Abstract

Experiments were performed with a two-dimensional flowcell to analyze the size and shape distributions of nonaqueous phase liquid (NAPL) blobs in water saturated porous media. Photographs were taken of NAPL blobs allowing for the quantification of blob characteristics using image analysis methods. Results demonstrated that the blobs ranged in size and shape. Although the median blob size was relatively small, the fewer large blobs contribute to most of the NAPL residual. It was observed that the shape and number of blobs in a given region changed during the dissolution process. Blobs tended to become less complicated in shape during dissolution. Large irregularly shaped blobs often broke into smaller blobs during the dissolution process. The longest lasting blobs originated from the breakup of initially large blobs.

Experiments were performed with the two dimensional flowcell and a column apparatus to observe the shape and length of the dissolution front. The propagation of the dissolution front was recorded through sketches, photographs and with an x-ray attenuation apparatus. In many experiments, the dissolution front did not remain stable and dissolution fingers were observed. The fingering process was found to be a function of the initial length of residual, media packing, flowrate, and media size. Gravity did not seem to effect the development of dissolution fingers. Dissolution fingering was observed in an experiment containing a NAPL mixture. In general, finger lengths and widths increased during the dissolution process. A mathematical analysis demonstrated that maximum finger length theoretically increases with increasing flowrate and finger radius. Maximum finger length was shown to be inversely proportional to transverse dispersivity.

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Notation

a	blob area
Adim	dimensionless blob area
Ana	interfacial area between the NAPL phase and the water phase
С	dissolved NAPL concentration in the bulk water solution
Cs	solubility limit of the NAPL in water
D_m	molecular diffusion coefficient of the NAPL species in water
dni	initial diameter for equal sized spherical NAPL ganglia
d_p	mean diameter of the porous media particle
Dt	transverse dispersion coefficient
d50	median particle diameter in cm
f	dimensionless form factor
J	mass flux of NAPL
Jo	Bessel function of the first kind of order zero
J_1	Bessel function of the first order
ki	mass transfer coefficient
KI	mass transfer rate coefficient
Lz	length of the mass transfer zone
m	mass of dissolved NAPL in water
$M_{ij}(t)$	the ijth moment of the residual TCE saturation distribution in space
Na	average photon counts (in a given time period) through the flowcell containing
	water saturated sand at location i
Nib	average photon counts (in a given time period) through the flowcell filled with
	sand, water and residual TCE at location i
Ne	average photon counts (in a given time period) through the flowcell filled with
	dry sand at location i
Nif	average photon counts (in a given time period) through the flowcell filled with
	sand saturated with TCE at location i
Ng	average photon counts (in a given time period) through the empty flowcell at
	location i
р	blob perimeter
Pc	capillary pressure
Pn	pressure of the NAPL phase
Pw	pressure in the water phase
r	radial distance from centerline of dissolution finger

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- R radius of the finger
- rc radius of curvature at the NAPL-water interface
- Re Reynolds number
- Sc Schmidt number
- SE() estimated standard error in ()
- Sin residual NAPL saturation at location i
- Sni initial residual NAPL saturation (before dissolution)
- Swirr irreducible water saturation for a porous media
- t time
- t' dimensionless dissolution time
- U Darcy flux
- U_i uniformity index of the porous media
- V bulk volume in the region of interest
- var() estimated variance in ()
- v_z velocity of the mass transfer zone
- xc location of the center of mass in the x direction
- X_{p}^{i} path length of the pore space at location i
- Xis path length of sand at location i
- X_t^i path length of TCE at location *i*
- y distance into the porous media containing residual NAPL
- y' longitudinal distance into the finger, moving coordinate system
- yc location of the center of mass in the y direction
- a_l longitudinal dispersivity
- $\alpha_n s$ roots of $J_o(R\alpha_n) = 0$
- a_t transverse dispersivity
- β relative permeability of the media (with and without NAPL residual)
- Ar radial thickness of the elemental volume
- $\Delta y'$ longitudinal thickness of the elemental volume
- Ew dynamic viscosity of water
- porosity at location i
- mass attenuation coefficient of sand
- mass attenuation coefficient of TCE
- mass attenuation coefficient of water
- θ_n NAPL volumetric content

- θ_{ni} initial NAPL volumetric content
- ρ_n density of the NAPL
- ρ_s particle density of sand

 ρ_t density of TCE

- ρ_w density of water
- σ spatial covariance tensor
- σ_t interfacial tension at the NAPL-water interface
- τ tortuosity of the porous medium
- vw kinematic viscosity of water
- ω contact angle (measured through the wetting liquid)
- ξ empirically determined exponent
- ψ exponent, equal to 0.518 + 0.114($d_{50}/0.05$) + 0.10 U_i for Powers et al. (1994)

1. Introduction

Groundwater is an essential natural resource utilized throughout the world. The reliance on groundwater resources has increased greatly in the last few decades. In the United States, groundwater supplies approximately one fourth of all water used and is the sole source of drinking water for more than 50 percent of the population (Rail, 1989). Groundwater contamination has received much attention due to the numerous well closures and contamination incidents throughout the country. The contamination of groundwater supplies has been detected with increasing frequency throughout the United States (Rail, 1989). Threats to groundwater quality include point sources, such as leaking underground storage tanks, as well as non-point sources associated with agricultural pesticides and fertilizers. The need for better protection and remediation of groundwater has prompted legislation including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA).

The remediation of groundwater at many contaminated sites is based on groundwater extraction followed by treatment of the extracted water prior to disposal (Mackay and Cherry, 1989). The most frequently occurring and persistent contaminants found in groundwater are immiscible or partially-miscible organic compounds (Mackay and Cherry, 1989). These organic compounds are often termed nonaqueous phase liquids, or NAPLs. The low aqueous solubilities of these NAPLs coupled with numerous other factors lead to extremely long remediation times and high cleanup costs.

Many groundwater contamination incidents begin with the introduction of a NAPL into the subsurface. Figure 1-1 shows the fate of a denser-than-water nonaqueous phase liquid (DNAPL) such as trichloroethylene, from a leaking underground storage tank. The DNAPL migrates downward due to gravity, until it reaches the water table. If the volume

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Figure 1-1: DNAPL subsurface migration

of the contaminant is sufficiently large to generate a suitable displacement pressure, the DNAPL will penetrate the water table (Schwille, 1988). The migration will continue downward until the volume of released fluid is exhausted or it reaches an impermeable layer, where it will spread creating a "pool". After the bulk of the contaminating fluid has migrated through the aquifer, a substantial fraction will remain held in the pore spaces, in a state of residual saturation. Residual exists as discontinuous NAPL blobs or ganglia that are trapped in the pore spaces due to capillary forces. Once a contaminant is introduced into the subsurface, the component chemicals can volatilize into the air space of the unsaturated portion of the aquifer, dissolve into the groundwater or sorb to the soil.

The purpose of this work is to examine one piece of the overall multiphase problem: the interphase mass transfer between a NAPL phase at residual saturation and the aqueous phase in saturated porous media. Experimental and mathematical investigations have been developed to describe mass transfer and transport in the saturated region of the subsurface environment (Miller et al., 1990; Powers et al., 1992, Geller and Hunt, 1993; Imhoff et al., 1994a; Powers et al., 1994). Much remains to be learned with respect to the factors affecting residual formation and removal. The objective of this work is to gain a qualitative and quantitative understanding of the fundamental nature of the interphase mass transfer process through laboratory investigations. More specifically, the study examines various microscopic and macroscopic characteristics of the mass transfer zone. In this technical report, the following questions are considered: (1) what is the morphology of the distribution of the immobilized NAPL blobs in the subsurface, (2) how does the NAPL blob morphology change during dissolution, and (3) how does the shape and length of the mass transfer zone change during dissolution? The findings of this study will lead to a better understanding of contaminant transfer and transport in the subsurface.

2. Background

2.1 Residual formation

In the subsurface environment, the solid media is usually considered strongly water-wet while NAPLs are considered nonwetting. Consider two immisible fluids such as water and NAPL in contact with the walls of a solid cylindrical tube (see Figure 2-1). Differences in the wettability between the water and solid phase and the NAPL and solid phase, results in a meniscus at the interface between the two immisible fluids (Wilson et al., 1990). The interfacial tension at the interface between the water and NAPL produces a pressure difference between the two phases called capillary pressure (p_c):

$$p_c = p_n - p_w = \frac{2\sigma_t}{r_c} = \frac{2\sigma_t \cos\omega}{r_t}$$
(2-1)

where p_n is the pressure of the NAPL phase, p_w is the pressure in the water phase, σ_l is the interfacial tension at the NAPL-water interface, ω is the contact angle (measured through the wetting liquid), r_c is the radius of curvature at the interface, and r_l is the radius of the tube.



Figure 2-1: The interface between two immiscible fluids (after Wilson et al., 1990)

Once introduced into the subsurface, a NAPL will migrate due to buoyancy forces and pressure gradients from water flowing through the region. It is well known that a substantial portion of the NAPL volume can become trapped within the pore spaces as discrete blobs by a displacement mechanism called snap off (Wilson et al., 1990, Dullien, 1992). The details of the trapping mechanism are complicated and not perfectly understood (Dullien, 1992). The NAPL entrapment mechanism has been found to be affected by factors including wettability, interfacial tension, viscosity, and pore geometry (Dullien, 1992). Once formed, capillary forces retain NAPL blobs, existing in highly complicated shapes (Mohanty et al., 1987).

2.2 Representative elementary volume

The porosity (ϕ) of a porous medium is a volume-averaged parameter defined as the volume of the voids divided by the total volume of the porous medium. A problem in defining the porosity of a porous medium is in choosing an appropriate volume over which the parameter should be averaged. If a microscopic volume is chosen to determine porosity, the value of porosity could be 1 or 0 depending upon if the chosen volume is located entirely within a pore or entirely within the solid media. As the averaging volume is increased about a point, the value of porosity will vary due to the local variations in pore structure. If the porous medium is truly homogeneous, the value of porosity should eventually stabilize as the averaging volume is increased. If the porous medium is heterogeneous, the value of porosity may continue to fluctuate as the averaging volume is increased. The averaging volume required to reduce the fluctuation in porosity for a nonuniform media may be many orders of magnitude greater than that for a uniform porous media (Mayer and Miller, 1992). The representative elementary volume (REV) has been defined as the averaging volume that is large enough such that the fluctuations from pore to pore are negligible. In addition, the averaging volume should be small enough such that the parameter variations from one domain to another may be approximated by continuous functions without introducing measurable error at the macroscopic scale (de Marsily, 1986). Utilizing the same reasoning, the concept of the REV can be applied to other volume averaged parameters such as residual NAPL saturation (S_n) , defined as the volume

of the NAPL within the pores divided by the total pore volume in a designated region (Mayer and Miller, 1992).

2.3 Permeability changes due to NAPL residual

The presence of NAPL at residual saturation reduces the permeability of a medium to water flow. An empirical expression relating the permeability of porous media with entrapped NAPL to clean porous media was developed by Wyllie (1962). This relationship is given by:

$$\beta = \left(\frac{1 - S_n - S_{wirr}}{1 - S_{wirr}}\right)^3 \tag{2-2}$$

where β is the relative permeability of the media (with and without NAPL residual), S_n is the residual NAPL saturation, and S_{wirr} is the irreducible water saturation for the porous media. Demond (1988) compared three different correlations to relative permeability data for a medium saturated with water and xylene and found that the Wyllie correlation best described the data. This correlation was also selected by Geller and Hunt (1993) to analyze their data.

2.4 Mass transfer coefficient

Groundwater models are often based on the simplified assumption that equilibrium always exists between phases (soil, water, and NAPL) in intimate contact (Mercer and Cohen, 1990; Miller et al., 1990). However, the equilibrium assumption has not been demonstrated as generally valid and the inappropriate use of this assumption could result in a substantial underestimation of aquifer remediation time (Powers et al., 1991). Recognizing the potential problems associated with equilibrium modeling, recent investigators have focused on rate limited-mathematical modeling of NAPL dissolution in porous media (Miller et al., 1990; Powers et al., 1992; Geller and Hunt, 1993; Imhoff et al., 1994a; Powers et al., 1994).

In rate-limited based approaches for describing mass transfer, the mass flux from NAPL blobs to water is commonly assumed to be proportional to the concentration gradient at the interface between the phases (Miller et al., 1990). A common form of the mass transfer relationship is:

$$J = \frac{1}{A_{na}} \frac{dm}{dt} = k_I (C_s - C) \tag{2-3}$$

where J is the mass flux of NAPL, A_{na} is the interfacial area between the NAPL phase and the water phase, m is the mass of dissolved NAPL in water, t is time, k_l is the mass transfer coefficient, C_s is the solubility limit of the NAPL in water, and C is the dissolved NAPL concentration in the bulk water solution. Dividing equation 2-3 by the *bulk* volume in the region of interest (V), and rearranging yields:

$$\frac{1}{V}\frac{dm}{dt} = \frac{A_{na}}{V}k_{l}(C_{s}-C) = K_{l}(C_{s}-C)$$
(2-4)

where K_l is the mass transfer rate coefficient. This definition of mass transfer rate coefficient was utilized by Imhoff et al. (1994a) and Powers et al. (1994). The mass transfer rate coefficient was defined slightly differently by Miller et al. (1990) (V was defined as the volume of the aqueous phase in the region of interest). Most experimental studies on the mass transfer rate from NAPL blobs to water involve the measurement of K_l rather than k_l because of the difficulties associated with determining A_{na} (Miller et al., 1990).

In recent years, numerous investigators have estimated K_l as a function of quantifiable system parameters and often present their empirical models in dimensionless form. In these models, K_l is often expressed through the dimensionless Sherwood number (Sh) defined as:

$$Sh = \frac{K_I d_p^2}{D_m}$$
(2-5)

where d_p is the mean diameter of the porous media particle and D_m is the molecular diffusion coefficient of the NAPL species in water. Often times, the Sherwood number is given as a function of other dimensionless parameters including porosity, residual NAPL saturation, NAPL volumetric content ($\theta_n = \phi S_n$), the Reynolds number (*Re*) and the Schmidt (*Sc*) number:

$$Re = \frac{d_p U}{v_w \phi(1 - S_n)} \tag{2-6}$$

$$Sc = \frac{\varepsilon_w}{\rho_w D_m}$$
(2-7)

where U is the Darcy flux, v_w is the kinematic viscosity of water, ϕ is the porosity, S_n is the residual NAPL saturation, ε_w is the dynamic viscosity of water, and ρ_w is the density of water.

2.5 Mass transfer zone

Assuming 1-D flow of water through a region of porous media containing uniformly distributed residual NAPL (single species) and rate-limited mass transfer, dissolution of the NAPL ganglia will occur over some length until the water passing through the contaminated porous media becomes saturated with dissolved NAPL. The length necessary for the water to reach equilibrium with the NAPL phase is the length of the mass transfer zone (L_z). It has previously been assumed that if the length of the NAPL contaminated region is long enough, the mass transfer zone will eventually develop to some fixed length and propagate with a constant velocity (v_z) given by:

$$v_z = \frac{UC_s}{\rho_n \phi S_n} \tag{2-8}$$

where U is the Darcy flux, C_s is the equilibrium concentration of dissolved NAPL in water, ρ_n is the density of the NAPL, ϕ is the porosity, and S_n is the residual NAPL saturation (Geller and Hunt, 1993). Geller and Hunt (1993) developed a relationship to predict L_z based on a correlation for rate-limited mass transfer from spheres, assuming residual NAPL could be modeled as initially equal-sized NAPL spheres that shrank during a 1-D dissolution process. For an initial residual NAPL saturation of 0.20 (made up of blobs with diameters equal to 0.1 cm), they predicted that the length of the fully developed mass transfer zone would be 0.3 cm and 1.38 cm for Darcy flow rates of 1 and 10 m/d, respectively.

2.6 Previous investigations

2.6.1 Blob size investigations

The distribution of NAPL blobs held in the pore spaces is important to the efficiency of contaminant removal and to mass transfer processes (Hunt et al., 1988). Powers et al. (1991) conducted a theoretical study of the significance of nonequilibrium dissolution from NAPL blobs. In their steady-state modeling efforts, it was found that solute concentration profiles were highly dependent on blob size and shape distributions. In transient modeling efforts, a first-order mass transfer rate relationship was assumed in a 1-D convection-dispersion mass balance equation incorporating temporal changes in blob configuration. Although the shrinkage of blobs during dissolution was included in this modeling effort, it was assumed that blobs retained their original shapes throughout the dissolution process and that the total number of blobs in a given region remained constant until the blobs dissolved away or until they were small enough to be advected downstream. These assumptions were made for mathematical simplicity and were not based on any physical observations of blob dissolution.

Because of the uncertainties associated with residual creation, many studies have been performed examining blob size distributions. Mayer and Miller (1993) reviewed the experimental and theoretical literature involving blob size distributions and found some common tendencies. For instance, often times a high percent of blobs trapped within a porous media are relatively small in size. However, most of the residual NAPL volume is contained within the fewer large blobs. Mayer and Miller (1992) performed a quantitative analysis of blob size distributions using 3 different sizes of glass beads (dp = 0.115, 0.385and 0.777 mm) with styrene monomer as the NAPL and found that blob volumes ranged over about 3 orders of magnitude. Although many investigators have examined initial blob distributions, no experiments have been performed to examine changes in blob configuration during dissolution (Imhoff et al, 1994a).

2.6.2 Recent experimental efforts to estimate the mass transfer rate coefficient

In the work of Miller et al. (1990) and Powers et al. (1992), the dissolution of NAPL blobs in porous media was examined under pseudo steady-state conditions (i.e., during the initial phase of dissolution before a significant change in interfacial area). Miller et al. (1990) mechanically stirred glass beads, water, and NAPL to create residual. Powers et al. (1992) examined this technique and found that it created NAPL ganglia that were smaller and more spherical in shape than blobs created with a more natural displacement mechanism used in their experiments. In both studies, effluent concentrations were used to estimate mass transfer rate coefficients in correlations involving characteristic system parameters.

In the approach taken by Geller and Hunt (1993), NAPL dissolution was modeled by representing the NAPL blobs as initially equal-sized spheres that shrank with time. Although changes in blob sizes were accounted for during the dissolution process, it was assumed that blob shape did not change. In this work, transient conditions were examined through effluent concentration measurements as multi-component NAPL blobs were

dissolved away. The modeling approach accounted for the bypassing of regions containing NAPL residual due to the reduced permeability of these regions.

Imhoff et al. (1994a) employed a gamma radiation attenuation system to measure changing NAPL saturation during complete dissolution experiments. This system allowed for nondestructive measurements of volume averaged properties such as porosity and residual saturation at discrete locations. Effluent concentrations were measured to provide an independent means of checking the gamma radiation measurements. This study found that the mass transfer zone lengthened as it moved through the porous medium and correspondingly, dissolution rates decreased with increasing distance into the porous medium.

In the work by Powers et al. (1994), mass transfer rates were calculated using effluent concentration measurements from transient NAPL dissolution experiments. It was found that the length of time required to dissolve NAPLs was many times greater than would have been expected based on equilibrium calculations. The resulting mass transfer model developed by Powers et al. (1994) was found to compare well with predictions made from the correlation developed by Imhoff et al. (1994a).

The mathematical modeling of NAPL dissolution has evolved from steady-state models to more complex transient models as the difficulties associated with predicting NAPL dissolution have become more apparent. Experimental techniques have also evolved to better mimic natural NAPL implacement mechanisms. A summary of the mass transfer models from the investigations discussed in the preceding paragraphs is provided in Table 2-1. The correlations given for Miller et al. (1990), Powers et al. (1992), and Geller and Hunt (1993) were adapted by Imhoff et al. (1994b) to provide better comparison. For all of the models given in Table 2-1, uniform flow and dissolution was assumed.

Reference	Correlation		
Miller et al., (1990)	$Sh = 12(\phi - \theta_n)Re^{0.75} \theta_n^{0.60} Sc^{0.5}$		
Powers et al., (1992)	$Sh = 57.7 [(\phi - \theta_n) Re]^{0.61} d_{50}^{0.64} U_i^{0.41}$		
Geller and Hunt, (1993)	$Sh = 70.5 Re^{\frac{1}{N}} \theta_n^{\frac{1}{N}} S_{ni}^{\frac{1}{N}} \phi^{-\frac{1}{N}} \left(\frac{d_p}{d_{ni}}\right)^{\frac{1}{N}}$		
Imhoff et al., (1994a)	$Sh = 340 \theta_n^{0.87} Re^{0.71} \left(\frac{y}{d_p}\right)^{-0.31}$		
Powers et al., (1994)	$Sh = 4.13 Re^{0.598} \left(\frac{d_{50}}{0.05}\right)^{0.673} U_i^{0.369} \left(\frac{\theta_n}{\theta_{ni}}\right)^{\psi}$		

Definitions

d50 is the median particle diameter in cm.

dni is the initial diameter for equal sized spherical NAPL ganglia

dp is the mean grain diameter

 U_i is the uniformity index of the porous media = $d_{60/d_{10}}$ (i% of the particles are $< d_i$)

y is the distance into the porous media containing residual NAPL

 θ_{ni} is the initial NAPL volumetric content

 ψ is equal to 0.518 + 0.114($d_{50}/0.05$) + 0.10 U_i

2.6.3 Dissolution fingering

As previously mentioned, it has commonly been assumed that the dissolution of NAPL blobs in porous media could be modeled as a 1-D process. Imhoff (1992) proposed that the dissolution process may be inherently unstable, leading to a fingered dissolution front. The physical factor driving this mechanism is the reduction of the permeability of the medium to water flow due to the presence of NAPL blobs (Imhoff, 1992). If the distribution of NAPL blobs in a porous medium is not perfectly homogeneous, water will flow faster in the regions containing fewer blobs, leading to higher dissolution rates in those regions. The higher dissolution rates in the regions containing fewer blobs further reduces the number of blobs in those regions, accentuating the differences in permeabilities between the regions with fewer blobs and the regions containing more blobs. This permeability-driven feedback mechanism results in a fingered dissolution front. The occurrence of dissolution fingering increases the length of the mass transfer zone. When dissolution fingers break through the contaminated portion of the porous media, the average rate of mass transfer decreases due to bypassing.

To explore the theoretical feasibility of fingered dissolution fronts, a mathematical analysis was performed by Imhoff et al. (1994c) in which a nonlinear model describing the dissolution of NAPL blobs was developed. A linear stability analysis was performed on the resulting moving free-boundary. The analysis indicated that instabilities may develop from a planar dissolution front. The fastest growing instabilities were found to decrease in width with increasing flowrate and increasing residual NAPL saturation (see Figures 6 and 8 of Imhoff et al., 1994c). Based upon this theoretical analysis, it was postulated that dissolution fingers formed in the experimental work of Imhoff et al. (1994a). The development of dissolution fingers would explain their observations of decreasing mass transfer with increasing distance into the zone of residual NAPL and the lengthening of the dissolution front it propagated through the medium. An objective of this study was to experimentally confirm the development of dissolution fingering.

3. Experimental Design/Methods

3.1 Materials

The water for all experiments was distilled and deionized using Corning Megapure systems, models PM11A and D2. The water was cooled to room temperature prior to use. In the experiments using the two-dimensional flowcell (2-D), the room temperature was approximately 20 to 23 °C. In the column experiment, the average temperature was 24.1 °C.

The NAPL used in most of the experiments was trichloroethylene (TCE), a denser than water chlorinated solvent. For one experiment in the 2-D flowcell, a mixture of 50% TCE and 50% toluene (by volume) was created. Toluene is a lighter than water contaminant. This ratio of TCE and toluene yielded a NAPL mixture that was slightly denser than water. Properties of these chemicals are listed in Table 3-1. The TCE and Tolune were supplied by EM Science, a division of EM Industries. The NAPLs were dyed to a concentration of 1 g/L with Oil Red O dye (certified biological stain), permitting visual observation of the NAPL blobs. The dyed NAPL was filtered with Whatman Co. number 40 filter paper to remove any insoluble dye. Mayer and Miller (1993) examined the effects of Oil Red O on NAPL properties. Results for perchloroethylene (used as an example NAPL) demonstrated that the dye did not have a statistically significant effect on dynamic viscosity. However, the dye lowered surface and interfacial tension. The surface tension was lowered from 32.0 to 31.0 dyne/cm due to the dye, and the interfacial tension was lowered from 47.0 to 40.0 dyne/cm due to the dye. This effect was attributed to the surfactant nature of dyes.

Table 3-	1: Chemical properties	
Property	TCE	Toluene
Specific gravity (g/cm3)	1.465 -	0.867*
Aqueous solubility (mg/L)	1270†	515*
Molecular diffusivity (cm ² /s)	8.4 × 10-6‡	8.0 × 10-6‡
	1.0 × 10-5+	

▲ Kirk and Othmer (1979), T = 20 °C

* Verschueren (1983), T= 20 °C

† Powers et al. (1994), with Oil Red O dye concentration = 0.5 g/L, T = 20-23 °C

‡ Calculated with method from Hayduk and Laudie (1974), T= 20 °C

Calculated with method from Wilke and Chang (1955), T= 24.1 °C

The four different types of porous media employed in the experiments consisted of sand (SiO₂) or spherical glass beads. The sand was purchaced from U.S. Silica Co. and the glass beads were purchaced from Thomas Scientific. For the experiments in the 2-D flowcell, the porous media was washed with water, oven dried, and then utilized either sieved or unsieved. For the column experiment, the media was not washed before use. A description of the types porous media used in the 2-D flowcell is given in Table 3-2. The grain size distributions for the unsieved 0.26-mm and 0.36-mm sands, media 1 and 2 respectively, are given in Figure 3-1.

Table 3-2: Porous media properties				
Media #	Туре	d _p (mm)	Grade	Porosity (± 0.01)
1	Sand	0.26	Unsieved	0.36
2	Sand	0.36	Unsieved	0.36
3	Sand	0.36	Sieved between 0.30 & 0.425 mm	0.36
4	Glass beads	0.78	Sieved between 0.71 & 0.85 mm	0.38



Figure 3-1: Grain size distributions for porous media 1 and 2

3.2 Methods

3.2.1 Two dimensional flowcell design/methods

The design of the 2-D flowcell allowed porous media to be packed between two glass plates. A schematic illustration of the flowcell is shown in Figure 3-2. In most of the experiments, the flowcell was oriented as shown in Figure 3-2 so that water flowed vertically through the flowcell. In experiment 6, the flowcell was rotated 90° so that water flowed horizontally through the flowcell. The back glass plate was mounted in an aluminum frame with Dow Corning Solvent Resistant Sealant (730). A Viton gasket was placed over the aluminum frame. Two stainless steel screens were secured in notches cut in the Viton gasket. The front glass plate was placed over the Viton gasket (the front glass plate was either 0.25" or a 0.5" thick). A Lexane frame was placed over the front glass plate and bolted to the aluminum frame, holding the assembly together. The apparatus thus provided a region bounded by the glass plates. Viton gasket, and screens, in which porous media could be placed. The apparatus was filled with porous media through two holes machined in the aluminum frame. Two constant head reservoirs were machined into the aluminum frame (each with three access ports) to provide uniform flow of water through the porous media. Two pressure ports were also machined in the aluminum frame. These pressure ports were covered with 1/16" thick porous stainless steel plates (pore size = 0.005 mm, purchaced from PSS Porous Stainless Steel, Pall Trinity Corporation), mounted flush to the aluminum frame with Dow Corning Solvent Resistant Sealant 730. All inlet and outlet ports were connected to Teflon tubing with brass or stainless steel Swagelock fittings.

To fill the 2-D flowcell, media was funneled through the fill holes into the apparatus. A rubber mallet was tapped against the top of the flowcell to assist the flow of media into the apparatus. To further increase the packing density, air was flowed through the apparatus from above and out through the bottom. By restricting the outlet flow of



Figure 3-2: 2-D Flowcell design (Lexane frame not shown)

air, the pressure in the flowcell was pulsed from 1 to 5 psi, yielding a tighter packing. The pressures used in this packing process caused the glass walls to bow slightly.

To determine the porosity of a packing, the following procedure was employed. First, the mass of the porous media used to fill the apparatus was carefully measured. With the mass of the porous media, the volume of media added to the apparatus could be determined. The particle density of the sand and glass media were measured at 2.66 g/cm³ (by John McBride) and 2.48g/cm³ (by Angela Frizzell), respectively. Next, CO₂ was flushed through the unit. Then deaired deionized water was injected by syringe into the apparatus from below until it just reached the lower boundary of the porous media. At this point, the injection of water was resumed and the volume of water required to fill the pores of the media was measured. Thus, a direct measurement of the pore volume of the packing was made. The porosity was then determined by dividing the pore volume by the total volume (i.e., the pore volume plus the volume of the solid media). The porous media was then dried by flowing air through the unit.

With the 2-D flowcell packed with dry porous media, CO₂ again was flushed through the apparatus. Deaired deionized water was pumped in from below (a minimum of 10 pore volumes of water) using a Masterflex peristaltic pump (model 7550-90 fitted with a 7519-10 pump head), leaving the media saturated with water. Dye tests were performed on each new media packing to confirm uniform flow through the 2-D flowcell. Blue-dyed water (Food Colors and Egg Dye, McCormick & Co., Inc.) was pumped through the apparatus, permitting visual observation of the flow field. A packing was rejected if the flow field was not reasonably uniform.

The first step in creating a region of residual NAPL saturation in the porous media was to displace most of the water in the pore space with NAPL. This was achieved by pumping NAPL in from below at a flowrate high enough to drain most of the water in the pore space (drainage stage). The flow was stopped when the NAPL had reached a desired distance (which varied by experiment) into the porous media. To create the residual

NAPL, water was pumped in from above to flush out the mobile NAPL (imbibition stage). Approximately 5 pore volumes of water were used to flush out the NAPL. Dye tests were performed to confirm uniform flow through the media containing residual NAPL. Bluedyed water (Food Colors and Egg Dye, McCormick & Co., Inc.) was pumped through the apparatus, to confirm uniform flow through the media containing residual NAPL. A dissolution experiment was started by flowing water from above at a specified rate.

3.2.2 Column design/methods

A schematic illustration of the column apparatus is shown in Figure 3-3. The end fittings were machined from Delrin. Viton O-rings provided seals between the Delrin end fittings and the glass tube. A perforated stainless steel plate was press fit into the lower end fitting. A stainless steel screen was spot welded to the perforated stainless steel plate and a Teflon screen (Spectra/Mesh filter, 0.150-mm mesh opening) was laid overtop the stainless steel screen. Pressure ports were machined into each of the end fittings.

A single experiment was performed with the column apparatus. In this experiment, the lower 95 cm of the column was filled with media 1. During this part of the filling process, a PVC tube with a screen covering the bottom end was placed within the glass column. Sand was pored into the PVC tube at a constant rate as the PVC tube was raised. Next, a 1.6-cm thick layer of finer sand ($d_p = 0.109$ mm) was added on top. The remainder of the column was filled with media 1. To increase the packing density, the top of the column was tapped with a rubber mallet during the final stage of the filling process.

The mass of the column apparatus was measured before and after it was filled with sand, providing the mass of sand added. The volume of solid material added was then determined assuming a particle density of 2.66 g/cm³ for the sand. The total volume occupied by the media was computed from the geometry of the apparatus (measurements





of the inner diameter and length of the glass tube and the dimensions of the upper end fitting). With this information, the average porosity was estimated at 37.1%.

With the column apparatus filled with sand, the unit was flushed with CO₂ and then deaired deionized water from below to saturate the media with water (a minimum of10 pore volumes were used). Blue-dyed water was passed through the column to ensure that the flow field was uniform. Next, TCE was pumped in from below at a flowrate of 26.4 m/d until the invading TCE was approximately 2 cm below the fine sand layer. The flow of TCE into the column was restarted at a flowrate of 0.08 m/d until a head of 40 cm of water was established across the fine layer of sand. The fine layer of sand served as a capillary barrier, allowing water to flow through but not TCE. Water was then pumped in from above to displace the mobile TCE at a flowrate of 8.13 m/d. The resulting mass of residual TCE was estimated at 450 g by mass measurement. The dissolution was initiated by flowing water through the column from above at an average flowrate of 7.64 m/d.

3.3 Measurements

3.3.1 Two dimensional flowcell

Flowrate and pressure drop

The 2-D flowcell was used to observe the dissolution of NAPL blobs at residual saturation in porous media. In the dissolution experiments, flowrate was monitored by measuring the mass of effluent over time. In some experiments, the pressure ports were connected to manometers to measure the pressure drop across the porous media.

Pressure-saturation

The drainage pressure-saturation curve for the packing of experiment 28 was measured in a multi-step experiment. The media was initially saturated with water and then drained through one of the perforated stainless steel pressure ports. The pressure head was controlled by manually lowering the outlet end of tubing from the pressure port. The mass of water drained from the pores was measured over time to determine when equilibrium had been established at each pressure head step.

Image analysis

Photographs were taken of NAPL blobs allowing for the quantification of blob characteristics by image analysis method. A Nikon N2020 camera with a Micro-Nikkor 105-mm f2.8 lens was used for the photographs. The camera was mounted on a tripod and positioned so that the plane of the film was parallel to the front glass plate of the flowcell. Kodak Ecktachrome 160 film was used to take color slides. Two 250-Watt tungsten light bulbs provided illumination for the photographs. The color slides were mounted on a light table and transformed into digital images by focusing a color video camera, equipped with a Nikkor 55-mm f2.8 lens, on a desired slide. The resulting image was displayed on a color monitor connected to an IBM AT personal computer. Image-Pro Color software was used to segment a color image (based on intensity differences) into a black and white image so that the blobs appeared black against a white background. Image-Pro Plus software was used to measure the area and perimeter of the blobs in a field of interest. The data was stored on floppy disk for future analysis.

Propagation of dissolution front

The propagation of the dissolution front was recorded through sketches and photographs. To create a sketch of the dissolution front, the boundary between clean sand and sand contaminated with NAPL was drawn on a plastic transparency laid over the front or back glass plate. This was done at various intervals through out the dissolution process.

Residual TCE saturation estimates

The sketches of the dissolution front were used to estimate the residual NAPL saturation's (given in Tables 4-1 to 4-4) by the following method. First, the sketches were used to estimate the area over which NAPL residual was removed during a known time

period. This area was multiplied by the plate spacing and the porosity of the porous media to estimate the total pore volume of the region where the NAPL had once existed. Next, the mass of NAPL removed from this region was estimated by assuming that the volume of water that had passed through this region became saturated with NAPL. The residual saturation was then estimated by dividing the estimated mass of removed NAPL by the total pore volume and NAPL density. This method could not be applied to experiments with very high dissolution flowrates (above 80 m/d) or large media (experiment 10 with media 4) because the boundary between the clean and contaminated media was not sharp and sketches could not be made. This method also could not be applied to experiment 29 in which a NAPL mixture was utilized.

X-ray measurements of the 2-D flowcell

In experiment 28, an x-ray attenuation method (McBride and Miller, 1994) was used to measure porosity and residual TCE saturation at various locations in the 2-D flowcell. A 160-kVp x-ray tube with a tungsten target was used as the radiation source. Photons were measured with a germanium detector connected to a high-throughput spectroscopy amplifier and a multichannel analyzer. The radiation beam passed through a filter of 20.1% CdCl₂ (by weight) in aqueous solution. Measurements were made with the x-ray generator at 32 kVp and 40 mA, yielding a photon peak energy of 26 keV. The system components are mounted on a movable platform, allowing for measurements at various locations on a fixed sample (placed between the radiation source and the detector).

The radiation beam was collimated to 5 mm by 5 mm. Attenuation measurements were made at 960 separate locations, using a programmed scanning pattern containing 40 columns and 24 rows. These measurements covered a 200 mm (horizontal) by 120 mm (vertical) region. The origin of the x and y axes for the attenuation measurements is shown in Figure 3-2. During a scanning cycle, the attenuation through a glass reference was periodically measured to monitor and adjust for drift in the radiation flux from the x-
ray generator. To increase the accuracy of the measurements, a scanning pattern of the flowcell in any given state (i.e., empty; filled with dry sand; filled with sand and water; filled with sand and TCE; filled with sand, water and residual TCE) was repeated two or three times. Averages were taken of the repeat measurements at each location.

The attenuation of photons through a sample can be described by Beer's law. Radiation attenuation measurements were made through the empty flowcell and then through the flowcell when it was packed with dry sand. The path length of sand at location *i* in the 2-D flowcell could then be determined from :

$$\chi_s^i = \frac{\ln(N_g^i / N_e^i)}{\mu_s \rho_s} \tag{3-1}$$

where X_s^i is the path length of sand at location *i*, N_e^i is the average photon counts (in a given time period) through the apparatus filled with dry sand at location *i*, N_g^i is the average photon counts (in a given time period) through the empty 2-D flowcell at location *i*, μ_s is the mass attenuation coefficient of sand, and ρ_s is the particle density of sand.

Next, scans were made with the 2-D flowcell filled with water saturated sand. TCE residual was created and the apparatus was scanned again. The path length of residual TCE at location *i* was then determined by:

$$X_t^i = \frac{\ln(N_b^i / N_a^i)}{\mu_w \rho_w - \mu_t \rho_t} \tag{3-2}$$

where X_{t}^{i} is the path length of TCE at location *i*, N_{b}^{i} is the average photon counts (in a given time period) through the flowcell filled with sand, water and residual TCE at location *i*, N_{a}^{i} is the average photon counts (in a given time period) through the flowcell containing water saturated sand at location *i*, μ_{w} is the mass attenuation coefficient of water, μ_{t} is the mass attenuation coefficient of TCE, ρ_{w} is the density of water and ρ_{t} is the density of TCE. The flowcell was scanned two times during the dissolution process to

record the location of the dissolution front as it propagated through the porous media (water flow was stopped during these scans).

When the dissolution experiment was completed, water was drained from the 2-D flowcell and the sand was dried by passing air through the apparatus. CO_2 and then TCE was flowed through the flowcell to saturate the pores with TCE. Attenuation measurements were then made with the flowcell filled with sand and TCE. The path length of the pore space at location *i* was determined using:

$$X_p^i = \frac{\ln(N_e^i / N_f^i)}{\mu_i \rho_i} \tag{3-3}$$

where X_{p}^{i} is the path length of the pore space at location *i* and N_{f}^{i} is the average photon counts (in a given time period) through the flowcell filled with sand saturated with TCE at location *i*.

With the above information, the porosity and residual TCE saturations at location *i* were determined in the 2-D flowcell with the following equations:

$$\phi^{i} = 1.0 - \frac{X_{s}^{i}}{X_{s}^{i} + X_{p}^{i}} \tag{3-4}$$

$$S_n^i = \frac{X_t^i}{X_p^i} \tag{3-5}$$

where ϕ is the porosity and S_n is the residual TCE saturation at location *i*.

Attenuation coefficients for the 2-D flowcell

For the polyenergetic x-rays used in the radiation attenuation measurement, the counts recorded within a counting window is the sum of the counts from discrete photon energies. When these photons are attenuated by the material of interest, the relative count of individual photon energies within the counting window changes because the lower-energy photons are attenuated more than the higher-energy photons. Consequently, the attenuation coefficient of the material is a function of the initial spectrum and the material

path length. The assumption of a constant attenuation coefficient leads to two sources of bias: one from the calibration procedure if the mean calibration path length of the material is different than the mean path length of this material in the porous media sample; and the other if the range of measurement path length is great relative to the mean measurement path length. The calibration procedure consisted of measuring the radiation transmitted through a series of calibration vials of known geometry. Attenuation measurements were performed (by John McBride) through calibration vials (filled with various path lengths of water, TCE, and sand) to estimate lumped values of $\mu_w \rho_w$, $\mu_t \rho_t$, and $\mu_s \rho_s$, for the x-ray measurements of the 2-D flowcell (experiment 28). A linear regression of transmitted counts versus known path lengths yielded estimates of $\mu_w \rho_w$, $\mu_t \rho_t$, and $\mu_s \rho_s$, as 0.4964 cm⁻¹, 0.4642 cm⁻¹, and 3.693 cm⁻¹, respectively. The standard errors in the estimates of $\mu_w \rho_w$, $\mu_l \rho_l$, and $\mu_s \rho_s$, were 0.0029 cm⁻¹, 0.0037 cm⁻¹, and 0.0012 cm⁻¹, respectively. In the 2-D flowcell experiment, the mean calibration path length was not equal to the mean measurement path length. The bias between the attenuation coefficient resulting from the calibration procedure and the attenuation coefficient at the mean measurement path length was determined by (1) performing an analogous calibration procedure using theoretical spectrum-weighted values of the attenuation coefficient at each discrete photon energy, and the observed spectrum through the empty calibration vials, and (2) comparing the result to the theoretical spectrumweighted value of the attenuation coefficient at the mean measurement path length. The bias due to the difference between the mean calibration path length and the measured path length was greater than the random error of the calibration procedure and was corrected for. The bias in the phase fraction measurement caused by the change in the attenuation coefficient within the measurement range was small and thus was not corrected for. The resulting adjusted estimates of $\mu_w \rho_w$, $\mu_t \rho_t$, and $\mu_s \rho_s$, are 0.4967 cm⁻¹, 4.718 cm⁻¹, and 3.730 cm⁻¹, respectively.

Estimates of error in the x-ray measurements of the 2-D flowcell

Random and systematic errors occur in the measurement of ϕ^i and S_n^i . Random errors are the sum total of all the small independent errors over which we have no control (Ku, 1966). Systematic errors are fixed deviations inherent in each measurement, throughout a particular measurement sequence (Ku, 1966). Table 3-3 provides error estimates in the measurement of ϕ^i and S_n^i . The equations used to calculate the error estimates are discussed below.

Table 3-3: Error estimates in x-ray measurements of 2-D flowcell			
Parameter	Estimated bound for systematic error	Estimated standard erro	
ø	0.0005	0.0024	
S _n ⁱ	0.0155	0.0050	

Substitution of equations 3-1 and 3-3 into equation 3-4 yields the following expression for ϕ^i :

$$\phi^{i} = 1.0 - \frac{\frac{\ln(N_{g}^{i} / N_{e}^{i})}{\mu_{s}\rho_{s}}}{\frac{\ln(N_{g}^{i} / N_{e}^{i})}{\mu_{s}\rho_{s}} + \frac{\ln(N_{e}^{i} / N_{f}^{i})}{\mu_{t}\rho_{t}}}$$
(3-6)

which demonstrates that the porosity estimate at a given location is a function of N_{e}^{i} , N_{f}^{i} , N_{g}^{i} , $\mu_{s}\rho_{s}$, and $\mu_{t}\rho_{t}$. Random errors in the measurements of N_{e}^{i} , N_{f}^{i} , and N_{g}^{i} , result in random variation in ϕ^{i} . Because the estimates of $\mu_{s}\rho_{s}$, and $\mu_{t}\rho_{t}$ were utilized in all porosity estimates, errors in these parameters will systematically bias porosity estimates.

To estimate the standard error in ϕ^i due to random errors in the measurements of N_e^i , N_f^i and N_g^i , the following formula was used (Ku, 1966):

$$\left(SE(\phi^{i})\right)^{2} = \left(\frac{\partial\phi^{i}}{\partial N_{e}^{i}}\right)^{2} \operatorname{var}\left(N_{e}^{i}\right) + \left(\frac{\partial\phi^{i}}{\partial N_{f}^{i}}\right)^{2} \operatorname{var}\left(N_{f}^{i}\right) + \left(\frac{\partial\phi^{i}}{\partial N_{g}^{i}}\right)^{2} \operatorname{var}\left(N_{g}^{i}\right)$$
(3-7)

where $SE(\phi^i)$ is the estimated standard error in ϕ^i , $var(N_e^i)$ is the estimated variance in N_{e}^i , $var(N_f^i)$ is the estimated variance in N_{f}^i , and $var(N_g^i)$ is the estimated variance in N_g^i . To estimate the bound for systematic error in the measurement of ϕ^i due to uncertainties in the measurements of $\mu_s \rho_s$ and $\mu_t \rho_t$, the following formula was used (Ku, 1966):

$$\left|\Delta\phi^{i}\right| = \left|\frac{\partial\phi^{i}}{\partial\mu_{s}\rho_{s}}\Delta\mu_{s}\rho_{s}\right| + \left|\frac{\partial\phi^{i}}{\partial\mu_{t}\rho_{t}}\Delta\mu_{t}\rho_{t}\right|$$
(3-8)

where $|\Delta \phi^i|$ is the estimated bound for systematic error in ϕ^i , $\Delta \mu_s \rho_s$ is the uncertainty in $\mu_s \rho_s$, and $\Delta \mu_t \rho_t$ is the uncertainty in $\mu_t \rho_t$. Estimating reasonable bounds for $\Delta \mu_s \rho_s$ and $\Delta \mu_t \rho_t$ is based on experience and judgment (Ku, 1966); twice the standard error of each of these parameters was used here.

Substitution of equations 3-2 and 3-3 into equation 3-5 yields the following expression for S^i_n :

$$S_n^i = \frac{\frac{\ln(N_b^i / N_a^i)}{\mu_w \rho_w - \mu_t \rho_t}}{\frac{\ln(N_e^i / N_f^i)}{\mu_t \rho_t}}$$
(3-9)

which demonstrates that the residual TCE saturation estimate at a given location is a function of N_{a}^{i} , N_{b}^{i} , N_{e}^{i} , N_{f}^{i} , $\mu_{t}\rho_{t}$, and $\mu_{w}\rho_{w}$. Random error in the measurement of N_{b}^{i} result in random variation in S_{n}^{i} . Measurements of N_{a}^{i} , N_{e}^{i} , and N_{f}^{i} , were used to estimate S_{n}^{i} at three different times during the experiment (i.e., the initial residual TCE

distribution and at two times during the dissolution process) and so, errors in the estimates of these parameters will systematically bias S_n^i estimates. In addition, the estimates of $\mu_s \rho_s$, and $\mu_t \rho_t$ were utilized in all S_n^i estimates and errors in these parameters will also systematically bias S_n^i estimates. To estimate the standard error in S_n^i due to random error in the measurement of N_b^i , the following formula was used (Ku, 1966):

$$\left(SE\left(S_{n}^{i}\right)\right)^{2} = \left(\frac{\partial S_{n}^{i}}{\partial N_{b}^{i}}\right)^{2} \operatorname{var}\left(N_{b}^{i}\right)$$
 (3-10)

where $SE(S_n^i)$ is the estimated standard error in S_n^i , and $var(N_b^i)$ is the estimated variance in N_b^i . To estimate the bound for systematic error in the measurement of S_n^i due to uncertainties in the measurements of N_a^i , N_e^i , N_f^i , $\mu_t \rho_t$ and $\mu_w \rho_w$, the following formula was used (Ku, 1966):

$$\left|\Delta S_{n}^{i}\right| = \left|\frac{\partial S_{n}^{i}}{\partial N_{a}^{i}}\Delta N_{a}^{i}\right| + \left|\frac{\partial S_{n}^{i}}{\partial N_{e}^{i}}\Delta N_{e}^{i}\right| + \left|\frac{\partial S_{n}^{i}}{\partial N_{f}^{i}}\Delta N_{f}^{i}\right| + \left|\frac{\partial S_{n}^{i}}{\partial \mu_{t}\rho_{t}}\Delta \mu_{t}\rho_{t}\right| + \left|\frac{\partial S_{n}^{i}}{\partial \mu_{w}\rho_{w}}\Delta \mu_{w}\rho_{w}\right| (3-11)$$

where $|\Delta S_n^i|$ is the estimated bound for systematic error in S_n^i , ΔN_a is the uncertainty in N_a^i , ΔN_e is the uncertainty in N_e^i , ΔN_f is the uncertainty in N_f^i , $\Delta \mu_t \rho_t$ is the uncertainty in $\mu_t \rho_t$, and $\Delta \mu_w \rho_w$ is the uncertainty in $\mu_w \rho_w$. Twice each parameter's standard error was used to estimate reasonable bounds for ΔN_a , ΔN_e , N_f^i , $\Delta \mu_t \rho_t$ and $\Delta \mu_w \rho_w$.

Effluent concentration measurements by gas chromatography

In experiment 28, the concentration of TCE in the effluent was measured by gas chromatography during the first half of the dissolution process. This provided a means of confirming the x-ray measurements of TCE residual saturation. The analysis was made on a Hewlett Packard 5890A gas chromatograph equipped with a flame-ionization detector (FID) and a 10-m DB-5 capillary column with a 0.53-mm inner diameter. The injector was set at 250 °C and the detector was set at 300 °C. The oven temperature was set to 60 °C for the initial 3 minutes and then ramped to 100 °C at a rate of 10°C/min. The flowrate of the carrier gas (He) was 9 ml/min and the flowrate of the make-up gas (N_2) was 21 ml/min. The FID was supplied with 43 ml/min of H₂ and 327 ml/min of air.

To create a sample for analysis, a volume of 1.0 ml of methanol was carefully pipetted into a 2-ml autosampler vial. Next, 0.8 ml of water was removed from the effluent with a 1.0-ml gastight syringe and added to the methanol in the autosampler vial. The vial was quickly sealed with a Teflon coated septum, shaken, and then stored upside down in a freezer until analysis. Effluent samples collected intermittently during the first half of the dissolution experiment using this procedure. Calibration standards were prepared to analyze the TCE concentrations in the samples (see Figure 3-4).

3.3.2 Column experiment

Flowrate, pressure drop and sketches

The column apparatus was used to make observations of the dissolution of NAPL at residual saturation in porous media at a larger scale. In this dissolution experiment, flowrate was monitored by measuring the mass of effluent over time. The pressure ports were connected to Omega PX800 10-psi pressure transducers to measure the pressure difference across the porous media through time. The propagation of the dissolution front was recorded through sketches along the glass wall of the column.

X-ray measurements of the column apparatus

The x-ray system was used to measure the path length of TCE residual at various locations in the column to determine the length of the mass transfer zone at various intervals during the dissolution experiment. The radiation beam was passed through a filter of 20.1% CdCl₂ (by weight) in aqueous solution and a 3-mm thick piece of aluminum. The radiation beam was collimated to 5 mm by 5 mm by lead plates. Measurements were made with the x-ray generator at 52.5 kVp and 20 mA, yielding a photon peak energy of 46 keV.



Figure 3-4: Gas chromatography TCE calibration curve

The x-ray attenuation system was used to measure porosity and residual TCE saturation along three vertical transects; along the centerline of the column, at 1 cm to the left of the centerline, and at 1 cm to the right of the centerline. The origin of the x and y axes for the attenuation measurements is shown in Figure 3-3. During a scanning cycle, the attenuation through a reference was periodically measured to monitor and adjust for drift in the radiation flux from the x-ray generator. To increase the accuracy of the measurements, a scanning pattern of the column in any given state (i.e., filled with dry sand; filled with sand and water; filled with sand, water and residual TCE) was repeated three times. Averages were taken of the repeat measurements at each location.

Radiation attenuation measurements were made through the column when it was filled with water saturated sand and TCE at residual saturation. The path length of residual TCE at location *i* was then determined with equation 3-2. Scans were done at four stages in the dissolution process to record the location of the dissolution front. At the end of the experiment, the column was drained of water and the porous media was air dried. Radiation attenuation measurements were made (by Paul Imhoff) through the column filled with dry sand and the path length of the pore space was determined with:

$$X_{p}^{i} = \frac{\ln(N_{e}^{i} / N_{a}^{i})}{\mu_{w} \rho_{w}}$$
(3-12)

where X_{p}^{i} is the path length of the pore space at location *i*, N_{e}^{i} is the average photon counts (in a given time period) through the flowcell filled with dry sand, and N_{a}^{i} is the average photon counts (in a given time period) through the flowcell filled with water saturated sand at location *i*. With this information, residual TCE saturations were determined at various locations in the column using equation 3-5. The porosity at various locations in the column was determined with:

$$\phi^i = \frac{X_p^i}{X_c^i} \tag{3-13}$$

where ϕ^i is the porosity at location *i*, and X_c^i is the path length of the cross section of the column at location *i*.

Attenuation coefficients for the column apparatus

Attenuation measurements were performed to determine lumped values for $\mu_w \rho_w$ and $\mu_t \rho_t$ for the column experiment. The radiation beam was passed through a filter of 20.1% CdCl₂ (by weight) in aqueous solution, a 3-mm thick piece of aluminum and eight 0.25" thick glass plates. The glass plates were added to reduce the x-ray flux. Measurements were made with the x-ray generator at 52.5 kVp and 20 mA, yielding a photon peak energy of 46 keV (the same as was used in the column experiment).

The inner dimensions of five rectangular glass vials were carefully measured. The vials were placed between the x-ray generator and the detector to determine the flux through the empty vials. One of the vials was filled with water, and the attenuation through all of the vials was measured. This procedure was repeated until four of the vials were filled with water. Next, six glass slides were placed within the fifth (empty) vial, and attenuation measurements were recorded. Slides were added (one at a time) and attenuation measurements were recorded, until the fifth vial contained eight slides. At this point, all the slides were removed from the fifth vial. Dyed TCE was added to the fifth vial and attenuation measurements were recorded. Six slides were again placed within the fifth vial (now containing TCE) and attenuation measurements were recorded, until the fifth vial contained eight slides.

With the attenuation measurements through the vials and water, a linear regression was performed to obtain an estimate of $\mu_w \rho_w$ equal to 0.2423 cm⁻¹ (see Figure 3-5). The standard error in the estimate of $\mu_w \rho_w$ was 0.0002 cm⁻¹. The measured estimate of



Figure 3-5: Calibration curve for $\mu_w \rho_w$ for the column experiment

 $\mu_w \rho_w$ required adjustment to account for the bias induced by the difference between the mean path length of water in the calibration vials and the mean path length of water in the column. This adjustment was made with the same method used to remove the bias in the attenuation coefficients for the 2-D flowcell. The resulting adjusted estimate of $\mu_w \rho_w$ for the column experiment equals 0.2424 cm⁻¹.

With the attenuation measurements through the vials, water, slides and TCE, a linear regression was performed to obtain an estimate of $\mu_t \rho_t$ equal to 1.0525 cm⁻¹ (see Figure 3-6). The standard error in the estimate of $\mu_t \rho_t$ was 0.0012 cm⁻¹. The measured estimate of $\mu_t \rho_t$ required adjustment to account for the bias induced by the difference between the mean path length of TCE in the calibration vials and the mean path length of TCE in the column. This adjustment was made with the same method used to remove the bias in the attenuation coefficients for the 2-D flowcell. The adjusted estimate of $\mu_t \rho_t$ for the column experiment equals 1.0634 cm⁻¹.

Estimates of error in the x-ray measurements of the column apparatus

Random and systematic errors occur in the measurements of ϕ^i and S^i_n . Table 3-4 provides error estimates in the measurement of ϕ^i and S^i_n . The equations used to calculate the error estimates are discussed below.

Parameter	Estimated bound for systematic error	Estimated standard error
ø	0.0022	0.0016
s_i	0.0022	0.0013



Figure 3-6: Calibration curve for $\mu_t \rho_t$ for the column experiment

Substitution of equation 3-12 into equation 3-13 yields the following expression for ϕ^{i} :

$$\phi^{i} = \frac{\ln(N_{e}^{i}/N_{a}^{i})}{X_{c}^{i}\mu_{w}\rho_{w}}$$
(3-14)

which demonstrates that the porosity estimate at a given location is a function of N_a^i , N_e^i , X_c^i , and $\mu_w \rho_w$. Random errors in the measurements of N_a^i and N_e^i , result in random variation in ϕ^i . Because the estimates of X_c^i and $\mu_w \rho_w$ were utilized in all porosity estimates, errors in these parameters will systematically bias the porosity estimates. To estimate the standard error in ϕ^i due to random errors in the measurements of N_a^i and N_e^i , the following formula was used (Ku, 1966):

$$\left(SE(\phi^{i})\right)^{2} = \left(\frac{\partial\phi^{i}}{\partial N_{a}^{i}}\right)^{2} \operatorname{var}\left(N_{a}^{i}\right) + \left(\frac{\partial\phi^{i}}{\partial N_{e}^{i}}\right)^{2} \operatorname{var}\left(N_{e}^{i}\right)$$
(3-15)

where $SE(\phi^i)$ is the estimated standard error in ϕ^i , $var(N_a^i)$ is the estimated variance in N_a^i and $var(N_e^i)$ is the estimated variance in N_e^i . To estimate the bound for systematic error in the measurement of ϕ^i due to uncertainties in the measurements of X_c^i and $\mu_w \rho_w$, the following formula was used (Ku, 1966):

$$\left|\Delta\phi^{i}\right| = \frac{\partial\phi^{i}}{\partial X_{c}^{i}} \Delta X_{c}^{i} + \frac{\partial\phi^{i}}{\partial \mu_{w}\rho_{w}} \Delta \mu_{w}\rho_{w}$$
(3-16)

where $|\Delta \phi^i|$ is the estimated bound for systematic error in ϕ^i , ΔX_c^i is the uncertainty in X_c^i and $\Delta \mu_w \rho_w$ is the uncertainty in $\mu_w \rho_w$. Estimating reasonable bounds for ΔX_c^i and $\Delta \mu_w \rho_w$ is based on experience and judgment (Ku, 1966). ΔX_c^i was estimated at 0.04 cm while twice the standard error of $\mu_w \rho_w$ was used for $\Delta \mu_w \rho_w$.

Substitution of equations 3-2 and 3-12 into equation 3-5 yields the following expression for S_n^i :

$$S_n^i = \frac{\frac{\ln(N_b^i / N_a^i)}{\mu_w \rho_w - \mu_t \rho_t}}{\frac{\ln(N_e^i / N_a^i)}{\mu_w \rho_w}}$$
(3-17)

which demonstrates that the residual TCE saturation estimate at a given location is a function of $N^i{}_a$, $N^i{}_b$, $N^i{}_e$, $\mu_t \rho_t$, and $\mu_w \rho_w$. Random error in the measurement of $N^i{}_b$ result in random variation in $S^i{}_n$. Measurements of $N^i{}_a$ and $N^i{}_e$, were used to estimate $S^i{}_n$ at five different times during the experiment (i.e., the initial residual TCE distribution and four times during the dissolution process) and so, errors in the estimates of these parameters will systematically bias the $S^i{}_n$ estimates. In addition, the estimates of $\mu_t \rho_t$, and $\mu_w \rho_w$ were utilized in all $S^i{}_n$ estimates and errors in these parameters will also systematically bias the $S^i{}_n$ estimate the standard error in $S^i{}_n$ due to random error in the measurement of $N^i{}_b$, equation 3-10 was used. To estimate the bound for systematic error in the measurement of $S^i{}_n$ due to uncertainties in the measurements of $N^i{}_a$, $N^i{}_e$, $\mu_t \rho_t$ and $\mu_w \rho_w$, the following formula was used:

$$\left|\Delta S_{n}^{i}\right| = \left|\frac{\partial S_{n}^{i}}{\partial N_{a}^{i}}\Delta N_{a}^{i}\right| + \left|\frac{\partial S_{n}^{i}}{\partial N_{e}^{i}}\Delta N_{e}^{i}\right| + \left|\frac{\partial S_{n}^{i}}{\partial \mu_{t}\rho_{t}}\Delta \mu_{t}\rho_{t}\right| + \left|\frac{\partial S_{n}^{i}}{\partial \mu_{w}\rho_{w}}\Delta \mu_{w}\rho_{w}\right|$$
(3-18)

where $|\Delta S_n^i|$ is the estimated bound for systematic error in S_n^i , ΔN_a is the uncertainty in N_a^i , ΔN_e is the uncertainty in N_e^i , $\Delta \mu_t \rho_t$ is the uncertainty in $\mu_t \rho_t$, and $\Delta \mu_w \rho_w$ is the uncertainty in $\mu_w \rho_w$. Twice each parameter's standard error was used to estimate reasonable bounds for ΔN_a , ΔN_e , N_f^i , $\Delta \mu_t \rho_t$ and $\Delta \mu_w \rho_w$.

4. Results

4.1 Microscopic scale

4.1.1 Introduction

In microscopic studies, pore-scale events are visualized and measured in model systems (Mohanty et al., 1987). For the pore-scale measurements in this investigation, the 2-D flow cell was used to quantify blob sizes and shapes at the interface between the glass walls and the porous media. Wardlaw and McKeller (1985) found that the blobs on the exterior surfaces of bead packs are larger than those in the interior but that their average orientation and shapes are similar to those in the interior.

In three experiments, photographs were taken of TCE blobs for the quantification of blob area and perimeter by image analysis. In experiment 10, a near monolayer of glass beads (media 4, $d_p = 0.78$ mm) served as the porous media. Photographs were taken of blobs existing entirely within a 6-cm by 4-cm region from the location shown in Figure 4-1. For more detailed observations (see section 4.1.6), a 1.9-cm by 1.5-cm portion of the original 6-cm by 4-cm region was magnified and examined (see Figure 4-1). In experiments 23 and 24, the spacing between the glass walls of the 2-D flowcell was filled, approximately two to three grains across, with media 2 (unsieved sand, $d_p = 0.36$ mm) and photographs were taken of blobs from within a 3-cm by 2-cm region as shown in Figure 4-2. The photographed regions shown in Figures 4-1 and 4-2 were oriented so that their upper boundaries corresponded to the boundary between clean media and the media containing NAPL residual.

To determine if the photographed regions were large enough to be representative, REV type analyses were performed. Figures 4-3 and 4-4 show the REV analyses for experiments 10 and 24, respectively. In both of these analyses, representative areas were chosen from the centers of the photographed regions and the total areas occupied by the



Figure 4-1: Locations of the photographed regions in experiment 10

<u>*</u>









Figure 4-3: Percent area occupied by blobs as a function of the representative area for experiment 10



Figure 4-4: Percent area occupied by blobs as a function of the representative area for experiment 24

blobs within the representative areas were determined. The representative areas (rectangular in shape) were increased about their centroids and the total blob areas within these larger representative areas were determined. Because the total area occupied by blobs per representative area appeared to stabilize within the photographed regions, it was assumed that the photographed regions were reasonably representative of their respective porous media.

The parameter data collected by image analysis was normalized to average particle size according to:

$$A_{\rm dim} = \frac{4a}{\pi d_p^2} \tag{4-1}$$

$$f = \frac{4\pi a}{p^2} \tag{4-2}$$

where A_{dim} is dimensionless blob area, a is blob area, d_p is the particle diameter of the media, f is the dimensionless form factor, and p is blob perimeter (from Mayer and Miller, 1993). The form factor is a measure of blob complexity or divergence of the blob shape from that of a circle, for which f = 1 (Mayer and Miller, 1993). Blobs with small form factors are highly complex in shape and are usually relatively large.

Detection limits for blob measurement varied between experiments due to differences in magnification and image clarity. The dyed TCE blobs left residual dye on the porous media as they dissolved away. It was difficult to distinguish residual dye from very small TCE blobs after significant dissolution had taken place. The porous media also contained some dark spots (due to irregularities in grain shape) that were difficult to distinguish from small blobs. Because of these problems, detection limits were set high enough as to prevent false readings of small blobs. To determine the detection limits, photographs were taken of porous media when only residual dye remained. Image analysis was performed on these photographs. Any object interpreted as a blob by the software had to be a false reading because only dye remained. The maximum size of these

false readings was set equal to the detection limit. For the blob measurements in the 6-cm by 4-cm region of experiment 10, the detection limit was 0.002 cm². For the more detailed observations from the 1.9-cm by 1.5-cm region of experiment 10, the detection limit was reduced to 0.0003 cm² because of increased magnification. The detection limit for blob measurements made from the 3-cm by 2-cm regions in experiments 23 and 24 was 0.0004 cm².

4.1.2 Initial distribution of blob size

Figures 4-5 and 4-6 show the initial cumulative frequency distributions and the initial cumulative fraction distributions of blobs from experiment 10 (6-cm by 4-cm region), experiment 24 (3-cm by 2-cm region), and from the work of Mayer and Miller (1993). To the author's knowledge, the research by Mayer and Miller (1993) provides the only comparable results of blob distributions. In the work presented for Mayer and Miller (1993), blobs were created by injecting tetrachloroethlyene (PCE) into porous media, consisting of a monolayer of glass beads saturated with water. Water flowed through the porous media and the injected NAPL separated into discrete blobs. Measurements of blob parameters were made with image analysis methods similar to those employed in this study.

If the initial frequency distribution for a given media is compared to it's initial fractional area distribution, it can be seen that the median blob size (from Figure 4-5) is significantly smaller than the blob size where the cumulative blob area contributes to 50% of the total blob area (from Figure 4-6). This demonstrates that while the median blob area is relatively small, the fewer large blobs contribute to most of the residual NAPL volume. This result is supported by the previous investigations of Mayer and Miller, 1993. It is important to remember that some very small blobs were not accounted for in the cumulative frequency and fraction distributions because of the detection limits. The inclusion of these smaller blobs would impact the shape of the cumulative frequency



Figure 4-5: Initial cumulative frequency distribution of blob size for Mayer and Miller (1993), experiment 10, and experiment 24



Figure 4-6: Initial cumulative fraction distribution of blob size for Mayer and Miller (1993), experiment 10, and experiment 24

distributions and lower the median blob size. However, the inclusion of these smaller blobs would have almost no impact on the cumulative fraction distribution.

Comparisons between experiments are complicated by factors including differences in NAPL properties, methods for creating the residual NAPL, and differences in the uniformity of the porous media. However, examination of Figure 4-6 appears to demonstrate a trend that larger media sizes produce *relatively* larger blobs (even when blobs are normalized with respect to particle size).

4.1.3 Repeatability of blob creation

In experiments 23 and 24, the same media packing was utilized, identical drainage and imbibition velocities were used in residual creation (see Table 3-4), and photographs were taken of blobs from the same location (3-cm by 2-cm region). Figures 4-7 and 4-8 show the initial cumulative frequency and initial cumulative fraction distributions of blobs from these experiments. The similarities in the blob distributions between experiments demonstrate that the pore-scale physics underlying residual creation can be highly repeatable in controlled systems.

4.1.4 Initial distribution of blob shape

Figure 4-9 shows the initial cumulative frequency distributions of form factor for experiment 10 (6-cm by 4-cm region), experiment 24 (3-cm by 2-cm region), and from Mayer and Miller (1993). Although the experiments show similar trends, the median form factor for the work of Mayer and Miller (1993) was about 0.6, while the median form factor for experiments 10 and 24 was closer to 0.5. This suggests that the blobs created in experiments 10 and 24 were more complex on average than those created by Mayer and Miller (1993). Figures 4-10 and 4-11 show the relationship between form factor and blob size for experiments 10 and 24. It can be seen that form factor is inversely proportional to



Figure 4-7: Initial cumulative freqency distribution of blob size for experiment 23 and experiment 24



Figure 4-8: Initial cumulative fraction distribution of blob size for experiment 23 and experiment 24



Figure 4-9: Initial cumulative frequency distribution of form factor for Mayer and Miller (1993), experiment 10, and experiment 24



Figure 4-10: Relationship between form factor and blob size for experiment 10



Figure 4-11: Relationship between form factor and blob size for experiment 24

blob size (i.e., small blobs have higher form factors while large blobs have lower form factors). This means that small blobs tend to be spherical while large blobs are more irregularly shaped.

4.1.5 Blob dissolution

After TCE residual had been established in each porous medium, dissolution experiments were initiated by passing water through the porous medium in the 2-D flowcell. Photographs were taken of the TCE blobs at various n of the TCE blobs at various time pe changes in blob morphology due to dissolution could be examined. In experiments 10 and 24, the length of the mass transfer zone extended well past the regions photographed for analysis (based on visual observations), and so, dissolution observations were made from within the mass transfer zones. In dissolution experiments, the amount of water passed through a region during dissolution is often expressed in pore volumes, defined as the volume of water passed through a specified region divided by the volume of the pores (without NAPL residual) within the specified region.

Figure 4-12 shows the cumulative blob size distribution for experiment 10 (6-cm by 4-cm region) before any dissolution had occurred and after 555 pore volumes of water passed through the region. Before dissolution, the total area occupied by blobs accounted for 24 % of the region's area. After passing 555 pore volumes of water through the region, the total area occupied by blobs was only 7% of the region's area. Figure 4-13 shows the cumulative blob size distribution for experiment 24 (3-cm by 2-cm region) before any dissolution had occurred and after 668 pore volumes passed through the region. The total area occupied by blobs accounted for 16 % and 8 % of the region's area before dissolution and after passing 668 pore volumes of water, respectively. In both experiments 10 and 24, median blob sizes decreased after periods of dissolution.



Figure 4-12: Cumulative fraction distribution of blob size before dissolution and after 555 pore volumes for experiment 10



Figure 4-13: Cumulative fraction distribution of blob size before dissolution and after 668 pore volumes for experiment 24

Figures 4-14 and 4-15 show the changes in cumulative frequency of form factor for experiments 10 and 24, after periods of dissolution (555 and 668 pore volumes, respectively). In both experiments, the median form factor increased after some dissolution. This demonstrates that the blobs on average became rounder or less complicated in shape during dissolution.

4.1.6 Blob Breakup

In examining the photographs taken of blobs before and after periods of dissolution, it was noticed that often times large complex blobs broke apart into smaller blobs during the dissolution process. To better quantify these observations, a 1.9-cm by 1.5-cm portion of the 6-cm by 4-cm region photographed in experiment 10 (see Figure 4-1) was magnified for more detailed examination. Blobs in this region were measured initially before any dissolution, and after 740, 1481, and 2221 pore volumes of water passed through this region.

Digitized images of blobs from this region (at various stages of the dissolution process) are provided in Figure 4-16. The initial blobs were labeled with numbers in order of decreasing size. By 740 pore volumes, some of the initial blobs completely dissolved away, some shrank in size, while others shrank and broke up into many smaller blobs. The blobs at 740 pore volumes were labeled by maintaining their previous number designation and adding on a letter extension. For example, blob 3A at 740 pore volumes came from blob 3 at 0 pore volumes. If a blob broke up into smaller separate blobs during dissolution, the resulting smaller blobs were given different letter extensions. For example, blobs 1A, 1B, 1C and 1D at 740 pore volumes resulted from the breakup of blob 1 at 0 pore volumes. In going from 740 to 1481 pore volumes, the resulting blobs were given new number extensions. For example, blob 3A1 came from blob 3A, and blobs 1A1 and 1A2 resulted from breakup of blob 1A. In going from 1481 to 2221 pore volumes,



Figure 4-14: Cumulative frequency distribution of form factor before dissolution and after 555 pore volumes for experiment 10



Figure 4-15: Cumulative frequency distribution of form factor before dissolution and after 668 pore volumes for experiment 24
Initial Conditions 24, 29--1 CM 17-•32

After 740 pore volumes



Figure 4-16: Digitized images of blobs at 0, 740, 1481, and 2221 pore volumes for experiment 10 (1.9-cm by 1.5-cm region)



Figure 4-16 cont.: Digitized images of blobs at 0, 740, 1481, and 2221 pore volumes for experiment 10 (1.9-cm by 1.5-cm region)

the resulting blobs were given new letter extensions. For example, blob 3A1A came from blob 3A1, and blobs 1A1A and 1A1B resulted from the breakup of blob 1A1.

Figure 4-17 shows histograms of the blobs from the 1.9-cm by 1.5-cm region of experiment 10 during the dissolution process. The blob labels from Figure 4-16 have been provided so that blob history can be tracked. In general, the total number of blobs decrease with increasing pore volumes. This shows that the rate of blob generation from breakup is less than the rate of blob removal from dissolution. In addition, it can be seen that the longest lasting blobs originated from the breakup of initially large blobs. This demonstrates that the initial large blobs dominate dissolution over the long term. This has been postulated by previous investigators (Imhoff et al., 1994a, Powers et al. 1994) but until now, no experiments have been performed which allowed direct observation of changing NAPL volume within a contaminated region as dissolution progressed (Imhoff et al., 1994a).

Figure 4-18 shows the relationship between form factor and dimensionless blob areas for the blobs initially, at 740, and at 1481 pore volumes and indicates the blobs that broke up sometime during the dissolution process between 0 and 2221 pore volumes. This figure demonstrates that many of the very large blobs with small form factors broke up while none of the very small blobs with large form factors broke up.

4.1.7 Comparison to other mass transfer investigations

Previous investigations of mass transfer from residual NAPL (Imhoff et al., 1994a, Powers et al., 1994) indicate that :

$$\frac{k_l A_{na}}{V} \propto S_n^{\xi} \tag{4-3}$$

where k_l is the mass transfer coefficient, $A_{n\alpha}$ is the interfacial area between the NAPL and water phases, V is the bulk volume of the region of interest, S_n is the residual NAPL saturation and ξ is an empirically determined value that varies with experimental











Figure 4-17 cont.: Blob size distributions at 0, 740, 1481, and 2221 pore volumes for experiment 10 (1.9-cm by 1.5-cm region)



Figure 4-18: Relationship between form factor and blob size at 0, 740, and 1481 pore volumes for experiment 10 (1.9-cm by 1.5-cm region)

conditions. It is expected that k_l is relatively constant as NAPL blobs shrink in size due to dissolution. Thus:

$$A_{na} \propto S_n^{\xi}$$
 (4-4)

Imhoff et al. (1994a) estimated ξ to be 0.87 for the uniform sand used in their experiments. Powers et al. (1994) estimated values of ξ between 0.75 and 0.96 depending on the porous media utilized.

A comparison to these models can be made if it is assumed that 2-D measurements of total blob perimeter and total blob area are proportional to A_{na} and S_n , respectively. With these assumptions, it would be expected that:

Total Blob Perimeter
$$\propto$$
 (Total Blob Area)⁵ (4-5)

during the dissolution process. Total blob perimeter and total blob area were determined at various times during dissolution in experiment 10 (6-cm by 4-cm region) and 24 (3-cm by 2-cm region). This was not done for experiment 23 because the length of the dissolution front did not appear to extend past the photographed region (due to the slow dissolution flowrate used in this experiment). Regression analyses were performed with the total blob perimeter and total blob area data to estimate ξ for experiments 10 and 24, using a log transformation of equation 4-5. Figure 4-19 shows the total blob perimeter and total blob area at various times during dissolution for experiments 10 and 24 along with their regression lines. For experiment 10, ξ was estimated at 0.81 with a 95% confidence interval of 0.665 to 0.953. For experiment 24, ξ was estimated as 0.90 with a 95% confidence interval of 0.862 to 0.932. These values of ξ are in qualitative agreement with the estimates in 3-D systems by Imhoff et al. (1994a) and Powers et al. (1994).



Figure 4-19: Relationship between total blob perimeter and total blob area for experiment 10 and experiment 24

4.2 Macroscopic scale

4.2.1 Introduction

In macroscopic studies, quantities are measured that are large compared to pore scale (Mohanty et al., 1987). In this study, the 2-D flowcell and the column apparatus were used to make observations at the macroscopic scale. Experiments were performed to determine if the dissolution of residual NAPL was an unstable process as suggested by Imhoff (1992). The 2-D flowcell was designed so that changes in the shape and length of the mass transfer zone (during the dissolution of NAPL at residual saturation) could be visually observed. The column experiment was performed to make observations at a larger scale.

4.2.2 Observations of dissolution fingering from the 2-D flowcell

Introduction

A series of experiments were performed with the 2-D flowcell in which the NAPL, media packing, Viton gasket thickness, drainage flowrate, imbibition flowrate, and dissolution flowrate varied. The Viton gasket thickness was varied to change the spacing between the glass plates. Tables 4-1 through 4-4 provide summaries of the parameters varied in experiments using the 2-D flowcell with porous media 1 through 4 respectively. In these tables, S_{ni} is the initial residual NAPL saturation. Some experiments utilized the same packing, as reflected in the tables. The experiments were performed to confirm the development of dissolution fingers as postulated by Imhoff (1992). In many of the experiments performed with the 2-D flowcell, the dissolution front did not remain stable and dissolution fingers were observed. Variations between experiments were made to develop an understanding of the factors affecting finger formation such the initial length of the NAPL contaminated region, media packing, flow orientation, flowrate, media size, and NAPL composition. Most of the experiments were performed with the spacing between the glass plates equal to 0.95 mm (see Tables 4-1 to 4-4). In these experiments, observations of the dissolution front were consistent between the front and rear glass plates indicating that the patterns were two-dimensional. However, in the experiments with the spacing between the glass plates equal to 3.34 mm (experiments 27a, 27b, 27c, 28 and 29), the observations on the front and back glass plates were slightly different, indicating that the dissolution patterns were three-dimensional.

Table 4-1: Experiments with Media 1								
Exp #	NAPL	Packing Utilized	Spacing (mm)	Drainage U (m/d)	Imbibition U (m/d)	Dissolution U (m/d)	S _{ni} (±0.03)	
19	TCE	Exp 19	0.95	336	75	8.44	0.19	
20	TCE	Exp 19	0.95	336	75	8.44	0.19	
26	TCE	Exp 26	0.95	336	75	8.44	0.16	

Table 4-2: Experiments with Media 2								
Exp #	NAPL	Packing Utilized	Spacing (mm)	Drainage U (m/d)	Imbibition U (m/d)	Dissolution U (m/d)	S _{ni} (±0.03)	
22	TCE	Exp 22	0.95	336	75	8.44	0.18	
23‡	TCE	Exp 22	0.95	336	75	0.86	0.18	
24‡	TCE	Exp 22	0.95	336	75	86.6	0.18*	
25	TCE	Exp 25	0.95	336	75	8.44	0.17	

‡Performed image analysis on these experiments

*Assumed equal to experiment 23

_		Tab	le 4-3: Exp	periments w	ith Media 3		
Exp #	NAPL	Packing Utilized	Spacing (mm)	Drainage U (m/d)	Imbibition U (m/d)	Dissolution U (m/d)	S _{ni} (±0.03)
1	TCE	Exp 1	0.95	N.M.	75	8.60	0.19
2	TCE	Exp 2	0.95	N.M.	75	8.51	0.10
3	TCE	Exp 2	0.95	N.M.	112	8.60	0.10
4	TCE	Exp 2	0.95	N.M.	112	8.81	0.10
5	TCE	Exp 2	0.95	N.M.	112	8.96	0.10
6	TCE	Exp 2	0.95	N.M.	112	8.37	0.10
12	TCE	Exp 12	0.95	373	112	8.51	0.20
17	TCE	Exp 17	0.95	373	112	84.4	0.20†
18	TCE	Exp 17	0.95	373	112	8.44	0.20
27A	TCE	Exp 27A	3.34	108	25	9.46	0.16
27B	TCE	Exp 27A	3.34	108	25	9.46	0.16
27C	TCE	Exp 27A	3.34	108	25	9.46	0.16
28	TCE	Exp 28	3.34	115	28	2.18	0.14
29	TCE/Tol	Exp 28	3.34	115	28	2.16	0.14*

†Assumed equal to experiment 18

*Assumed equal to experiment 28

Table 4-4: Experiments with Media 4									
Exp #	NAPL	Packing Utilized	Spacing (mm)	Drainage U (m/d)	Imbibition U (m/d)	Dissolution U (m/d)	S _{ni} (±0.03)		
10‡	TCE	Exp 10	0.95	N.M.	112	8.44	0.24*		

‡ Performed image analysis on this experiment

*Estimated from image analysis

Initial length of residual NAPL

In many of the dissolution experiments, the dissolution front remained fairly stable at early times but fingers developed as the dissolution front propagated through the porous medium. To demonstrate how the initial length of residual NAPL effects finger development, experiments 27a and 27b were performed. In these experiments, the same packing was used (media 3) but the initial length of residual TCE was varied by stopping the flow of TCE into the flowcell at different points. Figures 4-20 and 4-21 show the propagation of the dissolution fronts (as seen from the front glass plate) for experiments 27a and 27b, respectively. In experiment 27a (U = 9.46 m/d), the dissolution front remained fairly flat by t = 8 hr and did not become unstable until the dissolution front had passed further into the media. In experiment 27b (U = 9.46), the dissolution front was also fairly flat at t = 8 hr but fingers were not observed during the dissolution of the remaining residual TCE. This shows that fingers require some distance to develop and that finger growth may not occur in experiments with short regions of NAPL contaminated media.

Media packing

To examine the effects of media packing, repetitive experiments were performed using the same media packing. Figure 4-22 shows the propagation of the dissolution front in experiment 4 (media 3, U = 8.81 m/d) as residual TCE dissolved away from water saturated porous media. The dissolution front did not remain stable and a fingered pattern was observed. Similar finger patterns were achieved when residual TCE was reestablished in the same media packing and similar dissolution flowrates were used. For example, in experiment 5 (U = 8.96 m/d), residual TCE was created using the porous media packing from experiment 4 and the resulting fingered dissolution front was very similar to that of experiment 4, as shown in Figure 4-23. When different packings were created using the same type of porous media, dissolution fingers formed in different locations.



Figure 4-20: Propagation of the dissolution front for experiment 27a



Figure 4-21: Propagation of the dissolution front for experiment 27b



t = 0 hr



t = 5 hr



t = 7.5 hr



Figure 4-22: Propagation of the dissolution front for experiment 4



t = 0 hr



t = 4 hr



t = 7 hr

t = 12 hr



Flow orientation

To check the effects of gravity on the dissolution front, experiment 6 (U= 8.37 m/d) was performed. Residual TCE was re-established in the same media packing used in experiments 4 and 5. The 2-D flowcell was then rotated 90° so that water flowed horizontally through the porous media containing residual TCE. As can be seen in Figure 4-24, the propagation of the dissolution front in experiment 6 was very similar to experiments 4 and 5. This implies that gravity did not effect the growth of fingers in the 2-D flowcell.

Flowrate

Experiments were performed over a range of flowrates in an effort to observe the effects of flowrate on finger development. In experiments 22, 23, and 24, the same media packing was used in dissolution experiments with flowrates of 8.44, 0.86 and 86.6 m/d, respectively. Figures 4-25 and 4-26 show the propagation of the dissolution flowrates for experiments 22 and 23. The shapes of the resulting dissolution fingers were fairly similar between these experiments. In experiment 24 however, dissolution fingering was not observed. The dissolution appeared to occur over the entire length of TCE residual (about 12 cm) and the TCE residual appeared to dissolve away fairly uniformly. Perhaps dissolution fingers were not observed in experiment 24 because the length of the initial residual in the 2-D flowcell was shorter than the length of the mass transfer zone induced by the high water velocity. To examine the potential of dissolution fingering at flowrates as high as 86.6 m/d (as in experiment 24), a much longer flowcell would be needed.

Media size

Dissolution fingering was observed in experiments using porous media 1, 2, and 3, when TCE residual was dissolved away at a flowrate of U = 8.44 m/d. In experiment 10, TCE residual was established in porous media 4 (glass beads, $d_p = 0.78$ mm) and dissolution was initiated by passing water through the medium at a flowrate of U = 8.44 m/d. In this experiment however, dissolution appeared to occur over the entire length of



t = 0 hr



t = 4 hr



t = 7 hr

t = 12.5 hr

Figure 4-24: Propagation of the dissolution front for experiment 6





t = 0 hr

t = 7 hr



t = 17 hr











1 cm

-¥ŀ+





the TCE contaminated region and although the dissolution was not entirely uniform, distinct dissolution fingers were not observed. Dissolution fingers may not have been observed because the length of the mass transfer zone was longer than the initial length of residual TCE. To better examine the potential for dissolution fingering in experiments with large porous media, a much larger flowcell would be needed.

NAPL composition

In experiment 29, the possiblility of dissolution fingering in porous media containing a multi-component NAPL was explored. In this experiment, a NAPL mixture, consisting of 50% TCE and 50% Toluene was used to create residual saturation in porous media 3. The NAPL mixture was made by adding 50 ml of TCE to 50 ml of Toluene. The NAPL mixure was stirred and dyed to a concentration of 1 g/L with Oil Red O dye. Dissolution was initiated by flowing water at a flowrate of U = 2.16 m/d. The resulting fingered dissolution front as seen from the front glass plate is shown in Figure 4-27. Experiment 29 demonstrates that dissolution fingering is *feasible* in porous media containing NAPL mixtures.

Observed finger lengths and widths

Measurements were made of the mean finger lengths and widths from sketches of the boundary between the clean and contaminated media. The mean finger length was determined with the following method. First, the location of the farthest downward projection or bottom of a finger was determined (see Figure 4-28). Next the locations of the highest portions of the finger (to the left and right of the finger bottom) were determined. The distance between the highest portion of the finger on the left side and the finger bottom was averaged with the distance between the highest location of the finger on the right side and the finger bottom to obtain the mean finger length. The finger width was determined by the following method. Starting from the finger bottom, the vertical location corresponding to half the mean finger length was determined. The width of the finger was measured at this vertical location. Finger measurements were not made for







1 cm ->| k−











Water flow

Figure 4-28: Measurement of finger length and width

disturbances in the dissolution front less than 2 cm in length. Figure 4-29 shows the relationship between observed finger length and width for the experiments in the 2-D flowcell in which dissolution fingers formed. In general, finger width increased with increasing finger length. Wide fingers sometimes arose from the merging of 2 or more smaller fingers.

The flowrates, residual saturations and the particle sizes differed among experiments. To better facilitate comparison among experiments, dissolution times were normalized by:

$$t = t \left(\frac{U}{S_n d_p} \right) \tag{4-6}$$

where t' is dimensionless dissolution time, t is time, S_n is the residual NAPL saturation, d_p is the diameter of the porous media particle, and U is Darcy flux. Figure 4-30 shows the relationship between finger length and t' for a select number of individual fingers from various experiments. Fingers often increased in length with increasing t'.

4.2.3 Dissolution fingering observations compared to theory

The instability analysis of Imhoff et al. (1994c) provides predictions for the wavelengths of the fastest growing dissolution instabilities over a range of flowrates and residual NAPL saturations. This analysis applies only at very early times in the dissolution process. According to theory (see Figures 6 and 8 of Imhoff et al., 1994c), the wavelengths of the fastest growing dissolution instabilities are estimated between 0.2 to 0.9 cm (depending on the definition of longitudinal dispersion) for a residual NAPL saturation of 0.20 and a Darcy flux of 8.4 m/d. In experiments with residual TCE saturations near 0.20 and dissolution flowrates around 8.4 m/d, the observed dissolution fingers were typically 1 - 3 cm in width, corresponding to critical wavelengths of 2 - 6 cm.



Figure 4-29: Relationship between finger width and length in 2-D flowcell experiments



Figure 4-30: Relationship between finger length and t'

The differences between predicted and observed wavelengths may be due to the scale of the NAPL blobs in the porous media (Imhoff et al., 1994c). For example, in experiment 18 the scale of largest TCE blobs was on the order of 0.7 cm, which is the same scale as the predicted dissolution instability. The predicted fastest growing disturbances may not have been observed because they could have been disrupted by the large TCE blobs. Instead, longer-wavelength but slower growing instabilities occured. An alternative explanation is that the theoretical analysis may not be entirely valid since it assumed an infinitesimally thin dissolution front is violated (Imhoff et al., 1994c). Actual dissolution fronts (before instabilities developed) were on the order of 1 to 2 cm at a Darcy flux of 8.4 m/day, as determined by visual observation.

4.2.4 X-ray measurements of the 2-D flowcell

Introduction

In experiment 28, an x-ray attenuation method was used to measure porosity and residual TCE saturation at various locations in the 2-D flowcell. Attenuation measurements were made at 960 separate locations, using a programmed scanning pattern containing 40 columns and 24 rows. These measurements covered a 200-mm (horizontal) by 120-mm (vertical) region. The origin of the x and y axes for the attenuation measurements is shown in Figure 3-2. Inspection of the attenuation measurements revealed inconsistencies in the data from the last column of the scanning pattern (from x = 195 to 200 mm). A possible explanation for the inconstancies in the data is that the x-ray beam may have passed through the edge of the Viton gasket. Because of the problems with the data from the last column, the data from x = 195 to 200 mm will not be presented.

Porosity

Figure 4-31 shows the porosity contours (lines of equal porosity) for the 195-mm by 120-mm region over which reliable x-ray data was obtained. The average porosity



Figure 4-31: Porosity contours for experiment 28

from x-ray measurements was 0.355. This value compares well to the average porosity estimate of 0.356, based on mass and volume measurements. The porosity measurements were slightly lower on average towards the top (low y), as compared to the bottom (high y). Perhaps the packing at the top was slightly tighter because the apparatus was tapped with a rubber mallet along the top of the aluminum frame during the packing process. Despite the small differences in porosity in the vertical direction, the dye test performed on this packing showed that the flow field was very uniform.

Propagation of the dissolution front

Figure 4-32 shows the residual TCE saturation contours at t = 0 hr (initial conditions), at t = 44 hr, and at t = 66.5 hr into the dissolution process. The initial residual TCE distribution from x-ray measurement appeared reasonably uniform with an average residual saturation of 14.3%. A dye test confirmed that the flow field through the initial residual TCE was very uniform, suggesting that the overall initial residual saturation was uniform. Dissolution was initiated by flowing water through the flowcell at a Darcy flux of 2.2 m/d. By t = 44 hr, the dissolution front was fairly flat, but dissolution fingers were starting to develop. By t = 66.5 hr, dissolution fingers had developed resulting in an uneven distribution of residual TCE. The propagation of the dissolution front as seen along the glass walls was similar to the x-ray measurements. Figure 4-33 shows the propagation of the dissolution front as seen along the glass walls.

Mass balance

In experiment 28, the concentration of TCE in the effluent was measured intermittently by gas chromatography from t = 0 hr to t = 44 hr (see Figure 4-34). With flowrate and effluent concentration data, the total mass of TCE removed from the porous media during this time interval was estimated at 3.419 g. Because the x-ray measurements did not span the entire width of the porous media containing residual TCE, the estimate of the total mass of TCE removed using x-ray measurements was determined with the



t = 0 hr

Figure 4-32: Residual TCE saturation contours at t = 0, 44, and 66.5 hr for experiment 28



t = 44 hr

Figure 4-32 cont.: Residual TCE saturation contours at t = 0, 44, and 66.5 hr for experiment 28



Figure 4-32 cont.: Residual TCE saturation contours at t = 0, 44, and 66.5 hr for experiment 28







t = 44 hr



t = 66.5 hr





Figure 4-34: Effluent TCE concentration during dissolution for experiment 28

following procedure. First, the mass of TCE within the 195 mm by 120 mm region at t = 0 hr was calculated using the attenuation measurements. Because the porous media actually occupied a width of 202 mm, the mass of TCE in the unmeasured region was estimated and added on to the amount of mass estimated from the 195 mm by 120 mm region. Next, the mass of TCE that remained within the 195 mm by 120 mm region at t = 44 hr was calculated from attenuation measurements. The amount of mass remaining in the unmeasured region was re-estimated and this amount was added on to the amount of mass estimated in the 195 mm by 120 mm region. The total amount of mass removed between t = 0 hr and t = 44 hr was then estimated by subtracting the total estimated amount of mass at t = 0 hr. The resulting estimate of the total amount of TCE mass removed from t = 0 to t = 44 hr was 3.306 g, which compares well to the estimate based on effluent concentration measurements.

Spatial moment estimations

For the 2-D flowcell, the *ij*th moment of the residual TCE saturation distribution in space, $M_{ij}(t)$ is defined here, after Freyberg (1986), as:

$$M_{ij}(t) = \rho_l \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_n(x, y) \phi(x, y) x^i y^j dx dy dz$$
(4-7)

where ρ_t is the density of TCE, $S_n(x, y)$ is the residual TCE saturation field, $\phi(x, y)$ is the porosity field, and x, y, z are the spatial coordinates. Although the integrand is defined over all space, it will be non zero only over regions where the residual TCE saturation is non zero. Because the x-ray data provides average measures over z, the integration over z is dropped. Estimating spatial moments requires approximating the integrals of equation 4-7 using discrete data. In this report, the zeroth, first, and second moments (i + j = 0, 1, or 2, respectively) are examined. These moments provide measures of the mass of TCE, location of the center of mass, and the spread of the mass.

Physically, the zeroth moment M_{00} is equal to the mass of the TCE within the measured region (Freyberg, 1986). The first moment about the origin, normalized by the TCE mass present, defines the coordinate location of the center of mass (Freyberg, 1986):

$$x_c = M_{10} / M_{00} \tag{4-8}$$

$$y_c = M_{01}/M_{00}$$
 (4-9)

where x_c is the location of the center of mass in the x direction, and y_c is the location of the center of mass in the y direction. The second moment about the center of mass defines a spatial covariance tensor:

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{bmatrix}$$
(4-10)

$$\sigma_{xx} = M_{20}/M_{00} - x_c^2 \tag{4-11}$$

$$\sigma_{yy} = M_{02}/M_{00} - y_c^2 \tag{4-12}$$

$$\sigma_{xy} = \sigma_{yx} = M_{11}/M_{00} - x_c y_c \tag{4-13}$$

where the components of the covariance tensor are physically related to the spread of the residual TCE distribution about its center of mass.

The zeroth, first, and second moments were estimated using the x-ray data from the 195 mm by 120 mm region. Parameters derived from these estimates are provided in Table 4-5. The mass of TCE decreased over time due to dissolution. The effects of dissolution fingering can be seen by the movement of the center of mass. If the residual TCE had dissolved away uniformly, the center of mass should have remained roughly at the same x location and move steadily along y as dissolution occurred. In this experiment, the location of the center of mass moved steadily along y as dissolution occurred ($y_c =$ 67.3, 98.9, and 113.4 mm at t = 0, 44 and 66.5 hr, respectively), but the center of mass shifted significantly in x during the dissolution process due to the development of dissolution fingers ($x_c = 98.6$, 95.0, and 72.6 mm at t = 0, 44 and 66.5 hr, respectively). The estimates of the components of the covariance tensor show that the spread of the
mass decreased during the dissolution process. As the dissolution front propagated through the porous media, the region over which residual TCE existed became smaller and so, the magnitudes of σ_{xx} and σ_{yy} decreased over time.

	t = 0 hr	<i>t</i> = 44 hr	t = 66.5 hr
Mass of TCE (g)	5.13	1.93	0.29
x _c (mm)	98.6	95.0	72.6
<i>y_c</i> (mm)	67.3	98.9	113.4
$\sigma_{\rm rr} ({\rm mm}^2)$	3112.1	3101.4	2659.6
σ ₁₀ (mm ²)	914.6	165.5	-82.6
$\sigma_{\rm rv} ({\rm mm}^2)$	-51.0	16.6	-121.0

4.2.5 Relative permeability

In experiment 28, the pressure drop across the porous media was measured when the porous media was clean and after the media was contaminated with residual TCE. With this information, the relative permeability (β) of the porous media containing residual TCE was estimated at 0.56. To estimate the relative permeability using the Wyllie correlation (equation 2-2), estimates for the residual NAPL saturation and the irreducible water saturation (S_{wirr}) for the porous media are required. The residual TCE saturation for this experiment was estimated by x-ray measurements at 14.3 %, and S_{wirr} was estimated as 10.4% from the drainage pressure-saturation experiment performed on the media packing used in experiment 28 (see Figure 4-35). With this information, the relative permeability was estimated using the Wyllie correlation at 0.60, which agrees well with the measured value.



Figure 4-35: Drainage pressure-saturation curve for experiment 28

4.2.6 Results from the column experiment

Introduction

The column experiment was designed to examine the effects of dissolution fingering at a large scale. The x-ray attenuation system was used to make measurements (5 mm by 5 mm) of porosity and residual TCE saturations along three vertical transects; along the centerline of the column, at 1 cm to the left of the centerline, and at 1 cm to the right of the centerline. The residual TCE existed below the fine layer of sand (y = 50 mm to y = 1000 mm, see Figure 3-3 for location of the origin of the y axis). X-ray measurements were made contiguously at vertical locations from y = 50 mm to y = 210mm and from y = 230 mm to y = 945 mm. Scans of the region between y = 215 mm to y= 220 mm could not be used because this region was covered by a metal chain (used to secure the column). The bottom portion of the column (from y = 950 mm to y = 1000mm) could not be scanned due to the positioning of the column with respect to the x-ray apparatus.

Porosity

Figure 4-36 shows the porosity profiles along the length of the column at the three transects. The average column porosity from x-ray measurements was 0.374. This value compares well to the average porosity estimate of 0.371 based on mass and volume measurements. The porosity measurements were slightly lower on average near the top (low y), as compared to the bottom (high y) of the column. Perhaps the packing at the top was slightly tighter because the apparatus was tapped with a rubber mallet at the top of the column to increase the packing density. Another explanation is that some consolidation may have occurred between the fine layer of sand and the porous media in the lower part of the column.

Propagation of the dissolution front

Dissolution was initiated by flowing water through the column at a Darcy flux of 7.64 m/d. The dissolution front (as observed along the glass wall of the column) did not



Figure 4-36: Porosity profiles at the three horizontal locations in the column experiment

remain stable and dissolution fingers developed. Figure 4-37 shows the propagation of the fingered dissolution front as seen along the glass wall of the column.

The residual TCE saturation profiles in the column were determined before dissolution was initiated (S_{ni}) , and at 4 times during the dissolution process. Figures 4-38, 4-39, and 4-40 show the residual TCE saturation profiles at various times along the column centerline, at 1 cm to the left of the column centerline, and at 1 cm to the right of the centerline, respectively. These figures demonstrate that the length of the dissolution front increased with increasing distance into the porous medium. The length of the dissolution front is defined as the region over which active dissolution occurs. The leading edge of this front was defined by Imhoff et al. (1994a) as the largest y where $S_n \leq (S_{ni}$ three times one standard error in S_n), while the trailing edge is specified as the largest y where $S_n \leq$ (three times one standard error in S_n). Figure 4-41 shows how the length of the dissolution front increased during the dissolution process. The maximum recorded length of the dissolution front increased due to the development of dissolution fingers.

The x-ray measurements demonstrated that the leading edge of the dissolution front dissolution extended further into the porous media than was observed along the glass walls. After 54.1, 87.6, and 126.1 pore volumes, the boundary between clean sand and sand containing residual TCE (as observed along the glass wall of the column) extended down to y = 380, 580, and 850 mm, respectively (see Figure 4-37). According to x-ray measurements, the leading edge of the dissolution front extended down to y = 410, 645, and 945 mm after 54.1, 87.6, and 126.1 pore volumes, respectively.

Observed finger lengths and widths

Measurements were made of the mean finger lengths and widths from sketches of the boundary between the clean and contaminated media along the wall of the column. The fingers were measured using the same method described earlier for the 2-D flowcell measurements (see Figure 4-28). Because the sketches of the fingers were made along the







Figure 4-38: Residual TCE saturation profiles along the centerline of the column





Figure 4-39: Residual TCE saturation profiles at 1 cm to the left of the column centerline



Figure 4-40: Residual TCE saturation profiles at 1 cm to the right of the column centerline



Figure 4-41: Growth of the dissolution front with increasing pore volumes

outer surface of the curved glass wall, the finger widths were distorted because of the difference between the circumference along the inner diameter of the column and the circumference along the outer diameter (where the sketches were made). This distortion was adjusted for in the finger width measurements by multiplying the measured finger widths by the circumference of the inner diameter of the column and then dividing this value by the circumference of the outer diameter of the column. Figure 4-42 shows the relationship between observed finger length and width along the walls of the column. In general, finger width increased with increasing finger length. Wide fingers sometimes arose from the merging of 2 or more smaller fingers. Figure 4-43 shows that generally finger length increased with increasing t'.

Mass balance

From mass measurements, it was estimated that 450 g of TCE was trapped as residual within the column (before any dissolution). Because the x-ray measurements did not span the entire width or length of the porous media containing residual TCE, the estimate of the total mass of TCE in the column from x-ray measurements was determined with the following procedure. First, the TCE volumetric content ($\theta_n = S_n \phi_n$) was determined at each of the scanned locations. Next, the average TCE volumetric content was determined from the three horizontal measurements at each vertical location. By multiplying the horizontally averaged TCE volumetric contents by the cross sectional area of the column and the vertical thickness of the x-ray measurements (5 mm), the volume of TCE in each horizontal slice was estimated. The volumes of TCE in each of the horizontal slice was estimated to determine an estimate of the total volume of TCE within the scanned portion of the column. Because the x-ray measurements did not span the entire region swas estimated and added to the estimated volume of TCE in the scanned portion of the column, providing an estimate for the total volume of TCE in the



Figure 4-42: Relationship between finger width and length in column experiment



Figure 4-43: Relationship between finger length and t' for the column experiment

column. The estimate of the total volume of TCE in the column was multiplied by the density of TCE to obtain an estimate of the total mass of TCE in the column. The total mass of TCE in the column was estimated at 463 g, which compares well to the estimate based on mass measurements.

Remediation time

If equilibrium existed between the water phase and the residual TCE during dissolution, the amount of water required to clean out the column would be equal to the mass of TCE in the column divided by the equilibrium concentration of TCE in water (C_s = 1.27 g/L). The highest estimate for the mass of TCE in the column was 463 g (based on x-ray measurements). Using the equilibrium assumption, the amount of water required to remediate the column was estimated at 365 L. Based on visual observations along the glass wall, the last blob in the column dissolved after 402 L of water was passed through the column. Using the equilibrium assumption, the amount of water required to clean the column was under estimated by 10.1 %. This shows that fingering has a small but measureable effect on remediation time, at least in a uniform porous medium where the zone of contamination is 95 cm.

Pressure loss

The pressure loss across the porous medium was measured during the dissolution experiment. The pressure loss was expected to decrease as the residual TCE dissolved away but instead, it increased during the dissolution process as shown in Figure 4-44. The increase in pressure loss implies that clogging occurred somewhere in the system. After all of the residual TCE was dissolved away, blue-dyed water was pumped through the column to check the uniformity of the flow field. The blue-dyed water flowed uniformly through the column, demonstrating that clogging did not disturb the flow field. Because the clogging did not disturb the flow field, it should not have effected the dissolution process.



Figure 4-44: Relationship between pressure drop and pore volumes for the column experiment

4.2.7 Maximum finger length

The length of the dissolution front increased steadily during the dissolution process in the column experiment due to the growth of dissolution fingers. Imhoff et al. (1994c) proposed that finger growth should eventually be limited by transverse dispersion. Transverse dispersion from regions containing NAPL residual should contaminate the clean water flowing through a finger and decrease the driving force for dissolution at the end of the finger. To illucidate this argument, consider the flow of water through an infinitely long region of porous media containing NAPL residual in which an idealized fully developed finger has formed (see Figure 4-45). It is assumed that the water in contact with NAPL residual (where r >R) is fully saturated with dissolved NAPL. As clean water flows into the finger, the concentration gradient between the contaminated water and the clean water provides a driving force for a radially inward dispersive flux of dissolved NAPL in the aqueous phase. As water flows further into the finger, the concentration of dissolved NAPL in water along the centerline of the finger will gradually increase due to the accumulation of NAPL mass from the sides of the finger. Eventually, water traveling through the finger becomes saturated with dissolved NAPL, preventing further dissolution at the end of the finger.

A mathematical analysis was performed with the idealized conditions described above to estimate maximum obtainable finger lengths. Figure 4-46 shows an elemental volume located within the dissolution finger *with a coordinate system moving with the dissolution front*. Assuming only advective transport along the longitudinal axis and dispersive flux radially, the continuity equation for NAPL mass in the elemental volume at dynamic steady state is:



Figure 4-45: Fully developed idealized dissolution finger



Figure 4-46: Elemental volume within dissolution finger

$$\frac{\partial m}{\partial t} = 0 = U \pi \left[C \left(r, y' - \frac{1}{2} \Delta y' \right) - C \left(r, y' + \frac{1}{2} \Delta y' \right) \right] \left[\left(r + \frac{1}{2} \Delta r \right)^2 - \left(r - \frac{1}{2} \Delta r \right)^2 \right]$$

+2\pi D_t \phi \left[\left(\frac{\partial C \left(r + \frac{1}{2} \Delta r, y' \right)}{\partial r} \right) \left(r + \frac{1}{2} \Delta r \right) \Delta y' - \left(\frac{\partial C \left(r - \frac{1}{2} \Delta r, y' \right)}{\partial r} \right) \left(r - \frac{1}{2} \Delta r \right) \Delta y' \right]^{(4-14)}

where *m* is the mass of dissolved NAPL in the elemental volume, *t* is time, *U* is the Darcy flux through the finger, C(r, y') is the concentration of dissolved NAPL in the water at location (r, y'), *r* is the radial distance from the centerline of the dissolution finger, *y'* is the longitudinal distance into the finger, Δr is the radial thickness of the elemental volume, $\Delta y'$ is the longitudinal thickness of the elemental volume, D_t is the transverse dispersion coefficient, and ϕ is the porosity. Simplifying equation 4-14 and taking the limit as Δr and $\Delta y'$ go to zero yields:

$$\frac{\partial C(r, y')}{\partial y'} = \frac{\phi D_t}{U} \left[\frac{\partial^2 C(r, y')}{\partial^2 r} + \frac{1}{r} \frac{\partial C(r, y')}{\partial r} \right]$$
(4-15)

which can be rewritten as:

$$\frac{\partial C(r, y')}{\partial y'} = \frac{\phi D_t}{U} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C(r, y')}{\partial r} \right)$$
(4-16)

with boundary conditions:

$$C(r,0) = 0, \qquad 0 < r < R$$
 (4-17)

$$C(R, y') = C_s, \qquad y' > 0$$
 (4-18)

where R is the radius of the finger and C_s is the equilibrium concentration of dissolved NAPL in water. The solution to equation 4-16 with the above boundary conditions is given by Crank (1992):

$$C(\mathbf{r},\mathbf{y}') = C_s \left[1 - \frac{2}{R} \sum_{n=1}^{\infty} \frac{1}{\alpha_*} \frac{J_o(\mathbf{r}\,\alpha_n)}{J_1(R\,\alpha_n)} \exp\left(-\frac{\phi D_t}{U} \alpha_n^2 \,\mathbf{y}'\right) \right]$$
(4-19)

where J_o is the Bessel function of the first kind of order zero, J_I is the Bessel function of the first order, and the α_n s are the roots of:

$$J_{\alpha}(R\alpha_n) = 0 \tag{4-20}$$

which can be obtained from tables of Bessel functions. Equation 4-19 can be used to determine the concentration of dissolved NAPL at various distances into an idealized dissolution finger. When the concentration along the centerline of the dissolution finger (r = 0) approaches the NAPL solubility limit, the maximum finger length is obtained.

An estimate of transverse dispersion in the dissolution finger is required to solve equation 4-19. Transverse dispersion in clean porous media (i.e., containing no residual NAPL) has been expressed as:

$$D_l = \tau D_m + \alpha_l \frac{U}{\phi} \tag{4-21}$$

where D_t is the transverse dispersion coefficient, τ is the tortuosity of the porous medium, D_m is the molecular diffusion coefficient of the NAPL species in water, and α_t is the transverse dispersivity. Transverse dispersivity in clean porous media is typically in the range of 1/20 to 1/5 of longitudinal dispersivity , α_l (Freeze and Cherry, 1979). Longitudinal dispersivity has been measured in the range of 1 to 2 times the mean particle diameter in clean porous media (see Figure 7.4 of Bear, 1979).

Transverse dispersion in the dissolution finger may be different than that in clean porous media due to interactions at the interface between the contaminated sand and clean sand, along the walls of the dissolution finger. The convergence of flowlines at the finger inlet may also influence the effective transverse dispersion. With these factors in mind, an accurate estimate of transverse dispersion within a dissolution finger can not be made.

The concentration profile (from equation 4-19) along the centerline of a theoretical dissolution finger was plotted in Figure 4-47, assuming a porosity of 37 %, a tortuosity of 0.67, a mean particle diameter of 0.26 mm, a value of transverse dispersivity equal to 0.225 times the mean particle diameter of the porous media, a NAPL molecular diffusivity



Figure 4-47: Concentration profile along the centerline of an idealized dissolution finger

equal to 1.0 E -5 cm²/s, a finger radius of 1 cm, and a Darcy flux through the finger of 7.64 m/d. These conditions were chosen in a conservative attempt to simulate the conditions of the column experiment. The results from equation 4-19 show how the concentration of NAPL in the water phase asymptotically approach the solubility limit. This feature results from the fact that the dispersive flux is theoretically driven by a concentration gradient, requiring an infinite distance before the solubility limit can be obtained. If fingers are assumed to stop growing when the water reaches 98.5% of the solubility limit, a maximum finger length of 130.5 cm was predicted for the conditions described above. If the above conditions are representative of those in the column experiment.

Sensitivity analyses of equation 4-19 to changes in Darcy flux, finger radius, and transverse dispersivity were performed assuming finger growth stops when the water reaches 98.5% of the solubility limit (see Figures 4-48 through 4-50). These figures were prepared using the base state conditions given above, unless otherwise indicated. Figure 4-48 demonstrates that maximum finger length rises with Darcy flowrate at low flowrates but stabilizes at higher flowrates. Figure 4-49 shows that maximum finger length is proportional to the square of the finger radius. Figure 4-50 shows that maximum finger length is inversely proportional to transverse dispersivity.



Figure 4-48: Relationship between maximum finger length and flowrate



Figure 4-49: Relationship between maximum finger length and finger radius



Figure 4-50: Relationship between maximum finger length and transverse dispersivity

5. Conclusions and Recommendations

Quantification of blob size through image analysis demonstrated that the blobs ranged in size and shape. Although the median blob size may be relatively small, the fewer large blobs contribute to most of the NAPL residual. Results from image analysis demonstrated that the shape and number of blobs in a given region changed during the dissolution process. Blobs tended to become less complicated in shape during dissolution. It was observed that large irregularly shaped blobs often broke into smaller blobs during the dissolution process. The longest lasting blobs originated from the breakup of initially large blobs. This result is important because it indicates blob breakup is a dominant mechanism and should be accounted for in pore-scale models of NAPL dissolution.

In many experiments, the dissolution front did not remain stable and dissolution fingers were observed. The fingering process was found to be a function of the initial length of residual, media packing, flowrate, and media size. Gravity did not seem to effect the development of dissolution fingers. Dissolution fingering was observed in an experiment containing a NAPL mixture. In general, finger lengths and widths increased during the dissolution process. Results from the column experiment showed that the dissolution front can grow to 29 cm due to the development of dissolution fingers. In addition, flow bypassing due to dissolution fingering increased remediation time by 10.1%. A mathematical analysis demonstrated that maximum finger length theoretically increases with increasing flowrate and finger radius. Maximum finger length was shown to be inversely proportional to transverse dispersivity.

For future work, it is recommended that an effort be made to develop a method that would allow NAPL blob observations without having to dye the NAPL. This might reduce the detection limit and allow for observations of much smaller blobs. The experiments in this work were performed using homogeneous porous media. It is

recommended that future efforts investigate the effects of heterogeneous media packings and NAPL mixtures on blob distribution, dissolution fingering and remediation time.

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Wyllie, M. R. J., Relative Permeability, in Petroleum Production Handbook, Vol. II: Reservoir Engineering, McGraw-Hill, New York, N.Y., 1962 7. Appendix 1: Remaining raw data from experiments



t = 0 hr

_

t = 7 hr

.

1 cm

łk





t = 24 hr







t = 4 hr



t = 7 hr





1 cm

t = 4 hr



t = 8 hr

t = 12 hr













t = 24 hr



t = 0 hr

-

t = 12 hr





t = 22 hr














t = 0 hr

t = 7 hr

.





t = 23 hr

Propagation of the dissolution front for experiment 20





t = 0 hr

t = 8 hr





t = 24 hr

Propagation of the dissolution front for experiment 25





t = 21.5 hr

t = 26.5 hr

Propagation of the dissolution front for experiment 26





sand & water

t = 0 hr

t = 12 hr

1 cm

*





t = 28 hr

Propagation of the dissolution front for experiment 27c