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Pore-Scale Analysis of DNAPL Dissolution and Biomass Distribution

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PORE-SCALE ANALYSIS OF DNAPL DISSOLUTION AND BIOMASS DISTRIBUTION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

In

The Department of Civil and Environmental Engineering

by
Keegan L. Roberts
B.S., Louisiana State University, 2001
M.S., Louisiana State University, 2004
May 2009
DEDICATION

To my family for their enduring support
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ABSTRACT

A comparison of equilibrium and non-equilibrium dissolution of tetrachloroethylene (PCE) was conducted to ascertain how PCE saturation, individual blob properties (volume, surface area, sphericity), and PCE occupied pores are affected by two distinct dissolution regimes. One-dimensional columns were imaged at various dissolution stages using high resolution (~10 um) synchrotron x-ray tomography (XT) and image subvolumes were analyzed using a series of grain, pore network structure, and blob analysis algorithms. An analysis of algorithm-generated data was conducted to determine grain and pore statistics, PCE saturation and individual blob properties, and correlations between PCE blobs and pore network structure.

Grain and pore data demonstrated an accurate and consistent segmentation of grains and pores across experiments and a consistent packing between columns. PCE removal rates with pore volumes flushed in both equilibrium and nonequilibrium experiments were consistent until arrival of the primary dissolution front in equilibrium columns. Arrival of the primary dissolution front and number of pore volumes required to completely remove PCE from equilibrium experiments matched well with theoretical predictions. Nonequilibrium dissolution rates varied during the course of the experiment, with increased dissolution observed near the conclusion of the experiments. Blob properties within the equilibrium columns remained relatively constant for all dissolution steps prior to the arrival of the primary dissolution front. Changes in pore-level blob properties in the nonequilibrium experiments were correlated to small perturbations in the mass transfer rates. Deviations in mass transfer rates within the subvolumes occurred over relatively short timescales and are most likely due to the inability to image and analyze a representative elementary volume (REV).

XT was also used to investigate the feasibility of imaging biomass within a porous media system. Lugol’s iodine was used to dope the biomass and mass attenuation histograms were compared to those of an undoped biomass system and an abiotic system imaged with and without Lugol’s iodine filling the pore space. After pre-processing with an anisotropic diffusion program, the biomass could be identified within void space of the biotic columns. This insight will aid in the development of XT in exploring the effects of biomass on pore-scale aqueous flow paths.
INTRODUCTION

Over the past several decades, releases and ineffective disposal of Dense Non-aqueous Phase Liquids (DNAPLs) have become a concern to environmental practitioners. Due to the persistent nature, toxicity, and prevalence of DNAPLs as groundwater contaminants, the scientific community has directed a significant amount of research towards understanding the mass transfer kinetics and associated remediation techniques of these contaminants. While remediation of DNAPL releases is complex due to the subsurface migration properties of the liquids alone, the dearth of knowledge currently available concerning the effects of a subsurface environment on pore scale DNAPL mass transfer kinetics (e.g., encapsulation of residual DNAPL blobs by microbial growth, etc.) only serves to compound the complex issue of determining an effective, efficient means of DNAPL-contaminated groundwater remediation.

DNAPL migration through porous media is subject to heterogeneities of the porous media structure. As a result of these heterogeneities and pore geometries, downward movement of the contaminant through the saturated zone is typically accompanied by trapping of DNAPL blobs (i.e., residual) along the migration pathways by capillary forces. Under normal environmental conditions, the resulting media structure will include a combination of soil particles, water, isolated DNAPL blobs, and microorganisms. While the mass transfer kinetics of the residual DNAPL blobs have been investigated (e.g., Schnaar and Brusseau, 2006; Pan et al., 2007, etc.) and microbial degradation of groundwater contaminants is a widely studied field (e.g., Cope and Hughes, 2001; Yang and McCarty, 2002; etc), little is currently known concerning the mass transfer kinetics of residual DNAPL blobs in biotic porous media systems at the pore scale (on the order of $1 \times 10^2$ microns), nor has a direct experimental comparison of equilibrium and non-equilibrium DNAPL dissolution been conducted previously. The research described in this dissertation was conducted in an attempt to address selected components of these areas.

Current bioremediation research has demonstrated that certain mixed cultures possess the ability to both survive saturation concentrations of chlorinated hydrocarbons and to increase the rate of DNAPL dissolution (Cope and Hughes, 2001; Nielson and Keasling, 1999). The increased dissolution rates have typically been attributed to one of two factors: 1.) an increased concentration gradient resulting from biodegradation of the DNAPL, or 2.) increased solubilities of reductively dechlorinated hydrocarbons in comparison to parent compounds. Regardless, research has demonstrated that mixed culture microbiological communities can be effectively implemented in DNAPL remediation.

As bioremediation is often proposed as a remediation technique for contaminated groundwater, the effects of microbial communities on the mass transfer kinetics of residual DNAPL blobs on the pore scale are vital to understanding residual blob depletion and, ultimately, groundwater remediation in biotic systems. To facilitate an increased understanding of the associated abiotic DNAPL kinetics and provide insight into previously unproven biomass imaging techniques, this research employs high resolution x-ray tomographic imaging to non-destructively gather time-varying images of biotic porous media systems. These images were then analyzed to determine the
feasibility of visualizing biomass on the pore scale using x-ray tomography, a vital precursor to further biotic DNAPL dissolution studies requiring the use of XT.

To investigate the differences between equilibrium and non-equilibrium DNAPL dissolution, PCE was used to establish residual saturation conditions within a 40/50 Accusand-packed aluminum column (5 mm ID). These columns were then subjected to two distinct flow regimes, selected on the basis of theoretical calculations to ensure equilibrium and non-equilibrium mass transfer conditions within the columns. The results of these abiotic experimental sets were compared to ascertain differences experienced by the PCE when subjected to equilibrium and non-equilibrium dissolution. Specifically, grain, pore, and packing properties were investigated to ensure a proper segmentation of the grain and pore phases as well as ensure consistent packings between columns. PCE saturations, individual blob properties (volume, surface area), and PCE occupied pores were then analyzed to ascertain differences in these characteristics caused by the two distinct dissolution regimes.
1. DISSOLUTION BACKGROUND AND LITERATURE REVIEW

1.1 DNAPL Site Assessment and Remediation

Following a release, denser-than-water nonaqueous phase liquid (DNAPL) migration is controlled by subsurface heterogeneities. After the DNAPL source is depleted or removed, free-phase DNAPL will remain in the subsurface in the form of ganglia and pools. DNAPL aqueous phase solubilities are typically several orders of magnitude higher than the drinking water MCLs and, therefore, can cause persistent contamination of drinking water aquifers. DNAPL remediation is extremely difficult – as a result, there is growing interest in reducing the source zone mass flux rather than attempting to completely remove the DNAPL. For this approach to be successful, the DNAPL mass transfer processes must be better understood so that the appropriate relations can be applied in site assessment and remediation designs.

1.2 Motivation for DNAPL Mass Transfer Studies

DNAPL mass transfer kinetics complicate the issue of contaminated site remediation. Typically exhibiting low aqueous solubilities, DNAPLs pose long-term risks to human health due to their environmental persistence (Kennedy and Lennox, 1997) and were previously thought to dissolve into aqueous solutions at such a rate as to preserve a local equilibrium concentration between the pure phase and the solvent. While the theory of local equilibrium has long been held as an accurate assumption of the dissolution process for residual NAPLs, studies from the mid-80s showed that in many cases groundwater concentrations of DNAPL solutes were lower than expected under equilibrium conditions. Factors potentially responsible for these decreased concentrations included rate limited mass interfacial mass transfer and flow by-passing of the aqueous phase around the region of residual contamination due to either porous media heterogeneities or decreased permeability of the contaminated region (e.g., Abriola, 1989; Razakarisoa et al., 1989; Feenstra and Coburn, 1986; Wilson et al., 1988; Mackay and Cherry, 1989; Feenstra, 1990).

Early studies of sorption kinetics indicated the need for more detailed DNAPL mass transfer studies. Miller and Weber (1986) suggested that the local equilibrium assumption does not hold for mass transfer kinetics where regions of high dispersivities and/or high pore water velocities are present. Goltz and Roberts (1988) concluded that non-equilibrium descriptions of mass transfer kinetics are required for areas having immobile water and slow rates of diffusion.

1.3 Dissolution Studies

Interfacial mass transfer between two phases can be the result of a combination of processes, including advective, diffusive, and chemical kinetics. The first work on phenomenological models to describe residual NAPL dissolution in aqueous systems were performed in one-dimensional columns (e.g., Miller et al., 1990; Powers et al. 1992; Imhoff et al., 1993). Early models were based upon describing the mass transfer kinetics
as a solute flux from pure phase contaminant into the aqueous solvent. The most common mass transfer relationship has been defined as:

\[ J = k_l(C_s - C) \]  (1-1)

Where:
- \( J \) = mass flux from solute to solvent
- \( k_l \) = mass transfer coefficient
- \( C_s \) = solute concentration in the aqueous phase assuming equilibrium
- \( C \) = solute concentration in the actual bulk aqueous phase

Expansion of Equation 1-1 to include the stagnant film model yields (Miller et al., 1990):

\[ J = D_l \left( \frac{\partial C_f}{\partial \xi} \right)_f = \frac{D_l}{\delta} (C_s - C) \]  (1-2)

Where:
- \( D_l \) = solute diffusivity in water
- \( \xi \) = distance from boundary of stagnant film into bulk aqueous phase, normal to the NAPL/water interface
- \( \delta \) = thickness of stagnant film

Analysis of the stagnant film theory reveals that the mass transfer kinetics of a nearly immiscible liquid in an aqueous solution is highly dependent on the DNAPL/water interfacial area (Imhoff et al., 1993). Incorporation of the DNAPL/water interfacial area into Equation 1-2 gives (Miller et al., 1990):

\[ J = \frac{1}{A_{na}} \frac{dm}{dt} = k_l(C_s - C) \]  (1-3)

Where:
- \( A_{na} \) = NAPL/aqueous phase interfacial area
- \( \frac{dm}{dt} \) = mass rate of change of the aqueous phase

Equation 1-3 can be used to develop an equation for the local aqueous phase concentration change \( \frac{dC}{dt} \):

\[ \frac{1}{V} \frac{dm}{dt} = \frac{dC}{dt} = \frac{A_{na}}{V} k_l(C_s - C) = K_l(C_s - C) \]  (1-4)

Where:
- \( V \) = volume of the porous media
- \( A_{na} \) = NAPL/aqueous phase interfacial area
- \( k_l \) = mass transfer coefficient
- \( K_l \) = lumped mass transfer rate coefficient where \( K_l = \frac{A_{na}}{V} k_l = a_{na} k_l \)

A number of steady-state and transient 1-D column studies were performed to investigate the impact of various system properties on the rate-limited mass transfer (Johns and
Gladden, 1989, Miller et al., 1990, Powers et al., 1992, Powers et al., 1994, Imhoff et al., 1993) In all cases, the mass transfer relations were formulated in terms of a Sherwood number (Sh) as a function of the Reynolds number, Schmidt number, mean grain size and either the uniformity coefficient or the NAPL saturation. In addition to developing a Sh formulation for transient conditions, Imhoff et al., (1993) used gamma attenuation to non-destructively measure saturation profiles as a function of time. Because none of these studies could measure interfacial areas, only the lumped mass transfer coefficient could be determined. Finally, polymerization was used in several studies to look at NAPL morphology and interfacial areas at residual saturation (Conrad et al., 1992; Mayer and Miller, 1992) and during NAPL dissolution (Powers et al., 1992 & 1994).

Due to the complexity of the mass transfer process, these empirically-based equations are of limited use. Each was developed based on a relatively narrow range of experimental conditions and thus is limited in its applicability to real-world situations.

1.4 Non-destructive Imaging During NAPL Dissolution

Magnetic resonance imaging (MRI) and X-ray Computed Tomography (XT) have been used to non-destructively image systems undergoing NAPL dissolution. MRI studies (Johns and Gladden, 1999; Zhang et al., 2002) provided the first insights into the pore-scale flow and transport processes that were hypothesized in the 1-D larger-scale column studies. While MRI is only able to image the NAPL phase; and the resolution is not high enough to capture fine details, these studies were able to provide relatively detailed description of the changes in blob morphology and NAPL/water interfacial area as a function of saturation. Results showed that smaller ganglia typically experience a higher rate of dissolution than do larger NAPL features due to their increased surface area per unit volume. Furthermore, they have also shown that as dissolution occurs, an increasing number of advective flow paths develop, thereby decreasing flow bypassing and allowing for even greater NAPL dissolution.

Synchrotron XT is capable of providing high resolution, non-destructive, three-dimensional images of multiphase porous media systems that can be used to quantify not just the fluid phases and properties, but also the pore network structure and correlations between the two (Al-Raoush and Willson, 2005; Pradanovic et al., 2007). While capable of providing higher-resolutions than MRI, XT is not able to provide any details on the pore-scale flow field.

Schnaar and Brusseau (2005 and 2006) extensively examine pore scale dissolution of NAPLs through the use of synchrotron X-ray computed microtomography. The researchers create residual NAPL saturations within a 1-D column and monitored NAPL dissolution by means of synchrotron XT. An analysis of the resultant data reveals an initial NAPL saturation on the order of 12.7% in a 45/50 Accusand-packed column and sequential saturations of 6.8%, 1.6%, and 0.5% following the subsequent dissolution steps. Furthermore, the overall number of NAPL ganglia and blobs decrease with each dissolution step. Based on these conclusions, it is possible to monitor the dissolution of residual NAPL blobs on the pore scale over a series of time steps.
Schnaar and Brusseau also concluded that residual blob size correlates to blob morphology as singlets and doublets comprised the majority of smaller blob sizes (more complex ganglia shapes were associated with larger blob volumes). Furthermore, they also observed that more complex ganglia may become separated into smaller, more-sphere like blobs as a result of dissolution of the narrower sections of these NAPL shapes. The researchers were also able to confirm the existence of a linear relationship between NAPL-aqueous phase interfacial area and NAPL volumetric fraction and calculate a mass transfer coefficient using a steady-state, first-order mass transfer equation and assuming one-dimensional transport without dispersion (Equation 1-5) (Powers et al., 1992).

\[
\hat{k} = -\left(\frac{q}{L}\right)\ln\left(1 - \frac{C}{C_s}\right)
\]  

(1-5)

Where:

- \(L\) = length of porous media zone
- \(\hat{k}\) = \(k_{fa}\)

1.5 Pore Network Modeling

Microscale modeling is a complementary approach to quantifying pore-level NAPL dissolution that is able to provide insights into a number of the important pore-scale processes (blob morphology, flow velocities, fluid concentrations). Microscale modeling can be classified into two main categories: pore network models and lattice Boltzmann (LB) models. Pore network models have previously been employed in the study of residual DNAPL dissolution to supplement the information provided by column dissolution study results. Dillard and Blunt (2000), through the use of a rectangular lattice network model, provides a correlation for the modified Sherwood number and the Peclet number for the nonequilibrium dissolution of a residual NAPL. Chomsurin and Werth (2003), employing a pore network etched into silicon wafers, provide insight into such correlations as Non-Wetting Phase (NWP) interfacial specific surface area, Sherwood number, and modified Sherwood number to NWP saturation. However, these micromodels are 2-dimensional and not fully representative of a naturally-occurring actual pore network structure.

Pan et al. (2006) utilized a random three-dimensional sphere pack to investigate residual NAPL dissolution. Following a characterization of the NWP phase (volume, interfacial area, etc.), an aqueous flow field was generated for the pore structure using a lattice Boltzmann approach and correlated to the mass transfer of the system. While providing the first correlations of mass transfer in a 3-dimensional system to an aqueous flow field, it, too, is not representative of a naturally occurring pore network structure. Prodanovic et al. (2007) construct a pore network model of a naturally occurring media before examining quantitative blob characteristics and fluid interactions.

Despite the aforementioned efforts, no previous pore network models have employed the use of an actual porous media structure defined by a grain-base algorithm as input into a pore network model. Through the use of information garnered from x-ray computed
1.6 Image Processing

Regardless of the qualitative analysis packages used to examine tomographic images, some form of image segmentation is required to properly interpret the data. These segmentation techniques can include 1.) simple (or multiple for more than two “phases”), 2.) edge-based, 3.) region-based, 4.) watershed, and/or 5.) indicator-kriging. Unfortunately, each of these techniques exhibits its own advantages and disadvantages. For instance, while a simple thresholding technique requires relatively little computational time, it allows for the introduction of misclassification errors proportional to the percentage of overlapping values of a bimodal distribution for a two-phase system (e.g., solids and voids) (Oh and Lindquist, 1999). Edge- and region-based methods, while eliminating some errors associated with image noise, may misidentify a void or fracture feature within a grain particle as being solid. Watershed segmentation techniques excel at separating adjacent, individual objects into distinct items, but may erroneously separate a uniquely shaped (e.g., a dumb-bell shaped grain particle), single object into multiple entities. Indicator-kriging, while based on a geo-statistical analysis of the image, can be computationally expensive. All images analyzed for this research were subjected to indicator-kriging.

High resolution synchrotron x-ray tomographic images typically contain on the order of several million voxels, each with an assigned gray scale value which is dependent upon the density and chemical composition of the material within the voxel. This can be used to identify the phase of that particular particle based upon the mass attenuation coefficient of that material. Algorithms capable of quantitatively reconstructing the information (e.g., Thompson’s algorithm, 3DMA, and BLOB3D) are not abundant (Thompson et al., 2006).

BLOB3D is a data quantification software package that can be employed in the study of DNAPL blobs found in x-ray tomographic images. Ketcham (2005) describes the data processing sequence as 1.) segmentation, 2.) separation, and 3.) extraction. During segmentation, the unique x-ray attenuation energies of the materials present in the sample are subjected to thresholding (e.g., Expanded Seeding Thresholding—whereby a filter selects all voxels which lie within a gray scale range and subsequently expanding the selection to include voxels which fall within a second gray scale range and are connected to the first series of voxels within a finite distance). The separation module is then employed to segregate connected voxels into one or more objects before the data of interest (e.g., volume, etc.) is extracted for each object. While able to quantify many of the NAPL blob properties (Schnaar and Brusseau, 2005) BLOB3D cannot be used to quantify the porous geometry or topology.

3DMA is an image segmentation and analysis software package developed to produce geometrical analyses of gray-scale images from XCT systems. Typically employed in the characterization of void and grain phases, 3DMA is capable of image segmentation, medial axis modification and statistics, throat construction, and throat/pore body network construction and statistics. Lindquist (1999) describes the algorithm progression as 1.)
image input, 2.) file segmentation (3DMA supports four segmentation algorithms: simple thresholding, anisotropic diffusion, indicator kriging, and mardia-hainsworth [similar to indicator kriging but assumes Gaussian noise in the image and is an iterative method]), 3.) surface distance and medial axis file construction, 4.) throat file construction, and 5.) throat-pore body network file output.

3DMA-Rock is another package which can be used to analyze multiphase XT volumes. Users are allowed one of three thresholding techniques (simple, Mardi-Hainsworth, indicator kriging) before the medial axis of the volume is constructed. Throat and pore surfaces are then identified for use in the construction of a pore-throat network and for a generation of statistical rock properties. The fluid phase is subsequently segmented before discontinuous blobs are quantified and used in the determination of pore saturations (http://www.ams.sunysb.edu/~lindquis/3dma/3dma_rock/3dma_rock.html).

This package has and continues to be the foundation for a body of research investigating the characterization of pore structures as a foundation for exploring fluid-fluid interactions. For instance, Prodanovic et al. (2007) employ 3DMA-Rock in the characterization of Berea sandstone before using a Lattice Boltzmann model to investigate permeability values of the sandstone core. This work is then proceeded by the use of XT fluid phase data to investigate such fluid-fluid interactions as phase partitioning and permeability changes due to fluid additions.

1.7 Dissolution Subvolume Segmentation and Grain, Pore, and Blob Algorithms

To segment the subvolumes for the dissolution experiments in this research, an indicator kriging package written by our group is used. This package is similar to 3DMA in most regards but does have certain differences allowing it more flexibility when processing data. These differences include 1) the option of using a majority filter, 2.) the ability to change the size of the majority filter, and 3) the ability to use a larger sample size for kriging calculations (Bhattad, private communication). In this work, the majority filter is used as are the default values for the majority filter radius and the kriging window radius.

An algorithm developed by Thompson et al. (2006) allows for a quantitative reconstruction of the grain phase by means of a five stage process (ie, vox2grains). During the initial phase of data processing, solid- and void-phase particles are simultaneously labeled as either positive or negative integers, respectively, as the distance from each voxel to the phase interface is mapped. Local maxima are then taken to be the particle centers (or, in the case of the maximum being a cluster of voxels, the center is taken as the center of mass of the cluster in question) during the second stage of processing. Step 3, an iterative process, serves as an opportunity for refinement of the particle location (i.e., the particle center is independent of the particle shape). The center of the particle is defined as the location of the largest sphere that can be inscribed within the boundaries of the solid phase. Voxels which are located within the same particle are merged together thereby forming a single particle. During the fourth stage of the process, the grain particles are assembled before having their statistics calculated during the final stage of the algorithm.
A separate algorithm by Thompson (2008) creates the pore network structure by using the grain information and supplementing this data with pore information (i.e., voxgrains2net). Distance functions are taken as the distance from a point in the void space to the surface of a grain particle. The local maxima distance is then used as a baseline radius for an inscribed sphere within the void space before the maximum diameter inscribed sphere is determined through a series of optimization procedures. Pores are then merged if an inscribed sphere contains the center point of an adjacent inscribed sphere. Phase separated voxel clusters are then assigned to one of the previously defined grain or pore locations before the pore network structure, including throats, is constructed.

PCE blobs are characterized using a connected-component algorithm (Al-Raoush and Willson, 2005a) (i.e., vox2blobs). The algorithm proceeds by first identifying a voxel which contains the PCE following image segmentation. This voxel is labeled with the identifier “1”. The 26 adjacent voxels are then searched to determine if they contain PCE. Voxels containing the PCE and adjacent to the initially identified voxel are also labeled as “1”. Those voxels not containing PCE are originally designated as “0” and remain as such through this process. Inspection of adjacent voxels continues until the summation of all voxels adjacent to this PCE cluster totals 0, identifying an independent blob. This procedure is then repeated on an iterative process, with the next PCE voxel (that has not already been assigned to blob “1”) being identified as “2” until all NWP blobs have been identified.

PCE volume calculations are then made based upon a voxel count methodology. In such a case, the volume of a PCE blob is taken as the number of voxels assigned to that discontinuous blob multiplied by the voxel resolution. PCE surface areas are approximated by a marching cubes technique as this method has been proven to produce more accurate measurements than a simple face counting technique (Al-Raoush and Willson, 2005a).

1.8 Similarity Measure and Sphericity

The shape of PCE blobs can be used as an indication of PCE saturation. Pan et al. (2007) found that at higher NWP saturations, a larger distribution of NWP blob shapes can be observed as more multi-pore ganglia will exist at higher saturations. Similarity measure is a means of describing the shape of a NWP blob and is defined by Pan et al. (2007) as:

\[ \Psi = \frac{V_o}{V_c} \]

Where: $\Psi$ = similarity measure  
$V_o$ = volume of a three-dimensional object  
$V_c$ = volume of the smallest sphere which can enclose the object (center located at the centroid of the object)

Sphericity was used as a surrogate measure of quantifying the shape of the PCE blobs. The sphericity value of a perfect sphere is 1 and is defined by as Wadell (1935) as:
\[ \Psi = \frac{\pi^{1/3} (6V_p)^{2/3}}{A_p} \]  

(1-7)

Where: \( \Psi \) = sphericity

\( V_p \) = volume of the particle

\( A_p \) = surface area of the particle
2. BIOMASS BACKGROUND AND LITERATURE REVIEW

2.1 Effects of Biodegradation on DNAPL Mass Transfer Kinetics

Under typical bioremediation regimes involving chlorinated hydrocarbons, dehalogenating microbes are employed to reductively dechlorinate the contaminant of interest. In the presence of all necessary microbial species and substrates, tetrachloroethylene is biologically degraded, sequentially, to trichloroethylene, dichloroethylene, vinyl chloride, and, ultimately, ethene. As the degradation products have a higher aqueous solubility than does the tetrachloroethylene, the biologically degraded DNAPL can experience an enhanced dissolution rate (compared to the parent compound) and a lower level of environmental persistence (Yang and McCarty, 2002).

A reduction of the hydraulic conductivity in the saturated porous media system may result from increased microbial growth near the contaminant. As the microorganisms reproduce, a sufficient biomass may be generated such that clogging of the pore structure occurs. Once sufficient clogging has taken place, advective flow by-passing may occur, resulting in decreased DNAPL dissolution rates (Baveye et al., 1998).

Further complicating the issue of DNAPL mass transfer kinetics in biotic systems is the potential for gas generation during the biodegradation process (e.g., Baveye et al., 1998; Ronen et al., 1989). Methane produced during reductive dehalogenation can become trapped within the pore structure of the saturated media, resulting in advective flow by-passing (similar to the clogging process associated with accelerated microbial growth). Consequentially, a decrease in the dissolution rate of the entrapped DNAPL may be observed.

2.2 Biomass Imaging

At present, there exists a dearth of knowledge concerning imaging techniques which could be effectively used to image biomass yet still provide an accurate representation of an associated porous media structure. Problematic issues include the fact that biomass typically has a high water concentration, making differentiation of biomass and the aqueous phase extremely difficult. To address this issue, one of two approaches can be taken. First, a non-biomass diffusing dopant can be added to the aqueous phase, thereby creating three phases (ie, grain, doped aqueous, biomass) with distinctly different x-ray attenuation characteristics. Second, a dopant can be added to the aqueous phase which will preferentially sorb to the biomass, also creating three identifiable phases (ie, grain, aqueous, doped biomass).

At present, work is being conducted at Oregon State University to investigate the use of silver nano-particles as an aqueous phase dopant in biotic porous media systems (http://web.engr.oregonstate.edu/~wildensd/biofilm.html). This work hopes to employ silver coated, near neutral buoyancy spheres as a non-biomass partitioning aqueous phase tracer. It is hypothesized that the size of these spheres (~10-20 microns) will prevent their migration through biomass films.
The approach used in this research for the purpose of imaging biotic porous media is to dope biotic materials through the introduction of Lugol’s iodine into the system. As iodine is typically used in microbiological staining procedures, it is hypothesized that iodine ions will sorb to the biotic materials as Lugol’s iodine is flushed through the system, making these regions identifiable based upon their altered x-ray attenuation properties. An aqueous phase flush of water is then remove excess iodine solution from void spaces not occupied by biomass, thereby allowing these regions of the sample column to be identified and segmented from the aqueous and grain phases. The relative low cost and ease of acquisition of Lugol’s iodine make it the preferred candidate for these trials.

2.3 Biomass Imaging Subvolume Segmentation and Grain, Pore, and Blob Algorithms

Prior to image segmentation, biomass system subvolumes are subjected to an anisotropic diffusion program written by our group (Bhattad, personal communication). The anisotropic diffusion program removes noise in the image by first defining the edge of an object (in this case, a phase) according to a maxima gradient in grayscale values. A diffusion coefficient function is then constructed so that a maximum flux is assigned to the homogenous regions of the phase and a minimum flux is assigned to the edge (PoreSim, 2007). The region is then homogenized to a more discreet range of intensity values, allowing for image segmentation to continue.

The same segmentation packages and grain, pore, and blob (biomass in this case) were used to process biomass imaging subvolumes as are described in Section 1.7.
3. DISSOLUTION MATERIALS AND METHODS

3.1 Experimental Setup

Thin-walled aluminum columns (50 mm length by 6 mm outside diameter by 5 mm inside diameter) were packed with a washed 40/50 Accusand (Unimin Corporation) under ponded (de-ionized water), vibrating conditions. The sand was packed by pouring the grains in a series of 5 lifts while vibrating the column and manually tamping each sand layer between lifts. 20 μm high-density polyethylene frits (Kimble Chase) were used as bed support on both ends of the columns and in an effort to randomly distribute any flow entering the porous media. Stainless steel fittings (Swagelok) were used to connect both ends of the aluminum columns to Teflon tubing (Figure 3-1). Teflon tubing was selected for use as previous research has shown that Teflon tubing is the least sorbing commercially available flexible tubing when examining chlorinated hydrocarbons (Barcelona et al., 1985). The up-gradient end of the flexible tubing was affixed to a syringe pump loaded with de-ionized water while the downgradient end was connected to an effluent tube. In this configuration, de-ionized water was pumped vertically upward through the column at a Darcy velocity of 0.003 cm/sec for a minimum of 10 pore volumes (~0.37 cc/PV). Next, a second syringe, filled with a mixture of tetrachloroethylene (PCE) doped with 8% (volume:volume) 1-iodononane and a minimal amount of oil red dye was used to pump the PCE vertically upward through the column for 3 pore volumes in order to flood the column with DNAPL. Following the PCE flood, the column was flipped over and a syringe containing a mixture of de-ionized water and PCE at its aqueous solubility limit (~0.0002 g/cc) was connected to the column. This fluid was then pumped vertically downward through the column at a Darcy velocity of 0.003 cm/sec for 5 pore volumes in order to displace any mobile DNAPL within the porous media system and to establish a residual DNAPL saturation within the matrix.

For a PCE water system, a darcy velocity of 0.003 cm/sec corresponds to a Capillary number of approximately $10^{-5}$. This value is consistent with the range of values typically used for creating residual NWP systems (Schaar and Brusseau, 2005) and small enough
(< 10^{-3}) to not have any significant impact on the residual saturation (Morrow and Chatzis, 1982).

3.2 Flow Rates and Diffusion Fronts

Aqueous phase flow rates for the equilibrium dissolution experiments (Table 3-1) were based upon steady state mass transfer relationships provided by Powers et al. (1992). Non-equilibrium dissolution flow rates were chosen to ensure a non-equilibrium dissolution regime, albeit outside of the valid operating range of the Power’s relationship. Calculations of the equilibrium flow rate were based upon the following equations:

\[ Sh' = 57.7 \text{Re}^{0.61} d_{50}^{0.64} U_i^{0.41} \]  \hspace{1cm} (3-1)

Where: \( Sh' \) = modified Sherwood number

\( Re \) = Reynolds number

\( d_{50} \) = mean grain size

\( U_i \) = uniformity index

\[ \text{Re} = \frac{\rho_w q l_c}{\mu_w} \]  \hspace{1cm} (3-2)

Where: \( \rho_w \) = density

\( q \) = superficial velocity

\( l_c \) = characteristic length (d_{50})

\( \mu_w \) = viscosity

\[ U_i = \frac{d_{60}}{d_{10}} \]  \hspace{1cm} (3-3)

Where: \( d_{60} \) = grain diameter at which 60% of the mass of a grain distribution sample is smaller

\( d_{10} \) = grain diameter at which 10% of the mass of a grain distribution sample is smaller

(Schroth et al., 1996)

\[ Sh' = \frac{\hat{k}(d_{50})^2}{D_L} \]  \hspace{1cm} (3-4)

Where: \( \hat{k} \) = Lumped mass transfer coefficient (product of mass transfer coefficient and specific surface area)

\( D_L \) = Diffusivity
\[
\hat{k} = -\left( \frac{q}{L} \right) \ln \left( 1 - \frac{C}{C_s} \right)
\]  
(3-5)

Where:
\( q \) = Darcy velocity  
\( L \) = Column length  
\( C \) = Bulk aqueous phase concentration of solute  
\( C_s \) = Aqueous phase concentration of solute if at equilibrium

Dissolution experimental aqueous flow rates were selected to ensure that two distinct dissolution regimes would be achieved. The flow rate for the equilibrium dissolution regime was chosen as it allowed for dissolution conditions closely approximating those of an equilibrium dissolution regime but also allowed for the experiments to be completed within the available Advanced Photon Spurce (APS) beamline time constraints. While outside of ranges normally observed in experimentation, the non-equilibrium flow rate ensured that the dissolution conditions were of a non-equilibrium nature and were distinctly different than those of the equilibrium experiments.

<table>
<thead>
<tr>
<th>Table 3-1: Experimental Dissolution Conditions</th>
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<td>Dissolution Regime</td>
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</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>Non-Equilibrium</td>
</tr>
</tbody>
</table>

Imhoff et al., (1996) defines the primary dissolution front as the length over which the NWP saturation decreases from a value of \( S_{ni}\eta \) to \((1-\eta)S_{ni}\) where \( \eta \) represents the percentage of NWP expected to be removed via dissolution. The dissolution front length is a function of the NAPL, the porous medium, and the aqueous phase (Imhoff et al., 2003; Equation 3-6).

\[
L_{df} \approx \frac{2v_{af} \phi \eta^{1-\beta_1} - (1-\eta)^{1-\beta_1}}{\beta_0 S_{ni} \eta^{\beta_1}}
\]  
(3-6)

Where:
\( L_{df} \) = Length of dissolution front  
\( v_{af} \) = Final interstitial aqueous phase velocity  
\( \phi \) = Porosity  
\( \eta \) = Threshold parameter (Imhoff et al., 1996)  
\( \beta_0, \beta_1 \) = Equation constants (Miller et al., 1990)  
\( S_{ni} \) = Mean initial NAPL saturation
The primary equilibrium dissolution front length was considered to be where 90 percent of existing NAPL would be removed by dissolution. For the experimental conditions used here, the front was calculated to be approximately 0.5 mm in length and estimated to arrive within the scanned region of the column (approximately 1.6 cm from the influent end) at approximately 330 pore volumes flushed (PVF). While applicable for the equilibrium flow regime, this relationship does not hold for the non-equilibrium conditions.

Two columns were left at residual saturation and the remaining ten columns were divided into two subsets (equilibrium and non-equilibrium). Five equilibrium columns were flushed vertically downward with de-ionized water at a Darcy velocity of 0.003 cm/sec at multiples of 120 pore volumes (PV). For example, equilibrium column 2 was flushed for 120 pore volumes, equilibrium column 3 was flushed for 240 pore volumes and equilibrium column 6 was flushed for 600 pore volumes. After the appropriate number of pore volumes was flushed through the column, three PV of PCE-saturated water was flushed to prevent further PCE dissolution. After this step, the influent and effluent tubing was removed from the columns and they were capped in a water bath.

The five non-equilibrium columns were flushed vertically downward with de-ionized water at a Darcy velocity of 0.071 cm/sec for multiples of 150 pore volume flushes. For example, non-equilibrium column 2 was flushed for 150 pore volumes, non-equilibrium column 3 was flushed for 300 pore volumes and non-equilibrium column 6 was flushed for 750 pore volumes. As with the equilibrium columns, each of these columns was flushed with three volumes of PCE-saturated de-ionized water and then capped beneath a water bath.

The residual saturation columns were first imaged (Section 3.3) and then used for dynamic and dynamic replicate non-equilibrium experiments. These dynamic columns were flushed for 150 PV with de-ionized water, flushed with three PVs of PCE-saturated de-ionized water, capped, and imaged at the same region of the column as before. This process was repeated at 150 PVs until final imaging after 750 PV flushed.

3.3 Image Acquisition and Processing

XT images were collected at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. These images were collected by rotating the sample columns at 0.5° increments from 0° to 179.5° and collecting a 2-dimensional image at each increment at pre-determined energy levels above and below the iodine adsorption K-edge (33.169 KeV). The columns were then reset to a starting rotation of 0.25° and images were again taken at 0.5° increments from 0.25° to 179.75° above and below the iodine K-edge, for a total of 720 images (sample scanning arrangement in Figure 3-3). Images were taken at energies near the iodine K-edge as 1-iodononane had been added to the PCE. Due to the difference in absorption properties between water and iodine, such a procedure allows for the PCE to be easily distinguished from the wetting phase in XT images. These images were then converted to a 3-dimensional volumetric data set through algorithms developed by GeoSoilEnviroCars (Willson et al., 2004; http://cars9.uchicago.edu/gsecars/index.html).
All of the columns were imaged at energies both above and below the iodine K-edge, 33.269 KeV and 33.069 KeV, respectively. Two adjacent 5.2 mm sections were scanned at a resolution of 9.92 μm and identified as either “H1” (scan section closest to influent) or “H2” (scan section downgradient from H1; Figure 3-3). Those data points without an H1 or H2 designator are a composite of both scan heights.

The first scanned region of each column was located approximately 1.6 cm down-gradient from the influent end of the column. The inability to scan the initial reach of the column was due to the stainless steel column end fittings and the associated inability of the x-rays to penetrate this material. Column section scans were then labeled according to their dissolution regime, PVF, and scan location (Figure 3-3). (eg, “non-equilibrium-150-H2” is that scan height down gradient of but adjacent to scan height 1 which was subjected to non-equilibrium dissolution conditions and imaged following 150 pore volumes of deionized water being flushed through).
Following image acquisition and reconstruction, the XT volume was cropped and re-written from a 16-bit file to an 8-bit file using an IDL (Visual Information Solutions) routine at a minimum distance of one grain diameter from the inner column wall. The cropped subvolume (Figure 3-4) was created in an effort to create the largest possible subvolume exclusive of regions where possible wall effects may be present. The subvolume was cropped to a size of 350 voxels by 350 voxels by 350 voxels, creating a 0.04 cc subvolume.

A subvolume attenuation histogram generated by the routine was used to select threshold values for phase segmentation within the image (Figure 3-5). The histogram peaks shown in Figure 3-5 represent, from left to right, the aqueous phase, the grain phase, and the PCE phase. The X-axis is a scaled absorption value and the y-axis is the number of voxels in the subvolume containing a given absorption value.

The indicator kriging algorithm, described in Section 1.7, is then used to assign phase-dependent values to individual voxels. Initially, the PCE is segmented from the aqueous and grain phases. All PCE assigned voxels are then reassigned a value of 0 (with grain and aqueous phase voxels being assigned a value of 1). This segmented image was then multiplied by the original binary image and segmented again, separating the void phase from the grains. The two segmented images were then added together producing a subvolume as shown in Figure 3-6. Threshold values for all segmentations can be found in Table 3-2.
The segmented subvolume is then processed using a “remove islands/holes” algorithm which locates adjacent voxel clusters of a certain size grouping and phase designation and re-assigns those clusters to another phase. In order to optimize the data output and eliminate potential noise in the subvolume, PCE clusters smaller than 63,000 microns$^3$ (65 voxels) were re-assigned to the aqueous phase. This step had little affect on PCE saturation values while removing potential areas of image noise. This procedure was replicated for grain-phase clusters smaller than 20,000 microns$^3$ (20 voxels). Following the removing islands/holes processing, the resultant output was compared to the original binary image to ensure that processing had preserved the true image and not inadvertently removed an actual artifact.

Following phase segmentation and island/holes processing, the subvolume is input into a series of algorithms, beginning with a grain-based algorithm (Thompson et al., 2006) and concluding with the blob analysis (Al-Raoush and Willson, 2005a), as described in Section 1.7.
Figure 3-6: Segmented Three-phase Subvolume

Segmented phases in the above image are: red - grain, blue - aqueous, and purple - PCE.

Table 3-2: Dissolution Threshold Values

<table>
<thead>
<tr>
<th>Experiment</th>
<th>&quot;PCE&quot; Threshold Values</th>
<th>&quot;Grain&quot; Threshold Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium-0-H1</td>
<td>47.49</td>
<td>37.39</td>
</tr>
<tr>
<td>Equilibrium-0-H2</td>
<td>52.54</td>
<td>43.45</td>
</tr>
<tr>
<td>Equilibrium-120-H1</td>
<td>54.56</td>
<td>43.45</td>
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<td>Equilibrium-120-H2</td>
<td>45.47</td>
<td>37.39</td>
</tr>
<tr>
<td>Equilibrium-240-H1</td>
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<td>Equilibrium-360-H1</td>
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<td>Equilibrium-360-H2</td>
<td>41.43</td>
<td>31.33</td>
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<tr>
<td>Equilibrium-480-H1</td>
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<td>34.36</td>
</tr>
<tr>
<td>Equilibrium-480-H2</td>
<td>N/A</td>
<td>34.36</td>
</tr>
<tr>
<td>Equilibrium-600-H1</td>
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<td>38.40</td>
</tr>
<tr>
<td>Equilibrium-600-H2</td>
<td>N/A</td>
<td>34.36</td>
</tr>
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<td>Non-Equilibrium-0-H1</td>
<td>41.43</td>
<td>34.36</td>
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Table 3-2: Continued

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<th>&quot;Grain&quot; Threshold Values</th>
</tr>
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<td>Non-Equilibrium-450-H1</td>
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4. BIOMASS IMAGING MATERIALS AND METHODS

4.1 Experimental Setup

Thin-walled aluminum columns (50 mm length by 6 mm outside diameter by 5 mm inside diameter) were used to core sections from two separate samples for biomass imaging experiments. The abiotic sample was cored from a container comprised solely of a washed and water-saturated 40/50 Accusand (Unimin Corporation). The porous media was packed by depositing the grains into a small bucket (not the column itself) in one continual lift while vibrating the holder. The biotic sample was cored from a separate small bucket comprised of a washed and water-saturated 40/50 Accusand and an undefined mixed microbial culture. This culture was collected from the Baton Rouge Central Waste Water Treatment Facility (Baton Rouge, LA) and centrifuged at 9,400 x g for 5 minutes in order to create a dense biomass pellet and remove excess water from the biomass. This process was repeated numerous time in order generate a significant amount of centrifuged biomass. In excess of 1 pore volume (PV of small bucket) of biomass was generated and mixed with the washed 40/50 Accusand. A minimal amount of water was added to the Accusand/biomass mixture before the entire mixture was homogenized by hand, breaking the biomass pellets into sizes that could fit within the pore structure of the column. The biotic sample was then cored from the container using the afore-mentioned thin-walled aluminum columns.

20 μm high-density polyethylene frits (Kimble Chase) were used as bed support for the porous media on both ends of each of the columns and to randomly distribute the influent flow. These frits were inserted into the column ends following coring of the samples. Stainless steel fittings (Swagelok) were used to connect the aluminum columns to Teflon tubing. The up-gradient end of the flexible tubing was affixed to a syringe pump loaded with de-ionized water. Once the down-gradient terminus of the column was affixed with a stainless steel fitting and effluent tubing, de-ionized water was pumped vertically upward through the column at a Darcy velocity of 0.003 cm/sec for a minimum of 10 PVs (~0.37 cc/PV). This flow rate was identical to that which was used to construct the dissolution columns.

Following the 10 PV deionized water flush, each of the columns was scanned approximately 1.6 cm from the effluent end of the column (due to the inability to scan the stainless steel connection region of the column). One ~0.5 cm section was imaged in the abiotic column and two consecutive ~0.5 cm sections were imaged in the biotic column. Following scanning, each column was re-connected to a syringe pump and promptly flushed with 5 PV Lugol’s iodine at a Darcy velocity of 0.003 cm/sec. Sample columns were then re-sealed and the same effluent end regions of each column were re-scanned. Following scanning, each column was re-connected to a syringe pump and promptly flushed with 1 PV of deionized water at a Darcy velocity of 0.003 cm/sec. Sample columns were then re-sealed and the same effluent end regions of each column were re-scanned.

Both the abiotic and biotic columns experiments were scanned at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. These
columns were imaged at energies both above and below the iodine K-edge, 33.269 KeV and 33.069 KeV, respectively at a resolution of 10.03 μm. The scanned region of each column was located approximately 1.6 cm downgradient from the effluent end of the column.

Processing of the biomass imaging experimental results was similar to that of the DNAPL dissolution experiments. However, following the creation of the biomass system subvolume but prior to image segmentation, the subvolume was run through an anisotropic diffusion program (described in Section 2.3) in order separate two overlapping histograms peaks (Figure 4-1). The use of anisotropic diffusion was necessary as the original subvolume attenuation histograms for the biotic columns during and following Lugol’s iodine injection could not be separated by indicator kriging alone. Anisotropic diffusion homogenized regions within the subvolume which then allowed for phase segmentation.

Following anisotropic diffusion processing, the two overlapping histograms were separated into unique histogram peaks and were able to be segmented into separate phases for future processing (Figure 4-1). The x-axis of Figure 4-1 is cropped from a maximum value of 255 to 50 in order to better illustrate the peak separations.

![Figure 4-1: Pre- and Post-Anisotropic Diffusion Histograms](image-url)
4.2 Secondary Qualitative Biomass System Imaging Studies

Following the biomass system imaging experiments, a series of batch laboratory experiments were performed to: (1) determine if biomass volume would change in the presence of different aqueous phases; and (2) study the extent of iodine diffusion through biomass. The first set of experiments was specifically intended to determine if the addition of Lugol’s iodine may have altered the pore volume occupied by biomass within the sand after the Lugol’s flush. The second experiment was conducted with the intent of ascertaining the ability of a Lugol’s solution to diffuse through biomass and dope the entire biomass within a system (as opposed to doping only surficial portions of biomass directly contacted with Lugol’s iodine).

The biomass utilized in both sets of experiments consisted of granular activated sludge collected from a laboratory-scale sequencing batch reactor (SBR) configured essentially as described by McSwain et al. (2004) but with a working volume of 2.0 L. The synthetic wastewater fed to the SBR was as described by Moy et al. (2002) with the exceptions that meat extract (250 mg/L) and AlCl₃ (0.05 mg/L) were omitted. Sludge granules collected from the reactor were collected by straining through a sieve. The first series of qualitative experiments involved placement of approximately 4 mL of activated sludge granules within a test tube (15 mL nominal capacity). After allowing granules to settle for approximately 5 hours, supernatant was decanted, and then 4 mL of the following liquids were added to the top of each sample taking care not to disturb the settled biomass: de-ionized water, tap water, carbon-free feed solution, feed-solution with carbon sources added (1400 mg/L glucose and 400 mg/L peptone), Lugol’s iodine, and a sodium chloride solution with an ionic strength identical to that of Lugol’s iodine. The volume of the biomass was then visually observed at various intervals over a period of 24 hours to ascertain any changes in the original biomass volume. A control tube of approximately 4 mL of settled biomass with no solution addition was also monitored to provide a baseline comparison.

The second series of experiments employed two 15-mL test tubes containing approximately 4 mL of granular activated sludge biomass prepared as described above but with 4 mL and 8 mL, respectively, of Lugol’s iodine carefully ponded on top of the settled biomass. The tubes were then monitored for a period of 24 hours and the location of the iodine diffusion front through each biomass sample was recorded by tracking the staining of the white biomass by the brown Lugol’s iodine solution.
5. DNAPL DISSOLUTION PORE RESULTS

5.1 Grain Size and Packing Analysis Results

Using the vox2grains program (Section 1.7), grain data was calculated from all imaged and segmented subvolumes and compiled for comparison to sieve data provided by the Accusand manufacturer (Unimin Corporation). The first look at the grain and packing properties (porosity, inscribed radius (GIR), surface area, aspect ratio (GAR), and coordination number) was to ensure that segmentation techniques used to separate grain and void phases were consistent between subvolumes. As evidenced by the data in Table 5-1, grain segmentation was consistent between subvolumes as the largest standard deviation for a grain property was 3% of the average value (grain coordination number). A closer look at the grain data reveals what might be a slight inverse relationship between the lowest grain coordination numbers and their associated porosities. Those column sections with the lowest grain coordination numbers (eg, less than 6.0) displayed the highest porosity values (eg, ≥ 0.38).

Table 5-1: Grain and Packing Properties

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium-0-H1</td>
<td>0.36</td>
<td>118</td>
<td>3.59E+05</td>
<td>1.57</td>
<td>6.4</td>
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</tr>
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<td>Equilibrium-240-H2</td>
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<td>Equilibrium-360-H1</td>
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<tr>
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<td>Equilibrium-480-H1</td>
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<td>5.9</td>
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<td>5.8</td>
</tr>
<tr>
<td>Equilibrium-600-H1</td>
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<td>6.3</td>
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<td>3.43E+05</td>
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<td>Non-Equilibrium-0-H1</td>
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<td>3.49E+05</td>
<td>1.59</td>
<td>6.0</td>
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<td>Non-Equilibrium-0-H2</td>
<td>0.38</td>
<td>118</td>
<td>3.57E+05</td>
<td>1.55</td>
<td>6.3</td>
</tr>
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<td>6.0</td>
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<tr>
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<td>118</td>
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<td>5.9</td>
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<td>Non-Equilibrium-300-H1</td>
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</tr>
<tr>
<td>Non-Equilibrium-300-H2</td>
<td></td>
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<td>6.1</td>
</tr>
<tr>
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<td>118</td>
<td>3.60E+05</td>
<td>1.56</td>
<td>5.8</td>
</tr>
<tr>
<td>Non-Equilibrium-600-H1</td>
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<td>115</td>
<td>3.50E+05</td>
<td>1.57</td>
<td>6.3</td>
</tr>
<tr>
<td>Non-Equilibrium-600-H2</td>
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<td>117</td>
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<td>6.3</td>
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<tr>
<td>Non-Equilibrium-750-H1</td>
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<td>118</td>
<td>3.56E+05</td>
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<td>6.2</td>
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<tr>
<td>Non-Equilibrium-750-H2</td>
<td>0.38</td>
<td>120</td>
<td>3.61E+05</td>
<td>1.54</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Next, the grain size distribution, obtained from the images, was compared to a standard sieve analysis (provided by Unimin Corp.). An effective grain diameter (GED) for each grain was calculated (Equation 5-1)

\[
GED = \frac{(2 \times GIR \times GAR) + (2 \times GIR)}{2}
\]  

(5-1)

where GIR (grain inscribed radius) is the radius of the largest sphere which could be inscribed within a grain and GAR (grain aspect ratio) is calculated as a grain’s long axis divided by its short axis. Comparison of the grain size distribution calculated from the image data and that from the sieve analysis (Figure 5-1) suggests that the image-based grain size distribution does a decent job of capturing the median grain diameter \(d_{50}\) and the overall trend. However, the simplistic approach using Equation 5-1 seems to cause some under- and over-calculation of the actual grain sizes. This causes more spreading of the distribution. Furthermore, the agreement between the grain size distributions from a subset of experiments (Figure 5-1) provides further evidence of the consistency of the grain versus void thresholding.

## 5.2 Pore Network Structure Analysis Results

A review of the cumulative pore size distribution reveals a consistent pore size distribution between experiments (Figure 5-2). This would suggest a consistent packing and void identification during thresholding. As pore size distribution is independent of dissolution regime and is dependant upon media size and packing, it was expected that distributions would remain consistent between experiments. Approximately 50 percent of all pores have a pore inscribed radius (PIR) less than 50 microns. The average GED:pore inscribed diameter ratio for the sand packings in these experiments yielded a value of 2.5. A similar analysis of a natural sand with a similar average grain diameter (325 μm) yielded ratios of 3.5 and 2.4 for two samples, suggesting that the pores in these experiments are accurately segmented (Al-Raoush and Willson, 2005b).

Data from the pore network structure algorithms revealed an average pore inscribed radius of 0.047 mm and an average throat inscribed radius of 0.031 mm with standard deviations of 2 and 3 percent, respectively. The small standard deviation for these measures suggests a consistent packing and void thresholding across the experiments. Schnaar and Brusseau (2005) use the water-retention curve from a similar sand (ie, 45/50 Accusand) to estimate pore size distribution and find that approximately 90% of the pores in their systems have radii between 50 um and 100 um. Comparatively, pores with diameters between 50 and 100 um in these dissolution experiments comprised only 35%
of the pore size distribution (Figures 5-24 through 5-27). This discrepancy in pore size
distribution could be attributed to the wider grain/pore size distribution used in these
dissolution experiments. Al-Raoush and Willson (2005a) analyze a slightly larger media
($d_{50} = 500$ um) and find a similar cumulative distribution of pore radii 30 um or smaller
(~75% of total pores). However, their largest 25% of pores have a wider distribution of
values than those observed in these experiments. A water retention curve prediction for
pore sizes (Rowell, 1994) using published data for a 40/50 Accusand (Schroth et al.,
1996) is also calculated. This cumulative frequency prediction does vary from the
experimental data but displays a similar approximation of pore sizes. The variation from
experimental data could be attributed to the fact that pore size distributions estimated
from values from the Schroth et al. (1996) water retention curves do not include the
smallest pore sizes associated with the irreducible water content.

Table 5-2: Pore and Throat Properties

<table>
<thead>
<tr>
<th>Experiment (Both Scan Heights)</th>
<th>Avg. PV (um$^3$)</th>
<th>Avg. PIR (um)</th>
<th>Avg. PCN</th>
<th>Avg. TIR (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium-0</td>
<td>2.11E+06</td>
<td>45.55</td>
<td>5.87</td>
<td>30.48</td>
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<tr>
<td>Equilibrium-120</td>
<td>2.34E+06</td>
<td>47.67</td>
<td>5.93</td>
<td>31.73</td>
</tr>
<tr>
<td>Equilibrium-240</td>
<td>2.25E+06</td>
<td>47.09</td>
<td>5.93</td>
<td>31.37</td>
</tr>
<tr>
<td>Equilibrium-360</td>
<td>2.24E+06</td>
<td>47.17</td>
<td>5.93</td>
<td>31.31</td>
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<tr>
<td>Equilibrium-480</td>
<td>2.47E+06</td>
<td>49.26</td>
<td>5.96</td>
<td>32.84</td>
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<tr>
<td>Equilibrium-600</td>
<td>2.32E+06</td>
<td>48.14</td>
<td>5.81</td>
<td>32.24</td>
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<tr>
<td>Non-Equilibrium-0</td>
<td>2.25E+06</td>
<td>46.91</td>
<td>5.91</td>
<td>31.21</td>
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<tr>
<td>Non-Equilibrium-150</td>
<td>2.20E+06</td>
<td>46.66</td>
<td>6.22</td>
<td>30.41</td>
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<tr>
<td>Non-Equilibrium-300</td>
<td>2.2E+06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-Equilibrium-450</td>
<td>2.44E+06</td>
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<td>6.00</td>
<td>31.90</td>
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<td>Non-Equilibrium-600</td>
<td>2.08E+06</td>
<td>45.51</td>
<td>5.97</td>
<td>30.21</td>
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<tr>
<td>Non-Equilibrium-750</td>
<td>2.33E+06</td>
<td>47.62</td>
<td>5.97</td>
<td>31.46</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>2.27E+06</strong></td>
<td><strong>47.25</strong></td>
<td><strong>5.95</strong></td>
<td><strong>31.38</strong></td>
</tr>
<tr>
<td><strong>STANDARD DEVIATION</strong></td>
<td><strong>1.16E+05</strong></td>
<td><strong>1.12</strong></td>
<td><strong>0.10</strong></td>
<td><strong>0.80</strong></td>
</tr>
</tbody>
</table>

Where: $PV$ = pore volume  
$PIR$ = pore-inscribed radius  
$PCN$ = pore coordination number  
$TIR$ = throat inscribed radius
Figure 5-1: Calculated Effective Grain Diameter and Provided Sieve Analysis

Figure 5-2: Cumulative Pore Size Distribution
5.3 PCE Blob Analysis

5.3.1 Bulk PCE Characteristics Analysis

The PCE saturations in the two residually-saturated subvolumes range from 0.18 to 0.19 (Figure 5-3) with one standard deviation of 0.03 based upon data gathered from the vox2blobs algorithm (Section 1.7). This indicates good replicability between the systems and is reasonably consistent with residual PCE saturations found by previous researchers. Dobson et al. (2006) report saturations in 3 cm ID by 28 cm length columns ranging from 0.202 to 0.21 for a 40/50 Accusand and Schnaar and Brusseau (2005) identify saturations, using 0.46 ID and 0.58 cm ID by 4.4 cm length-mm columns, of 0.17 to 0.22 over a range of three porous media types, including a 45/50 Accusand.

The PCE saturations in the equilibrium static column subvolumes show a gradual decline with PVF followed by a drop to zero (or near zero) between 360 and 480 PVF (Figure 5-3). This is consistent with the theoretical arrival time of the primary dissolution front calculated from Equation 5-2 (~405 PVF) and the estimated number of PVs needed for complete removal of the PCE within a distance of 1.4 cm (~200 PVF) following arrival of the dissolution front. The slight deviation from the theoretical arrival of the primary dissolution front (defined as 90 percent removal of the initial PCE mass (Imhoff et al., 2003) can be attributed to two possible causes. The use of multiple independent columns to study the equilibrium dissolution will result in slightly varying conditions within each column (eg, PCE saturation, etc.). Furthermore, the inability to scan the initial 1.6 cm of the column precludes any understanding of the conditions in the upstream portions of these columns or the influent connections.

\[
PVF_{dfa} = \frac{(S_{PCE})(PV_{AOI})(\rho_{PCE})(\eta)}{(C_S)(PV_{col})}
\]  

(5-2)

Where: 
- \(PVF_{dfa}\) = pore volume flushes required for primary dissolution front arrival  
- \(S_{PCE}\) = PCE saturation  
- \(PV_{AOI}\) = pore volume of the area of interest  
- \(\rho_{PCE}\) = PCE density  
- \(\eta\) = threshold parameter  
- \(C_S\) = PCE solubility in aqueous phase  
- \(PV_{col}\) = pore volume of the column

The non-equilibrium static, dynamic, and dynamic replicate columns all experience similar PCE saturation versus PVF patterns (Figure 5-3). All three experimental series experience a relatively increased dissolution rate during one of the first dissolution steps, followed by a period of decreased dissolution, and then (under these experiment conditions) an increased dissolution rate in PCE saturations after 600 PV flushed.

The most obvious difference between the equilibrium and non-equilibrium systems is a result of the distinct arrival of the equilibrium dissolution front followed by a relatively rapid flushing of the imaged section. There does appear to be a continuous gradual decline in PCE saturation in the equilibrium subvolumes until the arrival of the
dissolution front (following 360 PVF). This indicates that there is some dissolution occurring despite the primary dissolution front being in the upstream portion of the column.

For comparison, Zhang et al. (2002) exhibits a steady decline in DNAPL volumetric fraction as function of PVF for a angular silica gel (d = 0.5 mm) in a 1.2 cm ID column at a darcy velocity of 1.83 m/day. Upon arrival of the primary dissolution front, Imhoff et al. (1993) observes a similar steady decline in TCE saturation within a 8.25 cm ID by 3 cm long column packed with 40/50 sand (d50 = 0.36 mm) and flushed at a darcy velocity of 0.91m/day. The unsteady changes in PCE saturation of the non-equilibrium columns for these dissolution experiments could possibly be attributed to the high aqueous flow rate and flow by-passing of entrapped PCE blobs.

![Figure 5-3: PCE Saturation vs Pore Volumes Flushed](image)

Mass transfer rate coefficients (MTRC) are calculated for the non-equilibrium dynamic and dynamic replicate experiments using the PCE saturation data (Figure 5-3). Steady state mass transfer is assumed to occur during the 150 PVF for each dissolution step and Equation 5-3 is used to calculate the mass transfer rate coefficient (Zhang et al., 2002). The capillary PCE specific surface area is used instead of the total PCE surface area in Equation 5-3 as Zhang et al. uses the total measure as a surrogate for the interfacial PCE specific surface area. The PCE concentration in the aqueous phase (C) is taken as the mass lost during each dissolution stage (150 PVF) divided by the volume of water flushed (~55 cc; PV multiplied by PVF) (Equation 5-4). Mass transfer rate coefficients for each dissolution stage are then calculated using the column system parameters and the interfacial specific surface area provided by the vox2blobs algorithm. An examination of
the PCE capillary SSA data reveals both experiments exhibit a strong linear relationship between the absolute change in PCE saturation and the calculated mass transfer coefficient (Figure 5-4).

$$k = -\frac{q}{a_i L} \ln \left( 1 - \frac{C_{x=L}}{C_s} \right)$$  \hspace{1cm} (5-3)

Where:
- $k$ = mass transfer rate coefficient
- $q$ = darcy velocity
- $a_i$ = PCE capillary specific surface area
- $L$ = distance of the imaging region over which mass transfer is occurring (1.4 cm)
- $C_{x=L}$ = concentration at position “L”
- $C_s$ = PCE solubility limit

$$C_{x=L} = \frac{\rho \Delta V}{Q \Delta t}$$  \hspace{1cm} (5-4)

Where:
- $\rho$ = PCE density
- $\Delta V$ = PCE volume change in image region
- $Q$ = aqueous volumetric flow rate
- $\Delta t$ = aqueous flushing time

Imhoff et al. (1993) conclude that as a clean aqueous phase is pumped into a system containing residual NWP, the length of the dissolution front increases and the longitudinally averaged dissolution rate decreases with distance into the region of residual NWP. An analysis of MTRC data for individual heights within the same column confirms a decreased dissolution rate as a function of increasing distance into the column following the 150 PVF (Table 5-3).

<table>
<thead>
<tr>
<th>Table 5-3: Scan Height Mass Transfer Rate Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Volumes Flushed</td>
</tr>
<tr>
<td>Non-Equilibrium Dynamic H1</td>
</tr>
<tr>
<td>Non-Equilibrium Dynamic H2</td>
</tr>
<tr>
<td>Non-Equilibrium Dynamic Replicate H1</td>
</tr>
<tr>
<td>Non-Equilibrium Dynamic Replicate H2</td>
</tr>
</tbody>
</table>
A selection of modified Sherwood number (Sh’) correlations (Pan et al., 2007) (Table 5-4) are plotted against non-equilibrium dynamic experimental Sh’ values (Figure 5-5). While all three referenced Sh’ correlations are not valid for the flow regime used in the non-equilibrium experiment, they are plotted for comparative purposes. The non-equilibrium dynamic subvolumes display a lower Sh’ value than the other correlations predicted. However, it is interesting to note that the experimental system does display a relatively constant Sh’ over the course of the experiments, suggesting quasi-steady state mass transfer conditions within the non-equilibrium dynamic subvolume.

Table 5-4: Modified Sherwood Number Correlations

<table>
<thead>
<tr>
<th>Modified Sherwood Number Equation</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sh' = 57.7 \left[ \phi (1 - S_n) \right] Re^{0.61} d_s^{0.67} U_i^{0.41} )</td>
<td>Quasi Steady-state</td>
<td>Powers et al., 1992</td>
</tr>
<tr>
<td>( Sh' = 340 Re^{0.71} \Theta_n^{0.87} \left( d_s / L \right)^{0.31} )</td>
<td>Transient</td>
<td>Imhoff et al., 1994</td>
</tr>
<tr>
<td>( Sh' = 141.4 Re^{0.56} \Theta_n^{0.86} )</td>
<td>Transient</td>
<td>Pan et al., 2007</td>
</tr>
</tbody>
</table>

Where:
- \( \theta_n \) = PCE volumetric content
- \( L \) = distance into region of residual PCE

\[
Sh = \frac{kl_c}{D_m}
\] (5-5)
Where: 
\[ k = \text{mass transfer rate coefficient} \]
\[ l_c = \text{characteristic length scale (d}_{50}) \]
\[ D_m = \text{molecular diffusivity} \]

\[ Sh' = \frac{Kl_c^2}{D_m} \]  \hspace{1cm} (5-6)

Where: \( K = \text{lumped mass transfer coefficient (product of k and PCE/water interfacial specific surface area)} \)

Experimental MTRC coefficients are then used to compute both the Sherwood number (Equation 5-5) and the modified Sherwood number (Equation 5-6) (Zhang et al., 2002). An analysis of the data reveals that both numbers are confined to a fairly consistent range of values over numerous PVF and PCE saturations, with the exception of two data points for the non-equilibrium dynamic replicate subvolumes (150 and 750 PVF) and one data point for the non-equilibrium dynamic subvolumes (300 PVF) (Figures 5-6 through 5-9). These outliers correspond to periods of increased dissolution within the subvolumes, as evidenced by the PCE saturation data (Figure 5-3). Pan et al. (2007) predicts a decrease in modified Sherwood number and a relatively constant Sherwood number, both as a function of decreasing saturation. However, Pan et al. also identifies a general trend whereby increasing Reynolds number relates to an increase in both Sherwood number and modified Sherwood number. Therefore, the outliers in the non-equilibrium dissolution data set could possibly be attributed to a localized alteration in the flow field and an associated change in Reynolds number due to dissolution during those PVF. A
comparison of the average number of pores occupied (APO) by a single blob at these PVF reveals a significant change in the respective APO trends at both the non-equilibrium dynamic 300 PVF and non-equilibrium dynamic replicate 750 PVF (Section 5.3.5), suggesting a change may have occurred in the local flow field.

Figure 5-6: Non-equilibrium Sherwood Numbers as a Function of PVF

Figure 5-7: Non-equilibrium Sherwood Numbers as a Function of Saturation
Figure 5-8: Non-equilibrium Modified Sherwood Numbers as a Function of PVF

Figure 5-9: Non-equilibrium Modified Sherwood Numbers as a Function of Saturation
5.3.2 General PCE Blob Properties and Blob Volume Analysis

A review of the general PCE blob properties reveals two distinct trends for each the equilibrium and non-equilibrium series of experiments (Table 5-5). When examining the initial (equilibrium-0) and final experiment (equilibrium-360) averaged PCE blob properties, it becomes apparent that the average number of pores occupied, surface area, and volume remain relatively constant over the course of the experiments. However, these same properties for the non-equilibrium series (xx-0 and xx-750) show a marked decrease over the number PVF. This confirms that the characteristics of the PCE blobs in the subvolumes of the equilibrium columns, while experiencing some dissolution over the experiments, are not significantly altered until the arrival of the primary dissolution front. However, the non-equilibrium series of experiments exhibit a marked change in averaged PCE blob properties over the course of the experiments.

Table 5-5: Averaged PCE Blob Properties

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PCE Saturation</th>
<th>Total # of Blobs</th>
<th>Avg # Pores Occupied per Blob</th>
<th>Avg Blob Surface Area (mm²)</th>
<th>Avg Blob Volume (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium-0</td>
<td>0.19</td>
<td>198</td>
<td>5.1</td>
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<td>0.030</td>
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<td>0.63</td>
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<td>0.63</td>
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<tr>
<td>equilibrium-600</td>
<td>0.10</td>
<td>454</td>
<td>1.6</td>
<td>0.18</td>
<td>0.007</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PCE Saturation</th>
<th>Total # of Blobs</th>
<th>Avg # Pores Occupied per Blob</th>
<th>Avg Blob Surface Area (mm²)</th>
<th>Avg Blob Volume (mm³)</th>
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</thead>
<tbody>
<tr>
<td>non-equilibrium-0</td>
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<td>5.4</td>
<td>0.78</td>
<td>0.035</td>
</tr>
<tr>
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<td>0.69</td>
<td>0.034</td>
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<tr>
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<td>210</td>
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<td>0.42</td>
<td>0.018</td>
</tr>
<tr>
<td>non-equilibrium-600</td>
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<td>154</td>
<td>2.9</td>
<td>0.39</td>
<td>0.018</td>
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<tr>
<td>non-equilibrium-750</td>
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<td>161</td>
<td>3.2</td>
<td>0.39</td>
<td>0.018</td>
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</table>

<table>
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<tr>
<th>Experiment</th>
<th>PCE Saturation</th>
<th>Total # of Blobs</th>
<th>Avg # Pores Occupied per Blob</th>
<th>Avg Blob Surface Area (mm²)</th>
<th>Avg Blob Volume (mm³)</th>
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<tr>
<td>non-equilibrium-dynamic-0</td>
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<td>0.78</td>
<td>0.035</td>
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<td>0.024</td>
</tr>
<tr>
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<td>3.5</td>
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<td>0.021</td>
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<tr>
<td>non-equilibrium-dynamic-700</td>
<td>0.10</td>
<td>161</td>
<td>3.2</td>
<td>0.39</td>
<td>0.018</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PCE Saturation</th>
<th>Total # of Blobs</th>
<th>Avg # Pores Occupied per Blob</th>
<th>Avg Blob Surface Area (mm²)</th>
<th>Avg Blob Volume (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-equilibrium-dynamic-replicate-0</td>
<td>0.19</td>
<td>198</td>
<td>5.1</td>
<td>0.68</td>
<td>0.030</td>
</tr>
<tr>
<td>non-equilibrium-dynamic-replicate-150</td>
<td>0.16</td>
<td>183</td>
<td>4.8</td>
<td>0.56</td>
<td>0.026</td>
</tr>
<tr>
<td>non-equilibrium-dynamic-replicate-300</td>
<td>0.16</td>
<td>180</td>
<td>5.8</td>
<td>0.60</td>
<td>0.027</td>
</tr>
<tr>
<td>non-equilibrium-dynamic-replicate-450</td>
<td>0.15</td>
<td>165</td>
<td>5.7</td>
<td>0.61</td>
<td>0.028</td>
</tr>
<tr>
<td>non-equilibrium-dynamic-replicate-600</td>
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<td>3.9</td>
<td>0.47</td>
<td>0.022</td>
</tr>
<tr>
<td>non-equilibrium-dynamic-replicate-700</td>
<td>0.10</td>
<td>454</td>
<td>1.6</td>
<td>0.18</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Both the equilibrium and non-equilibrium data sets display average PCE blob volumes (Figure 5-10) which are consistent with their respective PCE saturation trends (Figures 5-3). PCE blob size distributions within equilibrium columns (Figure 5-11) display a relatively consistent distribution over the course of the experiments given that independent columns were used for experimentation. One data point within Figure 5-10 that is inconsistent with the others is the average blob volume corresponding to the 120 PVF equilibrium dissolution step – it is higher than those of similar saturations. Further examination of the blob volumes in this dataset reveals that the average blob volume of the largest 10 percent of blobs within this column was 0.27 mm$^3$. By comparison, the largest 10 percent of blobs within the 150 PVF dynamic non-equilibrium column (which has a similar saturation and number of PVF) was found to be 0.22 mm$^3$, suggesting that the equilibrium 120 PVF data point may be skewed upwards by the presence of a few large blobs.

![Graph](image)

**Figure 5-10: Average PCE Blob Volume as a Function of PVF**

All three non-equilibrium columns experience average PCE blob volume trends that were similar to those observed for the PCE saturations within these respective columns (Figure 5-10). A period of declining average blob volume is proceeded by a relatively steady blob volume size. Towards the conclusion of the experiments, an additional decline in average blob volume is observed. Closer evaluation of the data reveals two data points that are not consistent with the others. First, the dynamic replicate column experiences a marked decrease in average blob volume following the final dissolution step. This reduction can be attributed to a large number of smaller volume blobs at this stage (Figure 5-14, Figures 5-12 and 5-13 for comparison). The abundance of smaller PCE blobs contributed to the skewing of the data towards a smaller average blob volume for
this particular data set. The second anomalous point is associated with the static non-equilibrium average blob volume at 450 PVF. This data point is markedly higher than others of a similar dissolution stage and saturation but is skewed by the presence of several relatively large blobs as compared to those found in other experiments. An analysis of the data revealed that the largest 10 percent of blobs in the imaged subvolume had an average volume of 0.28 mm$^3$. Conversely, the largest 10 percent of the blobs in the dynamic non-equilibrium replicate column at the identical dissolution step and similar PCE saturation had an average volume of 0.16 mm$^3$.

A review of the blob size distributions for the non-equilibrium columns reveals a consistent trend across all three data sets for blobs smaller than 0.005 mm$^3$. In each experiment, the percentage of blobs smaller than 0.005 mm$^3$ fluctuates as a function of PVF. This is consistent with observations of multipore blobs within the non-equilibrium columns being separated into multiple blobs and smaller blobs being removed by dissolution.

![Figure 5-11: Equilibrium PCE Blob Volume Distribution](image)

*Figure 5-11: Equilibrium PCE Blob Volume Distribution*
Figure 5-12: Non-equilibrium PCE Blob Volume Distribution

Figure 5-13: Non-equilibrium Dynamic PCE Blob Volume Distribution
5.3.3 PCE Blob Specific Surface Area

A strong linear correlation is found between the PCE specific surface area (SSA) and saturation (Figure 5-15). This is consistent with the experimental findings of Johns and Gladden (1999, 2000) and Schnaar and Brusseau (2006) and the numerical modeling work of Pan et al. (2007). There appears to be no distinguishable difference in this relation between equilibrium and non-equilibrium dissolution experiments. The only potential outlier in this plot, the dynamic non-equilibrium replicate experiment at an approximate saturation of 0.1, can be attributed to the unusually high number of smaller-than-average blobs in this subvolume (Table 5-5). These “small” blobs skew the data towards a higher value than what is observed in other subvolumes.

Capillary PCE specific surface area is defined here as that portion of PCE blobs which is exposed to the bulk aqueous phase per unit subvolume. The systems studied in the dissolution experiments all contain water wet sands. Therefore, the entire surface of each PCE blob is exposed to water either in the void space or in the film separating the blobs from the grains. However, as this film is impossible to detect with the XT resolution used here, capillary PCE SSA is taken as that portion of the PCE which is exposed to the bulk aqueous phase (i.e., not the film).
Figure 5-15: PCE Specific Surface Area as a Function of PCE Saturation

Figure 5-16: PCE Capillary SSA as a Function of PCE Saturation
A review of the PCE capillary SSA data reveals a linear relationship with PCE saturation for equilibrium dissolution conditions (Figure 5-16). This trend is consistent with data concerning PCE SSA (Figure 5-15). There also appears to be similar data trends for the equilibrium experiments between PVF and PCE capillary SSA (Figure 5-17) and the PVF and PCE saturation plot (Figure 5-3). Non-equilibrium dissolution data reveals a correlation between PCE saturation and capillary PCE SSA (Figure 5-16) with the exception of two data points (non-equilibrium-dynamic-600 and non-equilibrium-dynamic-replicate-750). Both of these outliers (at approximately 0.42 mm\(^{-1}\) PCE Cap SSA and 0.11 saturation) correspond to periods of increased MTRCs (Table 5-3). In the case of the non-equilibrium dynamic replicate subvolume, this increase can be attributed to the presence of numerous small, high specific surface area blobs (Table 5-5).

### 5.3.4 Blob Sphericity

The sphericity of individual blobs is calculated for every PCE blob within the subvolumes. A perfect sphere will have a sphericity of one. A comparison of the initial sphericity values to those at each experiment conclusion shows that in all systems that the blobs became more spherical as a function of PVF (Figures 5-18 through 5-21). Thus, it can be concluded that as dissolution is occurring, the blobs decrease in volume and become more spherical. While using the shape factor to look at blob shape, Pan et al. (2007) and Johns and Gladden (2000) found similar trends in that the blobs became more spherical as the NWP saturation decreased.
Figure 5-18: Equilibrium Blob Sphericity

Figure 5-19: Non-equilibrium Blob Sphericity
Figure 5-20: Non-equilibrium Dynamic Blob Sphericity

Figure 5-21: Non-equilibrium-Dynamic Replicate Blob Sphericity
5.3.5 Pores Occupied by PCE Blobs

The average number of pores occupied (PO) within equilibrium subvolumes display a general decline in average PO following the first dissolution step (i.e., 120 pore volumes flushed), followed by a relatively steady average PO between 240 and 360 pore volumes flushed (Figure 5-22). The average PO data point for the 120 PVF equilibrium dissolution step is higher than those of similar saturations but this can be attributed to the presence of larger blobs occupying a higher-than-average number of pores (Section 5.3.2 and Table 5-5). The equilibrium PO trends are consistent with the equilibrium average blob volume trends (Figure 5-11).

![Figure 5-22: Average Number of Pores Occupied by a PCE Blob](image)

Within the dynamic and dynamic replicate non-equilibrium subvolumes, a period of declining steady value of average number of pores occupied over two consecutive dissolution steps (Figure 5-22). Again, these trends are generally consistent with saturation data for these subvolumes. As stated in the previous section, the dynamic replicate subvolumes experience a marked decrease in average blob volume following the final dissolution step. This reduction in blob volume can be correlated with the fact that the average PO of this system is 1.6 while the other two non-equilibrium systems have average PO’s of approximately 3. The dynamic replicate subvolumes display an increase in the total number of blobs and a marked decrease in average blob volume from the previous dissolution step, indicating the presence of more, smaller blobs (Table 5-5), suggesting that multipore blobs are separating into multiple blobs during dissolution. The
abundance of smaller PCE blobs contributed to the skewing of the data towards a smaller average PO for this particular data set.

An examination of the distribution plots of the PCE occupied pores reveals that the PCE is predominantly found in the larger pore sizes for all experiments (Figures 5-23 through 5-26). This trend is consistent with previous researchers (eg, Willson et al., 2004) and expected based upon pore-scale multiphase physics (Lowry and Miller, 1995). Furthermore, it appears that relatively the same size distribution of pores remain occupied by PCE in the equilibrium dissolution experiments from the initial scanning (0 PVF) until the conclusion of the experiment (360 PVF). Such a finding is consistent with the average blob properties previously mentioned (Table 5-5).

A review of which pores were occupied by PCE blobs during various stages of the non-equilibrium dissolution experiments reveals that the distribution of PCE occupied pores varies as a function of dissolution stage (Figures 5-24 through 5-26). As dissolution occurs within the non-equilibrium system, the distribution of PO sizes shifts towards the smaller pores at the conclusion of the experiment (750 PVF). This trend would be expected as the largest pores would be most available to aqueous advective flow paths and, as such, experience increased PCE dissolution. This trend is not observed in the equilibrium columns as it appears that spatially uniform dissolution is occurring throughout the scanned subvolumes of the equilibrium columns.

Figure 5-23: Equilibrium PCE Occupied Pore Sizes
Figure 5-24: Non-equilibrium PCE Occupied Pore Sizes

Figure 5-25: Non-equilibrium Dynamic PCE Occupied Pore Sizes
Figure 5-26: Non-equilibrium Dynamic Replicate PCE Occupied Pore Sizes
6. BIOMASS SYSTEM IMAGING RESULTS

6.1 Grain, Pore, and Packing Properties

After image segmentation (i.e., converting the grayscale image to integers representing the grains, pores, biomass-filled pore space and non-biomass pore space), algorithms described in Section 1.7 (Thompson et al., 2006, Willson et al., 2004 and Thompson et al, 2008) were used to quantitatively analyze the granular packing, pore network structure, distribution and properties of the biomass, and correlation between the biomass and pore network structure. An analysis of quantitative grain results from the biomass imaging experiments (Table 6-1) reveals an agreement between the segmented grain information from the biomass imaging experiment and grain results from previous NAPL dissolution studies using the same porous media (40/50 Accusand) (Section 5.1). The grain size distribution also agrees with the previous distributions and with the sieve analysis data provided by Unimin Corporation. This indicates that the grains and pore space were properly segmented during image thresholding. Information concerning porosity, coordination numbers, or pore properties (Table 6-1) was not considered for determining proper segmentation as the two sets of experimental columns (biomass imaging and NAPL dissolution studies) were packed under different conditions.

Table 6-1: Biomass System Imaging Grain, Pore, and Packing Properties

<table>
<thead>
<tr>
<th>Column ID</th>
<th>Porosity</th>
<th>Avg. GIR</th>
<th>Avg. GSA</th>
<th>Avg. GAR</th>
<th>Avg. GCN</th>
<th>Avg. PIR</th>
<th>Avg. PCN</th>
<th>Avg. Pore/Throat AR</th>
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</thead>
<tbody>
<tr>
<td>Abiotic A</td>
<td>0.34</td>
<td>124</td>
<td>3.69E+05</td>
<td>1.51</td>
<td>6.8</td>
<td>46.1</td>
<td>5.7</td>
<td>0.624</td>
</tr>
<tr>
<td>Abiotic Iodine A</td>
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<td>6.7</td>
<td>45.3</td>
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<td>46.3</td>
<td>5.8</td>
<td>0.620</td>
</tr>
<tr>
<td>Abiotic A</td>
<td>0.35</td>
<td>121</td>
<td>3.62E+05</td>
<td>1.52</td>
<td>6.4</td>
<td>47.1</td>
<td>5.8</td>
<td>0.623</td>
</tr>
<tr>
<td>Abiotic Iodine A</td>
<td>0.35</td>
<td>122</td>
<td>3.53E+05</td>
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<tr>
<td>Abiotic Flush A</td>
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<td>122</td>
<td>3.54E+05</td>
<td>1.54</td>
<td>6.6</td>
<td>49.7</td>
<td>5.6</td>
<td>0.632</td>
</tr>
<tr>
<td>Biotic C</td>
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<td>3.69E+05</td>
<td>1.53</td>
<td>6.4</td>
<td>47.0</td>
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<td>0.621</td>
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<tr>
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<td>3.52E+05</td>
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<td>6.5</td>
<td>49.5</td>
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<td>0.625</td>
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<td>3.50E+05</td>
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<td>6.5</td>
<td>49.9</td>
<td>5.8</td>
<td>0.628</td>
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<td>AVERAGE</td>
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<td>3.62E+05</td>
<td>1.53</td>
<td>6.6</td>
<td>47.8</td>
<td>5.7</td>
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<td>ST. DEV.</td>
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<td>1.07E+04</td>
<td>0.01</td>
<td>0.2</td>
<td>1.81</td>
<td>0.1</td>
<td>0.00</td>
</tr>
</tbody>
</table>

AVERAGE (DIS EXP) 118 3.57E+05 1.55
ST. DEV. (DIS EXP) 2 7.11E+03 0.02

Note: All lengths in microns
GIR: = Grain Inscribed Radius GSA: Grain Surface Area
GAR = Grain Aspect Ratio
GCN = Grain Coordination Number
DIS EXP: results from the DNAPL dissolution experiments (Tables 5-1 and 5-2)
6.2 Biomass Detection and Quantification

A review of the attenuation histograms generated for the abiotic column (Figure 6-1) reveals no differences between the three experimental stages: 1.) prior to Lugol’s flush (column contains only deionized water and sand), 2.) following Lugol’s flush (column contains Lugol’s iodine and sand), and 3.) following a one PV deionized water flush (column contains deionized water, sand, and, presumably, some residual Lugol’s iodine). A visual inspection of the effluent during iodine injection confirmed that the discharging liquid was the same color as the influent Lugol’s iodine. Such a finding suggests that the iodine is not binding to any of the packing within the column (inorganic sands).

![Figure 6-1: Abiotic System Imaging Histograms](image)

A review of the attenuation histograms generated for the biotic column (Figure 6-2) reveals differences between the pre-Lugol’s flush stage and the post-Lugol’s and post-water flush stages. Prior to Lugol’s flush, the column contains only deionized water, sand, and undoped biomass; following the Lugol’s flush, the column contains Lugol’s iodine, sand, doped biomass, and, presumably, some deionized water; following a one pore volume deionized water flush, the column contains deionized water, sand, doped biomass, and, presumably, some residual Lugol’s iodine. The shape of the three histograms curves reveals several items of interest: (1) There is a definite shift in the lower peak towards higher attenuation values following the Lugol’s flush; (2) The post-Lugol’s and post-water flush histograms are nearly identical indicating that the portion of the pore space filled with iodine remains relatively constant following a one PV flush of water. This would seem to suggest that iodine-doped biomass retains the iodine staining...
that occurred during the Lugol’s flush; (3) The small bump in the post-Lugol’s and post-water flush histograms prior to the first peak most likely indicates the presence of pore space that does not contain concentrations of iodine above that in Lugol’s iodine. This last observation is consistent with the lack of any differences in the histograms shown in Figure 6-1 where the pre- and post-Lugol’s and post-water flush curves all show the same peak locations. Comparison of Lugol’s and water X-ray absorption coefficients (Figure 6-3) confirms that, because of the relatively low concentration of iodine in the Lugol’s solution used in these experiments, the peaks should not shift. In other words, the absorption coefficients of the water (0.299 cm²/g, 0.302 cm²/g) and Lugol’s solution (0.589 cm²/g, 0.342 cm²/g) are nearly the same at the energies (33.269 KeV, 33.069 KeV) used in this experiment (Figure 6-3). Calculation of the X-ray absorption coefficients at higher iodine concentrations (e.g., 5 times the iodine concentration of standard Lugol’s iodine) indicates that a peak shift would occur (Figure 6-3).

A visual inspection of the biotic column effluent during iodine injection revealed that the discharging liquid was the clear (as opposed to the brown effluent of the abiotic column). This is consistent with the comparison of the post-Lugol’s flush histograms in Figures 6-1 and 6-2 which suggests that the iodine concentration in the biomass phase is higher than the iodine concentration in the pore space. This conclusion comes from the observations that: (1) the lower peak in the abiotic column doesn’t shift to the right following either the Lugol’s or water flush, while the lower peak in the biotic column histograms shifts significantly to the right; and (2) the fact that the only difference in the two columns is the presence of biomass in the pore space.
Figure 6-3: Biomass System Imaging Attenuation Plots

Figure 6-4: Biomass System Imaging Slice
Segmented phases in the above image are: red - biomass, blue - water, and purple - grain.
Following anisotropic diffusion of the subvolumes and phase segmentation, the remove islands/holes program was used to reassign aqueous phase voxel clusters smaller than 25,000 continuous voxels to the biomass phase (Section 3-3). This was done in order to create a clearer segmented image (Figure 4-1) of the biomass system (Figure 6-4) and better visualize potential flow paths within the biomass/porous media (Figure 6-5). The ability to identify such flowpaths could prove useful as input in future pore network modeling examining how biomass affects aqueous flow fields and, consequentially, NWP dissolution.

6.3 Laboratory Batch Experiments

The results for the first series of qualitative biomass system imaging experiments indicate that the presence of Lugol’s iodine, sodium chloride solution, or tap water leads to a change in biomass volume (Table 6-2). In all three cases, the volume of the biomass increased from an initial volume of 4 mL to 4.5 mL after 6 hours and 5 mL after 24 hours (with all volumes being approximate). Furthermore, the tubes containing the two feed stocks exhibited marginal change (approximately 0.5 mL change over a 24 hour period) while the control and de-ionized water samples displayed no net change in observed biomass volume.

The qualitative Lugol’s iodine diffusion experiments reveal that the position of the dissolution front after 24 hours is approximately 5 mm and 10 mm into the biomass for the 4 mL and 8 mL iodine additions, respectively. In each case, the location of the
dissolution front was achieved after a period of 12 hours before appearing to stagnate for the remainder of the 24 hour observation period. While it is not expected that biomass thicknesses in XT column experiments will be of a similar thickness (approximately 4 cm), there does appear to be a limitation on the length over which the Lugol’s iodine solution will diffuse through a biomass.

Table 6-2: Observed Biomass Volume Change

<table>
<thead>
<tr>
<th>Liquid Addition</th>
<th>Approximate Observed Biomass Volume Change-6 hours (mL)</th>
<th>Approximate Observed Biomass Volume Change-12 hours (mL)</th>
<th>Approximate Observed Biomass Volume Change-18 hours (mL)</th>
<th>Approximate Observed Biomass Volume Change-24 hours (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>De-ionized Water</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Feed Stock (no carbon)</td>
<td>0</td>
<td>0</td>
<td>0-0.5</td>
<td>0-0.5</td>
</tr>
<tr>
<td>Feed Stock (w/carbon)</td>
<td>0</td>
<td>0</td>
<td>0-0.5</td>
<td>0-0.5</td>
</tr>
<tr>
<td>Tap Water</td>
<td>0.5</td>
<td>0.5-1</td>
<td>0.5-1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium Chloride Solution</td>
<td>0.5</td>
<td>0.5-1</td>
<td>0.5-1</td>
<td>1</td>
</tr>
<tr>
<td>Lugol’s Iodine</td>
<td>0.5</td>
<td>0.5-1</td>
<td>0.5-1</td>
<td>1</td>
</tr>
</tbody>
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7. CONCLUSIONS

7.1 DNAPL Dissolution Conclusions

Grain property and column packing data suggested that a consistent packing and grain segmentation was achieved for all experimental columns. Packing property (e.g. porosity and grain coordination number) statistics demonstrated packings were consistent between columns. Grain property statistics (average, standard deviation, and cumulative distributions) of the grain inscribed radii, grain surface area, and grain aspect ratio indicated consistent segmentation of the grain phase between experiments. Accurate segmentation of the grain phase was confirmed through comparison of the cumulative effective grain diameter data with mean grain diameter for the 40/50 Accusand sieve analysis data provided by the Unimin Corporation.

Average pore properties (e.g. pore volume, pore inscribed radius, pore coordination number) for all subvolumes were consistent between experiments. Consistency in these measures indicated a consistent segmentation of the void phase and a consistent packing between experiments. A comparison of the average GED:pore inscribed diameter ratio was consistent with that of a natural sand of a similar $d_{50}$ value (Al-Raoush and Willson, 2005b), suggesting an accurate segmentation of the pore phase. This information will prove useful as it will provide pore structure information of a naturally occurring media for use in pore network models, which have traditionally relied upon manufactured network structures.

PCE removal rates with pore volumes flushed in both the equilibrium and nonequilibrium experiments were similar until arrival of the primary dissolution front in the equilibrium column. Arrival of the primary dissolution front and number of pore volumes required to completely remove the PCE from the equilibrium experiment matched well with theoretical predictions. Nonequilibrium dissolution rates varied during the course of the experiment, with increased dissolution observed near the conclusion of the experiments. Blob properties within the equilibrium columns remained relatively constant for all dissolution steps prior to the arrival of the primary dissolution front. Changes in the pore-level blob properties in the nonequilibrium experiments were correlated to small perturbations in the mass transfer rates. The deviations in mass transfer rates within the subvolumes occurred over relatively short timescales and are most likely due to the inability to image and analyze a representative elementary volume (REV).

Differences in PCE saturation between time steps in the two imaged subvolumes of each nonequilibrium column were used to calculate the change in mass (concentration). Mass transfer rate coefficients (MTRCs) were calculated using this change in mass and flow properties. In nearly every case, the MTRC in the downgradient subvolume was lower than that of the upgradient subvolume and was consistent with nonequilibrium mass transfer theory and the work of Imhoff et al. (1993) and Schnaar and Brusseau (2006). Modified Sherwood numbers were calculated for each subvolume and were compared to a number of correlations (Powers et al, 1992; Imhoff et al., 1994; Pan et al., 2007). The
results were consistent with quasi-steady state mass transfer conditions within the non-equilibrium dynamic and non-equilibrium dynamic replicate subvolumes. Small perturbations in mass transfer rates were attributed to pore-level changes in blob properties. Experimental Sh values were lower than all theoretical projections but were most closely approximated by the Powers et al. (1992) steady state relationship. This was due to the nonequilibrium flow conditions being outside of the valid range for the relationships.

Average blob volume, average blob surface area, and blob size distributions reveal that the blobs within the equilibrium subvolumes exhibited little change over the course of the dissolution steps prior to arrival of the primary dissolution front. This could be attributed to the uniform dissolution that occurred within the equilibrium columns. PCE blobs within the non-equilibrium series of experiments displayed a general decline in average PCE blob volume over the course of the experiment and a fluctuation in the fraction of smaller blob sizes. This fluctuation was due to a separation of multipore ganglia into multiple blobs and the removal of smaller blobs during dissolution. This observation was confirmed by the fluctuation in blob count over the course of the non-equilibrium dynamic and non-equilibrium-dynamic-replicate experiments.

A strong linear correlation existed between PCE saturation and PCE SSA for both the equilibrium and non-equilibrium experiments. This finding was consistent with the work of previous researchers (Johns and Gladden, 1999; Schnaar and Brusseau, 2006; Pan et al, 2007). A linear relationship for capillary PCE SSA and PCE saturation was observed for the equilibrium experiments. A general decline of capillary SSA as a function of PCE saturation was observed for the non-equilibrium series of experiments. Outliers within this data set corresponded to increased experimental MTRCs and can be attributed to pore-scale changes in blob properties.

Both the equilibrium and nonequilibrium experiments exhibited a trend of increasing PCE blobs sphericity as a function of pore volumes flushed (PVF) and associated decreasing PCE saturation. Pan et al. (2007) observed a similar trend of NWP blobs approaching a more uniform spherical shape as a function of decreasing NWP saturation and Johns and Gladden (2000) observed that NWP blobs become smoother as a result of dissolution. The increase in sphericity also appeared to correlate with average number of pores occupied as a function of PVF.

Consistent with earlier work (Al-Raoush and Willson 2005b; Willson et al., 2004), results revealed that PCE blobs at residual saturation occupied the largest pores. Blob-occupied pore size distribution data showed that the blob-filled pores remained fairly constant over the course of the equilibrium experiments. In the non-equilibrium system, the blob-occupied pore size distribution shifted towards the smaller pore sizes as the dissolution progressed. Such behavior is expected due to the fact that 1.) uniform dissolution is occurring within the equilibrium columns and 2.) the largest pores will be most available to contact with the bulk aqueous phase during non-equilibrium flow velocities, allowing for increased dissolution to occur within these regions.
### 7.2 Biomass System Imaging Conclusions

A review of data concerning grain properties and column packings suggests that a consistent packing and grain segmentation is achieved for all experimental columns and is consistent with dissolution experiment results. A data analysis of packing properties (including porosity and GCN) indicates a good statistical agreement between columns for packing properties, suggesting that packings are consistent between columns. Grain properties, including average GIR, average grain surface area, and average GAR, also display good agreement between subvolumes and possess a maximum standard deviation of less than 3 percent. Such an agreement between subvolumes indicates a consistent segmentation of the grain phase between experiments. Furthermore, the cumulative effective grain diameter data agrees with mean grain diameter for the 40/50 Accusand sieve analysis data provided by the Unimin Corporation, suggesting an accurate segmentation of the grain phase in the subvolumes.

A review of average pore properties for all subvolumes indicates consistent average values for pore volume, PIR, PCN, and TIR between experiments. Consistency in these measures would indicate a consistent segmentation of the void phase and a consistent packing between experiments.

An examination of the biomass system imaging attenuation histograms suggests that the three phases within the system (ie, grain, void, biomass) can be identified and segmented. A review of post-anisotropic attenuation histogram reveals a definite shift in the lower peak towards higher attenuation values following the Lugol’s flush. The post-Lugol’s and post-water flush histograms are nearly identical indicating that the portion of the pore space filled with iodine remains relatively constant following a one PV flush of water. This would seem to suggest that iodine-doped biomass retains the iodine staining that occurred during the Lugol’s flush. This finding also correlates with the fact that column effluent for the biotic systems during the iodine flush was clear (suggesting biomass staining) while the abiotic system effluent during the Lugol’s iodine flush was brown (ie, the color of Lugol’s iodine). Furthermore, the small bump in the post-Lugol’s and post-water flush histograms prior to the first peak most likely indicates the presence of pore space that does not contain concentrations of iodine above that in Lugol’s iodine.
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