Investigation of NAPL dissolution and instability using a pore-scale network model: sensitivity analysis of porous medium characteristics

Yanhui Hu
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd
Part of the Chemical Engineering Commons

Recommended Citation
Hu, Yanhui, "Investigation of NAPL dissolution and instability using a pore-scale network model: sensitivity analysis of porous medium characteristics" (2002). Retrospective Theses and Dissertations. 379.
https://lib.dr.iastate.edu/rtd/379

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Investigation of NAPL dissolution and instability using a pore-scale network model: Sensitivity analysis of porous medium characteristics

by

Yanhui Hu

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Rodney O. Fox, Major Professor
James C. Hill
Robert Horton
W. Robert Stephenson
R. Dennis Vigil
Robert P. Ewing

Iowa State University

Ames, Iowa

2002
This is to certify that the doctoral dissertation of

Yanhui Hu

has met the dissertation requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program
Table of Contents

CHAPTER 1. INTRODUCTION 1
   1.1 NAPL movement and dissolution 1
   1.2 Dissertation organization 4
   1.3 References 4

CHAPTER 2. LITERATURE REVIEW 7
   2.1 Macroscopic scale studies 9
   2.2 Pore scale studies 20
   2.3 References 29

CHAPTER 3. INVESTIGATION OF NONAQUEOUS PHASE LIQUID DISSOLUTION AND INSTABILITY USING A NETWORK MODEL 40
   Abstract 40
   Nomenclature 41
   1. Introduction 42
   2. Model development 44
   3. Simulation results 51
   4. Conclusions 58
   References 60
   Captions for figures 66

CHAPTER 4. INVESTIGATION OF POROUS MEDIUM CHARACTERISTICS EFFECTS ON NONAQUEOUS PHASE LIQUID DISSOLUTION AND INSTABILITY 79
   Abstract 79
   1. Introduction 80
   2. Methodology 83
   3. Simulation results and discussion 87
   4. Conclusions 97
   References 99
   Captions for figures 105
   Appendix 114

CHAPTER 5. CONCLUSIONS 116
   1. Summary 116
   2. Recommendations 119

ACKNOWLEDGMENTS 122
CHAPTER 1. INTRODUCTION

1.1 NAPL movement and dissolution

Multiphase flow in porous media is a complicated yet common phenomenon in many fields of practical interest. An example in chemical reaction engineering is the trickled bed reactor, in which solid catalyst pellets are packed to form a porous medium. Two phases, usually one gas and one liquid, are introduced into the reactor, where they mix in the void space and react on the surface of the catalyst. Another example lies in the area of petroleum engineering, in which residual oil is recovered from reservoir rock via water flooding. Agricultural drainage and irrigation, in which water and air compete to occupy pores via capillary and buoyancy forces, is also a multiphase flow process. Multiphase flow processes can also be encountered in the environment, for example when organic solvents enter an aquifer due to leakage from underground tanks or accidental surface spills.

Organic chemicals can cause extensive water contamination. Many organic pollutants are hydrophobic, forming a separate nonaqueous phase rather than immediately dissolving into the groundwater, so they are referred to as NAPLs (nonaqueous phase liquids). The solubilities of many NAPLs are low, but still high enough to severely degrade water quality, causing long-term contamination. For example, the solubility for trichloroethylene (TCE, a commonly used degreaser and solvent) in water is around $10^3$ mg/L, while its maximum concentration limit (MCL) in drinking water is around $5\times10^{-3}$ mg/L, about $2\times10^5$ times less (Pankow and Cherry, 1996). The low solubility means that a spill takes a long time to dissolve; the high toxicity means that even extensive dispersion does not dilute it to safe levels. A list of the common organic groundwater pollutants and their MCLs can be found in Fetter (1994).
Following surface spills or underground tank leakage, NAPLs migrate into the underground porous media. NAPLs first infiltrate through the vadose zone (unsaturated zone), leaving disconnected residual blobs or ganglia behind their flow path when interfacial forces overcome viscous forces and gravity forces. Upon reaching the groundwater table, NAPLs lighter than water, known as LNAPLs, spread horizontally to form a floating pool. On the other hand, NAPLs denser than water, known as DNAPLs, migrate below the water table and into the saturated zone, leaving residual ganglia behind and forming a pool above an impermeable layer. As groundwater flows by these trapped ganglia and pools, NAPLs dissolve slowly into water, creating dilute contaminant plumes (Fig. 1). In the study of residual ganglia behavior, buoyancy forces resulting from density differences are generally insignificant at the scale of a few pores (Ioannidis et al., 1996), therefore they are ignored in this study.

When groundwater is contaminated, a decision must be made to either actively remediate the site, or to monitor it while natural processes accomplish the cleaning (PNNL, 2001). Both procedures are expensive and require a solid understanding of how contaminants move in the subsurface. Remediation used to be built around the processes of contaminant dissolution and recovery: the so-called pump-and-treat method, in which contaminated water is pumped out of the subsurface, and undergoes aboveground treatment, after which the clean water is released at the surface. However, pump-and-treat has been found to be ineffective in many practices (Pankow and Cherry, 1996), both because dissolution is a slow process when NAPL solubility is low, and because diffusion of dissolved contaminant from a water-NAPL interface to a region of higher-velocity water flow field is seriously rate limiting. Recent remediation methods also attempt to remobilize
the trapped NAPL ganglia or pools, with efforts concentrating on reducing capillary forces through the use of surfactants, or increasing the water velocity so the viscous forces will override the capillary forces that hold ganglia in place. Examples of these remediation techniques include water flooding and chemical-enhanced recovery using cosolvents and surfactants to reduce interfacial tension and/or increase NAPL solubility.

The NAPL entrapment process and the fate of the ganglia are affected by many factors, including porous medium characteristics, fluid properties, boundary conditions, and the NAPL spill (or leakage) and migration history. Due to the complexity and uncertainty in the nature of the NAPL dissolution and migration processes, investigations have been conducted on several scales. The largest scale is the field scale, at which a wide range of remediation techniques has been tested. However, in order to have a better understanding of the underlying processes, experimental investigations and numerical simulations typically are conducted at much smaller scales. Until recently, most experimental studies have focused on the measurement of continuous fluid properties on a macroscopic or laboratory scale (~10 cm). Along with these experiments, mathematical models have also been developed and relationships between continuous properties and transport characteristics have been proposed to describe multiphase flow and interfacial mass transfer in porous media.

Since the mass transfer process occurs at the NAPL-aqueous phase interfaces, investigation on the pore scale is useful for obtaining an accurate description of the transport processes. When the rocks are water-wet, capillary forces tend to restrict the residual NAPL blobs to the larger pores. Because these larger pores are often the locus of higher-velocity groundwater flow, the interplay between capillary and viscous forces acting on a ganglion is locally conditioned by the exact configuration of the ganglion, as determined by the porous
medium: size, structure and heterogeneity of the pores, aspect ratio, wetting angle, and so on. Among all the pore scale studies, pore-scale modeling is one of the most used investigation tools, since these models can explicitly take into account the effect of the porous medium on NAPL movement and dissolution, as well as provide an opportunity to test hypotheses that are difficult or expensive to test experimentally. This research investigates, via a pore-scale model, various aspects of NAPL dissolution and movement that have been overlooked in the past.

1.2 Dissertation Organization

The goals of this research are to better understand the mechanisms of stranded NAPL dissolution and remobilization using a pore scale model, and to characterize the effects of the porous medium, flow rates and fluid properties on those processes. Chapter 2 contains a thorough review of previous work. Chapter 3 describes the development and testing of a network model for investigating NAPL dissolution and instability. Chapter 4 presents a sensitivity analysis of various factors influencing NAPL dissolution and instability. Chapter 5 gives the conclusions from this research and recommendations for future work.

1.3 References


Figure 1. Schematic diagram of NAPL migration and research scales
Chapter 2. LITERATURE REVIEW

Nomenclature:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Specific interfacial area</td>
<td>[L^2 L^{-3}]</td>
</tr>
<tr>
<td>k_t</td>
<td>Mass transfer coefficient of NAPL in aqueous phase</td>
<td>[L T^{-1}]</td>
</tr>
<tr>
<td>k_f</td>
<td>Effective mass transfer coefficient</td>
<td>[L T^{-1}]</td>
</tr>
<tr>
<td>k_{rA}</td>
<td>Relative permeability of fluid phase A</td>
<td>[-]</td>
</tr>
<tr>
<td>l_c</td>
<td>Characteristic length</td>
<td>[L]</td>
</tr>
<tr>
<td>q_A</td>
<td>Darcy or superficial velocity of fluid phase A</td>
<td>[L T^{-1}]</td>
</tr>
<tr>
<td>C</td>
<td>NAPL concentration</td>
<td>[M L^{-3}]</td>
</tr>
<tr>
<td>C_{nw}</td>
<td>NAPL concentration at the interfaces</td>
<td>[M L^{-3}]</td>
</tr>
<tr>
<td>C_s</td>
<td>NAPL solubility in aqueous phase</td>
<td>[M L^{-3}]</td>
</tr>
<tr>
<td>D</td>
<td>Dispersion tensor</td>
<td>[L^2 T^{-1}]</td>
</tr>
<tr>
<td>D_m</td>
<td>Molecular diffusion coefficient</td>
<td>[L^2 T^{-1}]</td>
</tr>
<tr>
<td>F_A</td>
<td>Sources or sinks of fluid phase A</td>
<td>[M L^{-3} T^{-1}]</td>
</tr>
<tr>
<td>G</td>
<td>Gravitational acceleration vector</td>
<td>[L T^{-2}]</td>
</tr>
<tr>
<td>J</td>
<td>Mass flux of NAPL</td>
<td>[M L^{-2} T^{-1}]</td>
</tr>
<tr>
<td>K</td>
<td>Permeability tensor</td>
<td>[L^{-2}]</td>
</tr>
<tr>
<td>K_t</td>
<td>Mass transfer rate coefficient</td>
<td>[T^{-1}]</td>
</tr>
<tr>
<td>P_A</td>
<td>Pressure of fluid phase A</td>
<td>[M L^{-1} T^{-2}]</td>
</tr>
<tr>
<td>S_A</td>
<td>Saturation of fluid phase A, fluid volume/void volume</td>
<td>[-]</td>
</tr>
<tr>
<td>\alpha</td>
<td>Transverse dispersivity</td>
<td>[L]</td>
</tr>
<tr>
<td>\alpha_l</td>
<td>Longitudinal dispersivity</td>
<td>[L]</td>
</tr>
<tr>
<td>\delta</td>
<td>Diffusion length</td>
<td>[L]</td>
</tr>
<tr>
<td>\delta_k</td>
<td>Kronecker delta</td>
<td>[-]</td>
</tr>
<tr>
<td>\phi</td>
<td>Porosity of the porous medium, void volume/total volume</td>
<td>[-]</td>
</tr>
<tr>
<td>\rho</td>
<td>Density of fluid phase</td>
<td>[M L^{-3}]</td>
</tr>
<tr>
<td>\mu_A</td>
<td>Viscosity of fluid phase A</td>
<td>[M L^{-1} T^{-1}]</td>
</tr>
<tr>
<td>\omega</td>
<td>Mass fraction of NAPL in water</td>
<td>[-]</td>
</tr>
</tbody>
</table>

Subscript

\( \alpha = n, w \)  \( n: \) nonaqueous phase  \( w: \) water phase

As nonaqueous phase liquids (NAPLs) migrate through a porous medium, a portion of the NAPL is left behind as residual ganglia. The complicated NAPL migration and dissolution process, as well as the fate of the ganglia, are frequently characterized using several dimensionless groups. One of the most important dimensionless numbers to describe ganglion mobilization is the capillary number \( C_a \), as the ratio of viscous force to capillary
force. In general, for a specific system of porous medium and multiphase liquids, at some Ca, the viscous force will overcome the resistance posed by capillary force, and ganglia will move downstream. Another commonly used dimensionless group is the Bond number Bo ($Bo = \frac{(\rho_w - \rho_o)g l c^2}{\sigma_{nw}}$), the ratio of buoyancy force to capillary force. Buoyancy force is important in experimental and field study but not generally included in the pore level study.

Due to the complexity of, and uncertainty in, the underlying processes of the problem, a comprehensive investigation of all related factors in one study is rarely attempted. However, many researchers have studied some part of the whole problem, including the processes of residual ganglia mobilization, dissolution and remediation and various factors affecting those processes.

Melrose and Brandner (1974) used rheon to describe the episodic motion of the oil ganglion, sudden leaps in the direction of hydraulic pressure gradient with long periods of slow deformation of the interfaces in between. Ng et al. (1978) visualized the movement of residual blobs in a three-dimensional transparent porous media and found that non-aqueous phase liquid saturation in water-saturated zone was independent of the capillary number for $Ca < 2 \times 10^{-5}$. Above that point, NAPL saturation decreased with increasing Ca, and for $Ca > 5 \times 10^{-3}$, nearly all ganglia were displaced. Ng and Payatakes (1980) and Payatakes (1980) proposed a stochastic model to predict the fate of the residual ganglia in porous media during an immiscible displacement. Hundreds of one-step ganglion motions (rheons) were simulated using a two-dimensional network model with random sized unit cells, and the probabilities of mobilization, breakup, and stranding per rheon as functions of capillary number and ganglion sizes were obtained. It was found that larger ganglia can be mobilized
or broken up at lower $Ca$. For example, ganglia with a size of 15 pore units or larger are likely to be mobilized at $Ca > 10^{-3}$ while singlets cannot be mobilized until $Ca > 10^{-2}$. Later, experiments were performed on a two-dimensional chamber-and-throat etched glass apparatus by Avraam and Payatakes (1995a) and the effects of capillary number, flow-rate ratio, viscosity ratio and non-aqueous phase saturation on different flow regimes were investigated. Four main flow regimes were observed and mapped: large ganglion dynamics (LGD), small-ganglion dynamics (SGD), drop-traffic flow (DTF) and connected pathway flow (CPF). LGD (when the mean size of the moving ganglion larger than 10 chambers) corresponds to the small $Ca$ and moderate-to-high water saturation. On the other hand, SGD corresponds to the larger value of $Ca$ and/or smaller water saturation.

Besides the effect of the capillary number on the ganglion mobilization, porous medium characteristics such as pore sizes, shape, neck/body correlations and aspect ratios also have a significant impact on the NAPL movement mechanics. This is especially evident in the constitutive relationships, such as capillary pressure-saturation-relative permeability relationship (Reeves, 1997). These constitutive relationships play an important role on determining the final distribution and configuration of the NAPL ganglia (Mayer and Miller, 1992; Lowry and Miller, 1995).

2.1. Macroscopic scale studies

Various mathematical models have been developed and used to quantify multi-phase flow and NAPL dissolution into the aqueous phase (Kueper and Frind, 1991a, b; Powers et al., 1991; VanderKwaak and Sudicky, 1996). Many of the existing models are limited to simplified situations, such as only one NAPL species is considered, the porous medium is
homogeneous with only or two one spatial dimensions under consideration, local equilibrium of the NAPL aqueous phase concentration is assumed, or NAPL mass loss due to dissolution is neglected. The exceptions to these assumptions include a multi-region mass transfer model to describe more than one NAPL species (Garg and Rixey, 1999), a two-film model to incorporate surfactant interactions (Reitsma and Kueper, 1998), a rate-limited mass transfer model (Brusseau, 1992; Zhu and Sykes, 2000), a two-dimensional model (Mayer and Miller, 1996), and a NAPL pool dissolution and shrinkage model (Lee and Chrysikopoulos, 1998). A comprehensive review on multiphase flow and mass transport is given by Miller et al. (1998).

In general, it can be assumed that the microscopic balance law of continuum mechanics holds for each phase. Thus, a macroscopic mass balance law for isothermal multiphase flow in porous media can be formed by applying volume averaging techniques over a microscopic mass balance equation (Bear, 1972). This gives a mass balance equation for each fluid phase:

$$ \frac{\partial (\phi \rho_a S_a)}{\partial t} + \nabla \cdot (\rho_a q_a) = F_a $$  \hspace{1cm} (1)

where the subscript $a$ denotes the fluid phase, $\phi$ is the porosity, $S$ is the saturation, $q$ is the Darcy velocity, and $F$ is the source term.

Equation 1 can be used for an arbitrary number of fluid phases, with changing porosity or fluid densities. However, it is widely used for the common case of two-phase flow (aqueous and non-aqueous phases) with the solid phase being inert and immobile. Special cases like solid phase sorption and three-phases flow were studied by Abriola and Pinder (1985a,b) and Brusseau (1992).
For immiscible two-phase flow in a homogeneous and isotropic porous media, an extended version of Darcy's law can be used:

\[ q_a = -\frac{kk_{ra}}{\mu_a} \cdot (\nabla P_a - \rho_a g) \]  \hspace{1cm} (2)

where \( k \) is the intrinsic permeability tensor, describing the absolute permeability of the porous media, and \( k_{ra} \) is the relative permeability of phase \( a \).

A single governing equation for each fluid phase in multiphase flow can be attained by combining Eq. 1 and 2:

\[ \frac{\partial (\phi \rho_a S_a)}{\partial t} - \nabla \cdot \left( \rho_a \frac{kk_{ra}}{\mu_a} \cdot (\nabla P_a - \rho_a g) \right) = F_a \]  \hspace{1cm} (3)

For two-phase flow systems, Eq. 3 is needed for each fluid phase. In order to close the system, the following constraints must be satisfied:

\[ S_w + S_n = 1 \]  \hspace{1cm} (4a)

\[ P_c = P_n - P_w = P_c(S_a) \]  \hspace{1cm} (4b)

\[ k_{ra} = k_{ra}(S_a) \]  \hspace{1cm} (4c)

Eq. 4b gives the definition of capillary pressure. Constitutive relationships like Eq. 4b and 4c should account for the influences of all subscale phenomena and processes on immiscible fluid flow in porous media, such as porous medium characteristics and heterogeneity, wettability, and fluid properties. Both Eq. 4b and 4c are complex and hysteretic (Jerauld and Salter, 1990; Avraam et al., 1994; Avraam and Payatakes, 1995a), and the resultant flow equations are highly nonlinear and difficult to solve.

Due to the complex nature of the constitutive equations, many researchers try to find a more complete relationship for relative permeability. The relative permeability coefficient
not only depends on fluid saturation but also on other system parameters, such as the capillary number, flow rate ratio, viscosity ratio and contact angle. A generalized two-phase relative permeability coefficient form proposed by Avraam and Payatakes (1995b) explicitly takes into account the viscous coupling effects:

$$q_w = -\frac{kk_{rwm}}{\mu_w} (\nabla P_w - \rho_w g) - \frac{kk_{rnm}}{\mu_n} (\nabla P_n - \rho_n g)$$

$$q_n = -\frac{kk_{rwm}}{\mu_w} (\nabla P_w - \rho_w g) - \frac{kk_{rnm}}{\mu_n} (\nabla P_n - \rho_n g)$$

where $k_{rmn}$ and $k_{rww}$ are the generalized relative permeabilities for water and nonaqueous phases, and $k_{rwn}$ and $k_{rwn}$ are the viscous coupling effects. Note that original Darcy's law was originally developed to describe steady, saturated single-phase flow through a homogenous, isotropic porous medium, and the extension of Darcy's law to multiphase systems is for convenience rather than based on basic principles. Under certain conditions, the use of the extended Darcy's law leads to contradictions (Hassanizadeh and Gray, 1993). Therefore, caution is required when applying Darcy's law to build mathematical models.

Dissolution of NAPL in a porous medium can be characterized using the following mass balance equation:

$$\frac{\partial}{\partial t} \left( \phi \rho_w S_w \omega \right) + \nabla \cdot \left( \rho_w q_w \omega \right) - \nabla \cdot \left( \phi \rho_w S_w D \cdot \nabla \omega \right) = F$$

where $\omega$ is the mass fraction of NAPL in the aqueous phase and $D$ is the dispersion tensor. The first term represents the accumulation of NAPL in water, and the second term represents the advective transport of NAPL due to bulk flow. The third term describes the transport due to dispersion. The right-hand-side term accounts for all the sources, including interfacial mass transfer.
The dispersion tensor accounts for both mechanical dispersion and molecular
diffusion (Bear, 1972). For an isotropic medium, j,k-component of the dispersion tensor can
be expressed as:

\[ D_{jk} = \alpha_T \frac{|q_w|}{\phi S_w} \delta_{jk} + (\alpha_L - \alpha_T) \frac{q_w q_w}{\phi S_w |q_w|} + D_m \delta_{jk} \] (7)

where \( \alpha_T \) is the transverse dispersivity, \( \alpha_L \) is the longitudinal dispersivity, and \( D_m \) is the
molecular diffusion coefficient of NAPL in the aqueous phase.

Since most NAPLs of interest are only slightly soluble in the aqueous phase, the
spatial variation of aqueous phase density can be neglected, and \( \rho_w \) can be combined with the
mass fraction to yield solute mass concentration. This simplifies the mass transport equation
(Eq. 6) to:

\[ \frac{\partial}{\partial t} (\phi S_w C) + \nabla \cdot (q_w C) - \nabla \cdot (\phi D \cdot \nabla C) = F \] (8)

where \( C \) is the NAPL concentration in the aqueous phase. The source/sink term \( F \) has to
contain all the generation and consumption terms, which may include chemical
transformation due to reaction and the interface exchange of chemical species.

The mass flux of a species across an interface results from the different chemical
potentials of that species in the respective phases. A general assumption for mass transfer of
hydrophobic chemicals from the organic to the aqueous phase is that diffusion through a
boundary layer from the interface to the bulk aqueous phase is the rate-limiting step. Based
on this assumption, a single resistance, linear driving force model is widely used to describe
the interfacial mass transfer process (Miller et al., 1990; Powers et al., 1991).
where \( J \) is the mass flux of NAPL into the aqueous phase, \( C_{nw} \) is the NAPL concentration at the NAPL/water interface, \( \delta \) is the diffusion length, and \( k_l \) is the mass transfer coefficient.

Under most circumstances, concentrations at interfaces are not practical to measure. Therefore, it is convenient to define the mass transfer coefficient based on the solubility of NAPL, \( C_s \), in the aqueous phase:

\[
J = k_f (C_s - C)
\]

where \( k_f \) is the effective mass transfer coefficient.

In the situations where the only source or sink is interface mass transport, we have:

\[
F = Ja
\]

where \( a \) is the specific interfacial area defined as the interfacial area per unit volume of porous media. Combining Eq. 8, 10, and 11 yields:

\[
\frac{\partial}{\partial t} (\phi S_w C) + \nabla \cdot (\mathbf{q}_w C) - \nabla \cdot (\phi S_w D \cdot \nabla C) = k_f a (C_s - C)
\]

The governing equations for flow (Eq. 3) and mass transport (Eq. 12) are coupled through the volumetric flux term. Due to the strong influence of flow behavior on the interfacial mass transfer, it is difficult to solve Eq. 12 and obtain an accurate prediction.

Besides this linear mass transfer model, there are some other mass transfer models developed to describe the effect of a moving boundary on the mass transport, such as the pore-diffusion model (Baldwin and Gladden, 1996) and the shrinking-core model (Geller and Hunt, 1993). Baldwin and Gladden (1996) compared their experimental results with all three mass-transfer models, and found that the pore-diffusion model fit their data the best.
However, it remains an open question which model best describes any given physical situation.

In order to solve Eq.12, the value of \( k_f \) must be determined. Many investigators have proposed quantifying \( k_f \) through the use of correlation models, which describe the dependence of mass transfer on flow and diffusion. Those models generally involve dimensionless groups, such as Sherwood number (\( Sh \)), Reynolds number (\( Re \)), Schmidt number (\( Sc \)), and Peclet number (\( Pe \)).

\[
Sh = \frac{k_f l_c}{D_m} \quad \text{ratio of interface mass transfer to molecular diffusion.}
\]

\[
Re = \frac{l_c q_w \rho_w}{\mu_w} \quad \text{ratio of inertial force to viscous force.}
\]

\[
Sc = \frac{\mu_w}{(D_m \rho_w)} \quad \text{ratio of viscous force to molecular diffusional force.}
\]

\[
Pe = \frac{q_w l_c}{D_m} \quad \text{ratio of mass transfer by convection to diffusion.}
\]

Table 1.1 provides a list of mass transfer coefficient correlations.

Friedlander (1957) studied the mass transfer around a single solid sphere and a cylinder at low Reynolds numbers using boundary layer theory, and derived an expression for the Sherwood number in term of the Peclet number. His prediction is about 10 to 40% lower than the experimental data. Bowman et al. (1961) examined the mass transfer around a solid or fluid single sphere in Stokes flow using a theoretical approach similar to Friedlander's. Using a fluid sphere gave the opportunity to study the effect of internal circulation on the rate of mass transfer. He found that internal circulation could accelerate mass transfer at high Peclet number but not at low Peclet number. Both Pfeffer et al. (1964) and Nelson et al. (1975) predicted the mass transfer rate in a packed bed at low Reynolds number analytically, and found good agreement with published experimental results. They
also showed that the Sherwood number in a packed bed is a function of both porosity and the
Peclet number, and the effect of Peclet number decreases with decreasing porosity in the low
range of Peclet number. Wakao and Funakazi (1978) collected data of gas-liquid mass
transfer in packed beds from literature. They corrected those data for axial fluid dispersion
and then proposed a correlation for Sherwood number in the range $3 < Re < 10000$.

Other investigators have studied this issue from an experimental standpoint, including
Wilson and Geankoplis (1966) and Dwivedi and Upadhya (1977). Their correlation
relationships were developed from experimental results obtained from packed beds. They
found that mass transfer coefficients for multi-sphere systems were typically lower than those
from the extrapolation of correlations developed from single-sphere systems.

Researchers in the field of environmental engineering have also done experimental
work on different NAPL-water systems and derived similar correlation relationships. Due to
the complex nature of the NAPL-water porous media system, such as the changing of the
entrapped NAPL geometry and aqueous phase saturation due to NAPL dissolution, some
dimensionless numbers need to be modified or added into the correlations. Two widely used
dimensionless groups are the modified Sherwood number and modified Reynolds number:

$$Sh^* = \frac{K_i l_c^2}{D_m}$$

$$Re^* = \frac{q_w \rho_w l_c}{[\mu \phi (1 - S_n)]}$$

where $K_i = k_f a$ is the mass transfer rate coefficient, and $S_n$ is the nonaqueous phase saturation.
The reason for using $K_i$ instead of $k_f$ in the modified Sherwood number is that unlike
idealized chemical engineering systems in which interfacial area is well defined,
NAPL/water interfacial area in a geological setting is typically very difficult to measure.
accurately. It also should be noted that the mass transfer rate coefficient is not suitable for prediction of long-term dissolution in which the interfacial area changes with time.

Miller et al. (1990) investigated the mass transfer rate coefficient as a function of aqueous phase velocity, NAPL saturation, and porous media characteristics, and found that local equilibrium can be achieved rapidly over a wide range of NAPL saturation and aqueous phase velocities in a homogeneous system. Later Mayer and Miller (1996) developed a two-dimensional multiphase transport model to investigate the NAPL movement and dissolution in heterogeneous porous media, and found that changes in the variances of the porous media properties lead to significant variations of the mass transfer rate, which can be attributed to the existence of immobile regions of NAPL pools in the heterogeneous porous media. Geller and Hunt (1993) proposed a two-dimensional NAPL dissolution model using mass transfer coefficient correlation reported in the literature. Their model treats NAPL as discrete monosized spheres and accounts for the water flowing by the residual NAPL. They were able to reproduce the effluent NAPL concentration using mass transfer zone propagation.

Powers et al. (1991) investigated five different idealized blob shapes (singlets, doublets, fingers, large sphere, and cylinder), and assumed the effective surface area to be 1-50% of the blob surfaces (ignoring the diffusive mass transfer through immobile water). They developed a one-dimensional convection-dispersion mass transfer model to examine the steady state and transient behavior of the system. Sensitivity analysis of the model shows that the nonequilibrium effects are significant for situations with large blobs, relative high velocities and low NAPL saturation. Powers et al. (1992) studied initial stage ("steady state") residual NAPL dissolution for $7.3 \times 10^{-6} < \text{Ca} < 1.5 \times 10^{-7}$ and proposed a correlation model between $Sh^*$, $Re$ and grain size distribution measure $U_i$, consistent with the
experimental results of Geller and Hunt (1993). The effects of porous medium characteristics, NAPL type and aqueous phase velocity on dissolution rates were investigated. The results showed that the effluent NAPL concentration was below solubility in most cases, indicating nonequilibrium conditions. The results also revealed that the dissolution rate depends on the residual NAPL distribution, which is strongly affected by different porous medium types. Similar conclusions about the influences of blob size and aqueous phase velocities on mass transfer rate coefficient were drawn by Imhoff et al. (1994), who included an extra term in their correlation model to describe the location of NAPL blobs within the column. Later Powers et al. (1994a) extended their work to transient NAPL dissolution, and proposed a correlation model using the volume fraction of NAPL to indicate the change in specific surface area of the shrinking NAPL blobs. The correlation between the volume fraction and modified Sherwood number is a function of median grain size and grain size distribution (Table 1). Powers et al. (1994b) proposed a mathematical residual NAPL transient dissolution model, which treats mass transfer coefficient and specific surface area independently. The specific surface area is obtained by assuming spherical NAPL blobs with a distribution of diameters. This model relies on calibration of the porous medium, which may not be obtained easily in practice. A recent review (Khachikian and Harmon, 2000) discussed correlation relationships from both chemical engineering and environmental engineering literatures and concluded that the two disciplines arrived at similar descriptions of mass transfer behavior.
Table 1. Mass transfer correlations from the literature.

<table>
<thead>
<tr>
<th>System</th>
<th>Correlation</th>
<th>Valid for</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical work:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single sphere</td>
<td>Sh = 0.89Pe$^{1/3}$</td>
<td>Pe &gt; 1000</td>
<td>Friedlander [1957]</td>
</tr>
<tr>
<td>Single sphere</td>
<td>Sh = 0.978Pe$^{1/3}$</td>
<td>Pe &gt; 10</td>
<td>Bowman et al. [1961]</td>
</tr>
<tr>
<td>Packed bed</td>
<td>Sh = 2 + 9/16Pe + ...</td>
<td>0.08 &lt; Re &lt; 125</td>
<td>Williamson et al. [1963]</td>
</tr>
<tr>
<td>Packed bed</td>
<td>Sh = B($\phi$)Pe$^{1/3}$</td>
<td>1 &lt; Pe &lt; 1000</td>
<td>Pfeffer and Happel. [1964]</td>
</tr>
<tr>
<td>Packed bed</td>
<td>Sh = 0.18*[(1 - $\phi$)$^{2/3}$ - (1 - $\phi$)$^{1/3}$]ReSc$^{2/3}$</td>
<td>Re -&gt; 0</td>
<td>Nelson and Galloway [1975]</td>
</tr>
<tr>
<td>Packed bed</td>
<td>Sh = 2 + 1.1Re$^{0.6}Sc^{1/3}$</td>
<td>3 &lt; Re &lt; 10,000</td>
<td>Wakao and Funazkri [1978]</td>
</tr>
<tr>
<td><strong>Experimental work:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic acid-</td>
<td>Sh = 1.09Pe$^{1/3}/\phi$</td>
<td>0.0016 &lt; Re &lt; 55</td>
<td>Wilson and Geankoplis [1966]</td>
</tr>
<tr>
<td>water</td>
<td></td>
<td>0.35 &lt; $\phi$ &lt; 0.75</td>
<td></td>
</tr>
<tr>
<td>NAPL Ganglia</td>
<td>Sh* = 12Re$^{0.75}\theta_n^{0.6}Sc^{0.5}$</td>
<td>0 &lt; Re &lt; 0.1</td>
<td>Miller et al. [1990]</td>
</tr>
<tr>
<td>Toluene-water</td>
<td>Sh* = 3.18$\theta_n^{0.54}$Re$^{0.98}Sc^{0.5}$</td>
<td>0 &lt; Re &lt; 0.07</td>
<td>Guarnaccia J. F. et al. [1992]</td>
</tr>
<tr>
<td>TCE-water</td>
<td>Sh* = 57.7Re$^{0.61}d_{50}^{0.64}U_i^{0.41}$</td>
<td>0 &lt; $\theta_n$ &lt; 0.05</td>
<td>Powers et al. [1992]</td>
</tr>
<tr>
<td>TCE-water</td>
<td>Sh* = 3406$\theta_n^{0.87}$Re$^{0.71}(d_p/x)^{0.31}$</td>
<td>0 &lt; $\theta_n$ &lt; 0.04</td>
<td>Imhoff et al. [1994]</td>
</tr>
<tr>
<td>TCE-water</td>
<td>Sh* = 4.13Re$^{0.598}S^{0.673}U_i^{0.369}(\theta_p/\theta_{no})^{0.4}$</td>
<td>0.0012 &lt; Re &lt; 0.02</td>
<td>Powers et al. [1994a]</td>
</tr>
<tr>
<td>TCE-water</td>
<td>Sh* = 4.13Re$^{0.598}S^{0.673}U_i^{0.369}(\theta_p/\theta_{no})^{0.4}$</td>
<td>1.4 &lt; x/dp &lt; 180</td>
<td></td>
</tr>
<tr>
<td>Styrene-water</td>
<td>$\beta_d = 0.518 + 0.1148 + 0.10U_i$</td>
<td>10 &lt; Pe &lt; 170</td>
<td>Powers et al. [1994b]</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Sh = 77.6Re$^{0.658}$</td>
<td>0.001 &lt; Re &lt; 0.33</td>
<td>Powers et al. [1994b]</td>
</tr>
</tbody>
</table>

* $U_i = d_{50}/d_{10}$ uniformity index to describe grain size distribution. $d_{50}$: median grain size.

* x: distance into column. $d_p$: mean grain size. $\theta_n$: nonaqueous phase volumetric fraction.

* $d = d_{50}/d_M$ normalized grain size, $d_M$: the "medium" grain diameter.
2.2 Pore-scale studies

In order to solve the continuum-scale equations that describe two-phase flow and mass transport processes in porous media, a suitable way is required to average microscopic equations and appropriate constitutive relationships. Pore-scale models can be used to investigate the role of the individual physical and chemical properties and processes at the scale of NAPL-aqueous interfaces. Therefore, they play an important role in obtaining an accurate description of such processes. Also, pore-scale models can provide an opportunity to test hypotheses that are difficult to test on larger scales.

Pore-scale network models were first proposed by Fatt (1956), and have since been widely applied in fields like polymer, petroleum, environmental, and chemical engineering, hydrology, and soil science. An incomplete list of these applications includes deep bed filtration (Rege and Fogler, 1988), foam formation and flow (Kharabaf and Yortsos, 1997), porous catalysis (Hollewand and Gladden, 1992), polymer flow (Sorbie, 1990), mercury intrusion to characterize porous media (Tsakiroglou and Payatakes, 1990, 1991), Knudsen diffusion (Burganos and Payatakes, 1992), and pressure-saturation and permeability-saturation constitutive relationships (Jerauld and Salter, 1990).

Early pore-scale models used a bundle-of-tubes to describe the porous media (Berkowitz and Ewing, 1998). Although analytical expressions of fluid properties, such as permeability, can be derived easily from those models, they cannot characterize the topology or connectedness of the porous media. Fatt (1956) had the idea of arranging the tubes in two-dimensional or three-dimensional networks, referred to as network models.

Both two-dimensional and three-dimensional network models are widely used in practice. One common approach in 2-D experimental work is using a pair of glass plates
with mirror image networks of pores and throats etched on them and fused together. Experimental work on these two-dimensional micromodels can be performed under capillary, viscous and buoyancy forces similar to those found in the field. Also, some important fluid properties such as the NAPL saturation and interfacial area can be easily measured and quantified (Corapcioglu et al., 1998). These advantages made the two-dimensional network models widely used in investigations of both the immiscible displacement mechanism and NAPL dissolution (Chatzis et al., 1983; Conrad et al., 1992; Avraam et al., 1994; Avraam and Payatakes, 1999; Jia et al., 1999). Despite the advantages of those two-dimensional models, connectivity in a regular two-dimensional network model is significantly less than that found in a real porous medium (Wilkinson and Willemsen, 1983). More importantly, bicontinua cannot be modeled in 2D, although they commonly exist in 3D. Thus, a regular two-dimensional network model cannot represent a general three-dimensional system of interest. Modifications can be made on the transparent micromodels to increase the connectivity. For example, Zhong et al. (2001) used two pieces of roughened glass plates held together to represent a rough-walled fracture. The same plates can also be used to represent a two-dimensional granular porous medium. However, in general, in order to study the effect of pore geometry on multi-phase flow, NAPL dissolution, and the constitutive relationships, a three-dimensional model approach is necessary to capture the important features of a real porous medium.

Three-dimensional network models are usually cubic lattices of interconnected capillaries (Fig. 1). In general, important features of a three-dimensional network model include pore bodies (or sites), pore throats (or bonds), unit length, connectivity, aspect ratio, and wettability. In general, network models are applicable to granular porous media, whose
structure can be idealized as pore bodies and throats. The examples of such porous media include sand, bead packs and some consolidated rocks like sandstone. On the other hand, platelike structured media with significant intra-granular porosity, such as fractural rocks, cannot be represented by traditional network models without sufficient modification to account for their unique structure.

Pore bodies represent the large void space among the grains in a particular porous medium of interest, while pore throats represent the narrow channels between the pore bodies (Maier and Laidlaw, 1993). There are several approaches as to the choices of the pore body/throat shapes. The simplest approach is to use spherical pore bodies and cylindrical pore throats. Although models with this geometry are easy to handle, they lack some of the important features that exist in a real porous medium, such as the converging-diverging geometry of the pore throats, and the existence of crevices for wetting fluids. Dias and Payatakes (1986a, b) proposed a network of randomly sized unit cells of constricted tubes. The pore body is characterized by an effective chamber diameter $D$ and the throat is characterized by its narrowest cross-section diameter $d$; both $D$ and $d$ follow certain distributions. The throat wall shape follows a sinusoidal function, therefore the unit cells have completely smooth walls. The advantage of their approach is that the sinusoidal shaped throats capture the converging-diverging geometry. However, the disadvantage of this approach is its complexity. The diameter of the cross-section at a random location $z$ of the unit cell is determined by a function of $d, D, z,$ and unit length.

Reeves and Celia (1996) took a slightly different approach and proposed a model with biconical shaped tubes (Fig. 2). The constriction is located halfway between the two adjacent pore bodies, and throats are attached to pore bodies at 90° solid angle. Unlike
cylindrical tubes, which restrict the location of the fluid-fluid interfaces to the body/throat attachments, biconical throats allow the interfaces to be located anywhere within the throats as well as at the body/throat attachments. This approach neglects the crevices, however, which exist in the real porous media at the grain-to-grain contact points.

Dillard and Blunt (2000) proposed a model containing square pore bodies and rectangular pore throats with square cross sections. The advantage of this geometry is that the corners of the square cross sections can serve to represent the crevices in a real porous medium, providing channels for wetting fluid to flow around the nonwetting fluid blobs residing in the center of the pore space. However, their approach does not capture the converging-diverging geometry.

As mention earlier, another important feature of the network models is the connectivity, which represents the way in which pore bodies are connected. The connectivity is usually characterized by the coordination number, which represents the average number of throats a pore body is connected to. The coordination number of a simple cubic lattice is six or less (if throats are cut at random). However, the coordination number of a real porous medium can be higher than six. Experiments performed by Kwiecien et al. (1990) on serial sections of sandstone samples resulted in a range of coordination number from two to ten. Unconsolidated bead packs have an even higher connectivity than sandstone (Lin and Cohen, 1982). The coordination number obtained from an ideal packing of spheres can range from six to twelve (Dullein, 1992). Chatzis et al. (1983) found that the coordination numbers in the center of larger residual ganglia are in the range of three to eight. In order to accommodate higher connectivity, diagonal throats can be added to a regular three-dimensional network model, introducing complexity and, possibly, anisotropy. Dullien
(1991) argued that coordination number distributions should be included in realistic pore-scale models. Accordingly, a random network model was developed by Lowry and Miller (1995), which has regular shaped pore bodies and throats but random pore body locations and throat orientations, and a distribution of coordination numbers. It was thought that the chaotic topology of this three-dimensional network would more realistically capture the stochasticity of a porous medium. Their results indicate that connectivity has a significant effect on the residual NAPL saturation and its distribution in a porous medium: the higher the connectivity, the lower the saturation and the higher the specific interfacial area. This result is consistent with the finding of Jerauld and Salter (1990), who also concluded that the NAPL saturation is affected by the variability of the body and throat sizes. Increasing variability led to larger blobs.

Spatial correlations between pore body-body, body-throat and throat-throat are also important characteristics of a porous medium. Jerauld and Salter (1990) found that such correlations were important factors in determining the NAPL saturation and relative permeability-saturation relationships. Their results reveal that throat-throat correlation can increase the relative permeability of the nonwetting phase but decrease the relative permeability of the wetting phase. Also, the throat-throat correlation tends to decrease the breakthrough pressure and the NAPL residual saturation. They also tested the pore body-throat correlation for a consolidated porous medium (believing there is no correlation between bodies or throats for unconsolidated media), and found that the body-throat correlation has some minor effects on both hysteresis and relative permeability. Later Mani and Mohanty (1999) extensively investigated the effects of spatial correlations on fluid displacement. Three correlation structures for the pore body sizes were tested: uncorrelated,
spherical correlation, and the fractional Brownian motion (fBm) model. They found that for the cases of no correlation and short-range spherical correlation the permeability can be determined if the sample is sufficiently large. On the other hand, the pore-size distribution and the Hurst exponent (fBm parameter) alone cannot uniquely describe the capillary pressure curves. Another observation from their study is that the percolation cluster density increases with increasing Hurst exponents, but decreases with increasing system sizes for spherical correlation media. Local-scale structure alone therefore only changes macroscopic properties by a constant, whereas infinite-scale structure results in new kinds of behaviors.

Aspect ratio, defined as the ratio of the average pore body radius to the average pore throat radius, is considered the single most important feature of a porous medium with respect to fluid displacement and NAPL residual saturation, due to its significant effect on snap-off. Snap-off, a residual ganglion splitting mechanism in which the saddle-shaped interface in a pore-throat collapses before imbibition taking place, becomes more important at large aspect ratios. It is generally thought that snap-off is the result of wetting fluid flow through the crevices, or in films along the rough solid surfaces. Therefore, snap-off, unlike other mechanisms, is rate-limited by film flow and is not instantaneous. Much research has been devoted to understanding and characterizing the snap-off mechanism. Li and Wardlaw (1986a, b) found that in order for snap-off to occur in pore throats with constant cross sections, aspect ratio has to be at least 1.5 for perfectly wetting conditions (contact angle approaches zero), and at least 1.75 for a contact angle of 55°. Snap-off does not occur if the contact angle is above 70°. Mohanty et al. (1980) concluded that in a perfectly wetting system, the necessary aspect ratio for snap-off in a toroidal throat is around 3, but this number is throat shape dependent. Jerauld and Salter (1990) used $P_c < C\sigma/r$, as the critical
capillary pressure at which snap-off occurs, with \( C = 1 \) for consolidated media (high aspect ratio), \( C = 2/3 \) for intermediate consolidated media and \( C = 0.6 \) for unconsolidated media (low aspect ratio). They found that in the high aspect ratio media, NAPL residual saturation is mainly determined by snap-off (i.e. throat size), rather than by pore size distribution. Further, Lowry and Miller (1995) found that increasing pore size correlation results in an increase in the probability of snap-off and thus an increase in residual saturation.

Based on the displacement procedure, network models can be divided into two general types: quasi-static displacement models and dynamic displacement models (Celia et al., 1995). In quasi-static displacement models, a fixed capillary pressure is imposed on the field and the locations of all the interfaces are calculated using the pressure in each node. Here "quasi-static" means that the dynamics of the interfaces are ignored. Many drainage and imbibition processes are studied experimentally using a quasi-static displacement procedure. The corresponding quasi-static models simulate the drainage processes beginning with applying aqueous pressure \( (P_w) \) and non-aqueous pressure \( (P_n) \) on the two reservoirs. The macroscopic capillary pressure is \( P_c = P_n - P_w \). The capillary pressure is raised from zero to some small value and all interfaces are tested for stability. The unstable interfaces are advanced until they reach a stable position. This procedure is repeated with step-wise increases in the capillary pressure. In dynamic displacement models, a fixed flow rate is introduced into the field and the transient pressures in each node are calculated assuming laminar flow, followed by the calculation of the positions of the interfaces (Blunt and King, 1991; Chaouche et al., 1994). Therefore, dynamic models can be used to study the effect of capillary number. In the case of low capillary numbers, the results from the dynamic models are analogous to those of the quasi-static models with small steps of capillary pressure.
increase. But dynamic models, because they track interface positions explicitly, are needed if one is studying dissolution dynamics.

Although many of the existing network models are used to study the constitutive relationships for two-phase flow in porous media, network models are also used to address larger, more complex issues in multiphase flow. Celia et al. (1993) developed a two-scale model, in which a pore-scale model is imbedded into a continuum model. The advantage of multi-scale models is that they are inherently parallelizable, which provides an opportunity to study the complex nature of multiphase flow in porous media in a systematic way. Soll and Celia (1993) proposed a network model simulating three mobile fluids using a modified percolation approach, and a wetting film is considered. Zhang and Seaton (1994) studied simultaneous diffusion and reaction in a pore network. Ferrand et al. (1994) studied the dissolution of NAPL into an aqueous phase using a network model. A particle tracking method was used in the simulator to trace the movement of NAPL dissolved in the aqueous phase. Held and Celia (1998) modeled mass transfer from NAPL and predicted the dissolution front. Later, Held and Celia (2001) proposed a stagnant layer dissolution model, assuming no mobilization of the shrinking NAPL blobs during the dissolution. Their simulation results are in good agreement with the experiment results of Imhoff (1994). However, their model only accounts for the dissolution of NAPL caused by diffusion (driven by NAPL concentration gradient). In a real porous media, a significant portion of the dissolution of NAPL occurs due to convection rather than diffusion alone. Also, this model fails to address the ganglion instability induced by dissolution.

Column studies show the presence of immobile aqueous phase within small pores and at some grain contact points. Mass transfer through the immobile water occurs by diffusive
transfer, a much slower process than the convective transfer of mass to adjacent mobile water. Zhou et al. (2000) proposed a physically based model to study the dissolution of NAPL by taking into account both diffusion and convection. Corners are introduced into the pore throat geometry to accommodate the mobile water and provide a chance for convective mass transfer of the residual ganglia. The normalized NAPL effluent concentration then can be expressed as a function of a dimensionless time \( t_d = q_w d_{20} / v_w \xi^2 Pe \), where \( v_w \) is the water velocity in the corner and \( \xi \) is the corner length. Later Dillard and Blunt (2000) proposed a NAPL dissolution model using Zhou et al.'s (2000) \( t_d \) and obtained effluent NAPL concentrations and dimensionless group correlation relationships. Their simulation results are in good agreement with Powers' (1992) experimental results.

Although network models have been used to study different aspects of multi-phase flow in porous media, there are many issues that remain to be investigated. Baldwin (1997) observed the immobilization of ganglia occurring in the early stage of dissolution. He suggested that dissolution-induced mobilization was a significant mechanism that could help to explain the different rates of NAPL loss in Imhoff's column experiment (1994). Also, mobilization changes the topology of NAPL blobs, which changes the mass transfer rate by changing the interfacial area. This dissolution-induced instability has not been investigated using a network model before. However, Baldwin's observations could be explained as either initial snap-off or dissolution-induced instability. It is therefore not certain, from existing experimental evidence, whether Baldwin's proposed mechanism actually occurs.

The objective of this research is to simulate the ganglia dissolution process and study the stability of ganglia in porous media using a three-dimensional network model. The proposed network model should be able to represent and control the important features of a
porous medium, such as the converging-diverging geometry, aspect ratio, wetting angle, pore-size distribution and correlation structures. The model also should be able to explicitly track the interface positions, in order to investigate NAPL dissolution and instability. The model needs to test the stability dynamically during the NAPL dissolution. The influences of porous medium characteristics, flow rate, and different dissolution mechanisms on NAPL dissolution and instabilities are investigated.

2.3 References


Dwivedi, P. N., and S. N. Updhyay, Particle-fluid mass transfer in fixed and fluidized beds, 


Figure 1. Diagram of a regular 3D cubic network model, with pore bodies representing open void space in the porous medium and pore throats representing the narrow passages between pore bodies.
Figure 2. Biconical shaped pore unit. Six conical shaped throats are attached to the central spherical pore body at $90^\circ$ solid angles.
CHAPTER 3. INVESTIGATION OF NONAQUEOUS PHASE LIQUID DISSOLUTION AND INSTABILITY USING A NETWORK MODEL

A paper submitted to Water Resources Research

Yanhui Hu, Robert P. Ewing, Rodney O. Fox

Abstract

A pore-scale network model was developed to study nonaqueous phase liquid (NAPL) dissolution in a porous medium. The network is a cubic lattice with biconical shaped throats, so the interfaces can be tracked explicitly. Two dissolution mechanisms were investigated: stagnant layer diffusion to account for the local concentration gradient driven mass transfer through immobile water, and channel flow dissolution to account for the advection driven mass transfer by mobile water. Ganglion stability was investigated both before and during NAPL dissolution, and the effect of ganglion size, flow rate and porous medium characteristics on the instability types were established. Single ganglion numerical experiment results were converted into a column study using population analysis, and the correlation relationships between modified Sherwood number, Peclet number and Reynolds number were in good agreement with published results.

Keywords: NAPL, underground water quality, porous media, network modeling, dissolution, instability
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Specific surface area</td>
<td>$[L^{-1}]$</td>
</tr>
<tr>
<td>$c$</td>
<td>Hydraulic conductance of throat</td>
<td>$[T L^4 M^{-1}]$</td>
</tr>
<tr>
<td>$l_b$</td>
<td>NAPL blob length</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$l_c$</td>
<td>Characteristic length</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$m$</td>
<td>Number of column sections</td>
<td>[-]</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Number of ganglia of size $S_i$</td>
<td>[-]</td>
</tr>
<tr>
<td>$q_w$</td>
<td>Darcy aqueous phase velocity</td>
<td>$[L T^{-1}]$</td>
</tr>
<tr>
<td>$v_w$</td>
<td>Aqueous phase channel velocity</td>
<td>$[L T^{-1}]$</td>
</tr>
<tr>
<td>$w$</td>
<td>Weight in Eq. 1</td>
<td>[-]</td>
</tr>
<tr>
<td>$A_{nw}$</td>
<td>Interfacial area between NAPL/water</td>
<td>$[L^2]$</td>
</tr>
<tr>
<td>$C$</td>
<td>NAPL aqueous phase concentration</td>
<td>$[M L^{-3}]$</td>
</tr>
<tr>
<td>$C_{in, out}$</td>
<td>Inlet/outlet NAPL aqueous phase concentration</td>
<td>$[M L^{-3}]$</td>
</tr>
<tr>
<td>$C_s$</td>
<td>NAPL solubility in aqueous phase</td>
<td>$[M L^{-3}]$</td>
</tr>
<tr>
<td>$D_m$</td>
<td>Molecular diffusion coefficient in water</td>
<td>$[L^2 T^{-1}]$</td>
</tr>
<tr>
<td>$J$</td>
<td>NAPL mass flux</td>
<td>$[M L^{-2} T^{-1}]$</td>
</tr>
<tr>
<td>$J J$</td>
<td>Overall NAPL dissolution rate</td>
<td>$[M T^{-1}]$</td>
</tr>
<tr>
<td>$K$</td>
<td>Mass transfer coefficient</td>
<td>$[L T^{-1}]$</td>
</tr>
<tr>
<td>$L$</td>
<td>Unit length</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$L_{1,2}$</td>
<td>Length from body/throat attachment to throat constriction</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$N$</td>
<td>Total number of nodes in the field</td>
<td>[-]</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Capillary pressure</td>
<td>$[M L^{-1} T^{-2}]$</td>
</tr>
<tr>
<td>$P_{n,w}$</td>
<td>Pressure in NAPL/water</td>
<td>$[M L^{-1} T^{-2}]$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Water volumetric flow rate</td>
<td>$[L^3 T^{-1}]$</td>
</tr>
<tr>
<td>$R$</td>
<td>Radius at the body/throat attachment</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$R_{b,t,l}$</td>
<td>Radius of body/throat/contact line</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$S_i$</td>
<td>Ganglion size in nodes</td>
<td>[-]</td>
</tr>
<tr>
<td>$S_n$</td>
<td>NAPL saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Orientation of throat surface</td>
<td>[-]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Ratio of channel volume to ganglion volume</td>
<td>[-]</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Stagnant layer length</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$\mu_w$</td>
<td>Aqueous phase viscosity</td>
<td>$[M L^{-1} T^{-1}]$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Aqueous phase density</td>
<td>$[M L^{-3}]$</td>
</tr>
<tr>
<td>$\sigma_{nw}$</td>
<td>Interfacial tension</td>
<td>$[M T^{-2}]$</td>
</tr>
</tbody>
</table>

**Dimensionless numbers:**

- $Ca$: Capillary number ($\mu_w q_w / \sigma_{nw}$)
- $Pe$: Peclet number ($q_w l_c / D_m$)
- $Re$: Reynolds number ($\rho_w q_w l_c / \mu_w$)
- $Sc$: Schmidt number ($\mu_w / D_m \rho_w$)
- $Sh$: Sherwood number ($kl_c / D_m$)
- $Sh'$: Modified Sherwood number ($kal_c^2 / D_m$)
- $\tau$: Dimensionless time
1. Introduction

When non-aqueous phase liquids (NAPLs) spill onto the ground or leak from underground storage tanks, they may significantly degrade the groundwater quality and cause long-term contamination due to their low solubility and highly toxic nature. As a result, the migration, entrapment, dissolution and fate of NAPLs in the subsurface have drawn much attention in the last decade. Common examples of NAPLs include chlorinated solvents and hydrocarbons. In general, the multiphase flow and dissolution processes of NAPLs within porous media are governed by the chemical and physical properties of the liquids and the characteristics of the subsurface environment (Hunt et al., 1988a,b; Miller et al., 1990; Geller and Hunt, 1993; Imhoff et al., 1994; Chrysikopoulos, 1995; Mayer and Miller, 1996).

Many remediation techniques for NAPL contamination in the saturated zone require an accurate prediction of the NAPL dissolution rate, which is affected by such factors as the degree of NAPL saturation in the porous medium, NAPL/water interfacial area, aqueous phase velocity, solubility and solute concentration of NAPL, and various porous medium properties. A common approach in the study of NAPL dissolution is to use column experiments, with the NAPL dissolution rate coefficient expressed as a relation between the dimensionless numbers Sherwood number $S_h$, Reynolds number $R_e$, and Peclet number $P_e$. An alternative expression uses a modified Sherwood number, $S_h'$ (Miller et al., 1990; Powers et al., 1994), which is a function of the lumped dissolution rate coefficient, $K_a$, an easily measurable quantity. Although these column studies give some insight into NAPL dissolution, the resultant empirical correlation relations are generally limited to their own column settings.
A common assumption in the interpretation and simulation of dissolution processes is that ganglia are stable after becoming stranded from the bulk phase, i.e., dissolution changes the sizes but not the locations of the ganglia. Although this assumption is necessary in order to achieve a simplified correlation, it may not be correct. Baldwin (1997) observed ganglia displacement occurring in the early stages of dissolution and proposed that dissolution-induced remobilization was an important mechanism that could help to explain the different rates of NAPL loss in column experiments. Unfortunately, Baldwin’s experimental setup could not differentiate between the two possible time-dependent ganglion remobilization mechanisms: remobilization induced by dissolution, or snap-off resulting from gradually accumulating film flow. Johns and Gladden (2000) also studied the mobilization of small ganglia after dissolution using MRI and found that after dissolution to a critical size, similar to the size of pore throat, ganglia became unstable and could pass through the downstream pore constrictions. These observations suggest that ganglia remobilization induced by dissolution is an important aspect of remediation that cannot be overlooked. A thorough investigation of this phenomenon is therefore warranted in order to determine whether dissolution is able to induce remobilization. Due to the nature of the stability of the interfaces, we chose to investigate at the pore-level, so that the physical and chemical processes taking place at the interfaces could be studied explicitly.

Pore-scale network modeling, as a common microscopic investigation tool, has been widely applied in various aspects of multiphase flow processes in porous media. Proposed first by Fatt (1956a,b and c), pore-scale network models have been developed to investigate multiphase drainage and imbibition processes (Diaz and Payatakes, 1986a, b; Maier and Laidlaw, 1993; Mogensen and Stenby, 1998), single-phase and relative permeability
(Constantinides and Payatakes, 1989; Blunt and King, 1991; Reeves and Celia, 1996), pressure-saturation and permeability-saturation relationships (Jerauld and Salter, 1990; Ferrand and Celia, 1992; Dixit et al., 1997), mercury intrusion processes (Toledo et al., 1989; Tsakiroglou and Payatakes, 1990, 1991), and NAPL dissolution (Jia et al., 1999; Dillard and Blunt, 2000).

The focus of this research is to investigate ganglion dissolution and remobilization using a pore-scale network model, with emphasis on the characteristics of the stranded ganglia and the dissolution on remobilization at different flow rates. The numerical experiments modeling single ganglion are also compared, via population analysis, to those obtained from column experiments.

2. Model development

2.1 Porous medium

The porous medium is simulated using a regular cubic lattice, with pore bodies at the intersections and pore throats connecting them. Among the six boundaries of the domain, one is treated as the high hydraulic pressure end, the opposite is treated as the low hydraulic pressure end, and the other four are treated as periodic boundaries. Pore bodies are represented by spheres, which are connected to their neighbors with biconical throats (Reeves and Celia, 1996). All throats are attached to the pore bodies at a 90° solid angle. The distance between two neighbor bodies is a fixed unit length \( L \) (Fig. 1). The advantage of biconical shaped throats over commonly used cylindrical throats is that interfaces can be stable anywhere within the throats, thus giving more flexibility on the possible interface locations. This converging-diverging shape is also a more realistic approach, as it captures
the general shape of the void space seen between grains in the subsurface (Reeves and Celia, 1996).

Pore body sizes are generated randomly using the turning bands method (Tompson et al., 1989), assuming a stationary Gaussian distribution with a known decay correlation length. The parameters chosen to generate the porous medium follow the typical properties of consolidated sandstones. In order to capture body-throat correlation, pore throat radius sizes are first generated randomly from a Gaussian distribution. Then, the radius of each pore throat is chosen from the generated values based on the weight given by the two adjacent pore body sizes (Tsakiroglou & Payatakes, 1991):

\[
\omega = \frac{1}{2} \left[ \frac{R_{b,1} - R_{b,\text{min}}}{R_{b,\text{max}} - R_{b,\text{min}}} \right] + \left[ \frac{R_{b,2} - R_{b,\text{min}}}{R_{b,\text{max}} - R_{b,\text{min}}} \right]
\]

where \( R_{b,\text{min(max)}} \) represents the minimum (maximum) pore body radius. Since the throats are restricted to be no larger than the attached bodies, all throats sizes are adjusted to

\[ R_t = \min(R_t, R_{b,j}/\sqrt{2}). \]

2.2 Flow field

Under laminar flow conditions and assuming constant density within each phase, the net volumetric flow rate as a linear function of pressure drop \( \Delta P \) and hydraulic conductance \( c \) is zero for each node. The theoretical conductance for a biconical throat is (Reeves and Celia, 1996):

\[
c = \frac{8\mu \pi}{3\pi} \left[ L_1 \left( \frac{R_t^2 + R_t R_i + R_i^2}{R_t R_i^3} \right) + L_2 \left( \frac{R_t^2 + R_t R_i + R_i^2}{R_t R_i^3} \right) \right]^{-1}
\]
A system of linear equations of node pressures can be derived from the mass balance equations for each node using the conductance obtained above. The linear system has \( x_{\text{max}} \cdot y_{\text{max}} \cdot z_{\text{max}} \) equations, where \( x_{\text{max}}, y_{\text{max}}, \) and \( z_{\text{max}} \) are the numbers of nodes in the \( x, y, \) and \( z \) directions. Water pressure \( P_w \) at each node was calculated using a symmetric successive over-relaxation semi-iterative algorithm (SRSI) (Oppe et al., 1988).

2.3 Ganglion stability

A ganglion is stable if all of its interfaces are stable. A NAPL-water interface is at equilibrium if the capillary force across the interface satisfies the Young-Laplace equation:

\[
P_c = P_n - P_w = \frac{2\sigma_{sw}\cos(\theta + \alpha)}{R_l}
\]  

(3)

where the solid/water/NAPL contact line can be located at the body-throat attachment, the constriction point of the throat or anywhere in between (Fig. 2).

To initiate a simulation, a ganglion is irreversibly introduced into the flow field following a "piston drainage" mechanism. A node is selected randomly as the injection point of the ganglion. In order to eliminate boundary effects, the selection is limited to the central 60% of the domain in each of three dimensions. A predetermined NAPL volume is injected to fill that pore unit, and the required \( P_n \) \((= \frac{2\sigma_{sw}}{R_l} + P_w)\) for invasion through a throat constriction point is calculated for all water/NAPL interfaces. The remaining ganglion volume, if any, flows into the adjacent pore with the smallest \( P_n \). The injection process continues, pore by pore, until the total designated NAPL volume has been injected.

Since ganglion dissolution is a slow process compared to dynamic ganglion movement, the initial stable ganglion configuration is determined before dissolution takes
place. According to the energy stability analysis of menisci (Mohanty et al., 1980), a stable interface can persist under perturbation if it has positive $\frac{dP_c}{dV}$, where $V$ is the volume of the non-wetting phase at the menisci. A stable ganglion configuration resulting from stable configurations of all NAPL/water interfaces can be evaluated. Applying the stability criterion to the ganglion in the model, it follows that a stable ganglion has all its interfaces, except at most one upstream, located in the converging part of the throats. Thus the procedure for finding a stable location of the ganglion is as follows:

1. Find the highest ganglion pressure associated with one interface at the constricted point of its throat and all other interfaces in the converging sections of the throats. Calculate the ganglion volume corresponding to this stable configuration. If the calculated volume is larger than the predetermined volume, the capillary force of the interface at the constricted point is not strong enough to hold the ganglion, and the ganglion has to undergo a “Haines jump” through that constricted point.

2. Find the lowest ganglion pressure associated with one interface at the body-throat attachment while all other interfaces are in converging sections of the throats. Calculate the ganglion volume corresponding to this stable configuration. If the calculated volume is smaller than the predetermined volume, the capillary force of the interface at the body-throat attachment is not strong enough to hold the ganglion, and the ganglion has to retreat from that body.

3. If the ganglion is found stable in steps 1 and 2, then the stable interface locations and the corresponding ganglion pressure can be obtained using a bisection method to iterate between the highest pressure from step 1 and lowest pressure from step 2.
Ganglion instability can be classified based on the location of the unstable interface. "Tail retreat" happens when all interfaces of a tail node, defined as a node occupied by the ganglion with only one attached throat filled with NAPL, are unstable, so the pore body fills with water. "Breakup" occurs when all interfaces of a center node, defined as a node occupied by ganglion with more than one throat filled with NAPL, are unstable. "Snap-off" occurs when the selloidal interface in a NAPL-filled throat collapses. Breakup and snap-off will break a ganglion in two.

Many factors can induce instability in a stable ganglion, such as changes in the physical properties of the liquid phases due to a surfactant or cosolvent, increasing water flow rate, or volume reduction due to dissolution. The critical capillary pressures for the first two types of instabilities are given by Eq. 3, while the critical capillary pressure for the snap-off is:

\[ P_c = \frac{\sigma \cos \theta}{R_t} \]  

Eq. 4 captures the basic relationship between capillary pressure, contact angle and local configuration for the criterion of neck rupture, assuming a thin water layer between the NAPL and solid surface at the constricted point of the throat (Mohanty et al., 1980; Li and Wardlaw, 1986).

2.4 Ganglion dissolution

In real geological porous media, water directly in contact with a NAPL ganglion can be in either of two forms. First is water at the NAPL/water interfaces in pore throats, which like the entrapped ganglion is stagnant. Less obvious is the water in crevices and pendular structures in channels on the rock surfaces, and in the cracks and corners where rock grains
touch each other. Because this second form is continuous with the surrounding water but penetrates the ganglion, it represents a potentially effective means of transporting dissolved NAPL. Two competing conceptual models of NAPL dissolution have therefore evolved: one involving stagnant layer diffusion, which is called the stagnant layer dissolution model; the other involving flow in the channels and crevices through the ganglion, which is called the channel flow dissolution model.

The stagnant layer diffusion model assumes that the NAPL aqueous concentration at the interfaces is constant at the solubility limit, $C_s$; the mass flux is therefore simply:

$$ J = \frac{1}{A_{nw}} \frac{dm}{dt} = D_n \frac{\delta}{A_{nw}} (C_s - C) $$

where $C$ is the NAPL aqueous phase concentration in the adjacent water-filled pore body, within which the dissolved NAPL mixes completely with bulk water.

Dissolution rates at downstream interfaces are reduced by the presence of solute from upstream interfaces, so the details of how solute is routed from node to node are important. Historically, studies of routing methods have focused on fractures or fracture intersections. In fracture intersections, complete mixing in the nodes is never valid (Berkowitz et al., 1994), or valid only at low Peclet numbers (Hull and Loslow, 1986). In fractures, complete nodal mixing increases the modeled longitudinal and transverse dispersion in comparison to proportional routing (Ewing and Jaynes, 1995). However, in two-dimensional non-fractured porous media, complete nodal mixing and proportional routing were equivalent in their effect on effluent solute concentrations (Dillard and Blunt, 2000). Because this study involved a porous medium rather than fractures, and the critical
issue was the effect of the routing method on the dissolution rate, Dillard and Blunt's (2000) conclusion was accepted and complete nodal mixing was assumed.

The water channel dissolution model treats NAPL aqueous phase concentration as a function of water channel velocity, with high water velocity in the channel leading to nonequilibrium NAPL aqueous phase concentration after contacting a ganglion. Zhou et al. (2000) proposed a simplified approach to account for this phenomenon in a triangular-corner network model. A dimensionless time $\tau$ is used as a measure of the ratio of diffusion to channel water velocity: when $\tau>1$, the NAPL concentration in crevice waters reaches solubility after passing through a ganglion.

Pore throats in the current network model have a circular cross-section, with channel flow superimposed onto it. The ratio of channel volume to ganglion volume is $\beta$, and channel aqueous phase conductance of a throat is $\beta^2$ times the original conductance. Thus, from Zhou's definition (2000), the equivalent dimensionless time $\tau$ can be expressed as:

$$\tau = \frac{D_w l_b}{v_w R_t^2 \beta}$$

(6)

When $\tau < 1$, the solute concentration increase after passing a ganglion is approximately $\sqrt{\tau}$ times the maximum possible concentration increase had equilibrium been attained. When $\tau = 1$, the NAPL aqueous phase concentration increase reaches 90% of maximum possible concentration increase. Further increase in $\tau$ brings the NAPL aqueous phase concentration up to the solubility limit after passing a ganglion (Fig. 4, Dillard et al., 2000). It is expected that at the same Capillary number, water flow through a larger ganglion will approach NAPL solubility at the exit; while at a lower Capillary number water flow through
any size ganglion will reach NAPL solubility limit. \( \tau \) is calculated for each case, and for those cases with high flow rate and large \( \beta \), therefore small \( \tau \), the aqueous phase solute concentration is adjusted. This approach is an approximation of the channel dissolution process, with the purpose of accounting for the effect of water channel flow rate on the NAPL dissolution.

3 Simulation results

3.1 Single ganglion dissolution

Table 1 lists the parameters used in the single ganglion numerical experiments. The porous medium parameters represent a coarse-grained sand sample, and the NAPL was chosen to be styrene. Both the porous medium characteristics and the NAPL properties match the study settings of Powers et al., (1992) and Dillard et al. (2000). Therefore the results of this study can be compared to their published results.

Because the model introduces ganglia of pre-determined size into the porous medium starting from a randomly chosen node, the configuration of a ganglion results from the local porous medium configuration and the local hydraulic gradient. A stable ganglion is obtained when NAPL/water pressure drops across all interfaces are balanced by capillary pressures. Plotting the entrapped ganglion interfacial area as a function of the pre-determined sizes reveals a linear relationship on a log-log scale (Fig. 3). The regression slope is 0.7, slightly greater than 0.667, the slope for a perfect sphere. It indicates that the ganglion in the porous medium is slightly ramified, and thus, in column studies the common assumption of spherical ganglia may underestimate the area/volume ratio, particularly for large ganglia. Further investigation of the stranded ganglia configuration shows that they are slightly elongated in
the direction of the pressure gradient (Fig. 4). The differential elongation is not statistically significant, which indicates that the effect of hydraulic pressure drop across the entire ganglion on the configuration of the entrapped ganglion is less than the local effect of the porous medium.

In order to compare these two effects, the ratio of the two pressures is considered. At $Ca = 10^{-4}$, the highest Capillary number tested in this study, the hydraulic pressure drop across the entire domain (about 2 cm) is 180 kg m$^{-1}$ s$^{-2}$. Therefore, for a ganglion of size 40, spanning about six pore units in the direction of pressure gradient, the hydraulic pressure drop is around 27 kg m$^{-1}$ s$^{-2}$. On the other hand, the change of capillary pressure in two throats, assuming one radius is one standard deviation above mean and the other one is one standard deviation below the mean, is about 400 kg m$^{-1}$ s$^{-2}$. This change in capillary pressure between two throats is 15 times larger than the possible hydraulic pressure drop across a ganglion of size 40. At lower Capillary number, or for a smaller ganglion, this ratio would be even larger. Therefore, at the range of Capillary numbers in this study, the configuration of stable ganglion is mainly controlled by porous medium characteristics rather than by aqueous flow rate.

Numerous studies have shown that high aqueous flow can induce ganglion movement. For example, Ng and Payatakes's two-dimensional simulations (1980) found that ganglia were not stable when $Ca > 10^{-3}$, and may occasionally move even when $Ca = 10^{-5}$. Since an objective of this study is to find the dissolution effect on stable ganglia, a range of $Ca$ from $10^{-7}$ to $10^{-4}$ was chosen to ensure stable ganglia. In order to study the effect of flow and ganglion size on the stability of ganglia, the proportion of different instability types were recorded (Fig. 5). In the range of Capillary numbers studied, the aqueous flow effect on the
ganglion instability type is not significant. This seemingly surprising result can be explained again by the relatively small effects of aqueous flow compared to the effect of porous medium on ganglion stability. Fig. 5 also reveals that ganglion size plays a significant role on the initial ganglion stability. It is found that both initial tail-retreat and snap-off occurrences decrease with increasing ganglion sizes, and small ganglia are more likely to have initial tail-retreat than initial snap-off. Since the relative effect of hydraulic pressure drop is insignificant compared to the effect of capillary force, a growing ganglion tends to expand into a region with bigger throat sizes which pose less capillary pressure resistance, and the resultant average pore body radius of a larger ganglion is larger. Tail-retreat (water imbibition) is controlled by the size of the pore bodies (Eq. 3) and snap-off is controlled by the size of throats (Eq. 4). The smaller the pore body, the more likely it will be the node of retreat, and the smaller a ganglion-occupied-throat is, the more likely it will be the throat to snap off. Therefore, a larger ganglion is less likely to have tail-retreat or snap-off. Although both probabilities of tail-retreat and snap-off decrease with increasing ganglion sizes, the rate of decrease for tail-retreat occurrences is higher, therefore a larger ganglion is more likely to have snap-off.

A stranded ganglion undergoes dissolution due to diffusion at the water/NAPL interfaces and convection in the water channels passing the ganglion. Dissolution rates for the stagnant diffusion and channel convection mechanisms are dissimilarly affected by aqueous flow rate. Fig. 6 shows the effect of water channel on ganglion dissolution rate, given ganglion size 10. Three water channel volume fractions were investigated, β=0.05, 0.1 and 0.25. Neither the volume of the water channel nor the Capillary number strongly affects the stagnant layer diffusion rate. This result is reasonable since the stagnant layer diffusion is
a function of concentration gradient, which is not strongly affected by the flow in the water channel. However, when the Capillary number decreases to $10^{-7}$, the stagnant layer diffusion rates for all cases drops slightly, due to the resultant smaller concentration gradient. On the other hand, both the water channel volume and water flow rate affect the water channel dissolution rate greatly. It is shown that the channel dissolution rates increase about 10 times for every factor of 10 increase in the Capillary number except at high $Ca$ when $\tau << 1.0$. Fig. 6 also suggested a transition Capillary number at which the dissolution process switches from diffusion limited to channel dissolution limited.

In order to determine whether this transition between dominant mechanisms is a function of ganglion size, we examined the initial dissolution rate for both stagnant layer diffusion and channel flow dissolution as a function of ganglion size (Fig. 7). Only the case of $\beta = 0.1$ was examined here. The initial dissolution rates for both diffusion and channel dissolution are comparable at $Ca = 10^{-5}$, with channel dissolution dominating at larger $Ca$ and diffusion dominating at lower $Ca$. Therefore, in column ganglion dissolution studies, both diffusion through stagnant layer of water and convection in mobile water channel need to be taken into account when Capillary number is about $10^{-5}$. Only when aqueous flow rate is very high or very low can the dissolution process be reasonably approximated by a single mechanism.

Figure 7 shows not only the switch of control from diffusion to convection with increasing Capillary number, but also the interaction effect between aqueous flow rate and ganglion size on initial dissolution rate. The regression slope of initial dissolution rate on ganglion size on the log-log scale was obtained and plotted (Fig. 8). It is evident that the effect of ganglion size on diffusion is more pronounced at high than at low Capillary number.
Diffusion rate is defined as the product of diffusion flux and interfacial area, and interfacial area per unit volume is essentially the same when Capillary number increases from $10^{-7}$ to $10^{-4}$ (Fig. 4). Therefore, the regression slope would be fixed at 0.7, the slope of the interfacial area versus volume relationship, if the diffusion flux effect was constant across ganglion sizes and flow rates. However, flow rate affects the NAPL concentration in the aqueous phase, i.e., low aqueous flow rate causes higher NAPL concentration in the nodes around ganglia, which in turn decreases the diffusion flux. The larger the ganglion, the stronger is this effect. Thus, aqueous flow rate changes the effect of ganglion size on dissolution rate, and the curve in Fig. 8 is observed.

3.2 Dissolution induced instability

As dissolution occurs ganglion volume is reduced and NAPL/water interfaces retreat. Stability considerations indicate that ganglion pressure will change to accommodate changes in meniscus position. When a ganglion's internal pressure decreases to the critical pressure at which an interface will undergo an irreversible relocation, the ganglion becomes unstable. Depending on the type of the unstable interface, the ganglion may retreat, be invaded or have snap-off in a throat. In the range of Capillary number $10^{-7} < Ca < 10^{-4}$, dissolution-induced instabilities are mainly controlled by porous medium characteristics. It is found that the majority of the instability occurrences after dissolution are snap-off, with only a few occurrences of tail-retreat (Fig. 5).

The volume loss and dissolution time prior to instability are recorded in Fig. 9 and 10, respectively. The fraction of volume loss vs. ganglion size shows a descending trend, with no effect of flow rate within the range $10^{-7} < Ca < 10^{-4}$. This plot is consistent with the conclusion that the entrapped ganglion configuration and stability is more controlled by local
porous medium characteristics than by aqueous flow rates. On the other hand, the time to instability plot shows a significant effect of flow rate, a function of dissolution volume and dissolution rate.

3.3 Population analysis

Numerous column experiments and simulations have reported the ganglia dissolution process in a form of relationships between some dimensionless groups, such as $Sh'$, $Pe$, and $Re$. In order to compare the simulation results of this study with the known literature results, population information must be derived from single ganglion numerical experiments.

In general, ganglion size distribution in a porous medium can be described using percolation theory (Larson et al., 1981; Stauffer and Aharony, 1992). For a 3D lattice, the number of ganglia of size $S$ scales as $S^{-2.18}$. Therefore, the number of ganglia of size $S_i$ is

$$n(S_i) = S_i^{-2.18} \frac{S_n \times N}{\sum S_i^{1.18}}$$  (7)

The number of ganglia of size 40 is only about 0.021% of the total number of ganglia with size between 1 and 40. Therefore, it is assumed that ganglia larger than size 40 are rare and can be omitted from the study, and the summation in the denominator of Eq. 7 can go to 40 instead of infinity. The relationship between dissolution rate and ganglion size (Fig. 7) can be approximated using a linear log-log regression function, with $R^2 = 0.99$. In order to derive population information, the spatial distribution of different size ganglia in the column has to be assumed. Since the population analysis here is only an approximation, the goal of which is to determine whether the single ganglion numerical experiments gives reasonable estimation of dissolution rate, randomly distributed ganglia are assumed. Therefore, the overall dissolution rate from all ganglia is
In Eq. 8, the dissolution rate for regression is based on pure water inflow, which does not hold for an arbitrary ganglion in the middle of the column. Thus, the dissolution rate needs to be adjusted to account for the inflow NAPL concentration. The column is discretized into \( m \) small sections. For each section, the outlet concentration is

\[
C_{\text{out}} = C_{\text{in}} + \frac{JJ}{mQ} \left( 1 - \frac{C_{\text{in}}}{C} \right)
\]

The number of sections is increased until the effluent NAPL concentration at the end of the column approaches a constant, which is the "true" NAPL effluent concentration \( C(L) \). The steady state dissolution process in a column is described by

\[
q_w \frac{dC}{dx} = Ka(C_s - C)
\]

With the boundary condition \( C(0) = 0 \), effluent concentration is

\[
C(L) = C_s \left( 1 - \exp(-KaL/q_w) \right)
\]

Solving for \( Ka \) yields

\[
Ka = -\left( \frac{q_w}{L} \right) \ln \left( 1 - \frac{C(L)}{C_s} \right)
\]

Thus, the effluent concentration \( C(L) \) from discretization can be used in Eq. 12 to obtain \( Ka \), and the modified Sherwood number \( Sh' \) is also acquired assuming that the characteristic length, \( l_c \), is equal to one unit length minus the mean diameter of the pore.

The relationship between \( Sh' \) and \( Pe \) can be derived using the above population analysis (Fig. 11). Three curves from the simulation are shown: stagnant layer diffusion only, channel flow dissolution only, and the two mechanisms combined. The combined
curve is very close to the results of Dillard (2000) and Powers et al. (1992). Since $Pe$ is the ratio of convection to diffusion, when $Pe \gg 1$, convection is dominant, and when $Pe \ll 1$, diffusion is dominant. The curve for $Pe \gg 1$ appears to be log-linear with a similar slope as the ones from Dillard's and Power's; but the curve transitions to a larger slope at $1 < Pe < 10$.

Figure 12 shows the relationship between $Sh'$ and $Re$. Again, the simulation result from this study is within the range given by previous work (Miller et al., 1990; Parker et al., 1990; Powers et al., 1992; Guamaccia et al., 1992). The curve also shows a smaller slope for high $Re$ ($Re \gg 0.01$) and a larger slope for low $Re$ ($Re \ll 0.01$). Therefore, while the dissolution process in this study is based on individual ganglion, the population analysis still leads to results similar to those from various column experiments.

4. Conclusions

A pore-scale network model was developed to study the dissolution of residual NAPL blobs and the instabilities induced by dissolution. Residual ganglia with pre-determined sizes were introduced into the flow field and the instantaneous instability occurrences were recorded. Over the range of Capillary numbers investigated in this study ($10^{-7} \leq Ca \leq 10^{-4}$), the viscous force (or water flow rate) does not have a significant effect on the instantaneous instability types. The initial instability types were mainly affected by ganglion size and local porous medium characteristics. Small ganglia were more likely to have initial retreat than large ganglia.

The configurations of stable ganglia were also investigated, and ganglia were found to be ramified. Therefore, column studies, assuming spherical ganglia, may not be correctly calculating either initial, nor dynamically changing, interfacial area. Also, stable ganglia
tend to be slightly elongated in the direction of flow rate, although this elongation may not be significant at low flow rates.

Two dissolution mechanisms were studied: stagnant layer diffusion and water channel dissolution. The investigation of initial dissolution rate revealed that both the water channel volume ratio and the Capillary number had a strong effect on the initial water channel dissolution rate but not on the initial stagnant layer diffusion rate. The dissolution rate is approximately log-linear with ganglion size. At a water channel volume ratio of 0.1, stagnant layer diffusion dominates the dissolution process at $Ca < 10^{-5}$, while the channel flow mechanism controls dissolution at higher Capillary number. Both mechanisms should therefore be considered when investigating ganglion dissolution.

It is concluded that dissolution can indeed induce ganglion instability, mainly via snap-off. Larger ganglia become unstable earlier and at a lower fraction of dissolution volume, indicating that larger ganglia are more susceptible to dissolution-induced instability. The ganglion instability types were more controlled by the porous medium than the water flow rate within the range of Capillary numbers studied. The importance of the porous medium suggests further investigation.

The single ganglion experiments were also compared with column study literature results using population analysis. Based on the ganglion size distribution from percolation theory, the individual ganglion dissolution rates were combined into NAPL residual dissolution rate, and relationships between the modified Sherwood number, Peclet number and Reynolds number were established. These relationships were in good agreement with those from various experimental column studies.
References

Baldwin, C. A., Mobilization of NAPL ganglia due to dissolution: Effect of modeling, 

Berkowitz, B., C. Naumann, and L. Smith, Mass transfer at fracture intersections: An 

Blunt, M., and P. King, Relative permeabilities from two- and three-dimensional pore-scale 

Chryssikopoulos, C. V., Three-dimensional analytical models of contaminant transport from 
nonaqueous phase liquid pool dissolution in saturated subsurface formations, *Water 

Constantinides, G. N., and A. C. Payatakes, A three dimensional network model for 

Dias, M. M., and A. C. Payatakes, Network models for two-phase flow in porous media, Part 
1, Immiscible microdisplacement of non-wetting fluids, *J. Fluid Mech.*, 164, 305-336, 
1986a.

Dias, M. M., and A. C. Payatakes, Network models for two-phase flow in porous media, Part 


Dixit, A.B., S. R. McDougall, and K. S. Sorbie, A pore-level investigation of relative 

Ewing, R. P., and D. B. Jaynes, Issues in single-fracture transport modeling: scales, 


<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore body radius mean [m]</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pore body radius standard deviation [m]</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pore throat radius mean [m]</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pore throat radius standard deviation [m]</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Unit length [m]</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Correlation length [-]</td>
<td>2</td>
</tr>
<tr>
<td>Lattice size</td>
<td>$40^3$</td>
</tr>
<tr>
<td>NAPL density [kg m$^{-3}$]</td>
<td>900</td>
</tr>
<tr>
<td>NAPL solubility in water [kg m$^{-3}$]</td>
<td>0.23</td>
</tr>
<tr>
<td>Molecular diffusion of NAPL in water [m$^2$ s$^{-1}$]</td>
<td>$8 \times 10^{-10}$</td>
</tr>
<tr>
<td>NAPL/water interfacial tension [kg s$^{-2}$]</td>
<td>0.024</td>
</tr>
<tr>
<td>Residual NAPL saturation [-]</td>
<td>0.2</td>
</tr>
<tr>
<td>Water viscosity [kg m$^{-1}$ s$^{-1}$]</td>
<td>0.0009</td>
</tr>
<tr>
<td>Realization [-]</td>
<td>400</td>
</tr>
<tr>
<td>Percentage of water channel</td>
<td>0.05, 0.1, 0.25</td>
</tr>
<tr>
<td>Capillary number</td>
<td>$10^{-7} \sim 10^{-4}$</td>
</tr>
<tr>
<td>Normalized ganglion size</td>
<td>2 $\sim$ 40</td>
</tr>
</tbody>
</table>
Figure Captions:

Figure 1. Biconical shaped throat structure in 2D projection.

Figure 2. Possible stable interface locations shown in dashed lines.

Figure 3. Interfacial area of a stable ganglion on a log-log scale.

Figure 4. Stable ganglion configurations at Ca = 10^{-4} (x, y, and z represent the maximum span of a ganglion in the x-, y-, and z-directions).

Figure 5. Initial and dissolution induced instability types. (a) Ca = 10^{-4} (b) Ca = 10^{-7}.

Figure 6. Dissolution rates of a ganglion (size = 10) at different water channel volume ratio \( \beta \). The channel flow dissolution rates are corrected for \( t \).

Figure 7. Initial dissolution rates under stagnant layer dissolution model and channel flow dissolution model at 10^{-7} < Ca < 10^{-4}.

Figure 8. Regression slopes from Figure 7.

Figure 9. Fraction of ganglion volume dissolved before instability occurs.

Figure 10. Dissolution time required before instability occurs.

Figure 11. Correlation relationships of modified Sherwood number and Peclet number from this study, Powers et al. experiment (1992) and Dillard et al. simulation (2000). The curve denoted “Combined” includes both stagnant layer diffusion and channel flow dissolution.

Figure 12. Correlation relationships between modified Sherwood number and Reynolds number from this study and several reported experiments. The experimental curves (Miller et al., 1990; Parker et al., 1990; Powers et al., 1992; Guarnaccia et al., 1992) are adopted from Powers et al. (1992).
Figure 1
Figure 2
Figure 3

The graph shows the relationship between Ganglion Size and Interfacial Area (mm²). The equation for the line is given as:

\[ y = 0.8169 + 0.7003x \]

The graph includes data points for different Ca values: 10^-4, 10^-5, 10^-6, and 10^-7.
Figure 4
Figure 5
Figure 7

Figure 8
Dissolution Volume fraction to instability

![Graph showing dissolution volume fraction to instability with ganglion size on the y-axis and volume fraction on the x-axis. The graph includes data points for different Ca concentrations, indicating the relationship between ganglion size and dissolution volume fraction.]
Figure 10
Figure 11
Figure 12
CHAPTER 4. INVESTIGATION OF POROUS MEDIUM CHARACTERISTICS EFFECTS ON NONAQUEOUS PHASE LIQUID DISSOLUTION AND INSTABILITY

A paper to be submitted to Journal of Contaminant Hydrology

Yanhui Hu, Robert P. Ewing, and Rodney O. Fox

Abstract

Non-aqueous phase liquids (NAPLs) that move through aquifers leave residue in their migration pathway in the form of NAPL ganglia. It is known that porous medium characteristics can have a strong influence on the dissolution rate and fate of these ganglia, but this influence has not been systematically investigated. We systematically explored the effects of porous medium characteristics on isolated NAPL ganglia dissolution and instability using a three-dimensional network model. A full factorial experimental design was used to conduct a simulation experiment, and the significances of the effects of pore body sizes, pore size standard deviation, aspect ratio, correlation length and ganglion size were evaluated. NAPL ganglion dissolution is strongly affected by pore body size, Capillary number and ganglion size. NAPL dissolution increases with decreasing pore body size, increasing Capillary number and increasing ganglion size. Aspect ratio has the most important effect on the ganglion instability. With increasing aspect ratio, the instability type shifts from snap-off suppressed to snap-off dominated. However, the effect of aspect ratio is conditioned on the values of other parameters, such as the pore size standard deviation and correlation length.
1. Introduction

A common source of groundwater contamination is accidental spills and leaks of nonaqueous phase liquids (NAPLs) into the subsurface environment. Although NAPL solubilities are generally low, species with high toxicities tend to have regulated maximum concentration limits that are lower than their solubility limit. Therefore, NAPLs in underground porous media pose long-term contamination problems, frequently requiring the use of remediation techniques. These techniques are usually expensive, and a given technique may be successful at one site but ineffective at another. The lack of robustness of a remediation technique is primarily due to the underlying differences between porous media at different sites. Therefore, key to the development of a successful remediation operation is a thorough understanding of the mechanisms controlling NAPL migration and dissolution. Because NAPL migration and dissolution are complex processes involving the interaction of multiple forces interacting locally with the porous medium over time, it can be useful to examine them at the pore scale.

Since first introduced by Fatt (1956), pore-scale network models have been used extensively to investigate various aspects of residual NAPL ganglion formation, movement and dissolution. An incomplete list of possible factors in play includes pore geometry (pore body and throat sizes), solid surface wettability, interfacial tension, aqueous phase velocity, and NAPL solubility in water. The chief advantage of the pore-scale network model is its ability to explicitly take into account the details of the porous medium, so that the factors listed above can be investigated in a systematic and controllable manner.

Lowry and Miller (1995) studied the effects of pore scale geometric parameters on NAPL residual saturation, ganglion distribution and NAPL/water interfacial area using a
random network model. They found that smaller residual saturation could be obtained with larger connectivity, smaller aspect ratio (defined as the ratio of average pore body size to pore throat size), and/or smaller pore-size variability. They also concluded that high aspect ratio leads to smaller ganglia and smaller effective interfacial area. Jerauld and Salter (1990) studied effects of pore structure on the relative permeability-capillary pressure relationship. They found the body-to-throat aspect ratio is the most important factor in determining the degree of hysteresis, since aspect ratio controls the ratio of snap-off to retraction occurrences. They also found that spatial correlations are important in determining NAPL saturation and constitutive relationships: throat-throat correlation can increase the relative permeability of the nonwetting phase and decrease the relative permeability of the wetting phase and the NAPL residual saturation. These conclusions are consistent with those reached by Blunt (1997) when investigating long-range correlation effects.

Rajaram et al. (1997) studied the influences of two types of pore throat correlations on the constitutive relationships between capillary pressure, residual saturation and relative permeability: spatial correlation of throats along the same direction and cross correlation of throats originated from the same site but different directions. They found that increasing correlation leads to gradual (less steep) capillary pressure-saturation ($P_c$-$S$) relationships. However, the residual saturation decreases with increasing spatial correlation but increases with increasing cross correlation. They therefore concluded that correlation structure is necessary in order to successfully predict the capillary constitutive relationships for real porous media. Mani and Mohanty (1999) did an extensive investigation on the effects of spatial correlations on fluid displacement using a network model. Three correlation structures for the pore body sizes were tested: uncorrelated, spherical correlation and
fractional Brownian motion (fBm) based correlation. They found that for the cases of no correlation and short-range (spherical) correlation, the permeability can be determined with a large enough sample size. On the other hand, the pore-size distribution and the Hurst exponent (fBm parameter) alone cannot fully define the capillary pressure curves. They further observed that the percolation cluster density increases with increasing Hurst exponents, but decreases with increasing system sizes for spherical correlation media.

Ferrand and Celia (1992) investigated the effect of porous medium heterogeneity on the drainage capillary pressure-saturation curve. They studied three types of heterogeneity: alternating layers of two materials, one material embedded in a second material, and blocks of random properties. Their simulation results from a three-dimensional network model indicate that heterogeneity has strong influences on the relationship, and the approach of linear averaging of small-scale relationships to obtain an effective large-scale relationship may not be reliable.

The role of wettability in fluid displacement mechanisms has also been studied extensively, since the wettability of the rock surfaces may change over time during contact with oil. Blunt (1997) found that residual oil saturation following a waterflood is very sensitive to wettability of the solid surface. The flow pattern switches from snap-off dominating for water-wet, to cluster growth for weakly water-wet, to stable oil flow for oil-wet. Dixit et al. (1998) pointed out that hysteresis in water-wet and intermediate-wet porous media can be partially attributed to competition between snap-off in water-wet pores and piston-like advance in oil-wet pores. Blunt (1998) used a network model allowing both water-wet and oil-wet in a single pore and generated similar conclusions.
Pore-scale network models have long been used to study effects of the porous medium characteristics on multiphase flow displacement, but their use in the investigation of NAPL dissolution is more recent (Dillard and Blunt, 2000; Held and Celia, 2001). Existing pore-scale network models of NAPL dissolution tend to generalize macroscopic parameters, such as the lumped dissolution rate coefficient, and dimensionless groups, such as the Sherwood number and Peclet number, from pore-scale simulation, and then compare modeled macroscopic parameters with those from column studies. The results, in general, are in good agreement. However, the effects of porous medium characteristics have been overlooked. Hu et al. (2002) proposed a three-dimensional network model to study residual NAPL dissolution and instability, and found that the NAPL initial instabilities (before dissolution taking place) and dissolution-induced instabilities may be strongly influenced by the properties of the porous medium. The objective of the present research is therefore to examine effects of porous medium characteristics, such as pore body size, pore throat size, correlation, and aspect ratio, on residual ganglion dissolution and instabilities using the network model developed by Hu et al. (2002).

2. Methodology

2.1 Model description

The network model used in this study was described in some detail in Hu et al. (2002). A regular cubic lattice is used to simulate the porous medium, with spherical pore bodies and biconical shaped pore throats. Of the six boundaries of the cubic domain, one side is the high hydraulic pressure end, the opposite side is the low hydraulic pressure end,
and the other four are treated as periodic boundaries. Biconical throats are used rather than cylindrical, because they allow continuously stable interfaces.

The turning bands method (Tompson et al., 1989) was used to generate pore body sizes from a Gaussian distribution with a known decay correlation length. Given an aspect ratio $a_r$, throat radii are defined as:

$$R_t = \min\left(\frac{R_{b1}}{\sqrt{2}}, \frac{R_{b2}}{\sqrt{2}}, \frac{R_{b1} + R_{b2}}{2a_r}\right)$$

where $R_{b1}$ and $R_{b2}$ are the radii of the two adjacent pore bodies. Under laminar flow conditions, the conductance of a biconical throat can be theoretically defined (Reeves and Celia, 1996), and pressures at each node (pore body) can then be found based on mass balance equations using an iterative successive over-relaxation algorithm.

A stable interface at equilibrium satisfies the Young-Laplace equation

$$P_c = P_n - P_w = \frac{2\sigma_{nw} \cos(\theta + \alpha)}{R_i}$$

where $P_c$ is the stable capillary pressure, $P_n$ and $P_w$ are the pressures of nonaqueous and aqueous phases, $\sigma_{nw}$ is the NAPL/water interfacial tension, $R_i$ is the radius at the contact line, $\theta$ is the contact angle, and $\alpha$ is the angle defined by throat radius, body radius and throat length. Individual ganglia are introduced into the flow field pore-by-pore following a "piston drainage" mechanism. Once injection is complete, ganglion stability is tested based on an energy analysis of the menisci (Mohanty et al., 1980). Given the volume of the ganglion, the local porous medium geometry, and the flow field, the stable ganglion pressure can be determined uniquely (Hu et al., 2002). It is noted that ganglia are also subject to "snap-off".
which corresponds to the collapse of a selloidal interface in a NAPL-filled throat. The critical capillary pressure for snap-off is

\[ P_{c,\text{snap}} = \frac{\sigma \cos \theta}{R_i} \]  

(3)

In real porous media, water directly contacts a NAPL ganglion in two forms: mobile and immobile. Consequently, two NAPL dissolution models operate in parallel: a stagnant layer diffusion model for immobile water, and a channel flow dissolution model for mobile water. The stagnant layer dissolution model describes the concentration gradient driven NAPL diffusion through stagnant (immobile) water between the NAPL/water interfaces and the exit of the pore throats. The channel flow dissolution model describes the convective mass transfer of NAPL to surrounding mobile water in crevices. Hu et al. (2002) used population analysis to derive modified Sherwood, Peclet, and Reynolds numbers, and found that the relationships between them were in good agreement with those from column studies of NAPL dissolution.

Residual NAPL instability can be divided into two categories: initial instability and dissolution-induced instability. Initial instability means that the ganglion as injected is not stable; the resulting instability can be classified as initial-retreat (water invades a singly connected NAPL-filled pore body), initial-advance (NAPL invades a water-filled pore body), and snap-off (the selloidal interface in a NAPL-filled throat collapses). Dissolution-induced instability occurs only after the ganglion shrinks due to dissolution, and can be divided into retreat, snap-off, and breakup (water invading a multiply connected NAPL-filled pore body) (Fig.1). The breakup of an existing ganglion can create two or more smaller ganglia.
2.2 Statistical approach

We investigated six parameters: mean pore body radius, relative standard deviation of the pore body radius, aspect ratio, pore body correlation length, capillary number, and ganglion size (Table 1). The two levels of the mean pore body radius are 0.07 and 0.3 mm, typical values for a consolidated sandstone. The pore body standard deviation is made dimensionless by taking the ratio of the pore body radius standard deviation to its body mean. Because an aspect ratio of two is a cutoff value for snap-off used by Held and Celia (2001) for biconical shaped throats, the two levels of aspect ratio were chosen to be 1.7 and 3. The dimensionless correlation length is defined as the number of units (mean distance between pore bodies) for correlation in the turning bands method (Tompson et al., 1989), and was given values of 1 (no correlation) and 5, at which value the percolation threshold decreases to an asymptotic value (Renault, 1991). Table 2 lists those porous medium and aqueous and NAPL phase properties which are held constant across all simulations.

In order to investigate the effects of these six factors as well as their interactions on NAPL dissolution and instabilities, a six-factor full factorial numerical experiment was conducted. This experiment consists of all \(2^6 = 64\) combinations of the six factors, each taking two levels. Independent realizations were run for each treatment combination to get 300 stable ganglia. If in a given treatment the initial ganglia are always stable, there are exactly 300 runs implemented. However, if the initial ganglia are not always stable, more than 300 initial trials are needed in order to obtain 300 stable ganglia.

The continuous outputs from the simulation (ganglion area, dissolution volume, dissolution rate, and dissolution time) can be treated as normally distributed random variables. Therefore, a least square regression can be performed on each of these random
variables with respect to the treatments (defined as a combination of the factor levels, a total of $2^6 = 64$ treatments). The resultant coefficients for each treatment can be tested for significance against the mean square error obtained from the pooled sample variances from the runs. If the two levels of each treatment factor are coded as $-1$ and $1$, then the resultant model matrix is orthogonal, as are the effects of all the treatments (Wu and Hamada, 2000). Therefore, the sum of squares associated with each treatment is the product of $2^6$ and the square of the estimate of the coefficients, which are independent of each other and can then be used to decompose the total sum of squares contributed by all treatments. On the other hand, for the discrete outputs from the simulation (the occurrences of different types of instabilities), the two levels of each treatment factor are coded as $0$ and $1$. The resultant different types of instabilities are then fitted with respect to all treatments using logistic regression, and the coefficients from the regression give a measure of the association of the instabilities with those explanatory variables.

3. Simulation results and discussion

3.1 Continuous outputs – area, volume and dissolution flux

Each run generates 300 observations of the continuous variables of interest, such as interfacial area and dissolution volume, which can be summarized by mean and sample variance. There are a total of 64 runs, therefore, 64 means and sample variances ($y_i$, $s_i^2$) for each continuous output from the model. The least squared estimates of the coefficients for all treatments can be obtained as $2^6 M'Y$, where $M$ is the $64 \times 64$ orthogonal model matrix generated from the experiment design, and $Y$ is the vector of the 64 means (Appendix A). The pooled variance, $s^2$, is defined as the average of all 64 sample variances. All estimated
coefficients therefore have the same variance, $s^2/N$, where $N$ is the total number of observations ($= 19200$). T-tests with $2^6 \times 299$ ($= 19136$) degrees of freedom can be performed on each estimated coefficient to test its significance.

For interfacial area, the pooled variance is 0.4544. The t-values of the estimated coefficients using this pooled variance are quite large, with 29 terms larger than 2. In other words, 29 out of 64 treatments have significant effects on interfacial area at significance level 0.05, although some of those terms are found significant due to the multiple comparisons. Among the 29 significant terms, some are four-factor and five-factor interactions. In order to have a better understanding of both the main factor effects and their interactions on the interfacial area, a half-normal probability plot (Fig. 2) is used for visualizing effect significance (Wu and Hamada, 2000). The change in slope of the half-normal plot signifies a break between significant and non-significant effects, thus, the significant effects are the main effects, and two- and three-factor interactions of pore body size (A), ganglion size (F) and aspect ratio (C).

It is a trivial observation that the larger the ganglion, the larger will be the interfacial area. Specific interfacial area (defined as interfacial area/ganglion volume) was therefore used to normalize this effect with respect to ganglion size (Fig. 2). Significant factors for the normalized area include the main effects of pore body mean, ganglion size, and aspect ratio, as well as the two-factor interactions of (pore size mean)*(ganglion size) and (pore size mean)*(aspect ratio) (Table 3). The sum of squares of these five effects is 99.2% of the total sum of squares from all treatments. The pore body mean has the most significant effect (75.3%), with larger pore bodies having smaller specific area. The second most important effect is the normalized ganglion size, with a negative effect similar to that of the pore body
mean. A ganglion volume, $V$, is defined as the product of normalized ganglion size and the pore body mean, so $V$ increases with either of these two factors. The specific interfacial area is roughly scaled to $V^{-1/3}$, therefore both pore body mean and normalized ganglion size have negative effects on the specific interfacial area. On the other hand, higher aspect ratio leads to lower interfacial area, which in turn will cause lower diffusion rate. The two-factor interaction terms are less significant, and indicate that the effect of pore body mean is less pronounced for larger ganglia and/or larger aspect ratio.

Normalized dissolution volume (volume dissolved before instability/initial ganglion volume) is primarily affected by pore body standard deviation, aspect ratio, and ganglion size; and the two-factor interaction of the first two terms (Table 3). Aspect ratio is the single most significant factor, accounting for 84% of the total variance: larger aspect ratio leads to lower normalized dissolution volume, which may be due to the destabilizing effect of high aspect ratio (discussed below). This effect is conditioned on the value of pore body standard deviation: smaller pore body standard deviation enhances this effect. The normalized dissolution volume is larger for a smaller ganglion in a more uniformly distributed porous medium, simply because such a ganglion is more stable, and so requires relatively more dissolution before it becomes unstable.

Fluxes due to stagnant layer diffusion and channel flow dissolution fluxes are also strongly affected by the porous medium characteristics (Table 3). Pore body mean, Capillary number, and their interactions are the three most significant effects on diffusion flux. The diffusion flux decreases with increasing pore body mean, because the thickness of the stagnant layer length increases with increasing pore body size. The negative effect of Capillary number can be attributed to the higher solute concentration in the local aqueous
phase at low flow rates (low Capillary number), which effectively reduces the concentration gradient. The significant interaction term indicates that the negative effect of pore-body mean at high Capillary number is not as strong as that at low Capillary number. As to the channel flow flux, the most significant effect is the Capillary number, accounting for 87% of the variance. This high association is natural since the dissolution flux in channel flow is directly dependent on the aqueous flow rate: the slower the aqueous flow rate, the closer the NAPL solute concentration is to solubility.

3.2 Discrete outputs – instability

The simulation results will be examined from two perspectives. First, the various factors that contribute to a given instability type will be assessed statistically: for example, the inputs affecting initial retreat. And second, the aggregate effects of the significant inputs will be presented graphically: for example, the impact of correlation length on the various types of instability. The simulation output indicates that the aspect ratio is crucial to both the initial instability and the dissolution induced instability types. Therefore, the analysis of treatment effects is presented separately for the two levels of aspect ratio.

Regression analysis: low aspect ratio

When aspect ratio is 1.7, snap-off is totally suppressed, consistent with the critical value used by Held and Celia (2001). The initial instabilities are either retreat or advance. The counts of initial tail retreat range from 0 to about 500. In order to investigate the effects of the five explanatory variables on initial retreat, a logistic regression (Appendix B) is performed on the likelihood of initial retreat. To reduce bias and avoid infinite values, 0.5 is added to all initial retreat counts, and 1 is added to all total instability counts (Cox, 1970). Therefore the likelihood of initial retreat, \( P_{re} \), can be defined as the ratio of those two
adjusted counts. The final regression model coefficients, based on the BIC (Bayesian information criterion) (Schwarz, 1978), are presented in Table 4.

In this model three main effects and three two-factor interactions are significant at 0.05. The coefficients in the model are related to the log of the odds ratio, with a positive coefficient meaning a positive effect of the corresponding factors on the likelihood. For example, the coefficient of body size standard deviation, 2.27, indicates that high pore size standard deviation ($\sigma_p$) leads to higher likelihood of the initial retreat. In fact, the odds of having initial tail retreat increase about 10 ($\approx e^{2.27}$) times from $\sigma_p$ 0.15 to 0.25, when other factors are held at their low levels. Due to the existence of the significant two-factor interaction terms, the interpretation of the effect of any individual factor is not straightforward, but needs to take into account the levels of other factors. For example, although increasing $\sigma_p$ makes initial retreat more likely, this effect is more pronounced with a small ganglion in a correlated porous medium. Similarly, the effect of correlation is strongly negative (-2.26) for a small ganglion in a porous medium with small $\sigma_p$; this effect decreases with increasing $\sigma_p$. The odds of initial retreat decrease slightly ($e^{-0.5} = 0.6$ times) with increasing ganglion size in an uncorrelated porous medium with small $\sigma_p$. However, in a correlated porous medium, the odds of initial retreat increase about 2.5 ($\approx e^{0.92}$) times with increasing ganglion size.

The effects of $\sigma_p$, correlation length and ganglion size on the likelihood of initial retreat can be attributed to their influences on the local pore sizes and the internal ganglion pressure. High $\sigma_p$ leads to a wider variance of the local pore sizes a ganglion occupies, which in turn, leads to a higher probability of a small pore body occupied by a ganglion. The
smaller the pore body, the more likely a ganglion experiences initial retreat. Similarly, the smaller the correlation length, the more likely a ganglion occupies a small pore body, and the more likely the initial retreat. On the other hand, the effect of ganglion size is shown in two opposite ways. First, when a ganglion expands from its initial injection point, it prefers to invade through the large pore throats (pore bodies). Consequently, the average size of the pore bodies occupied by a large ganglion is larger than the average size of the pore bodies occupied by a small ganglion (in fact, the average pore body size of a size 20 ganglion is about 10% higher than the average pore body size of a size 3 ganglion). Secondly, this biased sampling is also reflected in the ganglion internal pressure: a larger ganglion has a higher internal pressure, and can resist water imbibition (initial retreat) better. Under the competition of both mechanisms, the ganglion effect appears to be negative (second mechanism dominates) when the porous medium is random (high $\sigma_p$ and no correlation), but positive (first mechanism dominates) when the local porous medium is more uniform (low $\sigma_p$ and high correlation).

Table 4 also presents the coefficients of the regression model for initial advance instability. It is shown that in an uncorrelated porous medium, the odds of initial advance are 3.3 ($\approx e^{1.2}$) times higher for a larger ganglion than for a small one. However, this ratio reduces to around 2.2 when the correlation length is five. On the other hand, the effect of correlation length on the odds of initial advance is positive (0.13) for a small ganglion, but negative (-0.3) for a large ganglion. Finally, when $\sigma_p$ increases from 1.5 to 2.5, the odds of initial advance increase 1.4 ($\approx e^{0.34}$) times.

The initial advance is controlled by the sizes of the pore throats where the NAPL/water interfaces reside: the larger the sizes, the more likely the initial advance.
Following the previous argument, the positive effect of \( \sigma_p \) can be explained as the higher probability of large pore throats with high \( \sigma_p \). Similarly, the positive effect of ganglion size on the initial advance can be attributed to the high internal ganglion pressure of a large ganglion.

Since there is no occurrence of snap-off when aspect ratio is 1.7, all of the 300 dissolution-induced instabilities are either breakup or retreat. Consequently, only breakup likelihood is analyzed here. The resultant regression model (Table 4) suggests that the main effects of \( \sigma_p \), ganglion size, and correlation length are the only significant effects. The odds of dissolution-induced breakup increase \(( \approx e^{1.26} \)) with increasing ganglion sizes. On the other hand, the odds of breakup decrease with increasing \( \sigma_p \) or correlation length.

**Regression analysis: high aspect ratio**

For the case of high aspect ratio, the dissolution-induced instabilities are mainly snap-off (> 99%). It is also found that high aspect ratio increases initial instability by approximately 1.6 times, that is, ganglia are more likely to be unstable right from the outset. The initial instabilities in this case are mostly retreat or snap-off, with initial advance being very rare.

The final regression model (Table 4) indicates that the frequency of initial tail retreat at high aspect ratio is affected by the main effects of \( \sigma_p \), ganglion size, and correlation length as well as two-way interactions between these factors. The model of initial retreat at high aspect ratio gives similar trends of effects as those given by the model at low aspect ratio. With other factors being held at their low levels, the odds of having initial retreat increase about 6.7 \(( \approx e^{1.9} \)) times with increasing \( \sigma_p \), and this effect is more pronounced for a large
ganglion in a porous medium with a large correlation length. The effect of correlation is negative (odds ratio = 0.34) for a small ganglion in a porous medium with low $\sigma_p$; however, this negative effect is reduced with increasing ganglion size or $\sigma_p$. In fact, for a ganglion size 20 in a porous medium with $\sigma_p$ 2.5, the effect of correlation length is not important anymore (odds ratio $\approx$1). At high aspect ratio, the negative effect of ganglion size is much stronger than that at low aspect ratio. In fact, the effect of ganglion size is kept negative across all levels of other factors. This trend indicates that the high aspect ratio enhances the increase of ganglion internal pressure when it expands.

The regression model for initial snap-off (Table 4) shows that the odds with increasing $\sigma_p$ are 0.5 ($= e^{-0.66}$) times less when other factors are at low levels. This is due to the competition between the effects of $\sigma_p$ on initial snap-off and on retreat. The counts of both initial snap-off and initial retreat increase with increasing $\sigma_p$. However, since the positive effect of $\sigma_p$ on initial retreat is stronger, the effect on the probability of initial snap-off appears negative. Regression also reveals a weak positive effect of correlation length on the odds of initial snap-off, and this effect is slightly enhanced when $\sigma_p$ is large. When $\sigma_p$ is small, ganglion size has a strong negative effect on the odds of initial snap-off (-2.03). However, when $\sigma_p$ is large, the effect of ganglion size on the odds of initial snap-off is diminished. Although the counts of initial snap-off decreases with increasing ganglion size, the negative effect of ganglion size on initial retreat is much stronger, therefore the ganglion size effect on the odds of initial snap-off is not pronounced.
Aggregate effects of significant inputs

In the previous two sections statistical analysis has been conducted on the likelihood of individual instability types and the resultant significant inputs are investigated. It is found that besides aspect ratio, the main effects of $\sigma_p$, correlation length and ganglion size, as well as their interactions affect the instability strongly. In this section, the aggregate effects of each of these factors on instability are investigated.

The main effect of $\sigma_p$ conditioned on the two levels of aspect ratio is presented in Fig. 3. When aspect ratio $= 1.7$, initial instability is either retreat or advance; and high $\sigma_p$ increases the occurrences of both types of initial instability. Also, the dissolution-induced instability maintains roughly the same proportion of retreat to breakup with increasing $\sigma_p$. When aspect ratio $= 3$, initial instability is mainly retreat or snap-off with initial advance being very rare, and the dissolution-induced instability is all snap-off. Similar to the case of low aspect ratio, here $\sigma_p$ still has a strong positive effect on the frequency of initial retreat due to the higher variability of the local pore sizes. The main effect of correlation length is presented in Fig. 4. The results from no correlation (Fig. 4 a, b) are similar to those from high $\sigma_p$ (Fig. 3 c, d) likewise, results from high correlation length (Fig 4 c, d) are similar to those from low $\sigma_p$ (Fig. 3 a, b). This similarity can be attributed to the fact that both correlation length and $\sigma_p$ are measures of porous medium homogeneity: the smaller the correlation length or the higher the $\sigma_p$, the more heterogeneous the porous medium.

The main effect of ganglion size is different at different aspect ratio (Fig. 5). When aspect ratio $= 1.7$, larger ganglia have more initial instability and the likelihood of initial advance increases increasing ganglion size, due to the increase of ganglion internal pressure
in a large ganglion. However when aspect ratio = 3, small ganglia have more initial
instability (more retreat and snap-off), again due to the effect of ganglion internal pressure.

Since the effect of $\sigma_p$ and correlation length can be summarized as the effect of
porous medium heterogeneity, only the two-way interactions between ganglion size and
porous medium heterogeneity is investigated (Fig. 6). Initial retreat is favored by a small
ganglion in a heterogeneous porous medium at either aspect ratio. When aspect ratio is
small, the initial advance is favored by large ganglion in a heterogeneous porous medium.
When aspect ratio is high, the initial snap-off is favored by a small ganglion in a more
uniform porous medium.

3.3 Intermediate aspect ratios

The previous results show a strong transition from snap-off dominated (aspect ratio =
3) to snap-off suppressed (aspect ratio = 1.7) instabilities. A closer look at aspect ratio
effects on the types of instability, therefore, is necessary. In order to investigate the aspect
ratio effect, simulations are conducted at aspect ratio = 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, and 2.7.
For each aspect ratio, four cases were investigated: $\sigma_p = (0.15, 0.25)$ and correlation length =
(1, 5). The pore body mean was held at 0.3 mm, ganglion size was held at 3, and the
capillary number was $10^{-4}$.

Aspect ratio $\approx 2.0$ is the cutoff value for snap-off at all levels of $\sigma_p$ and correlation
lengths (Fig. 7). Although this cutoff value is not explicitly defined in the program but
generated based on the stability criteria, it is in good agreement with the value used by Held
and Celia (2001). When aspect ratio is below the cutoff point, there is no snap-off (initial or
dissolution induced). With increasing aspect ratio, snap-off becomes more frequent and
eventually dominates the dissolution-induced instability. Also, increasing aspect ratio leads
to more initial retreat but fewer initial advances. Finally, dissolution-induced retreat is much more frequent than breakup, although both of them are less likely at high aspect ratio due to the dominance of snap-off at high aspect ratio. Overall, the initial instability is minimized when aspect ratio ≈ 2.2. This is the result of the competition between initial snap-off and retreat at high aspect ratio and initial advance at low aspect ratio.

Effects of aspect ratio on instability are conditioned on levels of $\sigma_p$ and correlation length. For example, the decreasing rate of dissolution-induced retreat with increasing aspect ratio is the largest in the most homogeneous porous medium (low $\sigma_p$ and high correlation length) and the smallest in the heterogeneous porous medium. Also, there is a much higher probability of initial retreat with high $\sigma_p$ and small correlation length; consequently, the most heterogeneous porous medium has the most initial instability occurrences.

4. Conclusion

A three-dimensional network model has been used to investigate the effects of porous medium characteristics on the stranded ganglia dissolution and instabilities. A two-level full factorial simulation experiment using six factors, including pore body size mean, pore body size standard deviation, aspect ratio, correlation, Capillary number and ganglion size, is performed.

The statistical analysis of the continuous outputs revealed that correlation length does not affect ganglion configuration or dissolution, but Capillary number strongly increases dissolution fluxes. Diffusion flux is affected by pore body size, due to the increases of the stagnant layer length with increasing pore size. It is also found that aspect ratio, due to its destabilizing effect, is the single most important factor on the normalized dissolution volume,
and ganglion size poses a negative effect on both the specific interfacial area and normalized dissolution volume.

Logistic regression models are obtained to study the associations between instabilities and explanatory variables. It appears that the aspect ratio is the most significant parameter on determining the ganglion stability. When aspect ratio is small (1.7), there is no snap-off (initial or dissolution-induced). But when aspect ratio is large (3), the dissolution-induced instability is dominated by snap-off. Therefore, the analysis is separated based on the levels of aspect ratio. When aspect ratio is small, it is found that a less uniformly distributed porous medium (high body standard deviation with no correlation) leads to higher probability of initial retreat, and therefore more initial instability occurrences. The likelihood of initial advance and the likelihood of dissolution-induced breakup increase with increasing ganglion size in a heterogeneous porous medium. Overall, large ganglia have more initial instability. When aspect ratio is high, initial advance becomes rare, and snap-off dominates the instability. Large ganglia are less likely to have initial snap-off and initial instability, unlike the case with low aspect ratio. It is concluded that the effects of \( \sigma_p \), correlation length, and ganglion size on the probabilities of instability can be explained as the combined effects of local porous medium heterogeneity, porous medium sampling difference of a ganglion, and ganglion internal pressure.

Due to the significant effect of aspect ratio on instabilities, several intermediate aspect ratio levels were also investigated. It is found the cut-off point of aspect ratio for snap-off is around 2, and that the minimum initial instability occurs at aspect ratio 2.2. It appears that the frequencies of all instability types are strongly affected by aspect ratio, and this effect is increased in the presence of greater porous medium heterogeneity.
References


Table 1. Six-factor full factorial experiment at two levels

<table>
<thead>
<tr>
<th>Factors</th>
<th>Level</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-1)</td>
<td>(+1)</td>
<td></td>
</tr>
<tr>
<td>A: pore body mean, $\mu_p$, [mm]</td>
<td>0.07</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>B: pore body standard deviation, $\sigma_p$, [-]</td>
<td>0.15</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>C: aspect ratio, $asp$, [-]</td>
<td>1.7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>D: correlation length, $\lambda$, [-]</td>
<td>1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>E: Capillary number, $Ca$, [-]</td>
<td>$10^{-4}$</td>
<td>$10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>F: ganglion size, $G$, [-]</td>
<td>3</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Simulation parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit length [-]</td>
<td>4</td>
</tr>
<tr>
<td>Medium size</td>
<td>40^3</td>
</tr>
<tr>
<td>Percentage of water channel</td>
<td>0.1</td>
</tr>
<tr>
<td>NAPL density [kg m(^3)]</td>
<td>900</td>
</tr>
<tr>
<td>NAPL solubility in water [kg m(^3)]</td>
<td>0.23</td>
</tr>
<tr>
<td>Molecular diffusion of NAPL in water [m(^2) s(^{-1})]</td>
<td>8*10^{-10}</td>
</tr>
<tr>
<td>NAPL/water interfacial tension [kg s(^{-2})]</td>
<td>0.024</td>
</tr>
<tr>
<td>Water viscosity [kg m(^{-1}) s(^{-1})]</td>
<td>0.0009</td>
</tr>
<tr>
<td>Wetting angle [rad]</td>
<td>0</td>
</tr>
<tr>
<td>Realization [-]</td>
<td>300</td>
</tr>
</tbody>
</table>
Table 3. Percentages of sum of squares of the treatments for continuous outputs

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Specific interfacial area [L^-1]</th>
<th>Dissolution volume [-]</th>
<th>Diffusion flux [ML^-2T^-1]</th>
<th>Channel flux [ML^-2T^-1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore mean</td>
<td>75.3 (-2.61)</td>
<td></td>
<td>49.8 (-3.60)</td>
<td></td>
</tr>
<tr>
<td>Pore standard deviation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>6.6 (-0.77)</td>
<td>84.1 (-0.093)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ganglion size</td>
<td>10.9 (-0.99)</td>
<td>4.7 (-0.022)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mean)*(aspect ratio)</td>
<td>2.4 (0.47)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mean)*(Ca)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mean)*(ganglion size)</td>
<td>4.0 (0.60)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pore std)*(aspect ratio)</td>
<td></td>
<td></td>
<td>3.2 (0.018)</td>
<td></td>
</tr>
<tr>
<td>(Ca)*(ganglion size)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SS(%)</td>
<td>99.2</td>
<td>98.1</td>
<td>96.1</td>
<td>95.0</td>
</tr>
</tbody>
</table>

The values in the table are the percentages of the effects sum of squares over the total sum of squares of all effects. Large values indicate more significant effects. The values in the parentheses are coefficients of the effects.
Table 4. Logistic regression coefficients for the probabilities of different instability types

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Initial instability</th>
<th>Dissolution-induced instability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aspect ratio=1.7</td>
<td>Aspect ratio=3</td>
</tr>
<tr>
<td></td>
<td>Tail retreat</td>
<td>Tail retreat</td>
</tr>
<tr>
<td></td>
<td>Advance</td>
<td>Snap-off</td>
</tr>
<tr>
<td>pore standard deviation</td>
<td>2.27</td>
<td>1.9</td>
</tr>
<tr>
<td>correlation length</td>
<td>-2.26</td>
<td>-1.07</td>
</tr>
<tr>
<td>ganglion size</td>
<td>-0.5</td>
<td>-3.3</td>
</tr>
<tr>
<td>(pore std)*(correlation)</td>
<td>0.95</td>
<td>0.27</td>
</tr>
<tr>
<td>(pore std)*(gsize)</td>
<td>-0.66</td>
<td>1.42</td>
</tr>
<tr>
<td>(correlation)*(gsize)</td>
<td>1.42</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The values are the coefficients of the final logistic regression models and can be interpreted as the log of the odds ratios. Only significant treatments (terms) are listed. Note all factors can take values 0 or 1 only.
Figure captions:

Figure 1. A cartoon showing different instability types.

Figure 2. Half-normal probability plot of the six-factor effects on interfacial area and the specific interfacial area.

Figure 3. The main effect of pore size standard deviation. initial retreat, initial advance, initial snap-off, dissolution retreat, dissolution breakup, dissolution snap-off.

Figure 4. The main effect of correlation length. Key is the same as Figure 3.

Figure 5. The main effect of ganglion size. Key is the same as Figure 3.

Figure 6. The interactions between ganglion size and porous medium heterogeneity. Key is the same as Figure 3.

Figure 7. The effects of aspect ratio on ganglion instabilities. (a) pore body standard deviation = 0.15, correlation length = 1, (b) std deviation = 0.15, correlation length = 5. (c) std deviation = 0.25, correlation length = 1. (d) std deviation = 0.25, correlation length = 5.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Appendix

1. Orthogonal model matrix for a continuous output \( y \) (\( y \) can be interfacial area, dissolution volume, etc.).

A two-level six-factor full factorial design has \( 2^6 = 64 \) treatment combinations. Therefore, the response vector \( Y \) is defined as \( Y' = [y_1, y_2, \ldots, y_{300}] \), where \( y_i \) is the mean of the 300 observations under treatment \( i \), and the coding of treatment \( i \) denotes the levels of each factor treatment \( i \) has (1 at low level and 2 at high level). The effects are defined as follows. The intercept is \( I \), the main effect of factor \( A \) is \( a \), the two-way interaction of factor \( A \) and \( B \) is \( ab \), the three-way interaction of \( A, B, \) and \( C \) is \( abc \), and the six-way interaction is \( abcde \). The 1x64 coefficient vector \( \Theta \) is then defined as \( \Theta' = [I, a, ab, \ldots] \). For a treatment \( i \), the coefficient of a factor at its low level is 1, else -1, and the coefficient for an effect is the product of those individual coefficients, with intercept being 1 always. For example, for treatment 112122, the 64 coefficients are as follows. The coefficient of intercept is 1, \( a = -1 \), \( c = 1 \), \( ab = 1 \), \( ac = -1 \), \( abc = 1 \), and \( abcde = 1 \). Then, the 64x64 model matrix \( M \) is defined; each row of which corresponds to a treatment, and contains the 64 coefficients defined as before.

The model \( Y = M\Theta + \varepsilon \), where \( \varepsilon \) is the independent normal distributed error vector, can be solved as: \( \hat{\Theta} = 2^{-6} M' Y \). The variance of any individual term of \( \Theta \) is \( \hat{\sigma}^2 / N \), where \( \hat{\sigma}^2 = s_p^2 \) is the pooled variance and \( N (= 2^6 \times 300) \) is the total number of observation. The \( t \)-statistic for an individual term, \( \theta_i \), is \( t = \frac{\hat{\theta}_i}{\sqrt{s_p^2 / N}} \). This \( t \)-statistic can be compared to \( t(0.025, 2^6 \times 299) \) to test the significance of the effect.
2. Logistic regression model

Logistic regression model is a type of generalized linear models, used to find the association between the response probability and a set of explanatory variables. The logistic model used in this research is:

\[
\text{logit}(P) = \log \left( \frac{p}{1-p} \right) = \sum_{i=1}^{n} \beta_i x_i
\]

where \( x_i \) is the \( i \)-th term of the explanatory variables (with value 0 or 1), and \( \beta_i \) is the regression coefficient. The logit transformation maps the probability interval \((0, 1)\) onto the real value interval \((-\infty, \infty)\). The coefficient \( \beta_i \) of a main effect \( x_i \) can be interpreted as the log of the odds ratio when \( x_i \) changes from 0 to 1 and other explanatory variables are held at 0:

\[
\beta_i = \log \left( \frac{p}{1-p} \right)_{x_i=1} - \log \left( \frac{p}{1-p} \right)_{x_i=0} = \log \left( \frac{p_{x_i=1}}{1-p_{x_i=1}} \right) = \log \left( \frac{p}{1-p} \right)_{x_i=0} = \log(\text{odds ratio})
\]
Chapter 5. CONCLUSIONS

5.1 Summary

Nonaqueous phase liquids (NAPLs) in underground aquifer pose a long lasting contamination problem. Many factors affect the transport and fate of NAPLs in water-saturated porous media. Understanding NAPL behavior requires knowledge of the physical and chemical processes taking place at the NAPL/water interfaces, at the pore scale. A three-dimensional pore-scale network model was therefore developed to investigate ganglion dissolution and instability.

The proposed network model uses biconical shaped pore throats to accommodate stable interfaces everywhere within a throat. After the porous medium is decorated and the water flow field established, residual ganglia with predetermined sizes are introduced into the medium and tested for stability. Once a stable ganglion is found, dissolution takes place until dissolution-induced instability occurs. Monte Carlo simulations are conducted to obtain data with statistical meaning.

Two dissolution mechanisms were investigated: stagnant layer diffusion and channel flow dissolution. The former mechanism describes the slow diffusive transfer of NAPL from interfaces to the flowing aqueous phase due to a concentration gradient across an immobile water region, while the latter describes the faster convective transfer of NAPL to surrounding mobile water. Channels of mobile water penetrating the ganglion area were introduced into the model in order to capture the second mechanism. Several variables describing the residual ganglion configuration, dissolution and instability are generated from the simulation.

It is found that the stable ganglion is slightly ramified, with higher specific interfacial area than a sphere. Furthermore, within the range of Capillary numbers being investigated
(10^{-7} \sim 10^{-4}), stable ganglia are slightly elongated in the direction of the hydraulic pressure gradient. Analysis of dissolution rates reveals that both Capillary number and channel volume fraction have strong effects on the channel flow dissolution rates: larger channel volume fraction and higher Capillary number lead to higher channel flow dissolution rates. However, this effect is not as strong when \( C_a > 10^5 \) and channel volume fraction >0.1, because at this point the effluent concentration of NAPL after passing through a ganglion is no longer at the solubility limit due to the high flow rate. The effect of Capillary number on the diffusion dissolution rate is not noticeable until \( C_a < 10^6 \). This is attributed to dissolution being diffusion limited when aqueous flow rates are not sufficient to maintain low NAPL concentrations in the water surrounding the ganglion. The big picture is that, with increasing Capillary number, dissolution switches from stagnant layer diffusion dominant to channel flow dissolution dominant.

Simulation results also show that normalized dissolution volume decreases with increasing ganglion size. Analysis of ganglion instabilities reveals that the Capillary number does not affect the type of instability, but ganglion size does. Large ganglia initially more stable: both initial tail-retreat and snap-off occurrences decrease with increasing ganglion sizes. This ganglion size effect is due to how small ganglia sample the medium in an unbiased manner, but large ganglia are biased as to which pores they grow into. This indicates the importance of porous medium characteristics on ganglion instability.

A population analysis conducted on results from the single ganglion numerical experiments compares simulation data with the results from column studies in the literature. Using percolation theory, the ganglion size distribution was obtained, and relationships between the commonly used dimensionless groups (modified Sherwood number, Peclet
number, and Reynolds number) were generated. Relationships from the population analysis were in good agreement with relationships from various published experiments.

The importance of porous medium characteristics on ganglion dissolution and instability suggested further investigation. A six-factor two-level full factorial design was used to conduct a simulation experiment to examine the importance of pore body mean, body size standard deviation, aspect ratio, correlation length, Capillary number and ganglion size. Statistical analysis enabled us to limit the significant effects to main effects and several two-way interactions only. It is found that correlation length did not affect stable ganglion configuration or dissolution, and that Capillary number also did not affect ganglion configuration, but had a strong positive effect on the dissolution flux. Aspect ratio is the most important parameter on normalized dissolution volume due to its destabilizing effect. Pore size and ganglion size all pose negative effect on the specific interfacial area. The most important factor on instability is the aspect ratio: snap-off is suppressed when aspect ratio is 1.7, and snap-off dominates when aspect ratio is 3. Initial retreat is favored in a more heterogeneous porous medium (high pore size standard deviation and no correlation). It is also found that the likelihood of initial retreat and initial snap-off decreases with increasing ganglion size, but the likelihood of initial advance increases with increasing ganglion size.

A further set of simulations focused on the influence of aspect ratio was conducted. With increasing aspect ratio, initial advance decreases but both initial snap-off and initial retreat increases. It is found that a ganglion has the minimum initial instability occurrences when aspect ratio is around 2.2. At low aspect ratio, the dissolution-induced instability is mainly retreat than breakup. The effect of aspect ratio on instability is subjected on the
levels of body size standard deviation and correlation length. The most heterogeneous porous medium leads to the most initial instability.

The work completed thus far provides a good simulator of ganglion dissolution and instability. This work also demonstrated that sensitivity analysis could be performed on this simulator to acquire valuable information and draw reasonable conclusions concerning the interactions between multiple variables, such as the porous medium characteristics, fluid and flow properties and the fate of the ganglia. The work clearly demonstrates that dissolution does induce instabilities, and this process is complex and affected by many factors. It also shows that detailed knowledge of the porous medium characteristics is needed to properly understand the NAPL dissolution and movement processes and so to improve remediation techniques.

5.2 Recommendations

Recommendations resulting from this work address several areas including the model itself, model applications, and model validation.

The objective of this work was to investigate the possibility of dissolution-induced instability of residual NAPL ganglia. Pursuant to this objective, the three-dimensional pore scale model used in this research attempted to capture those features of a real porous medium, which are related to the configuration of NAPL/water interfaces. However, the model we initially developed did not take water channels and channel flow dissolution into account. Although conceptual water channels were later introduced into the model, the model would be more robust if the water channels were a built-in feature of the model’s geometry, as for example, using pore throats with a square or triangular cross-section.
The work has shown that porous medium properties play a significant role in NAPL/water transport processes; however, the parameters used in this model are typical of a consolidated sandstone, a very specific porous medium. Given detailed knowledge of a particular porous medium, this model can be tuned to simulate a real system and analysis can be more porous medium-specific. The model output can then be used to parameterize a larger-scale continuum model.

The model developed in this work lays a foundation for future work. Chapter 4 discussed the effects of some specific porous medium characteristics on ganglion dissolution and instabilities. Other medium characteristics may also impact the dissolution rate and instability types. For example, contact between NAPL and the rock surface over time can change the solid surface wettability. In fact, the rocks in an oil reservoir oftentimes change from water-wet to oil-wet. This change in wettability can significantly alter the behaviors of the two interacting liquid phases in the porous medium. Since the network model keeps track of local contact angle, with slight modification this model could be used to investigate NAPL dissolution and instability in mixed-wettability porous media. A practical application related to wettability is surfactant-based remediation. By changing the NAPL solubility and solid contact angle over time, this model could be used to mimic the NAPL drainage-water flushing-surfactant remediation process.

Up to this point, the model has been used to investigate stranded ganglia behavior only. Stranded ganglia are only a small part of the whole NAPL migration and dissolution processes. Ganglia are stranded as a result of NAPL migration through the porous medium, and the dissolution of stranded ganglia can cause a string of events, including instability (breakup and migration downstream), small ganglia coalescence, small NAPL blobs flushing
out the system, and NAPL cleanup through dissolution (pump-and-treat). Since the NAPL transport history affects the formation of stranded ganglia and thus the subsequent dissolution, and since dissolution can affect the stability and fate of the ganglia, it is recommended that both the upstream and downstream processes be incorporated into this model in order to present a whole picture of the fate of NAPL after entering the underground aquifer.

The author is greatly concerned about model validation. This model emphasizes residual ganglia dissolution and instabilities, which have not been systematically investigated either experimentally or numerically. Validation of this model through comparison with results from the literature is therefore both indirect and incomplete. Due to this limitation, the analysis in this work emphasizes sensitivity for a general case, rather than the simulation of a real system. In order to have a good validation of the model, single ganglion experiments in a porous medium with known characteristics would be very helpful. Any further investigation using this model should follow an accompanying experimental setup, and use experimental data to calibrate and validate the model.
ACKNOWLEDGMENTS

First and foremost, I thank Dr. Robert Ewing for being my mentor. Without his advice in both my academic and personal life, I would not have been able to conquer the difficulties I faced in the last five years or to finish this program. I would also like to thank my major professor Dr. Rodney Fox for taking on this project and for helping me meet the requirements for this project. To all committee members, I thank you for your services and support through this project. I acknowledge Mirrya Fontenot, my officemate and former research groupmate, for her encouragement and many insightful discussions. I would also like to acknowledge my friends and family for their support and happy times, which I will cherish. Finally, I am deeply grateful to my fiancé, Brian, for his love, patience, encouragement and support. You make me realize that sharing the joy and difficulties with you in life is the best gift I have ever received.