, there is increased interest in using network models in a predictive sense (in contrast to studies which aim to uncover qualitative phenomenological behavior). However, apart from comparisons to selected bulk parameters measured by experiment, there is surprising little information available about the performance of network models in a quantitative and/or predictive sense.

One of the key difficulties in image-based network modeling is the ambiguity in the physical or geometric definition of what is termed a pore or pore throat in various types of materials. This ambiguity prevents the development of a universal definition of network structure. Consequently, multiple network structures can be created for the same material or 3D data set and there exists no straightforward way to define whether one network is more correct than another (without validation from a rigorous sub-pore-scale model).

In this paper we examine the structure of different networks that are created from the same set of porous media and quantify the impact of these differences on selected network model
simulations. Three materials are used: a random packing of spheres, a random packing of non-spherical grains, and a random packing of cylinders. All three materials were imaged using XCT, thus providing detailed 3D structural data. Image-based network models were created using in-house algorithms, and the differences in network structure, single-phase flow, and quasistatic displacement were studied in an effort to quantify the impact of variations in network structure.

5.2 Background

5.2.1 Network Modeling

The earliest network models are attributed to Fatt (1956) and consisted of highly simplified two-dimensional networks of tubes arranged on square or hexagonal lattices. The networks had fixed coordination number and the pores were located at the intersection of the tubes but were considered to have no volume. Experimentally obtained pore-size distributions were imposed onto the networks by randomly assigning the tube size distribution. Later, Chatzis and Dullien (1977) reported that three-dimensional networks of tubes differ substantially from 2D networks for immiscible displacement and the breakthrough condition for multiphase flow depends on the interconnectivity and dimensionality of the network. Similar models have since been used to simulate two- and three-phase imbibition and drainage (Blunt et al. 1992; Blunt et al. 1994; Fenwick and Blunt 1998). To create more realistic networks, connectivity is often varied by randomly removing bonds from the underlying lattice structure. Pore-size distributions can be assigned based on experimental porosimetry results (e.g., Wardlaw et al. (1987), who decorated networks using pore and pore-throat size correlations measured from Berea sandstone).

A second generation of network models was developed beginning with Bryant et al. (1993; 2003) in which the network is mapped directly from the void structure in a three-dimensional packing instead of creating a statistically equivalent network on a lattice structure. This approach
can be used with actual materials if the detailed particle structure is available (Bryant et al. 1993) or on computer generated materials (Thompson and Fogler 1997; Al-Raoush et al. 2003; Hilpert et al. 2003). The advantage of physically representative networks is that pore-scale spatial correlations are incorporated into the network (which are most likely missed if a statistical approach is used). Additionally, because the network is a direct mapping of a well-defined 3D structure, it reduces the ability to incorporate adjustable parameters into the model.

More recently, a third-generation of network modeling has evolved in which the network is mapped directly from a high-resolution digital map of a porous medium. This approach has the same advantages described in the previous paragraph (incorporation of spatial correlations, elimination of adjustable parameters). However, it is much more flexible in that it can be applied to essentially any type of pore structure rather than only those that can be described in simple geometric terms, such as a packing of spheres. The digital data can be obtained from either computer-generated or real structures. The former approach represents a unique tool for material design; the latter approach, termed image-based network modeling, offers obvious appeal because of the opportunity to study real materials. 3D images of real porous media can be obtained using serial sectioning (Lymberopoulos and Payatakes 1992; Silin and Patzek 2006; Jiang et al. 2007), which can give very high resolution in the plane of the slices but is destructive and less amenable to automation. Hence, the more popular approaches are non-destructive imaging techniques such as XCT (Petrovic et al. 1982; Spanne et al. 1994; Auzerais et al. 1996; Al-Raoush and Willson 2005; Al-Raoush and Willson 2005; Ruffino et al. 2005; Neethirajan and Jayas 2008), MRI (Baldwin et al. 1996; Botto et al. 1996; Kose 1996; Pauli et al. 1997), and confocal microscopy (Mickel et al. 2008). Resolution in these techniques typically ranges between 0.1 to 100 microns, and the final data sets provide quantitative descriptions of the pore structure in a wide range of porous media.
5.2.2 Image-Based Network Generation

Transforming the voxel description of the void space into a network is a challenge for a number of reasons. In the original data, the void space can be described by upwards of one billion voxels on a regular grid, whereas the network is an unstructured grid with orders of magnitude fewer discrete elements. Additionally, this transformation from voxels to a pore network must be performed in a way that retains the essential features of the pore structure, despite the fact that no definitive rules have been established for how to discretize the continuum void space into a series of pores and pore throats.

The various algorithms proposed in literature for extracting pore networks from 3D images fall into two broad categories: skeletonization algorithms and geometric algorithms. Skeletonization algorithms typically employ a voxel-scale approximation of the medial axis to create a graph of the pore space. Pores are placed at the nodal junctions of the skeleton and pore throats are defined by the curved elements of the skeleton that connect these nodes. The skeleton is decorated with network parameters such as pore sizes, which define the pore morphology. This approach has been used to calculate single phase permeability (Prodanovic et al. 2007), and model multiphase effects such as capillary pressure curves and relative permeability and other multiphase phenomena on sandstone and carbonate rock images. Alternatives to the medial axis include geometrical thinning or hybrids of the two techniques (Saito and Toriwaki 1994; Pudney 1996, 1998; Jiang et al. 2007; Prodanovic et al. 2007).

The other major approach to network generation uses some type of geometric analysis to define pore locations, and then builds the network structure from this information. Prior to the development of voxel-based techniques, the Delaunay tessellation (Bryant et al. 1993; Thompson and Fogler 1997) or a modified Delaunay tessellation (Al-Raoush and Willson 2005) were used to define both pores and network interconnectivity. Delaunay-based techniques have been used
to study packed beds and natural porous media, including phenomena such as dynamic and quasi-static imbibition (Gladkikh and Bryant 2003, 2005, 2007), interfacial area (Gladkikh and Bryant 2003), drainage (Thompson and Fogler 1997), and relative permeability (Bryant and Blunt 1992). Al Roush et al. (2003) compared pore structural properties of networks using medial-axis-based transforms versus modified Delaunay tessellation schemes on computer generated regular and random packing of spheres, and found that the modified Delaunay tessellation results closely match the theoretically calculated parameters. Silin and Patzek (2006) proposed a voxel-based maximum-inscribed sphere approach to map pore network structures. Thompson et al. (2008) developed a Delaunay-based method that can be used with voxel data if the locations of particles in a packing are known. Al-Kharusi and Blunt (2007, 2008) have used the maximal inscribed sphere technique developed by Silin and Patzek (2006) to generate networks from tomography image of sandstone and other natural rocks, and modeled two- and three-phase relative permeability and capillary pressure curves.

One of the problems in network generation and network modeling is the lack of a specific definition for what constitutes pores and pore throats in real materials with complicated pore geometries, combined with our limited knowledge about how differences in the discretization affects network modeling. The purpose of this work is to examine a series of significantly different network structures (generated from real materials) in an effort to begin understanding the sensitivity of network models to varying types of discretization. It should be emphasized that the goal is not to compare skeletonization versus geometric techniques; all networks discussed below are created using geometric-based algorithms.
5.2.3 Grain-Based Algorithm

The grain-based approach for network generation is a two step process: 1. computationally reconstruct particles from the XCT image; 2. use the particulate structure as a template to create the pore and pore-throat network. The rationale for this approach is that pores are formed by clusters of grains or particles in an unconsolidated granular material. Hence, using particles as a template ensures that the correct characteristic scale is used to define the pore structure.

The grain reconstruction step is performed by an algorithm called vox2grains. It transforms a binary image (e.g., solid-phase voxels equal 1; void-phase voxels equal 0) into a grain-scale map in which each solid-phase voxel is tagged with the grain number to which it belongs. Grain identification is a non-trivial procedure for most any material except idealized sphere packings. The algorithm uses a combination of erosion followed by nonlinear optimization to search for the maximal inscribed sphere that is contained inside each grain. Once the grain centers are located (which correspond to the locations of the maximal inscribed spheres, not the centers of mass of the grains), voxels belonging to that particular grain are collected from the center moving outward using a variant of the watershed algorithm. Details can be found in Thompson et al. (2006). Once every solid-phase voxel is tagged with its respective particle number, any particle or grain in the packing can be reconstructed from the digital image simply by retrieving the corresponding cluster of voxels. This approach allows a number of physical properties of the material to be computed, including total particle surface areas, fraction of surface areas exposed to the void phase, number of grain-grain contacts and the surface area of these contacts (limited by voxel resolution), grain volumes, grain orientations, grain locations, and grain aspect ratios.

The second step in the grain-based network-generation process is to create the pore and pore-throat map of the void space using the granular structure of the material as a template. For sphere packings and other materials made from compact grains, clusters of four or more particles create
pores in the void structure. This same particle cluster that forms a pore also has smaller gaps that lead into and out of the central pore (which are pore throats). Hence, using the granular structure as a template for the network structure is a more physically appealing approach than working directly from the voxel map itself. Mellor (1989), Bryant et al. (1993), and Thompson and Fogler (1997) have used the Delaunay tessellation as a mathematical tool for transforming the continuous, interconnected void space in a sphere packing into a discrete set of pores and pore throats. This approach was modified by Al-Raoush et al. (2003) to allow more flexibility in the network structure, including variable pore coordination numbers (as opposed to the fixed value of four that is dictated by the Delaunay tessellation). In the current approach, the modified Delaunay tessellation (MDT) approach is used in an implementation that operates on voxel images. In summary, it is comprised of four steps:

1. The Delaunay tessellation (operating on the granular structure in the material) is used to locate possible locations of pores.
2. The pore locations are confirmed and refined using a non-linear optimization procedure that locates maximal inscribed spheres in the void space.
3. Voxels belonging to a given pore are collected by moving from the center outward using a watershed-type algorithm.
4. The pore-network structure is created from the tagged voxels in the pore space.

Parameters that describe the pore network include inscribed pore radii, pore volumes, throat radii, throat cross-sectional areas, throat surface areas, throat wetted perimeters, throat hydraulic conductances, and of course the connectivity of the network itself. More details about how the grain-based network generation algorithm is applied to real materials can be found in Thompson et al. (2008).
5.2.4 Voxel-Based Algorithm

The algorithm described in the previous section can be applied to unconsolidated granular or particulate materials. However, it is not designed to operate on many other types of materials including fibrous materials, carbonates, highly consolidated materials, or solid foams. In these situations, the only viable approaches at present are voxel-based network generation techniques.

In this work we use an algorithm called vox2net, which creates a pore-network mapping of the void space directly from a binary (phase segmented) voxel image. Because the grain identification and Delaunay tessellation process cannot be used as a template, the main difference in the voxel-based algorithm is identification of pores. Once the set of maximal inscribed spheres is found, the network generation process is completed in the same way as it is with the grain-based algorithm.

As with the grain-based algorithm, each pore is characterized by a maximal inscribed sphere (i.e., a hypothetical sphere that is constrained from both movement and growth by its contact with surrounding solid phase). In all cases, we find the maximal inscribed spheres using the same nonlinear optimization process used with the grain-based algorithm. However, because this optimization procedure is computationally expensive, we have devised a number of different schemes to define subsets of seed voxels from which to run the optimization. In the present work, we employ three approaches:

Perform a voxel burn (Lindquist et al. 1996; Lindquist and Venkatarangan 1999) or erosion process in the void phase to define voxels that are local maxima in the distance function (from the surface). These voxels are viewed as potential (or at least near) locations for pore centers. This approach is designated VB1 below. Use all void-phase voxels as potential seeds for the nonlinear optimization, but eliminate all voxels that are contained inside a maximal inscribed
sphere once is it found. The premise for this approach is that other seed locations from inside a
given maximal sphere would likely converge to the same location. Because these spheres occupy
a significant fraction of the total void volume, this approach is dramatically faster than using
every voxel as a seed. This approach is designated VB2 below. Use all void-phase voxels as
seeds for the nonlinear optimization. This approach is slow but comprehensive. It is designated
VB3 below.

Unfortunately, there is no easy way to determine whether one approach is more correct than
another. For a sphere packing, there exists a finite number of maximal inscribed spheres, which
can all be located by a simple search procedure. However, for non-spherical particles, this set can
increase significantly. Furthermore, when particles are described by a voxel image, the particle
surfaces are not defined exactly, which can compromise the accuracy of the processes. In
general, the number of maximal inscribed spheres (and their locations) that are fed to the
network generation algorithm are determined by the method used to locate them and how
aggressive the merging process is for overlapping spheres. Once the set of maximal inscribed
spheres is found (and any merging procedures are applied), the network is constructed in the
same manner as with the grain-based algorithm (see steps 3 and 4 in the procedure outlined in
the previous section).

5.3 Materials and Methods

Three types of packing materials were chosen to create the porous media: (i) smooth soda-
limed glass spheres (250-297 microns, Mo-sci specialty products LLC); (ii) sand particles of
similar size as the spheres but with more irregular grain shapes (210-297 microns, Accusand,
Unimin corporation); (iii) cylinders that were packed randomly to create a simulated high-
porosity fibrous material (diameter 90-100 microns and aspect ratio 10-20, Mo-sci specialty
products LLC). The random packings were created by adding the packing media into plastic columns, and then shaking the columns using a vortex mixer to help remove macroscopic heterogeneity (the goal being to obtain microscopically heterogeneous but macroscopically uniform packings). The columns were imaged using synchrotron XCT to obtain three-dimensional gray-scale images (energy 35 keV and resolution 6.603µm/voxel; see acknowledgements for imaging facilities). Internal sections of the 3D images of size 350×350×520 were selected from the centers of the columns to avoid wall effects. A combination of anisotropic diffusion and indicator kriging was used for image segmentation (Bhattad et al. 2010). A non-linear anisotropic diffusion algorithm was used for image de-noising (Frangakis and Hegerl 2001; Weickert and Scharr 2002; Scharr and Spies 2005) and the modified gray-scale images were segmented using an indicator-kriging thresholding algorithm similar to Oh and Lindquist (1999) to obtain binary images containing void and solid phases. The phase-segmented data are shown in Figure 5-1. From each segmented image, four networks were created. Network properties were computed after cropping a length of one particle diameter from all sides of a network structure to avoid including information associated with partial pores at the network surfaces.

Figure 5-1: Segmented image of packings. left to right: spheres, sand and cylinders. Image size = 350×350×520. Resolution = 6.603µm/voxel side.
5.4 Pore Networks

Four networks were generated from each of the XCT images (spheres, sand, and cylinders). One network from each XCT image was generated using the grain-based approach. The other three were created using the more general voxel-based approach, which is not limited to granular materials. The differences between the latter three networks is the methodology used to locate pores. Varying the pore search technique causes more than two orders of magnitude variation in the number of pores, which in turn leads to differences in other network parameters. Specific parameters used in the network-generation process are given in Table 5-1. Thin cross sections of four different networks (from the sphere pack) are shown in Figure 5-2 using stick-and-ball depictions.

Due to excessive computation times for the VB2 and VB3 networks in the high-porosity cylinder packs, the cylinder data were cropped to 150×150×150 size and all four networks were generated from the smaller image for consistency in comparison. The smaller networks were tested against the larger networks for GB1 and VB1, and these tests indicate the 1503 data were sufficient to generate representative volumes (see the Section 5.8).

Table 5-1: Parameters used in the generation of four networks.

<table>
<thead>
<tr>
<th></th>
<th>GB1</th>
<th>VB1</th>
<th>VB2</th>
<th>VB3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algorithm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain-based</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voxel-based</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Pore Search Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tessellation of grains</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burn maxima</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Subset void voxels</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>All void voxels</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Burn Coordination number</td>
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</tr>
<tr>
<td>Merge Criteria</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Center contained</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Throat connections</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All connections</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
5.4.1 Network GB1

For the two particulate materials, the grain-based approach is expected to create a physically representative network with the appropriate characteristic scales because the network is built using the granular structure as a template. For the cylinders, there is no physical basis for using this algorithm, but it is used nonetheless for the purpose of comparison. (It should be noted that while the grain reconstruction and tessellation process are used to define seeds for locating pores, the final pore locations are defined using the XCT data. Hence, even with the cylinder packing, the network pores are indeed maximal inscribed spheres in the image.) For all three materials, pairs of pores are merged if the center of one pore is contained inside a neighboring pore.

Figure 5-2: Ball-and-stick representation of section of pore networks generated using the sphere-pack data.
5.4.2 Network VB1

All three VB networks are created using the voxel-based approach. For network VB1, pore seeds are identified from the local maxima in the local void-phase-burn number, and the nonlinear optimization algorithm refines these initial seeds so that pores correspond to maximal inscribed spheres. Pairs of pores are merged if the center of one pore is contained inside a neighboring pore. Because the burn maxima is a somewhat “quick and dirty” method for locating potential pores, this algorithm runs quickly and it results in the lowest pore density of any of the networks studied here. Because the algorithm does not rely on discretization of the solid phase into individual grains, it is appropriate for both the particulate and fibrous materials.

5.4.3 Network VB2

For the VB2 network, every void-phase voxel is a potential seed for the nonlinear optimization procedure that locates maximal inscribed spheres. However, to save computation time, each time a maximal sphere is located, the voxels inside this sphere are removed from the list of possible seeds (the rationale being that most of these voxels would lead to the same maximal inscribed sphere, thus creating redundancy in the search). This strategy creates a medium-density network. It is slower than the VB1 approach, but dramatically faster than using every void-phase voxel as a potential seed. As with the previous two approaches, pairs of pores are merged if the center of one pore is contained inside a neighbor.

5.4.4 Network VB3

To create the VB3 network, every void-phase voxel is used as a seed to locate maximal inscribed spheres. Additionally, every unique maximal inscribed sphere (pore) is retained, regardless of the degree of overlap with a neighboring pore. This strategy produces the maximum pore density of any combination of parameters in our set of algorithms, which typically results in overlapping spheres that form caterpillar-like structures that wind through the
pore space (see Figure 5-2d). This network generation process is very slow. It should also be noted that the large number of unique maximal inscribed spheres are due in part to the approximate distance functions that must be used in a voxelized structure, combined with the staircase-like surfaces that are found in any voxel-based data set.

All of the above algorithms differ only in how the pores are located. The subsequent network generation process (i.e., defining network structure by connecting the pores and computing pore geometric parameters) is the same for all networks, as summarized above and described in more detail elsewhere (Thompson et al. 2008).

5.5 Results and Discussion

The networks were analyzed using three different comparisons: physical structure, single-phase flow (permeability), and quasi-static drainage (which generates the primary drainage branch of a capillary pressure curve).

5.5.1 Network Structure

Figure 5-2 and Figure 5-3 are ball-and-stick representations of thin sections of selected networks, which provide qualitative insight into the different structures. The balls in the images are the maximal inscribed spheres associated with each pore. The sticks simply denote pore-throat connections between pores; no attempt is made to denote pore-throat diameter in these illustrations. The images shown are thin sections of the 3D networks, which allows easier visualization of the network structure. Average network properties are given in Table 5-2 and are discussed below.
Figure 5-3: Ball-and-stick representation of section of pore networks.
Table 5-2: Physical properties of pore networks generated from the sphere, sand and cylinder data.

<table>
<thead>
<tr>
<th></th>
<th>Sphere</th>
<th>Sand</th>
<th>Cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GB1</td>
<td>VB1</td>
<td>VB2</td>
</tr>
<tr>
<td>Domain Volume</td>
<td>1.83E10</td>
<td>1.83E10</td>
<td>1.83E10</td>
</tr>
<tr>
<td>Before cropping</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Domain Volume</td>
<td>1.03E10</td>
<td>1.03E10</td>
<td>1.03E10</td>
</tr>
<tr>
<td>Before cropping</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity before</td>
<td>35.50</td>
<td>35.50</td>
<td>35.50</td>
</tr>
<tr>
<td>Porosity after</td>
<td>34.76</td>
<td>34.67</td>
<td>34.85</td>
</tr>
<tr>
<td>Number of</td>
<td>654</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Particles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle radii</td>
<td>125.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of</td>
<td>3243</td>
<td>2363</td>
<td>35403</td>
</tr>
<tr>
<td>Pores</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. Pore</td>
<td>1.11E06</td>
<td>1.52E06</td>
<td>1.02E05</td>
</tr>
<tr>
<td>volume</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coordination</td>
<td>5.95</td>
<td>5.98</td>
<td>5.34</td>
</tr>
<tr>
<td>Number</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inscribed</td>
<td>41.77</td>
<td>39.92</td>
<td>16.63</td>
</tr>
<tr>
<td>Pore radii</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inscribed</td>
<td>27.12</td>
<td>25.90</td>
<td>14.80</td>
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<tr>
<td>Throat radii</td>
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<td></td>
</tr>
<tr>
<td>(µm)</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>0.13</td>
</tr>
<tr>
<td>Inscribed</td>
<td>0.22</td>
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<td>0.12</td>
</tr>
<tr>
<td>Pore Radii</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dimensionless</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inscribed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Throat Radii</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimensionless</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore/Throat</td>
<td>1.54</td>
<td>1.54</td>
<td>1.12</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

64
5.5.1.1 Pore Density

As shown in Figure 5-2 and Table 5-2, varying parameters in the network-generation algorithms results in pore densities (number of pores per unit volume) that span more than two orders of magnitude. Because no definitive rules exist for discretization of a network into pores and pore throats, choosing whether one network generation scheme is more appropriate than another is largely speculative (at least until the modeling community begins to accumulate additional data about these effects). Furthermore, the decision about which network is best will depend on the situation. For instance, if the network model is to be used for characterization (pore size distribution, pore coordination number, etc.), one might argue that the high-pore-density structure shown in Figure 5-2d is not consistent with our typical view of pores and pore throats. However, if the network structure is viewed as nothing more than a numerical discretization scheme for flow modeling, then the best network should be the one that provides the best accuracy, irrespective of whether it has representative pore-size distributions or coordination numbers. Finally, it should be emphasized that the ability to define strict discretization rules depends largely on the type of data describing the porous medium. For example, computer-generated packings of spheres and cylinders give exact description of the void space, and each of these packings has a finite number of maximal inscribed spheres (Zhang 2006). This fact might be used to place an upper bound on pore density. However, voxel-based data introduces error into the description of the void-space geometry, which gets passed on to computations, such as the medial axis or the location of maximal inscribed spheres.

For the glass spheres and the sand, an argument can be made that the GB1 networks are physically reasonable because the pore locations are derived from a Delaunay tessellation of the grain locations, which is an accepted method for discretizing the pore space in granular materials.
These networks contain 4.96 and 6.50 pores/particle for the sphere pack and sand pack, respectively. These values are lower than the strict Delaunay pore densities because of the merging process. Pore densities for the VB1 network, which relies on the burn maxima to locate pores, are 15 to 30 percent lower than GB1 network (the voxel-based medial axis should produce similar numbers). However, pore densities are order $10\times$ and $100\times$ higher for the VB2 and VB3 networks respectively because they employ direct searches of the void voxels to identify maximal inscribed spheres. For the sand (which has irregular grains), it is likely that some of these additional pores are true maximal inscribed spheres (constrained by the grain structure); however, a significant fraction may be constrained numerically because of the approximate distance function computations that must be made using voxel data.

The trends for the cylinder packing are similar: the VB1 network gives the lowest pore density and the range spans approximately two orders of magnitude. The GB1 data are shown for completeness. However, because this algorithm is designed for use with granular materials, the data cannot be used as a baseline for comparison as it was with the spheres and sand.

Finally, we note that the network porosity is correct for all materials (and is independent of pore density) because the volume assigned to each pore is computed independently of the size of its associated maximal inscribed sphere. For some pore/network combinations, the volume of a pore will be larger than the volume of the maximal sphere. For other pore/network combinations the reverse would be true.

### 5.5.1.2 Pore Radius

Pore radius is calculated using the maximal inscribed spheres that are associated with each
pore. The pore-size distribution for the sphere pack is shown in Figure 5-4 for each of the networks. Average pore sizes are reported for all materials and all networks in Table 5-2. As expected from visualization of the networks, the GB1 and VB1 networks give very similar pore size distributions for the granular materials. The distribution in the very high density network is shifted toward smaller pores, which is consistent with the ability to find smaller maximal inscribed spheres from a complete voxel search (as opposed to burn maxima or the Delaunay tessellation, both of which will identify the largest pore spaces). The most interesting differences are for the VB2 network, which show markedly different pore size distributions and average pore sizes. The reason for the difference is that the VB2 network is created from a direct voxel search for maximal inscribed spheres. But, once a sphere has been found, no voxels that lie inside that sphere are used for additional searches. The result is that the dramatic increases in pore density (~10× in moving from the VB1 to the VB2 networks) were created mostly by the addition of small pores, which were found by exploring the void voxels in the tighter void spaces. This effect shifts the number-average pore size downward (Table 5-2) and the pore-size distribution to the left (Figure 5-4).

These differences are evident in visualizations of the network structures. Comparing the VB1 and VB2 networks in Figure 5-2, notice that the networks share many of the same large “anchor” pores. In the lower-density network, these anchor pores are connected via single pore throats. In the higher-density VB2 network, these anchor pores are connected via strings of small pores. (In further contrast, the very high density networks contain large numbers of both small and large pores, so the entire void space is filled with caterpillar-like strings of spheres.) While the VB2 and GB1 networks have significantly different pore-size distributions and network structures, it is not possible to declare one more correct than another, at least in the absence of a strict
definition for a pore. In fact, it is likely that one network may be more appropriate for some
applications and another network more appropriate for others.

5.5.1.3 Throat Radius

Throat radius is calculated as the radius of the maximal inscribed sphere whose center lies on
the surface separating two pores. (Pore throats have no volume in our network scheme; therefore
the volumes assigned to any two neighboring pores meet at a surface that in principle should be
at the tightest constriction in the connecting passage.) For granular materials, the throat size
distributions for three of the four networks are essentially same (Figure 5-4), despite the orders
of magnitude difference in the number of throats. The one network structure with a different
distribution is the VB2 network. For the fibrous material, the throat size distributions are not as
consistent across networks as evidenced by the values in Table 5-2, which shows that the high
density network has a larger average throat size. This effect is attributed to the large fraction of
overlap between maximal inscribed spheres in the more wide open pore space in the cylinder
packing.

5.5.1.4 Pore Coordination Number

The pore coordination number is the number of pores that are directly connected to a given
pore. Determining the pore coordination number from voxelized image can be challenging
because the pore boundaries are represented by the Cartesian voxel system, which does not allow
for simple surfaces between pore boundaries. This problem is further complicated by a
dependence on the voxel resolution, by the range of pore geometries found in natural porous
media, and by the network bonds not being aligned with the Cartesian voxel geometry.

The distributions of pore coordination numbers are shown in Figure 5-4. The mean values for
three of the networks are similar to the mean value determined for granular materials using other techniques (Yanuka et al. 1986; Jerauld and Salter 1990; Al-Raoush et al. 2003). The high-density network exhibits larger values due to the overlap between pores. The tails of the distributions contain coordination numbers that are larger than one might expect from a geometric standpoint. This is caused partly by large pores (which naturally can link to a larger number of small neighbors). It is also a consequence of voxel-based network generation algorithms; similar results have been reported anecdotally for network-generation algorithms from other research groups.

Figure 5-4: Comparison of structural properties of pore networks generated from the sphere-pack data: (a) pore size; (b) pore-throat size; (c) pore-throat length; (d) pore coordination number.
5.5.2 Single-Phase Flow

Permeability is a spatially averaged parameter that quantifies the macroscopic hydraulic conductance of a porous medium, and is the most basic parameter associated with flow. Consequently, permeability prediction is one of the primary objectives of predictive image-based modeling. In network modeling, the permeability is governed by the hydraulic conductance values assigned to each pore throat, along with the way in which these pore throats are interconnected. Hence, it is difficult to imagine that varying the pore or pore-throat density by two orders of magnitude would not have some adverse effect on permeability prediction.

It should be noted that the main goal in the current work is not to validate the quality of permeability predictions. Instead, it is to understand how different network structures created from the same materials affect permeability. However, for reasonably simple structures, such comparisons can be made using empirical equations. These values are reported with the permeability values (Table 5-3) for the sake of comparison, simulations are performed for low-Reynolds-number single-phase flow. Constant-pressure boundary conditions are applied on opposing faces of the network and no flow boundary conditions are applied on the remaining faces. The flow rate $q_{i,j}$ between pore i and j is described using Equation (5-1). The term $g_{i,j}$ is the hydraulic conductance between pore i and j. Imposing mass conservation for each pore using Equation (5-2) creates a system of algebraic equations that can be solved for pressure in each pore. The pressure field can be used to solve for flow between individual pores as well as total flow rate through the network for the applied pressure gradient. This allows permeability to be predicted using the one-dimensional form of Darcy’s law (Equation 5-3).

$$q_{i,j} = \frac{g_{i,j}}{\mu} (P_j - P_i) \quad (5-1)$$
This procedure was repeated with pressure applied to the other two pairs of opposing faces, thus giving permeabilities along the principal coordinate axes. No significant variations in these directional permeabilities were observed for the granular materials (spheres and sand). For the cylinder packing, permeability is anisotropic. It is dominant in the x direction, somewhat reduced in y (7-21% smaller values depending on the network), and significantly reduced in z (35-54% smaller values). This suggests a horizontal alignment of fibers, as would be expected.

In order to use Equation (5-1), hydraulic conductances must be assigned to each pore throat in the network. In the past, networks were decorated with hydraulic conductances that were selected randomly from mathematical distributions. However, for image-based modeling, the hydraulic conductances are physical quantities associated with a region of the pore space, and therefore must be estimated from local pore geometry. Many equations have been proposed for this task, which use various combinations of pore and pore-throat radii, pore or pore-throat surface areas, throat cross-sectional areas, throat lengths, shape factors, etc. We have selected three different equations to use in the current study: a single-parameter model (Equation (5-4)), two-parameter model (Equation (5-5)), and three-parameter model (Equation (5-6)). The Ewing-Gupta equation is a function of pore radii only. The Byrant-Blunt equation is a function of both pore-throat radius and length. The Thompson-Fogler equation is a function of pore-throat radius, length and pore to pore-throat aspect ratio.
5.5.3 Permeability Results

Figure 5-5 shows permeabilities for all three porous materials. For each material, permeabilities for the four different networks combined with the three equations for estimating hydraulic conductances are reported. The permeability results lead to a number of important observations:

1. Although the number of pores (and pore throats) in the networks varies over two orders of magnitude for any one material, permeability variation is much smaller: at worst approximately a factor of two; in most cases significantly less. If we remove the highest-pore-density networks from the results, then we see nearly constant permeability values even as the number of pores changes by a factor of 10 to 20. This result is encouraging, especially in the absence of a definitive technique for pore discretization. It means that the image-based modeling algorithms are doing their job in the sense that variations in network structure are being balanced by the pore-geometry-based schemes used for flow modeling. Reasons for this behavior are discussed below.

2. The highest-pore-density network gives higher permeability estimates when the one-
parameter and two-parameters conductance models are used. However, by including the pore throat aspect ratio (which accounts for the converging-diverging geometry of the throats), this trend is reversed and the highest-pore-density networks exhibit lower permeability than the other three networks (at least for this particular set of conductance formulas).

3. The Ewing-Gupta and Thompson-Fogler equations show different trends when moving from the lower porosity granular materials to the higher-porosity cylinder pack. However, the Bryant-Blunt equation gives very consistent behavior for the three different pore morphologies: essentially constant permeabilities for three of the four networks, but higher permeability for the highest-pore-density network.

5.5.4 Network Factors Affecting Permeability Computations

The insensitivity of permeability to pore density has been observed previously, (Thompson et al. 2008) and was attributed to an effect where the increased number of pore throats is balanced by higher hydraulic conductivities for those throats. Specifically, as the number of pores and pore throats increases, this corresponds to a larger number of series resistances for flow (which would suggest a lower permeability). But, the higher pore density likewise corresponds to shorter pore throats, which decreases the resistance of each throat, thus counteracting the first effect.

Current results show that this explanation alone is insufficient: networks that use the one-parameter conductance model exhibit similar insensitivity to pore density despite the fact that they do not exhibit any throat-length dependence. In fact, the trend is opposite what would be expected from this argument because they give higher permeabilities as the number of resistances in the network increases. Further analysis suggests that some combination of the following six factors contributes to the permeability in an image-based network model.
Table 5-3: Single phase permeability (mD) calculated using three hydraulic conductivity models in a single phase flow simulation. Permeability values calculated using empirical equations are reported for the sake of comparison.

<table>
<thead>
<tr>
<th></th>
<th>Sphere</th>
<th>Sand</th>
<th>Cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GB1</td>
<td>VB1</td>
<td>VB2</td>
</tr>
<tr>
<td>Ewing-Gupta</td>
<td>4.34E+04</td>
<td>4.71E+04</td>
<td>4.73E+04</td>
</tr>
<tr>
<td>Bryant-Blunt</td>
<td>1.71E+04</td>
<td>1.67E+04</td>
<td>1.62E+04</td>
</tr>
<tr>
<td>Thompson-Fogler</td>
<td>3.43E+04</td>
<td>3.35E+04</td>
<td>3.06E+04</td>
</tr>
<tr>
<td>Blake-Kozeny</td>
<td>3.88E+04</td>
<td>3.84E+04</td>
<td>3.92E+04</td>
</tr>
<tr>
<td>Jackson James Perm</td>
<td>9.73E+05</td>
<td>9.68E+05</td>
<td>9.78E+05</td>
</tr>
</tbody>
</table>

Figure 5-5: Comparison of scalar permeability calculated using single-phase flow simulations on the networks generated from (a) spheres; (b) sand; (c) cylinders.
5.5.4.1 Pore Density

A larger pore density leads to a larger number of pore throats, which in turn creates a larger number of series resistances that are encountered during flow across the length of the network. In the absence of other factors, this effect would decrease the computed permeability.

5.5.4.2 Pore-Throat Length

A larger pore density would generally lead to shorter pore-to-pore distances. Assuming the hydraulic conductance equation accounts for the pore-throat length (e.g., the Bryant-Blunt and Thompson-Fogler models shown above), then individual pore-throat conductances should increase with pore density.

5.5.4.3 Inlet/Outlet Pore Density

An increase in the overall pore density will also lead to an increased pore density on the inlet/outlet faces of the domain (see Table 5-4) as well as an increased density on interior cross sections of the network. To illustrate this effect on fluid conductivity, consider a 2D square lattice with bonds of uniform length and conductance. Assume flow in the x-direction, entering at x=0 and exiting at x=1. Now consider doubling the linear density of nodes along the x-direction, which will double the number of resistors in series between x=0 to x=1. A single-parameter conductance model that depends only on bond diameter would cause the overall resistance to double. However, to retain the isotropic structure of the square lattice, one would also need to double the y-direction nodal density. This change would provide twice the number of inlet-to-outlet flow paths along the x direction, which would exactly offset the increased number of series resistances in the permeability calculation (because each x-direction path would carry half the volumetric flow compared to the original, less-dense lattice).
It would appear that this effect allows the single-parameter conductance model to remain relatively insensitive to pore density. On a 3D cubic lattice, doubling the linear nodal density while keeping the isotropic structure would create four times the number of flow paths from one face to the opposing face. For the 3D image-based networks, we can use the number of inlet/outlet pores as a surrogate measure of this effect. Comparing the VB1 and VB2 networks from the sphere pack (because they have essentially the same permeabilities based on the one-parameter Ewing-Gupta model), the network statistics suggest a change in linear pore density of approximately \((35403/2363)^{1/3}=2.47\). The expected increase in inlet or outlet throats would therefore be factor of \((2.47)^2=6.08\). Comparing these two networks, the actual increase is 5.69, suggesting that this effect may contribute substantially in maintaining consistent permeabilities for different networks.

### 5.5.4.4 Pore Coordination Number

The argument given above relies on the assumption that as the pore density increases, pores remain connected to one another in a manner similar to the lower-density networks. In the networks generated from real images, the average pore coordination number remains relatively constant (for any given material) for the GB1, VB1, and VB2 networks, suggesting that this
assumption is reasonable. However, pore coordination number increases significantly for the highest-density VB3 networks relative to the other three.

5.5.4.5 Pore Connectivity

In addition to the average coordination number (above) the spatial connectivity is important because the total macroscopic flow associated with the material permeability can be dominated by a relatively small fraction of the pore space that provides the most conductivity pathways for flow. The transition from the GB1 network (or the VB1 network) to the VB2 network involves the addition of a very large number of pores (approximately 10 times as many), most of which are small pores that fill in between the large pores in the low-density networks: see Figure 5-2 and Figure 5-4. If these additional pores interrupt the connectivity of the dominant flow channels, it would impact the permeability. In contrast, if the dominant flow channels remain connected as the pore density increases, the addition of the small pores should have little consequence.

5.5.4.6 Conductance Equation

The various throat conductance models available in literature include different combinations of pore-throat geometry as shown by the three conductance formulas chosen for this study. Hence, the choice of conductance formula can impact the relationship between pore parameters and permeability.

The results and discussion in this section should highlight a few important points:

- Because the relationship between network structure and permeability depends on a number of related factors, it is difficult to anticipate a priori how a change in network structure will affect fluid flow.
• It is reasonable to assume that networks having dramatically different structures can generate consistent permeability predictions if they are properly designed.

• The use of fundamental, geometric-based computations to assign network properties may be an effective way to help ensure that flow computations are independent of the specific network generation algorithm that is chosen.

5.6 Quasi-Static Drainage

Generally, multiphase flow is more sensitive to pore structure than single-phase flow because of the large impact of pore structure on the dynamics and location of fluid-fluid interfaces. To help assess the impact that network structure has on interfacial phenomena (i.e., different networks for the same porous material), quasi-static displacements were performed on the set of models. These simulations model immiscible displacement starting at a saturation $S_w = 1$ (pore space saturated with wetting phase) to a final point where a large fraction of the pore space has been invaded by the nonwetting phase. Quasi-static simulations neglect fluid viscosity, which in turn means that the model does not depend on time. The physical interpretation of the quasi-static displacement is a capillary-pressure-dominated invasion of the non-wetting phase, which is sufficiently slow so that pressure gradients do not develop in either fluid phase. In our simulations the effect of gravity is neglected, although this restriction can easily be removed.

To generate macroscopic capillary pressure curves using a network model, local pore capillary pressure functions (versus saturation) are needed for each pore. Unlike the monotonically increasing macroscopic capillary pressure curve (as $S_w$ decreases), the pore-scale capillary pressure function can undergo a minimum, which separates equilibrium and non-equilibrium branches of the curve. At the smallest non-wetting phase saturations, the local
capillary pressure can be large if the non-wetting phase has squeezed into the pore through a small pore throat. This configuration represents a non-equilibrium state: once entry has started, the interface will rapidly invade (a Haines jump), retract (if the local capillary pressure drops), or become disconnected and trapped due to a snap-off event. At some intermediate saturation value, the capillary pressure reaches a minimum, which corresponds to a fluid-fluid configuration with the minimum allowable curvature (constrained by local geometry and contact angles). Then, to further increase the non-wetting-phase saturation requires larger capillary pressures that squeeze interfaces into corners of the pores. The branch of the curve between the minimum capillary pressure and $S_w \to 0$ is an equilibrium branch.

Capturing this pore-scale behavior in a local capillary pressure function is difficult because of the strong dependence on pore geometry, invasion sequence, and surface properties (e.g., contact angle), and also because part of the curve reflects the fast, non-equilibrium behavior associated with the Haines jumps. For simplicity, most networks of immiscible displacement ignore the fast dynamics, and capture only equilibrium behavior. In our simulations we also neglect snap-off behavior, and we use the capillary pressure function for a cubic pore to provide the basic functionality for the pore capillary pressure function as described by Thompson (2002).

To perform the quasi-static drainage simulation, a positive capillary pressure is applied on one face of the network. A search is performed to find any pore-throats on the inlet face that are accessible at this capillary pressure, and invasion is allowed into the connecting pores. Invasion continues as long as newly accessible throats can be invaded at the current capillary pressure. Once an equilibrium point is reached, the applied capillary pressure at the inlet is increased and the process continues.
Figure 5-6: Capillary pressure versus saturation relation calculated using quasi-static drainage simulation: (a) spheres; (b) sand; (c) cylinders.
Figure 5-7: Saturation map showing distribution of water (black) and hexadecane (white) in the networks generated from the sphere-pack data. The saturation is averaged over the thickness of the network.
The capillary pressure curves generated from quasi-static drainage simulations are shown in Figure 5-6. For all three porous materials, the GB1 and VB1 curves overlap, suggesting that the pore and pore throat size distributions (along with how the pores are connected) are similar for both the grain-based approach and the fast voxel-based approach. As the pore density increases, the elbow in the capillary pressure curve becomes less sharp. This is not unexpected: a larger number of pores and connections should provide for a smoother transition across the saturation range. Figure 5-7 helps illustrate the effect; it shows a 2D saturation map averaged over the thickness of the networks at four different saturations for the different networks structures of the sphere packing. The low-density networks show larger and more distinct pockets of wetting phase as the displacement progresses. Whereas, the fluid phases are distributed more evenly in the high density networks. This suggests that at a given saturation (e.g., Sw = 0.4), the higher density networks were able to provide for a fluid configuration in which the non-wetting phase did not yet have to access the smallest pores, which in turn corresponds to the less-sharp elbow: Sw reaches a value of 0.4 at a lower capillary pressure.

Capillary pressure curves are commonly used to compute pore size distributions. This computation is instructive in the current study because, while a set of networks created for a given material may have significantly different pore size distributions, the differences in the capillary pressures obtained from these curves are much less pronounced. Hence, it is of interest to determine whether any of the differences in network pore-size distribution are recovered from the capillary pressure curves.

Pore size distributions were computed from the capillary pressure curves using the van-Genuchten model (van Genuchten 1980; Van Genuchten et al. 1991). The continuous form of
van-Genuchten model allows for greater flexibility compared to the discontinuous form of the Brooks-Corey model (Brooks and Corey 1964) over a wide range of pore size distribution. The parameters $\alpha$, $m$, and $n$ allow one to fit the entire capillary pressure curve and ensure a smooth transition at the air-entry pressure and residual saturation. In the equations shown below, $\alpha$ is related to air entry pressure, $n$ is related to pore-size distribution, $m$ is related to overall symmetry of the characteristic curve and is constrained to $m = 1 - 1/n$ (thus resulting in greater stability during parameter optimization), $\sigma$ is interfacial tension, $\Delta \rho$ is the density difference, $\theta$ is the contact angle, and $g$ is the gravitational constant. Non-linear optimization was performed to obtain fitting parameters for each of the four capillary pressure curves obtained from simulation of the sphere-pack networks and were then used to compute the pore-size distributions accordingly (Charbeneau 2007).

\[
S = \frac{1}{[1 + (\alpha P_c)^n]^m} \quad (5-7)
\]

\[
f(r) = \frac{nm\Delta \rho g}{2\alpha \sigma \cos \theta} \left[ \left( \frac{2\alpha \sigma \cos \theta \Delta \rho g r}{\Delta \rho g r} \right)^{n+1} \right] \left[ 1 + \left( \frac{2\alpha \sigma \cos \theta}{\Delta \rho g r} \right)^n \right]^{m+1} \quad (5-8)
\]

Figure 5-8 is a comparison of the pore-size distributions obtained directly from the networks versus those computed from the capillary pressure curves. The network distributions are rougher, reflecting the discrete data sets, and they also demonstrate the large differences from one network to the other (especially the VB2 network, as discussed above). In contrast, the capillary-pressure-curve-based pore-size distributions are more similar to one another. Of particular note is that the VB2 distribution no longer has the pronounced peak at the far left, which indicates that the very large number of small pores in the network structure did not unduly influence
simulation of the immiscible displacement process. The peaks in the pore-size distribution are slightly larger when they are computed from the capillary pressure curve (for networks GB1 and VB1). This is a difficult effect to trace through the full-circle computation (network pore size to capillary pressure curve back to pore-size distribution) because it can depends on the definition of the pore size in the network (maximum inscribed diameter), computation of the pore-scale capillary pressure in the quasi-static displacement algorithm, and interpretation of pore or pore-throat size in the van Genuchten model. The width of the peaks are larger for the VB2 and VB3 networks, which is consistent with the differences in the network structures and is translated though the less-sharp shoulder for the higher density networks as discussed above.

![Figure 5-8](image.png)

Figure 5-8: Pore-size distributions of networks generated from sphere pack data: (a) obtained from the pore network geometry; (b) calculated from capillary pressure curves (shown in Figure 5-6).

### 5.7 Conclusion

Image-based network modeling is becoming a widely applied tool for understanding pore-scale behavior in porous media. A number of network-generation strategies have been proposed, but it is not yet clear how critical the network generation process is to the success of the
subsequent network modeling procedure. We have used XCT images of three different porous media to begin understanding the impact of differences in network structure on modeling. For each porous medium, four different networks were created, which exhibit dramatically different network properties (in particular, the number of pores, which is reported as pore density). Analysis of network structure, simulation of single-phase permeability, and simulation of quasi-static drainage were used to interpret the impact of the network structure on simulation results.

We argue that with the exception of the simplest types of materials (e.g., structured sphere packings), no one network model is correct; in continuum pore spaces composed of converging-diverging and interconnected channels, it is difficult to prescribe definitions for pores and pore throats precisely. This problem is further exacerbated by the necessary use of voxelized data to describe the original pore structure, which contain both experimental error and limitations in resolution. These errors/uncertainties prevent the precise computation of parameters, such as distance functions (i.e., void locations to surfaces), pore diameters, or the location of a maximal inscribed spheres.

In the networks we use here, the large variations in pore density are a result of two factors: different methods for seeding the search for pores (i.e., defined as maximal inscribed spheres), and different settings in the merge criteria (that merges overlapping inscribed spheres to create single pores). Generally, the fast algorithms create low-density networks will little or no overlap in inscribed pores, and therefore also generate longer pore throats. More complete pore searches are slow, resulting in higher pore densities and shorter pore throats. In the highest density case, the pore networks are caterpillar-like structures of overlapping pores that snake through the pore space. In all cases, the pore and pore throat parameters are measured directly from the
surrounding material. Hence, porosity, total pore volume, and surface area are conserved (and correct) relative to the original voxel image. The pore density affects secondary parameters, such as pore-size distribution and pore interconnectivity. However, the relationship is not always proportional or obvious. For instance, the lowest and highest density network shown here have similar pore size distributions, while the peak in the pore-size distribution from the middle-density VB2 network is shifted far to the left (for reasons explained in the paper).

The most important result shown is the relative insensitivity of predicted single-phase permeability for a given material in spite of orders-of-magnitude changes in pore density, even for the most primitive pore-throat conductance formulas. We view this insensitivity is a beneficial trait (i.e., since the original sample has only one correct permeability) and attribute it to the use of physically representative network modeling, that, when applied correctly, precludes the use of adjustable parameters for modeling and maps dimensional geometric quantities onto the network structure.

Capillary pressure curves for quasi-static drainage are moderately sensitive to network structure. This result is expected given the sensitivity of interfacial phenomena to pore structure, some of which is captured in the network modeling algorithms. Generally, the low-pore-density capillary pressure curves have a sharper shoulder at the transition from the plateau capillary pressure to the steep rise. This is caused by fewer options for the invasion pattern when simulating the injection of nonwetting phase. When pore-size distributions are generated from the capillary pressure curves, the results of these differences include narrower peaks at larger pore sizes for the lower-density networks.

We expect that the correctness or quality of one network versus another (for the same porous
material) will depend on the application for which it is used. For example, the VB2 networks shown in this paper, which contain sharp peaks at very small pore sizes, are not the best choice for characterization. However, it is not difficult to believe that this same structure might prove effective as a pore-space discretization for modeling transport because the network better conforms to the tight regions of the pore space.

5.8 REV for Porosity and Permeability

The data for the cylinder packing (350×350×520 voxels) has approximately 72% porosity and thus contains more than 45 million void voxels. For the VB3 network algorithm, each void voxel is searched as a potential seed, which requires a non-linear optimization to calculate the inscribed sphere radius. This makes the process computationally expensive. To be able to calculate pore structure properties and to compare between all four networks, a smaller image of size 150×150×150 was chosen in this study. To confirm that the smaller size image contains a representative elementary volume (REV) for porosity and permeability, we randomly sampled various sized images from the large image, and created networks using the VB1 algorithm. Figure 5-9 shows a comparison of porosity and single phase permeability of various small images with the original large image, confirming that the image size 150×150×150 is sufficiently large.
Figure 5-9: Test for REV for cylinder image. Dashed line indicates the properties of 350×350×520 image: (a) porosity and (b) permeability. Error bars show variation of five randomly sampled locations from the same image.
CHAPTER 6 TRANSIENT IMBIBITION

6.1 Results and Discussion

Three types of plots/graphics are used to present the 3D data below. The first type is 3D visualization of the wetting phase, which gives a qualitative picture of the dynamic front at the moment it was frozen in place by polymerization. The second type consists of a series of 2D horizontal slices showing segmented data (solid, wetting, and non-wetting phase distributions) at specific elevations in the columns. Generally the first image in the sequence will correspond to the top-most slice where any imbibed wetting phase was found. Subsequent slices represent lower elevations (farther behind the tip of the imbibition front) and are spaced at one-particle-diameter intervals. These slice sequences are valuable in showing the geometry of the wetting phase at or above the bulk front. They also show demonstrate how rapidly the saturation increases as a function of elevation, which is indicative of the sharpness of the advancing front.

The third way the data are presented is by plotting saturation (averaged over a horizontal slice or region of slices) versus height in the column (presented in particle diameters). In these plots, the height scale is not tied to a global reference for the various images. Instead, the plots are superimposed to line up the location of the bulk front when possible, which allows for easier comparison of the saturation gradients from different experiments.

We have used the following terminology to aid in describing the observed behavior. The bulk front is the part of the imbibition front where the wetting phase has increased to its maximum value; the only non-wetting phase found behind the bulk front is trapped as disconnected ganglia. Its approximate location can be inferred from the plateau on the saturation versus height curve. However, since it is not necessarily horizontal, a detailed picture of its shape and location can come only from analyzing the 3D image data. The term sharp is used to describe a bulk front
that has little or no wetting phase in front of it; at the pore scale, it separates empty pores from fully saturated pores. In contrast, a diffuse front exhibits a transition zone consisting of pores that are partially saturated with wetting phase, and which moves ahead of the bulk front. It is worth noting that, since these are pore-scale definitions, a front can be sharp irrespective of whether it is flat, tilted, or non-planar at the column scale. And, it can be sharp irrespective of the fraction of trapped non-wetting phase that is left behind the front. Finally, we note that the terminology wetting films is used loosely in the following discussion to include essentially all wetting-phase geometries inside a partially saturated pore (pendular rings, corner geometries, films, etc.); it does not imply thin wetting films on a surface, which provide little or no hydraulic conductance.

6.1.1 Shape of the Dynamic Front

All of the imbibition experiments discussed in this paper are viscous- and gravity-stable displacements, because the displacing phase has a higher viscosity than the displaced phase and the higher-density displacing phase is injected from the bottom upwards in the column. Hence, in the absence of other effects, we would expect a piston displacement with a horizontal bulk front. We are interested in deviations from this behavior during dynamic imbibition, which would be attributed to some combination of capillary forces and/or material heterogeneity.

We focus first on the shape of the displacement front at the column scale. For smooth spheres, a plot of saturation versus height (Figure 6-2a) is steep and independent of capillary number over the range shown. Physically this implies that the dynamic front is reasonably piston-like. A 3D plot of the wetting phase (Figure 6-1) confirms this fact, and suggests that the saturation gradient in Figure 6-2a might be even sharper except for the influence of wall effects.

Roughening the spheres has two effects on the dynamic displacement front: the saturation
gradient is not as steep as it is in the smooth spheres and it is no longer independent of capillary number in the range tested. Changes in this height-averaged saturation gradient could be caused by one or both of two factors: 1) the front is tilted or non-planar at the column scale; 2) the front is horizontal, but it is not sharp at the pore scale; in other words, individual pore saturations vary in the vicinity of the front, creating a smearing of the saturation value in the longitudinal direction. Figure 6-1 indicates that the surface roughness induces both these effects. At high Ca, the front is sharp at the pore scale for both the smooth and rough spheres. However, the bulk front in the smooth spheres is much closer to being horizontal. Quantitatively, the height-averaged saturation gradient occurs over 3-4 diameters in the smooth spheres versus 6-7 diameters in the rough spheres. At lower Ca values, the same column-scale effect occurs, but in addition the front is smeared by pore-scale saturation gradients. This effect is discussed in the next section.

The main distinction between the rough spheres and the sand is the variation in particle size and shape in the sand, which in turn leads to greater pore-scale heterogeneity. The Ca values for the sand do not correspond exactly with the spheres, but the range does overlap sufficiently to allow direct comparisons. At the higher capillary numbers, the saturation plots and the 3D images of the dynamic fronts are qualitatively similar (Figure 6-2a and Figure 6-2b respectively), but there are subtle differences at the pore scale. Also, the low-capillary-number behavior for the sand is dramatically different, as seen in Figure 6-2c. These last two observations are discussed more in the next section.
Figure 6-1: 3D visualization of segmented wetting phase showing the dynamic front at the moment it was frozen in place by polymerization. Left to Right: High, Intermediate, and Low capillary numbers.
Figure 6-2: Plots showing average saturation vs. height at various three capillary numbers.
(a) Smooth spheres, (b) Rough Spheres, (c) Sand and (d) Cylinders

6.1.2 Wetting-Phase Advance Ahead of the Bulk Front

In this section we address one of the main objectives of the research, which is to better understand the conditions that allow wetting films to move ahead of the advancing bulk front during imbibition, and the consequence of this behavior on the overall displacement process.

6.1.2.1 Sphere Packings

In the packings of smooth spheres, the front is sharp at all conditions tested, including the low value $Ca = 1.4 \times 10^{-7}$. At this capillary number, the interstitial velocity in the pack is $5.0 \times 10^{-7}$ m/s, which translates to $2.0 \times 10^{-3}$ dia/s. This suggests that a pore has on the order 500s from the
time that it first is contacted by the wetting phase to the time when it will be filled by an advancing front or will have been invaded by a Haines jump. The fact that there is no evidence of the formation of wetting films ahead of the front, even with this relatively long characteristic pore filling time, suggests that the pore geometry, rather than a capillary-number limitation, prevents the films from forming in the smooth spheres. This observation is consistent with what has been observed in static situations (Dullien et al. 1989).

The rough spheres show a sharp (although not flat) front at the highest capillary number tested, and a slightly less sharp front at the intermediate capillary number. At the low capillary number \((Ca = 1.2 \times 10^{-7})\) the advancing interface is diffuse. The sharp front can be seen in Figure 6-3 which contains horizontal slices starting at the uppermost elevation that wetting phase had reached when it was polymerized, and moving downward. The slices are spaced at one particle diameter intervals, and each shows the wetting and nonwetting phases at that particular elevation. For the sharp front, note that pores are either filled with wetting phase or absent of wetting phase – there are no intermediate saturations at the pore scale. (Specific cases that demonstrate this behavior are the smooth-spheres at any \(Ca\) value and the rough spheres at high \(Ca\).) For the case of the sharp front, the distinction of whether any given pore in a horizontal slice is filled depends on the column-scale configuration of the interface as it passes that particular elevation, rather than on the local pore geometry.

Two observations in Figure 6-4 indicate the formation of a diffuse front at low \(Ca\). First, wetting films are apparent in numerous pores in the slices nearest the top elevation. Second, classic blob-like geometries are apparent in the non-wetting phase structure starting around the fifth slice in the downward sequence of images. These blob-like structures are indicative of
wetting phase having invaded via crack, crevice, or pendular ring type geometries. It should be noted that most of these apparent blobs are not yet trapped ganglia (even if they are isolated in the 2D plane). The effect of the front geometry on disconnection and trapping of the nonwetting phase is discussed below.

The intermediate capillary number in the set of rough-sphere experiments is $Ca = 2 \times 10^{-6}$, and the slice images suggest that this value may be near the transition from a sharp to a diffuse front. Images at this capillary number show limited evidence of films approximately one particle diameter ahead of the bulk front. Additionally, signs of the blob-like geometries described in the previous paragraph can be seen in the slice images from this capillary number.

![Series of 2D horizontal slices at high capillary number of three granular packing media, showing segmented data showing solid (gray), wetting (white), and non-wetting phase (black) distribution. The first image in the sequence (Left to Right) correspond to the top-most slice where any imbibed wetting phase was found.](image)
Figure 6-4: Series of 2D horizontal slices at low capillary number of three granular packing media, showing segmented data showing solid (gray), wetting (white), and non-wetting phase (black) distribution. The first image in the sequence (Left to Right) correspond to the top-most slice where any imbibed wetting phase was found.

6.1.2.2 Sand Packings

The sand exhibits significantly different behavior than the spheres, evidenced most dramatically by the saturation versus height plot for low $Ca$ (Figure 6-2c). Examining slices from this displacement shows evidence of some partially saturated pores, meaning they are being filled via crack and crevice flow prior to become completely invaded by wetting phase. However, the majority of the pores are either empty or filled (with wetting phase). This observation means that the long saturation gradient in Figure 6-4 is a different type of diffuse-zone structure than in the rough spheres. The wider distribution of pore sizes and shapes appears to dominate the physics, allowing the wetting phase to move far ahead of the bulk front via connected paths of small pores.

At higher capillary numbers, the same behavior is apparent ahead of the front (i.e., some
wetting films are evident, but the advance filling of smaller pores is more prevalent). However, the range that this diffuse zone extends ahead of the bulk front decreases. As the capillary number increases from $10^{-7}$ to $10^{-5}$ to $10^{-4}$, the corresponding size of the diffuse front decreases from approximately 90 to 8 to 5 particle diameters respectively. This is consistent with the expected physics of the process as the viscous forces driving the bulk front become larger in comparison to the interfacial forces pulling fluid ahead of the front into the smaller pores.

6.1.3 Trapping Behind the Bulk Front

At the high and intermediate capillary numbers tested, the smooth spheres exhibit a fairly uniform distribution of trapped nonwetting phase behind the bulk front, as evidenced by the plateaus at approximately $S_w = 0.92$ in the saturation versus height plot. In the rough spheres, the fraction of trapped nonwetting phase is significantly higher, and it is also less uniformly distributed. Specifically, note the saturation values for the high-capillary number displacement, which fluctuate in the range $0.8 < S_w < 0.96$ along a 15-20 sphere-diameter length of column (behind the bulk front).

The previous observation would not be surprising except for the fact that at $Ca \approx 2 \times 10^{-5}$ the displacement fronts are sharp in both the smooth and rough spheres. This implies that the extra non-wetting phase trapping is not associated with wetting films and snap-off behavior at the pore scale, but instead may be associated with the shape of the bulk front at the column scale (which is the major difference between the smooth and rough spheres at the highest capillary number). This argument is bolstered by the fact that even the low-capillary displacement leads to a similar fraction of trapped phase ($S_w \approx 0.9$), despite the fact that this imbibition front contains a diffuse region with distinct wetting films.
Figure 6-5: Grayscale image of sand packing showing Sand grains (Red), Air (Blue), and Wetting phase (Green) at low capillary number (1E-7). Left: Top of the column and Right: Bottom of the column.

The fraction of non-wetting phase trapped behind the bulk front (as disconnected ganglia) is known to be larger for secondary imbibition as compared to primary imbibition. This phenomenon is associated with the swelling of wetting films during the secondary imbibition process, which in turn leads to snap-off or re-connection of wetting phase structures. These events either disconnect non-wetting phase completely, or block escape routes for the nonwetting phase. Figure 6-5 shows a cross section from the large diffuse region in the low-Ca experiment in the sand. Qualitatively, this image is similar to an image of residual wetting phase saturation. However, this diffuse zone wetting phase saturation does lead to larger fractions of trapped non-wetting phase behind the front as it would if the fluid were residual wetting phase.

We believe the reason for this difference is the pore-scale distribution of fluids. The residual wetting phase is distributed more evenly: wetting phase exists at essentially all grain-grain contacts, and some fraction of wetting phase is found in nearly every pore. In contrast, the wetting phase structure in the diffuse front consists of connected paths of wetting fluid that fills many smaller pores. At the same time, other pores contain no wetting phase.

Given these differences in wetting phase structure, we would indeed expect a difference in trapping behavior as the bulk front moves through these two different zones. The diffuse zone ahead of the imbibition front contains a connected network of nonwetting pores that, because
they contain no wetting phase at all, cannot be cut off by swelling films. Thus, an increased number of non-wetting phase escape routes exists as the bulk front advances through the diffuse zone in comparison to when it moves through a zone with residual wetting phase saturation.

6.1.4 Cylinder Packings

The displacement patterns in the cylinder packings are significantly different than in the granular materials, which is attributed to the particle structure: high-aspect-ratio particles with smooth surfaces (at least in the current experiments). The particle geometry affects the structure of the packing, mainly by inducing local alignment of the cylinder. The impact of this alignment on the fluid transport problem is twofold.

First, the local alignment of as few as three cylinders creates a long narrow conduit between them, which not only generates the necessary capillary force for imbibition, but also provides an uninterrupted path (many cylinder diameters) for the imbibed fluid to traverse in one motion. (Contrast this with the granular materials, in which movement of an interface over many particle diameters requires the repeated stops, starts, and re-equilibrations associated with the Haines jump processes.)

A second effect of alignment is the creation of bed-scale heterogeneity, which is evident in Figure 3-3 and even more so in the images of wetting fluid (Figure 6-6). During imbibition, the long conduits described in the previous paragraph can rapidly transport fluid to a different region of the packing, which may exhibit tighter or looser packing, anisotropy with different orientation, or other types of heterogeneity. Hence, the snapshots of the dynamic fronts captured in these CT images show vertical transport well ahead of the bulk front, but with a vastly different wetting phase structure than in the spheres or sand. Characteristic of the cylinders are vertical conduits
that may be narrow or wide, but which can transport fluid to higher regions of the bed. This produces regions of high saturation above regions of low saturation, even though the fluid is moving from bottom to top. This behavior produces the non-monotonic saturation profiles seen in Figure 6-2d.

![3D image showing segmented wetting phase in cylinder packing. Left to Right: High, Medium, and Low capillary number.](image)

Figure 6-6: 3D image showing segmented wetting phase in cylinder packing. Left to Right: High, Medium, and Low capillary number.

Many fibrous materials used are more homogeneous than what we were able to obtain in the limited-diameter columns. Hence, the large scale bypassing seen in these experiments may not be the main culprit for nonwetting phase trapping, which is a practical problem in some engineering applications.

### 6.2 Conclusion

For high capillary numbers, the primary imbibition front during invasion is sharp, meaning it separates completely filled pore from completely empty pores. However, as the capillary number becomes sufficiently low, wetting phase can pull ahead of the bulk front in the form of pendular
rings and crevice-filling wetting films. The extent of this diffuse interface and the pore-scale structure of the films in this region depend on particle roughness, pore structure, and capillary number. In a packing of smooth spheres, the front remained sharp at all capillary numbers tested (the minimum value being $Ca = 1.4\times10^{-7}$). For a packing of spheres with surface roughness, a transition between a sharp and diffuse front was seen at approximately $Ca = 2\times10^{-6}$, and the extent of the diffuse zone (ahead of the bulk front) increased as the capillary number decreased.

The ability of wetting films to advance ahead of the dynamic front appears to have little or no effect on the fraction of non-wetting phase that becomes trapped behind the bulk front, which is somewhat surprising given the large impact that residual wetting phase saturation has on trapping of the non-wetting phase (i.e., primary versus secondary imbibition). This conclusion is drawn from experiments in the sand and the rough spheres; in both cases the fraction of trapped nonwetting phase remained relatively consistent with capillary number, despite operating in displacement regimes where we observed significant wetting phase moving ahead of the bulk front.

Despite the qualitative similarities between the wetting phase that moves ahead of a dynamic front and equilibrium residual wetting phase after drainage, their structure and impact on imbibition are different. The presence of residual wetting phase can increase significantly the fraction of trapped non-wetting after an imbibition front moves through. However, the presence of wetting phase ahead of a bulk front during primary imbibition does not have this same effect. The reason for this difference appears to be the pore-scale structure of the wetting phase: residual wetting phase saturation is distributed more evenly throughout the pore space, which allows swelling of films, snap-off, and/or the blockage of escape paths. In contrast, the wetting phase
that pulls ahead of a bulk imbibition front consists of a more bimodal distribution of pore saturations (many pores completely filled; many pores completely empty). This distribution allows the non-wetting phase to retain connected escape routes even as the wetting-phase saturation becomes high.

Differences in the fraction of non-wetting phase trapping were observed, but as a function of surface roughness (and pore structure) rather than capillary number, shown most clearly by the plateaus in Figure 6-2 (smooth vs rough spheres; intermediate and high Ca). At the higher capillary numbers, the main difference in the dynamic fronts for the smooth versus rough spheres is the flatter piston-like front for the smooth spheres. This observation suggests that nonwetting-phase trapping during primary imbibition is associated more with bypassing effects than snap-off or interface stability effects.

Not surprisingly, the pore space formed by cylindrical particles induced dramatically different behavior than in the granular particles. In the present experiments, the main effects were associated with the preferential alignment of cylinders in the dry packing. This alignment creates uninterrupted flow passages for the wetting phase, which allows the wetting phase to traverse many pore diameters in a single Haines-jump type event. If fluid is transported vertically (upwards) by this phenomenon, then bypassing on the column scale can occur, with pockets of high wetting-phase saturation forming above regions of low wetting-phase saturation. Because of the heterogeneity, the conclusions drawn from the cylinder packings are less general than conclusions from the granular materials. Similar experiments but in more homogeneous fibrous materials would be of interest to better understand wetting phase transport in this high porosity materials.
CHAPTER 7 SUMMARY AND FUTURE RESEARCH

A novel UV initiated polymerization technique to freeze the wetting front in a real porous medium was successfully implemented to study transient imbibition behavior using a noninvasive high-resolution XCT. Specialized image processing and image based characterization algorithms were developed to quantify: pore, wetting phase, and nonwetting phase structure from 3D XCT images.

The objective of transient imbibition experimental technique developed in this research was to achieve a rapid phase change upon irradiation with UV light to arrest the progress of the wetting front. 1,6-Hexanediol diacrylate was the principal component of the polymerizable wetting phase fluid along with Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide / 2-hydroxy-2-methylpropiopehnone 50/50 (Initiator) and 2,3-Dibromopropyl acrylate (Dopant). Dopant was added so that absorption edge imaging could be performed at the X-ray energies above and below the bromine absorption edge (13.47 keV). The details of absorption edge imaging can be found in Appendix II. Phase change was achieved in 2-3 seconds using this polymerizable mixture.

In order to study the effects of pore structure and surface roughness on the wetting front, four packing materials (smooth sphere, rough spheres, irregularly shaped sand particles and high aspect ratio cylinders) were used. Spontaneous imbibition experiments were performed on each of the packing materials to determine the limits of the flow regimes (viscous dominant, capillary dominant and transition between viscous to capillary dominant flow). Transient imbibition experiments were conducted in the UV chamber and the polymerized columns containing transient imbibition front were imaged using synchrotron XCT. The grayscale XCT images were segmented in to three phases (solid, wetting phase and nonwetting phase) using a combination of
an anisotropic diffusion algorithm and a modified indicator kriging algorithm. Geometric structure of these three phases was done using an image based network generation algorithm and qualitative arguments on the shape of the wetting front are made based on the visual inspection of the segmented 3D images.

In the following section, summaries of important result from each section (Chapter 4, 5, and 6) are presented. Key finding on the transient imbibition front, which was the main goal of this research, is presented first, followed by our contribution in the development of essential image based tools to accomplish this research.

7.1 Transient Imbibition

- **During primary imbibition, are wetting films able to advance ahead of the bulk imbibition front, and if so what factors most strongly influence this effect?**

For high capillary numbers, the primary imbibition front during invasion is sharp, meaning it separates completely filled pore from completely empty pores. However, as the capillary number becomes sufficiently low, wetting phase can pull ahead of the bulk front in the form of pendular rings and crevice-filling wetting films. The extent of this diffuse interface (films and pendular rings ahead of the bulk wetting front) and the pore-scale structure of the films in this region depend on particle roughness, pore structure, and capillary number. In a packing of smooth spheres, the front remained sharp at all capillary numbers tested (the minimum value being $Ca = 1.4 \times 10^{-7}$). For a packing of spheres with surface roughness, a transition between a sharp and diffuse front was seen at approximately $Ca = 2 \times 10^{-6}$, and the extent of the diffuse zone increased as the capillary number decreased.

The pore space formed by cylindrical particles induced dramatically different behavior than
in the granular particles. This alignment creates uninterrupted flow passages for the wetting phase, which allows the wetting phase to traverse many pore diameters in a single Haines-jump type event. If fluid is transported vertically (upwards) by this phenomenon, then bypassing can occur, with pockets of high wetting-phase saturation forming above regions of low wetting-phase saturation. Because of the heterogeneity, the conclusions drawn from the cylinder packings are less general than conclusions from the granular materials. Similar experiments but in more homogeneous fibrous materials would be of interest to better understand wetting phase transport in this high porosity materials.

- **What is the pore-scale structure of wetting phase that has advanced ahead of the bulk imbibition front?**

  Wetting phase in the diffuse zone ahead of the bulk wetting front consists of pendular rings and crevice-filling films along with the cluster of the saturated small pores. The wetting phase in this region is not uniformly distributed in the cross section, but present in the form of cluster of filled pores and cluster of completely unsaturated pores, with few pores showing films and pendular rings near the top of the column. The wetting phase in the diffused front is all connected to bulk front and no isolated pendular rings were observed.

- **Does wetting phase that has advanced ahead of the bulk front play a similar role as residual wetting phase that was already present in the pore space during secondary imbibition?**

  The ability of wetting films to advance ahead of the dynamic front appears to have little or no effect on the fraction of non-wetting phase that becomes trapped behind the bulk front, which
is somewhat surprising given the large impact that residual wetting phase saturation has on trapping of the non-wetting phase in secondary imbibition. This conclusion is drawn from experiments in the sand and the rough spheres; in both cases the fraction of trapped nonwetting phase remained relatively consistent with capillary number, despite operating in displacement regimes where we observed significant wetting phase moving ahead of the bulk front.

- **Is trapping of the nonwetting phase during primary imbibition associated more with pore-scale snap-off events (where wetting films have advanced) or by the bypassing of pores by the bulk imbibition front?**

The presence of wetting phase ahead of a bulk front during primary imbibition does not have the same effect as secondary imbibition with residual wetting phase saturation. The reason for this difference appears to be the pore-scale structure of the wetting phase: residual wetting phase saturation in the secondary imbibition is distributed more evenly throughout the pore space, which allows swelling of films, snap-off, and/or the blockage of escape paths. In contrast, the wetting phase that pulls ahead of a bulk imbibition front during the primary imbibition consists of a more bimodal distribution of pore saturations (many pores completely filled; many pores completely empty). This distribution allows the non-wetting phase to retain connected escape routes even as the wetting-phase saturation becomes high.

Differences in the fraction of non-wetting phase trapping were observed, but as a function of surface roughness (and pore structure) rather than capillary number. At the higher capillary numbers, the main difference in the dynamic fronts for the smooth versus rough spheres is the flatter piston-like front for the smooth spheres. This observation suggests that nonwetting-phase trapping during primary imbibition is associated more with bypassing
effects than snap-off or interface stability effects.

7.2 Image Segmentation

Nonlinear anisotropic diffusion effectively removes noise from porous media images and preserves the local structure in the data. All of the filters tested showed effective noise removal without blurring the edges when used with an appropriate edge stopping parameter and stopping criteria. Manual selection of an edge stopping parameter is difficult in the low contrast multi-phase images, but automatic selection by eigen value analysis provides effective noise removal. The peak separation and reduction in the grayscale variance of each peak increases the accuracy of the image segmentation using an indicator kriging algorithm. A comparison with above- and below-edge images show that, this segmentation approach is effective and useful for separating phases in low contrast XCT images.

7.3 Image Based Pore Network Generation

A number of network-generation strategies have been proposed, but it is not yet clear how critical the network generation process is to the accuracy of the subsequent network modeling procedure. XCT images of three different porous media were used to begin understanding the impact of differences in network structure on modeling. For each porous medium, four different networks were created, which exhibit dramatically different network properties (in particular, the number of pores, which is reported as pore density). Analysis of network structure, simulation of single-phase permeability, and simulation of quasi-static drainage were used to interpret the impact of the network structure on simulation results.

In the networks we use here, the large variations in pore density are a result of two factors: different methods for seeding the search for pores (defined as maximal inscribed spheres), and
different settings in the merge criteria (which merges overlapping inscribed spheres to created single pores). Generally, the fast algorithms create low-density networks will little or no overlap in inscribed pores, and therefore also generate longer pore throats. More complete pore searches are slow, resulting in higher pore densities and shorter pore throats. In the highest density case, the pore networks are caterpillar-like structures of overlapping pores that snake through the pore space. The pore density affects secondary parameters such as pore-size distribution and pore interconnectivity. However, the relationship is not always proportional or obvious. For instance, the lowest and highest density network shown here have similar pore size distributions, while the peak in the pore-size distribution from the middle-density VB2 network is shifted far to the left (for reasons explained in the Chapter 5).

The most important result shown is the relative insensitivity of predicted single-phase permeability for a given material in spite of orders-of-magnitude changes in pore density, even for the most primitive pore-throat conductance formulas. We view this insensitivity is a beneficial trait (since the actual sample has only one correct permeability) and attribute it to the use of physically representative network modeling, which when applied correctly precludes the use of adjustable parameters for modeling and maps dimensional geometric quantities (pore and pore-throat diameters, pore volume, throat length, coordination numbers, etc.) onto the network structure.

Capillary pressure curves for quasi-static drainage are moderately sensitive to network structure. This result is expected given the sensitivity of interfacial phenomena to pore structure, some of which (e.g. pore size distribution) is captured in the network modeling algorithms. Generally, the low-pore-density capillary pressure curves have a sharper shoulder at the
transition from the plateau capillary pressure to the steep rise. This is caused by fewer options for the invasion pattern of the nonwetting phase. When pore-size distributions are generated from the capillary pressure curves, the results of these differences include narrower peaks at larger pore sizes for the lower-density networks.

We expect that the correctness or quality of one network versus another (for the same porous material) will depend on the application for which it is used. For example, the VB2 networks shown in this paper, which contain sharp peaks at very small pore sizes, are not the best choice for characterization. However, it is not difficult to believe that this same structure might prove effective as a pore-space discretization for modeling transport because the network better conforms to the tight regions of the pore space.

7.4 Future Research
In the following section we present some research ideas to build on the work presented in this research on the advancing wetting films during imbibition.

7.4.1 Reversible Instantaneous Freezing of Immiscible Displacement Front
The experiments conducted in this research deals with a fast and irreversible phase change of the wetting front from liquid to solid. However, characterization of immiscible displacement with respect to time in a 3D porous medium, such as change in distribution of the wetting and nonwetting phase to evaluate relative permeability or transition from viscous dominant to capillary dominant flow regime during spontaneous imbibition, is not possible with this technique. In the absence of real time 3D imaging techniques, and building upon the work done in this research to freeze the wetting front in time, it is logical that the next step would be to bring about phase change reversibly (solid during the 3D image acquisition and liquid during the
displacement).

The use of an electrical field to instantaneously increase the viscosity of fluids when the electrical field is applied, and return to its lower viscosity state when the electrical field is removed have been tested on the past on polar liquids (Andrade and Dodd 1939; Sossinski 1939). This phenomenon of controlling the flow properties of fluid with the use of electrical field is called electrorheology. Another approach to bring about phase change using electrorheological properties of slurries with suspended nanoparticles was also reported in literature (Halsey 1992; Whittle and Bullough 1992; Wen et al. 2003). The application of electrical field brings about three dimensional alignment of the particles suspended in a nonpolar fluid to form gel like structure. The gel returns to the original fluid state when the electrical field is removed. The second approach is suitable in the study of the dynamic imbibition, drainage and relative permeability. In all three experiments the changes in the structure and the composition of the fluid phase present in the pore space determine flow characteristics. The influence of electric field on X-rays during XCT imaging might add to the experimental and image acquisition challenges.

7.4.2 Subsurface Transport of Contaminants

Transport of contaminant such as microbes (Wan and Tokunaga 1997, 2005), oil spills (Guiguer 1991) and nuclear waste (Poeter and Gaylord 1990; Tokunaga et al. 2003) across the unsaturated subsurface layer (Vadose zone) into groundwater have environmental and health consequences. Groundwater rises into the subsurface layer due to the capillary action in the form of films, pendular rings and cluster of small saturated pores.

The effect of the films in the trapping of nonwetting fluids is well understood. However, the
stability of the water films surrounding the trapped contaminants, and hydraulic conductivity of the films in transporting the colloidal particles into ground water is an attractive area where this research could contribute.

Air-water interface in unsaturated zone provide suitable conditions for microbial growth, another important area of research would be bacterial mediated breakdown and transport of non-aqueous contaminants. Effect of surface roughness and pore scale heterogeneity on the redistribution of the wetting phase can also be explored to maximize the air water interface, such that suitable microorganisms to breakdown harmful contaminants.

7.4.3 Incorporating Effects of Advancing Films in Imbibition Simulations

Image based physically representative pore network model is an important tools in simulating multiphase flow phenomenon in porous media. Pore network simulations have been extensively used to simulate drainage phenomena, however, very few studies have been published on imbibition simulations using physically representative pore-networks. Primary and secondary imbibition phenomena are difficult to simulate in a real porous medium due to the discontinuities (Haines jump), the splitting and merging of interfaces and the effects of film flow along the surface roughness. Gladkikh and Bryant (2003, 2005, 2007) use pore-network generated from computer generated packing to simulate secondary imbibition. Level set method (Prodanovic and Bryant 2006) has recently been used to addressing the challenge splitting and merging of interfaces during imbibition.

The effect of the film flow ahead of the bulk front has not been studied in a real 3D porous media. Our experiments capture the imbibition front and diffuse zone ahead of the imbibition front in microscopic details. The pore network can be constructed from the segmented image
using image based pore network generation techniques. The results from our experiments can be used to simulate and fine tune the imbibition model using level set method based simulation. Incorporating these effects in 3D image based imbibition simulations would help in the design and optimization of operating conditions to address following issues:

- Air trapping in fiber reinforced plastics molding during primary imbibition (Ruiz et al. 2006; Alms and Advani 2007)
- Effect of film flow on the relative permeability of reservoir rock samples (Arns et al. 2003; Øren and Bakke 2003)
- Decreased mass transfer and reduction in the efficiency of porous proton exchange membrane due to film formed by the condensing of water vapor in fuel cells (Nam and Kaviany 2003; Koido et al. 2008)
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APPENDIX I X-RAY COMPUTED MICRO-TOMOGRAPHY

I.1 X-Ray Computed micro-Tomography

X-ray Computed micro-Tomography (XCT) is a noninvasive and a nondestructive technique to study the structure of a sample in three dimensional microscopic details. A typical synchrotron XCT setup (Figure I-1) consists of a synchrotron source of a collimated X-ray beam, a sample rotation stage, a scintillator to convert the transmitted X-ray into visible light, a lens assembly to magnify the image and a CCD camera to capture the image in digital form. The digital image collected by the CCD camera is what is called a 2D projection. During scanning, a series of projections are collected by rotating the stage by a small angle increment \(0.25^\circ\) up to \(180^\circ\). The series of projections along with the background projections collected with the sample out of the field of view, which is subtracted from the image to remove background, are then used to calculate the 3D volumetric image using GRIDREC (Dowd et al. 1999) projection reconstruction algorithm.

Figure I-1: Typical synchrotron X-Ray CT setup

X-ray imaging works on the principle of Beer’s law (Equation I-1) and the X-ray absorptivity of a sample is governed by the mass attenuation coefficient \((\mu)\), the density \((\rho)\) and, the width of a sample \((x)\) though which the X-ray passes. Most materials of engineering interest are of
heterogeneous composition and the resulting 2D projection is composed of the absorption of each of the phases. For example, in the XCT image of a porous medium, the solids present in the natural porous media typically contain minerals with high X-ray mass attenuation coefficient resulting in a higher absorption compared to void which is typically air and has a lower attenuation coefficient. The total absorption in composites captured in the projection is the linear summation of the absorptivity and the effective length of each of the phases along the path of the X-ray beam.

\[
\frac{I}{I_0} = \exp\left(\frac{\mu}{\rho}x\right) \\
\frac{I}{I_0} = \sum \exp\left(\frac{\mu}{\rho}x\right)
\]

(I-1)  
(I-2)

**I.2 Linear Attenuation Coefficient**

The ratio \(\mu/\rho\) is known as the linear attenuation coefficient and is an important parameter in determining the contrast between various phases present in the 3D XCT image of a composite material. Higher linear attenuation coefficient results in higher absorption values in the resulting image. Besides the density and chemical composition of the material being imaged, the linear attenuation coefficient also depends on the energy of the incident X-ray beam and decreases exponentially with the increase in the X-ray energy. Typical linear attenuation coefficient values of the materials used in this research are shown in Figure I-2.
For the most part, the linear attenuation coefficient \( \mu/\rho \) of an element / compound decreases exponentially with the increase in the X-ray energy as shown in the Figure I-2. However at the resonant energies of an element present in the compound(s), the absorption attenuation increases discontinuously and is often referred to as an absorption-edge. Differential absorption tomography makes use of the absorption-edge information to focus on a specific element or phase present in the sample. To accomplish this, the sample is imaged at two different energies, above and below the absorption edge of the element or phase of interest. Because the two energies are chosen to be just below and above the absorption edge, only the attenuation coefficient of the element of interest changes significantly. Therefore, the phase of interest can then be identified by subtracting the below edge image from the above edge image. In cases...
where the element present in the phase of interest does not have an absorption edge in the desired energy limit, the fluid is often doped with chemicals containing an element with high attenuation in the desired energy limit.

For example, potassium iodide is often used as a doping agent to image water present in the porous medium and differential absorption tomography is performed above and below the iodine resonant energy (33.17 keV). In Figure I-3, the porous media containing water doped with the 8% (wt.) potassium iodide was imaged at the energies below (Figure I-3a) and above (Figure I-3b) the iodine absorption edge. The histogram (Figure I-3c) shows how the two images highlight different phases. Due to similar absorption values in the doped-water and air phase at the below-edge energy (33.07 keV), the solid phase is clearly highlighted. At the above-edge energy (33.27 keV), the doped water has a similar absorption to the solid phase making the air phase easy to identify and segment.

Figure I-3: Section of the image acquired at two energies, above and below the Iodine absorption edge (33.17 keV): (a) Below edge image at energy 33.07 keV, (b) Above edge image at energy 33.27 keV, (c) Histogram of the below and above iodine resonant energy.
APPENDIX II PHOToinITIATED POLYMERICANIZATION

Photo-initiated polymerization is a class of polymerization reaction initiated by UV, visible, or laser light. Highly corsslinked polymers can be readily synthesized by this technique and widely used in industrial applications such as: protective coating for wood and paper, varnishes, printing ink, adhesives dental filling and microelectronics (Pappas and McGinniss 1980; Ravve 2006). A typical polymerizable mixture consists of monomers or pre-polymers and one or more initiator molecules. Upon exposure to UV, or visible light, the polymerizable mixture undergoes rapid phase transformation from liquid to solid. The main advantage of polymerization started by photoinitiators is temperature independence and easy control and solventless formulations. Polymerization reaction can start at very low temperatures and can be stopped simply by removing the light source.

II.1 Photoinitiator

Photoinitiators are compounds which form polymerization initiating species upon irradiation with light energy (visible and UV). The polymerization initiating species can be free radical, ionic or both. Upon UV irradiation the free radical are produced by hemolytic cleavage of C-C bonds or by H-abstraction from a donor molecule(Sluggett et al. 1995; Starokadomskii and Solov'eva 2002). Based on the mechanism by which the initiation species are formed, the photoinitiators are generally divided into two types. Type-I initiators can themselves absorb the light energy and undergo a unimolecular cleavage to form free radicals(Ravve 2006). Type-II initiators undergo bimolecular reaction where the photoinitiator in excited state interacts with a second molecule (coinitiator) to generate free radicals. UV initiators of both Type-I and Type-II are available, however photoinitiator for visible light photopolymerization belong exclusively to Type-II class(Ravve 2006). Examples of Type-I photoinitiators include benzoin esters, benzil
ketals, alpha-dialkoxy acetophenones, alpha-hydroxy-alkylphenones, alpha-amino alkylphosphine, acylphosphine oxides. Examples of Type-II photoinitiators include benzo phenones, amines, thioxanthones,amines, titanocenes. An efficient photoinitiator must exhibit a large absorption in the emission range of the light source so as to generate high yield of initiating species. The initiator used in this research are both Type-I initiators and form the free radicals as shown in the Equation (II-1) - (II-3).

\[ \text{Initiator} + h\nu \rightarrow R. \]  

(II-1)

\[ \text{UV light} \]

\[ \text{UV light} \]

\[ \text{UV light} \]

(II-2)

\[ (\text{II-2}) \]

(II-3)

\[ (\text{II-3}) \]

**II.2 Polymerization Reaction**

The reactive species (free radicals) generated upon photo-cleaving of the initiator molecules, initiate the cross linking of the monomer molecules. The reaction is similar to that of conventional thermal polymerization, however reaction rates are much higher due to the large number of initiator species generated by the intense UV radiation.
The rate of reactions also depends on the reactive and number of functional groups participating crosslinking reaction to form a polymer. The reactivity of the functional groups increases in following order (see Figure II-2):

Vinyl ether > Allyl ether > Alkane > Acrylates

The monomer used in the formulation also affects both polymerization rate and extent of conversion as well as the physical properties of the crosslinked polymer. Increase in the reactive functional group accelerates reaction rate at the expense of the overall conversion (see Figure II-
3). From physical properties viewpoint, the increase in the functional groups leads to increased crosslink density to provide harder and polymer and increases solvent resistivity.

Figure II-3: Influence of the monomer functionality on the UV induced polymerization of acrylic resin.(Decker 1996)
VITA

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