Multiphase Flow and Transport Modeling in Heterogeneous Porous Media: Challenges and Approaches

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We review the current status of modeling multiphase systems, including balance equation formulation, constitutive relations for both pressure-saturation-conductivity and interphase mass transfer, and stochastic and computational issues. We discuss weaknesses and inconsistencies of current approaches based on theoretical, computational, and experimental evidence. Where possible, we suggest new or evolving approaches.

Notation

Roman Letters

c_α	specific heat of the α phase $[L^2T^{-2}K^{-1}]$
$D_{m\alpha}$	molecular diffusion coefficient of α phase $[L^2T^{-1}]$
d_i	grain diameter for which i% of particles are smaller than d_i $[L]$
d_M	diameter of a "median" sand grain as defined by USDA $[L]$
d_{ni}	initial NAPL ganglia diameter after entrapment but before onset of dissolution $[L]$
d_p	geometric mean particle diameter $[L]$
F	mobile fraction of aqueous phase $[-]$

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g	gravitational acceleration $[LT^{-2}]$
Ga_α	Galileo number of α phase ($Ga_\alpha = d_p^3 g \rho_\alpha^2/\mu_\alpha^2$) $[-]$
$\mathcal{I}_\alpha^\iota$	interphase mass transfer rate of species ι to the α phase $[ML^{-3}T^{-1}]$
$\mathbf{J}$	mean hydraulic (aqueous-phase) gradient
$\mathbf{j}_\alpha^\iota$	nonadvective flux vector for species ι in the α phase $[ML^{-2}T^{-1}]$
k	intrinsic permeability of porous media $[L^2]$
k^*	scaled intrinsic permeability of porous media $[L^2]$
k_α	effective permeability of porous media to α phase $[L^2]$
$k_{r\alpha}$	relative permeability of porous media to α phase $[-]$
$k_{\alpha\beta}$	mass transfer coefficient (from α phase to β phase) $[MT^{-1}]$
$K_{\alpha\beta}$	mass transfer rate coefficient (from α phase to β phase) $[ML^{-1}T^{-1}]$
$K_{\alpha\beta}^*$	scaled mass transfer rate coefficient $[ML^{-1}T^{-1}]$
K_e	effective hydraulic conductivity $[LT^{-1}]$
K_g	geometeric mean hydraulic conductivity $[LT^{-1}]$
l	pore-connectivity parameter in Brooks and Corey [40] p-S-k model $[-]$
m	empirical parameter in van Genuchten [291] p-S model $[-]$
n	empirical parameter in van Genuchten [291] p-S model $[-]$
n_d	number of spatial dimensions $[-]$
n_p	number of phases $[-]$
n_s	number of species $[-]$
p_α	α phase pressure $[ML^{-1}T^{-2}]$
$p_{\alpha-\beta}$	capillary pressure between the α and β fluid phases ($p_{\alpha-\beta} = p_\alpha - p_\beta$) $[ML^{-1}T^{-2}]$
Pe_α	Peclet number in α phase ($Pe_\alpha = v_\alpha d_{50}/D_{m_\alpha}$) $[-]$
$\mathcal{R}_\alpha^\iota$	α phase production rate of species ι due to reactions $[ML^{-3}T^{-1}]$
Re_α	Reynolds number in α phase ($Re_\alpha = V_\alpha d_{50}/\nu_\alpha \phi S_\alpha)$) $[-]$
$\mathcal{S}_\alpha^\iota$	α phase production rate of species ι due to sources $[ML^{-3}T^{-1}]$
S_α	saturation of fluid phase α $[-]$
$\bar{S}_w$	effective saturation of wetting phase ($\bar{S}_w = (S_w - S_{wr})/(S_{ws} - S_{wr})$; same definition used for effective saturation of aqueous phase, $\bar{S}_a$, where the aqueous phase is the wetting phase$[-]$
s_i	spatial separation vector in the i-direction $[L]$
Sc_α	Schmidt number in alpha phase ($Sc_\alpha = v_\alpha/D_{m_\alpha}$) $[-]$
S_f	fraction of immobile aqueous phase contacting both the mobile aqueous phase and the gas phase $[-]$
$Sh_{\alpha\beta}$	Sherwood number ($Sh_{\alpha\beta} = K_{\alpha\beta} d_{50}^2/D_{m_\beta}$) $[-]$
$Sh'_{\alpha\beta}$	modified Sherwood number ($Sh'_{\alpha\beta} = k_{\alpha\beta} d_{50}/D_{m_\beta}$) $[-]$
T_α	temperature of the α phase $[K]$
u	pore-connectivity parameter in Parker et al. [224] S-k model $[-]$
U_α	internal energy of phase α $[L^2T^{-2}]$
U_i	uniformity index ($U_i = d_{60}/d_{10}$) $[-]$
v	pore-connectivity parameter in Kaluarachchi and Parker [152] S-k model $[-]$

$\mathbf{V}$	aqueous phase Darcy velocity vector $[LT^{-1}]$
V_α	magnitude of α phase Darcy velocity vector $[LT^{-1}]$
$\mathbf{v}_\alpha$	α phase velocity vector $[LT^{-1}]$
v_α	magnitude of α phase velocity vector $[LT^{-1}]$
$\mathbf{x}$	position vector $[L]$
x, y, z	spatial coordinates $[L]$

Greek Letters

α	index of capillarity in van Genuchten [291] p-S model $[M^{-1}LT^2]$
δ	normalized grain size ($\delta = d_{50}/d_M$) $[-]$
ϵ	index of capillarity in Brooks and Corey [40] p-S model $[M^{-1}LT^2]$
$\eta_i(\gamma)$	correlation length of γ in the i-direction $[L]$
γ	dimensionless scaling function $[-]$
λ	empirical parameter in Brooks and Corey [40] p-S-k model $[-]$
μ_α	dynamic viscosity of fluid phase α $[ML^{-1}T^{-1}]$
ν_α	kinematic viscosity of fluid phase α $[L^2T^{-1}]$
ω_α^ι	mass fraction of species ι in the α phase $[-]$
ϕ	porosity $[-]$
ρ_α	α phase density $[ML^{-3}]$
$\sigma^2(\gamma)$	variance of γ $[-]$
θ_α	α phase volume fraction $[-]$

Subscripts

α	phase qualifier
a	aqueous-phase quantity
Δ	quantity evaluated at reversal point on p-S curve
g	gas-phase quantity
ar	irreducible, residual, aqueous-phase quantity
n	nonaqueous- or oelic- phase quantity
ne	entrapped nonaqueous phase quantity
ni	initial-residual nonaqueous-phase quantity – after entrapment but before onset of dissolution
nw	nonwetting-phase quantity
nwt	total nonwetting-phase quantity
s	solid phase quantity
t	total liquid-phase quantity
w	wetting-phase quantity
wr	irreducible, residual, wetting-phase quantity
ws	wetting-phase quantity at $p_{nw-w} = 0$

Superscripts

α	phase qualifier
a	system contains aqueous phase
d	quantity evaluated on main drainage curve of p-S relation
di	quantity corresponds to a drainage to imbibition saturation path change
e	energy
g	system contains gas phase
ι	species qualifier
i	quantity evaluated on main imbibition curve of p-S relation
id	quantity corresponds to a imbibition to drainage saturation path change
n	system contains nonaqueous phase
t	temperature is dependent variable
$*$	scaled or modified parameter

Abbreviations

C	Corey [75,76] p-S-k relations
CMC	critical micelle concentration
Comp	compressibility
BC	Brooks-Corey [40] p-S-k relations
Dim	dimensions
DNAPL	dense nonaqueous-phase liquid (denser than water)
E	Eckberg's [40] S-k relationship
EOS	equations of state
FO	First-order interphase mass transfer relation
h-VG	hysteretic van Genuchten pressure-saturation relation
IMT	interphase mass transfer
Immob	immobile
KP	Kool and Parker [162] p-S-k relations
LB	lattice Boltzmann
LNAPL	light nonaqueous phase liquid (less dense than water)
LP	Lenhard and Parker [178,176] p-S-k relations
LE	local equilibrium
Mob	mobile
NAPL	nonaqueous phase liquid
NWP	nonwetting phase
ns	not specified
ODE	ordinary differential equation
OO	object oriented
P	Parker [223,224] p-S-k relations
PCE	tetrachloroethene

PDE	partial differential equation
PLH	Pope, Lake and Hirasaki p-S-k models as described in [54]
p-S	pressure-saturation relation
p-S-k	pressure-saturation-permeability relations
REV	representative elementary volume
S	Stone scaling for three-phase relative permeability
S-k	saturation-permeability relation
TCE	trichloroethene
t S-k	tabulated saturation-permeability relation
t p-S	tabulated pressure-saturation relation
USDA	United States Department of Agriculture
VG	van Genuchten [291] p-S relation

1 INTRODUCTION

This special journal issue highlights current areas of research for flow and transport phenomena in multiphase systems. We believe that several critical issues deserve particular consideration and that they will require some novel approaches to resolve. Some existing and evolving approaches are encouraging, but much work remains to achieve a mature level of understanding.

The inherent complexity of multiphase systems and the marked heterogeneity that is characteristic of most natural environments [82,60,108], often over multiple scales [79], results in a large and difficult set of problems that must be resolved before accurate simulation of multiphase subsurface transport phenomena can be expected. We know of no work that structures these crucial issues and offers potential approaches for advancement.

The objectives of this work are (1) to provide a conceptual framework for considering the current issues in multiphase flow and transport phenomena; (2) to provide examples from past and recent work that illustrate these issues; and (3) to outline useful approaches that may resolve some of the remaining questions.

It is not our intention to provide a complete review of the vast multiphase literature. Instead, we will present and discuss the significant challenges and promising approaches for resolving them, focusing more on evolving rather than traditional aspects of multiphase systems. Several issues and approaches discussed are novel or in the early stages of development. Because of the breadth of this effort, we cite other sources for details whenever possible. In some cases, no published sources are available, and we include a minimal amount of detail to support our observations herein.

This work is organized with the following framework: (1) standard formulation approach, (2) continuum balance equation issues, (3) constitutive relation issues, (4) stochastic issues, and (5) computational issues.

2 STANDARD FORMULATION APPROACH

2.1 Overview

As a starting point for considering current issues in multiphase flow and transport modeling, we briefly review the standard approach for simulating both fluid flow and species and energy transport in subsurface systems. We consider two aspects of this formulation, which provides the organizing structure for this work: continuum balance equations and closure relations (equations of state and constitutive relations). We use results from models based on this formulation to support our review and comment on alternatives to this traditional approach.

The standard formulation approach is presented in a general manner, relying on fundamental balance equations and functional forms of closure relations, which may appear abstract. In this way, the approach may be applied to as much of the published work as possible. Similar approaches to multiphase model formulation have been taken in the general porous media [25] and enhanced oil recovery literatures [170]. Additional details, a critique of standard approaches, and a discussion of evolving approaches for various aspects of this approach are presented in the sections that follow.

2.2 Continuum balance equations

We first consider a general compositional formulation of multiphase flow and transport for systems comprised of n_p phases and n_s species in which capillarity, interphase mass transfer, and complex phase behavior may be important. We use the term "compositional formulation" to denote that the solution sought includes both the composition and the volumetric fraction of each phase as a function of space and time and not merely the volumetric fraction distribution of each phase in space and time.

A general species mass balance equation for a multiphase, multispecies system is [77,16,3,1,70]

$$\frac{\partial}{\partial t}\left(\theta_\alpha \rho_\alpha \omega_\alpha^\iota\right) = -\nabla \cdot \left(\mathbf{j}_\alpha^\iota + \theta_\alpha \rho_\alpha \omega_\alpha^\iota \mathbf{v}_\alpha\right) + \mathcal{I}_\alpha^\iota + \mathcal{R}_\alpha^\iota + \mathcal{S}_\alpha^\iota \tag{1}$$

where θ is a volume fraction; ρ is a density; ω is a mass fraction; $\mathbf{j}$ is a non-advective flux vector, accounting for dispersive and diffusive transport; $\mathbf{v}$ is a macroscopic phase velocity vector; $\mathcal{I}$ is a general interphase mass transfer term, representing the set of all possible transport pathways between binary groupings of phases; $\mathcal{R}$ is a general species reaction term, representing chemical and biological reactions; $\mathcal{S}$ is a solute source, representing mass added from outside the system; α is a phase qualifier, and ι is a species qualifier.

Summing (1) over all species yields a phase mass balance equation for each phase of the form

$$\frac{\partial}{\partial t}(\theta_\alpha \rho_\alpha) = -\nabla \cdot (\theta_\alpha \rho_\alpha \mathbf{v}_\alpha) + \mathcal{I}_\alpha + \mathcal{S}_\alpha \tag{2}$$

where the following identities

$$\sum_\alpha \theta_\alpha = 1,\ \sum_\alpha \mathcal{I}_\alpha^\iota = 0,\ \sum_\iota \omega_\alpha^\iota = 1,\ \sum_\iota \mathbf{j}_\alpha^\iota = 0,\ \sum_\iota \mathcal{R}_\alpha^\iota = 0 \tag{3}$$

and definitions

$$\sum_\iota \mathcal{I}_\alpha^\iota = \mathcal{I}_\alpha,\ \sum_\iota \mathcal{S}_\alpha^\iota = \mathcal{S}_\alpha \tag{4}$$

are used. We will use phase qualifier $\alpha = n, a, g, s$ to denote a nonaqueous phase liquid (NAPL), and aqueous, gas, and solid phases; other phases are possible as well (e.g., colloidal, microemulsion).

A separate momentum balance equation is not typically included in balance equation formulations of multiphase systems. It is traditional in both the environmental and petroleum literature to substitute a multiphase form of Darcy's law into a flow equation of the form given by (2). While the relationship between this approach and a formal momentum balance approach has been established for the limiting case of low Reynolds number in single-fluid systems [85,300], the common multiphase extension of Darcy's law to multiphase systems is not rigorously based [125,126]. Deviation from Darcy's law at high Reynolds numbers is also well established; the Forchheimer's equation is a well-recognized and useful alternative [75,94].

Most multiphase environmental model formulations published to date do not consider an energy balance, but there are some notable exceptions [98,99,221]. A general energy balance equation about a volume may be stated as

$$\frac{\partial}{\partial t}\left[\theta_\alpha \rho_\alpha \left(U_\alpha + \frac{v_\alpha^2}{2}\right)\right] = -\nabla \cdot \left[\theta_\alpha \rho_\alpha \mathbf{v}_\alpha \left(U_\alpha + \frac{v_\alpha^2}{2}\right)\right] + \nabla \cdot (\theta_\alpha \mathbf{T}_\alpha \cdot \mathbf{v}_\alpha)$$

$$- \nabla \cdot \mathbf{j}_\alpha^e + \theta_\alpha \rho_\alpha \mathbf{g} \cdot \mathbf{v}_\alpha + \mathcal{I}_\alpha^e + \mathcal{R}_\alpha^e + \mathcal{S}_\alpha^e \tag{5}$$

where U is the internal energy; v is the magnitude of the velocity vector; $\mathbf{T}$ is the fluid stress tensor; $\mathbf{j}^e$ is an energy transport vector comprised of dispersive and conductive components; $\mathbf{g}$ is the gravity vector; $\mathcal{I}^e$ represents the exchange of energy across interfaces; $\mathcal{R}^e$ denotes energy produced from reactions; $\mathcal{S}^e$ represents sources of energy, such as radiative; and α is a phase qualifier.

The energy balance equation is often written as a balance equation expressed in terms of temperature for a phase α about a volume [85] as

$$\frac{\partial}{\partial t} \left(\theta_\alpha \rho_\alpha c_\alpha T_\alpha \right) = -\nabla \cdot \left(\mathbf{j}_\alpha^t + \theta_\alpha \rho_\alpha c_\alpha T_\alpha \mathbf{v}_\alpha \right) + \mathcal{I}_\alpha^t + \mathcal{R}_\alpha^t + \mathcal{S}_\alpha^t \tag{6}$$

where c is a specific heat, T is temperature, and the superscript t denotes that temperature is the dependent variable, used to qualify the dispersive and conductive transport term, interphase transfer, reaction, and source terms in the energy equation. The energy balance equation is usually omitted by either explicitly or implicitly assuming the system to be isothermal.

In the most general case, the standard compositional approach results in some unique combination of $n_p n_s$ mass balance equations. It should be noted that the vector quantities $\mathbf{v}_\alpha$ and $\mathbf{j}_\alpha^\iota$, as well as the scalar quantity $\mathcal{I}_\alpha^\iota$ represent multiple unknowns. Even though Equation (3) is used to reduce the number of unknowns, and $\mathcal{S}_\alpha^\iota$ is usually assumed to be specified, many more unknown quantities exist than in balance equations. The actual number depends on the details of interphase mass transfer, reactions, and other considerations discussed below. Solution of the system requires that the balance equations be supplemented with closure relations.

Even in a multiphase system of moderate complexity, which may have three or four phases and several species, system size can become a problem. If each potential balance equation were formulated and solved, modest-sized systems would overwhelm currently available supercomputers—even using the most efficient numerical methods known. Therefore, the full formulation is necessarily simplified. Such simplification requires approximations, the effects of which on the solution are not always clear.

2.3 Closure relations

2.3.1 Focus

Closure of the system of balance equations requires a sufficient number of equations such that all unknowns can be determined. It is accomplished by providing equations of state (EOS) and constitutive relations. We briefly summarize standard formulations for EOS and constitutive relations in order to provide a more complete basis for our review. More detailed summaries of the state of the art for these relations are provided in §4.

2.3.2 Simplifying assumptions

Accurate solution of many current heterogeneous, field-scale multiphase flow and transport problems is beyond our current computational capabilities, since the overall system of mass balance equations requiring solution becomes too large. Thus, the judicious application of simplifying assumptions is both appealing and essential. The issue turns from whether or not such assumptions are required to considering which assumptions should be made and what effect they have on the overall accuracy of the model.

There are several major classes of simplifying assumptions that are made in compositional modeling: (1) the solid phase is immobile; (2) the solid phase is inert; (3) a portion of the components in the system are not of interest and do not affect the solution; (4) the relevant species in a system can be represented by a smaller subset of lumped species; and (5) local chemical equilibrium exists among phases. In addition to these major classes, other minor assumptions are also frequently applied: for example, spatial gradients in liquid densities are assumed to be small in comparison to those in liquid velocities.

The assumption that the solid phase is immobile ($\mathbf{v}_s = 0$) eliminates three unknowns and the need to specify a constitutive relation to express this motion—either elastic or inelastic—in terms of other system variables, such as fluid pressures [85,27]. Including solid phase motion implies that the pore structure changes as a function of time. Significant changes in pore structure will in turn lead to changes in pressure-saturation-permeability (p-S-k) relations; p-S-k relations refer to the concept and the general functional form of interdependence among these three quantities. The appropriate constitutive relations to describe solid phase motion and the resulting changes in p-S-k relations is still an open research question. However, solid phase motion is of secondary importance for shallow, unconfined sand and gravel aquifers.

In situations where geochemical interactions between the solid and fluid phases are insignificant, the solid phase can be assumed inert. This assumption greatly simplifies the analysis of compositional multiphase systems compared to situations in which geochemical reactions are important. When this assumption is applied, the composition of the solid phase is characterized by a lumped species that includes all mineral and natural organic species as well as species related to the NAPL phase. The assumption of an essentially inert solid phase is a necessary condition but not sufficient to ensure that the solid phase is immobile.

By ignoring species that have a minimal effect on the species of interest, the total number of unknowns and balance equations requiring solution can be reduced. Following are some common cases in which such an assumption may be applied: the gas phase can be adequately characterized by only a single lumped species and a volatile organic species—and oxygen if needed for a reaction relation; some species do not sorb substantially to the solid phase; and some species are considered insoluble in the aqueous phase.

Species lumping is a simplifying procedure whereby the total number of species is reduced by combining species with similar physicochemical characteristics into so-called pseudospecies [170]. Pseudospecies selection in the oil industry is typically based on results from laboratory experiments and a Gibbs free energy minimization procedure. This procedure has been used to reduce complex hydrocarbon systems that contain more than 100 species to systems that are adequately represented by 10–50 pseudospecies. Such approaches may also be used to simplify systems that contain a NAPL phase consisting of many fewer species.

The assumption of local chemical equilibrium is common for compositional multiphase modeling [3], but its validity has been frequently questioned [201,192,239,236,237,235,202,20
It relies on the reasoning that the time required to approach local chemical equilibrium is short in comparison to the rate at which transport occurs. The assumption of local equilibrium presupposes that the solute mass fraction, or concentration, in one phase implies the mass fraction in all other phases. When local equilibrium among phases is assumed, species transport equations may be summed over all phases and solved in terms of a single mass fraction.

2.3.3 Equations of state

EOS express the equilibrium relationship between pressure, volume, and temperature [170,196]; these relations are typically based on thermodynamic models that are empirical in origin [243]. Recent advances suggest that statistical mechanics and molecular dynamics may become increasingly important for establishing such relations, but the EOS commonly used in the hydrologic and petroleum literature are well-established relations that are adequate for most systems.

The molar volume behavior of pure liquid-vapor systems over a wide range of pressures and temperatures is often described using EOS that express pressure as a cubic function of molar volume [243,170]. These methods have been extended to complex mixtures for volume relationships and other thermodynamic system properties [243].

A general functional form for an EOS is

$$\rho_\alpha = \rho_\alpha(p_\alpha, T_\alpha, \omega_\alpha^\iota), \text{ for } \iota = 1, ..., n_s \tag{7}$$

where p_α is the pressure of the α phase. Note that p_α does not appear in the original balance equations, although all other quantities do. Therefore, adding EOS introduces an equivalent number of unknowns and new equations. However, these same unknowns also appear in the traditional momentum equations (extended form of Darcy's law).

For systems in which composition changes are small (e.g., dilute systems), EOS may be expressed by the functional form

$$\rho_\alpha = \rho_\alpha(p_\alpha, T_\alpha) \tag{8}$$

For systems that are also in local thermal equilibrium, EOS may be expressed by

$$\rho_\alpha = \rho_\alpha(p_\alpha, T) \tag{9}$$

or for dilute, isothermal systems by

$$\rho_\alpha = \rho_\alpha(p_\alpha) \tag{10}$$

where EOS are specified at a constant composition and temperature.

2.3.4 Constitutive relations

Typical constitutive relations for compositional multiphase systems are p-S-k, interphase mass transfer, and solute reaction relations. Interphase mass transfer refers to the movement of mass from one phase to another, with the total number of these relations determined by the number of phases present and the wetting properties of the media. Reactions may be of either a reversible (e.g., inorganic speciation) or irreversible nature (e.g., organic chemical transformation) and be chemical or biochemical in origin.

Constitutive relationships are approximate and often uncertain. While derivations of these relationships from first principles are theoretically possible in some cases, they are usually empirically based. EOS and constitutive relations increase both the number of equations and the total number of unknown quantities; they do, however, supply sufficient information to close the system of equations by expressing unknown quantities in the balance equations in terms of accessible parameters.

Some common constitutive models lead to systems of mass balance equations that must be solved at some smaller (micro) scale to resolve some of the unknowns (e.g., [227]), further expanding the number of equations requiring solution. Such approaches are computationally demanding but may be needed in certain cases to provide an accurate description of phenomena occurring at a smaller scale than that being simulated.

2.4 Model Formulation Summary

In summary, the standard steps taken to formulate a compositional multiphase model include specification of the following:

(i) the minimum set of balance equations needed to describe the behavior of the system of interest after applying some reasonable set of simplifying assumptions to the system regarding the relevant species and their behavior;
(ii) a multiphase form of Darcy's law in a mass balance equation to specify fluid velocities as a function of fluid pressures and saturations;
(iii) EOS, supplemented by the thermodynamic relations needed to resolve composition effects on system state;
(iv) relations among fluid pressures, saturations, and permeabilities for flow through the media;
(v) relations for diffusion, dispersion, and conduction (if energy transport is considered);
(vi) thermodynamic equilibrium and mass transfer rate relations for all relevant binary phase-species combinations;
(vii) all relevant reversible and irreversible reaction relations;
(viii) all sources and sinks; and
(ix) auxiliary conditions needed to form a well-posed problem.

Within this general framework, many specific examples are possible, ranging from relatively simple cases such as Richards' equation or two-phase flow (e.g., to describe water infiltration in the unsaturated zone) to compositional three-fluid-phase flow and species transport for nonisothermal systems (e.g., to describe steam flooding recovery of a NAPL). We summarize some previous efforts to model multiphase systems in the next section.

2.5 Flow and Transport Models

Notable multiphase flow and transport models published to date are summarized in Tables 1 and 2. Table 1 is a listing of multiphase flow models, meaning that phase composition is not included in the formulation. Table 2 is a listing of models for both flow and transport, meaning that phase composition is included in the formulation. These tables are intended to be illustrative of recent approaches taken in environmental research, but they are not a complete listing of multiphase models in the field. A few entries from the petroleum literature are included as well. From these tables we can note several common trends in multiphase flow and transport modeling of environmental systems:

(i) several two- and three-fluid-phase flow models have been published for both two and three spatial dimension systems;
(ii) all of the cited multiphase flow models simulate nonhysteretic p-S-k relations;
(iii) most multiphase flow and transport models in the environmental field use nonhysteretic forms of the p-S-k relations;
(iv) most models assume local equilibrium, but some first-order mass transfer formulations have been presented; and
(v) typical reported simulation sizes are on the order of 10^2 to 10^4 nodes (data not shown in table).

Table 1
Multiphase flow models, no transport

	Flowing		Constitutive Relations	
Work	Phases [a]	Dimensions	Compressibility	p-S-k[b]
[102]	a, n	2	a, n, s	BC
[103]	a, n	3	a, n, s	BC
[167,168]	a, n	2	none	BC
[139]	a, g, n	3	a, g, n, s	VG/S,t S-k

[a] phases: a=aqueous, n=NAPL/oelic, g=gaseous, s=solid

[b] when present, a slash indicates p-S/S-k

BC=Brooks and Corey-type p-S-k relations [40]; VG=van Genuchten p-S relation [183]; S=Stone's [268] three-phase extensions for p-S-k relations; and t S-k = tabulated S-k.

Table 2
Multiphase flow and transport models

	Mob./Immob.		Species		Constitutive Relations		
Work	Phases [a]	n_s	Into	Dim.	Comp.	p-S-k [b]	IMT [c]
[233]	$a, m, n/s$	6	a, m, n, s	1	ns	other/t S-k	LE
[310]	a, g, n	17	a, g, n	1	a, g, n	other	LE
[3,4]	$a, n_1, n_2/g, s$	1	a, g, n_1	1	a, n_1, n_2	Co	LE
[247,54]	$a, m, n/s$	19	a, m, n, s	3	a, m, n, s	PLH	LE
[73,17]	$a/g, n, s$	8	a, g, n, s	1	none	other	LE
[106]	$a, n/g$	1	a, g, n	2	s	other/t S-k	LE
[259]	$a, g/n$	1	a, g	2	g	VG/BC	FO
[30]	$a, m, n/s$	32	a, m, n, s	3	a, n, g, s	BC	LE
[151]	$a, n/g, s$	2	a, g, n, s	2	a, g, n	P	LE
[98,99]	$a, g, n/s$	3	a, g, n, s	1	a, g, n	VG/S,C	LE
[116]	a, n	2	a, n	2	none	h-VG/KP	FO
[193]	a, n	1	a, n	2	a, n	VG/P	FO
[7]	$a, g, n/s$	ns	a, g, n, s	3	a, g, n, s	C/P	LE
[260,261]	a, g, n	3	a, g, n	3	a, g, n	BC,VG/BC,P	LE
[42,86]	$a, m, n/s$	4	a, m, n, s	3	none	BC	LE
[155]	a, m, g, n	19	a, m, g, n	3	a, g, n	VG/other	LE
[242]	any 2	3	a, g, n	2	a, n, g	VG/P	LE
[288]	a, g, n	1	a, g, n	2	a, g, n	h-VG/LP	LE
[258]	a, n_1, n_2	3	a, n_1, n_2	1	none	t p-S/E	LE
[301,175]	$a, n/g, s$	1	a, g, n, s	3	ns	h-VG,LP	LE

[a] phases: a=aqueous, n=NAPL/oleic, g=gaseous, m=(micro-)emulsion and s=solid; [b] when present, a slash indicates p-S/S-k; [c] mass transfer types, LE=local equilibrium and FO=first-order; t p-S = tabulated p-S, t S-k = tabulated S-k; ns = Not Specified; PLH, VG, C, BC, P, Co, LP, KP, S, and E refer to specific p-S-k data or relations and are defined in the Notation.

3 CONTINUUM BALANCE EQUATION ISSUES

3.1 Overview

Use of the traditional balance equation approach outlined above leaves unresolved issues. For example, the above balance equations must be supplemented to describe important aspects of multiphase flow and transport phenomena in some complex systems. In addition, more complete systems of balance equations are being developed than those used in standard formulation approaches.

3.2 Complex Systems

The simulation of complex systems is an important, evolving area of multiphase flow and transport modeling. Following are some examples of such systems:

(i) multiphase surfactant systems in which a significant mass of surfactant is added to a system and is subject to bulk movement and distribution among the phases present;
(ii) multiphase cosolvent systems in which a significant fraction of the aqueous phase consists of a miscible species, such as an alcohol; and
(iii) nonisothermal systems in which significant changes in temperature occur.

Systems of this nature are important for environmental applications because developing so-called enhanced remediation methods is desirable. These methods are intended to be more effective than traditional methods of subsurface restoration, such as pump-and-treat [241,143]. The common feature of each of these complex systems is that they significantly affect many aspects of the physicochemical behavior of a multiphase system.

While such systems have been routinely considered in the oil industry under the rubric of enhanced oil recovery [170], the modeling of such systems in the environmental field is much more recent [42]. It is also important to recognize that there are important differences in motivation between the two fields, leaving many unresolved issues for environmental applications.

Surfactant systems are especially significant because they require the consideration of balance equations for any additional phase(s). The standard approach for such systems is to formulate balance equations for a microemulsion phase in addition to the other phases present [42]. This complexity, together with the dramatic effects of surfactants on constitutive relations, leaves many unresolved issues [42,228,2,229].

Common approaches for modeling surfactant systems fail to describe another potentially important transport mechanism: macroemulsion transport. Macroemulsions have a characteristic dimension larger than one micron and are either unstable or mesostable, while microemulsions have a characteristic dimension smaller than one micron and are thermodynamically stable [188,220,217]. If macroemulsion transport is important, balance equations will need to be formulated and solved to describe such cases accurately.

We have recently conducted a series of experiments in which residual tetrachloroethene (tetrachloroethene, PCE) was flushed from uniform glass bead media using 10 and 100 g/L Triton X-100 in water feed solutions [217]. Results showed that up to 30% of the PCE originally present in the solution was transported out of 20-cm long columns as a macroemulsion phase. To model such systems accurately, balance equation formulations other than those used to date in the environmental field will be required.

In other experiments conducted by our group, surfactant flushing was examined in a two-dimensional flow cell, 15.0 cm $\times$ 0.334 cm $\times$ 20.2 cm (length $\times$ width $\times$ height) packed with glass beads, $d_{50} = 0.078$ cm. Residual PCE trapped in the otherwise water-saturated porous medium was removed with a water flush ($V_a = 1.7$ m/day) containing 10 g/L of a 1:1 mixture of sodium diamyl sulfosuccinate and sodium dioctyl sulfosuccinate. Although 68% of the PCE in the porous medium left the system as mobilized NAPL, 15% was transported out of the system in macroemulsions and 17% either in microemulsions or dissolved in the aqueous phase. Macroemulsion transport was important just as in the column experiments noted above. As the mobilized PCE moved downward through the apparatus because of gravity, it did not form a continuous NAPL phase over many contiguous pores. Instead, PCE predominantly moved as isolated droplets before forming a NAPL bank at the bottom of the cell. This transport mechanism is shown in Figure 1. The movement of mobilized PCE as isolated droplets violates the assumption first made by Richards [244] that disconnected fluid cannot flow through a pore network. While compositional models can account for this movement through appropriately defined relative permeabilities [15,14], experimental studies in pore networks indicate that these relative permeabilities will be a function of the flow regime in addition to phase saturations [14]. Avram and Payatakes [14] conclude that the traditional description of fluid flow is quite unsatisfactory for this situation: the parameters that are used to predict the flow rate, i.e., relative permeabilities, are strong functions of the flow rates themselves.

3.3 Evolving Approaches

Gray and Hassanizadeh have pointed out several inconsistencies in the standard formulation approach, especially for the cases of flow in the unsaturated zone [114,115] and two-phase flow [125,126]:

(i) the constitutive theory used to close the traditional balance equations, such as Darcy's law, has evolved as a series of extensions to a relationship that was empirically derived for a single-phase system;
(ii) microscopic thermodynamic notions are often used to discuss macroscopic systems in which they are no longer meaningful (e.g., contact angle);

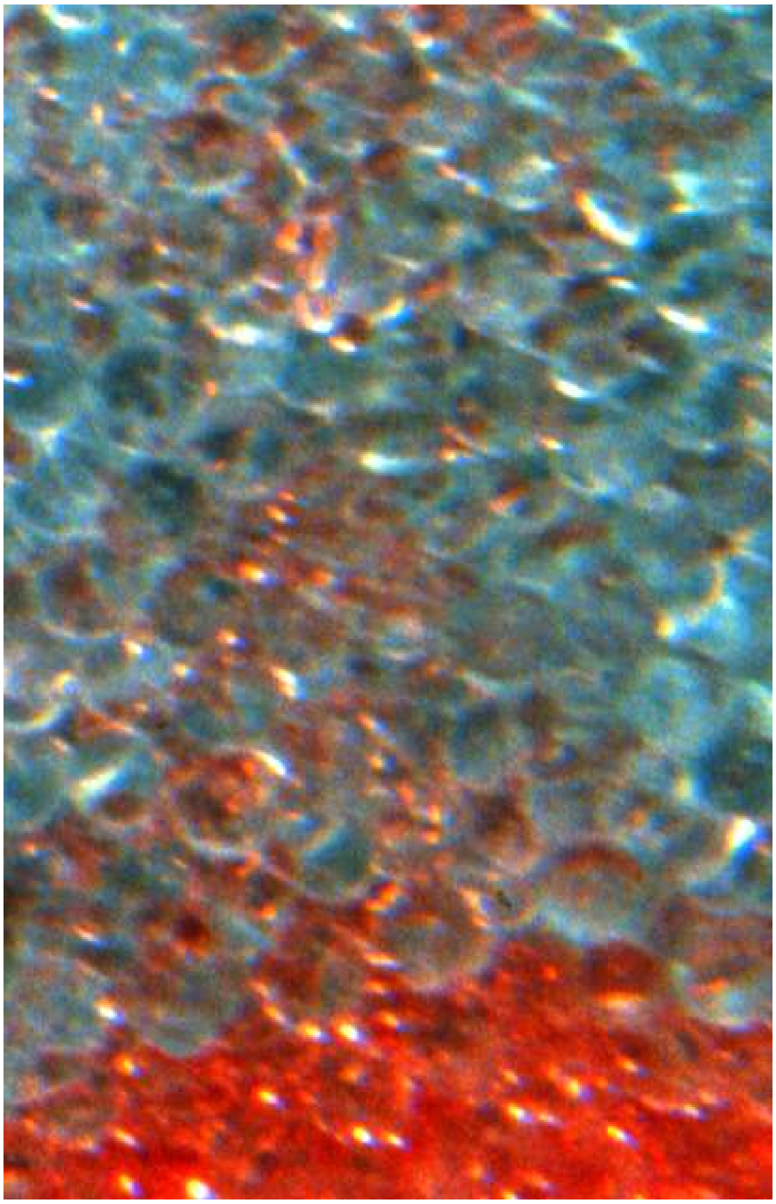


Fig. 1. Gravity-driven mobilization of PCE ganglia while flushing with a surfactant solution.

(iii) the traditional quasiequilibrium approach may be inadequate;
(iv) there is an inconsistency between traditional EOS (e.g., §2.3.3) and expressions for saturation dependence on capillary pressure; and
(v) the different nature of the forces (e.g., existence of preferential wetting of the solid phase) in a multiphase system compared to those in a single-phase system are not represented in current formulations. This discrepancy may be observed by examining the static equilibrium equation forms typically used.

A more complete approach can be based on integration over a representative elementary region to produce mass, momentum, and energy balance equations that are formulated about volumes, interfacial areas between each pair of phases, and contact lines for all unique three-phase intersections [122–124,112,114,115,126]. These balance equations are supplemented with constitutive relations, which are constrained by an entropy inequality relation, the second law of thermodynamics, and certain other equilibrium thermodynamic relations [71,124].

While this approach is theoretically appealing and promises to resolve the inconsistencies in current compositional modeling approaches, much more remains to be done. These formal averaging approaches lead to large systems of equations, which must be substantially simplified in order to be tractable with currently available computational resources. The need to simplify the system of equations resulting from traditional approaches was pointed out in the previous section; this same concern is even more important for formal averaging approaches.

Consider the case of formal averaging applied to two-fluid-phase flow [126,113]. The following steps are taken:

(i) mass, momentum, and energy conservation equations are written about a representative elementary volume (REV) for each phase—leading to 15 equations in 17 primary unknowns;
(ii) the volume balance laws are supplemented by constitutive relations, leading to an additional 63 secondary quantities;
(iii) mass, momentum, and energy conservation equations are written about representative elementary areas (REA) for all three phase-pair combinations, resulting in an additional 15 equations and 18 additional primary unknowns;
(iv) the area balance laws are supplemented by constitutive relations, leading to an additional 48 secondary quantities; and
(v) the overall system of 30 conservation equations in 35 primary unknowns and 111 secondary quantities is simplified using entropy inequality constraints.

The above description of a relatively simple multiphase system clearly demonstrates that formal averaging introduces considerable complexity into the formulation, which has not been fully developed and tested. Indeed, much more is required to bring a consistent thermodynamic basis to multiphase flow and species transport in porous media. Experimental work will be extremely difficult, and computational experiments will play a significant role; some preliminary efforts have been made to investigate relationships among fluid saturation, capillary pressure, and interfacial area [113].

While on the surface, the complexity of formal averaging approaches appears overwhelming for any realistic compositional multiphase problem, the complex, computationally demanding approaches of one era often become the guiding principles of the next. We believe that the application of these approaches promises an improved understanding of complex systems. For example, Cushman and his co-workers have already demonstrated this potential for improvement by using formal averaging methods to derive some enlightening results for swelling clay systems [5].

4 CONSTITUTIVE RELATION ISSUES

4.1 Overview

Compositional multiphase models require multiple constitutive relations to close the system of equations. Constitutive relations serve to describe the essential features of a given system at the scale of interest while decreasing the number of variables needed to describe it if one started from a smaller scale. In mathematical terms, constitutive relations should serve as a projection operator from a smaller scale to the scale of interest, implying minimal loss of important information and mathematical rigor. In reality, for complex multiphase systems, it would be more accurate to refer to the current practice as "scaling relations," since significant approximation is usually involved.

Since the purpose of constitutive relations is to reduce the number of unknowns through scaling essential system behavior from smaller scales to that of interest, several features of these relationships are important: (1) the range of scales of concern, (2) the scale and conditions for which the relations were developed, (3) the scale of measurement and parameter identification, (4) the scale of applications, and (5) the mathematical consistency of the relations.

While constitutive relations can be considered entirely within the conceptual framework of scaling relations, a detailed investigation must be linked to the experimental basis on which these observations are founded and the manner in which these relations are applied. In the following sections, we do the following:

(i) consider issues of scale that relate to porous media systems in general;
(ii) discuss aspects of p-S-k, aqueous-solid phase mass transfer, Nonaqueous-aqueous phase mass transfer, and mass transfer involving a gas phase;
(iii) summarize issues inherent in the experimental observations of multiphase systems; and
(iv) discuss evolving methods for the development of constitutive relations.

Porous media that occur in natural systems typically have a wide distribution of grain sizes, falling within the broad range of 10^{-6} to 10^{-1} m [104]. For most natural porous materials, a wide range of grain sizes results in a similarly wide range of pore sizes and a complex pore morphology [94]. While it is desirable to describe fluid flow and species transport in terms of this complex morphology, it is generally impossible to describe this pore structure. Even if it could be described, the resulting system of equations could not be solved for any system of more than a few thousand pores. Therefore, it is necessary to utilize constitutive relations for porous media systems that do not rely on knowledge of detailed pore morphology.

For multiphase systems, constitutive relations are usually derived from laboratory experiments performed at a scale of 10^{-2} to 10^{0} m. These experiments often use procedures that result in a solid phase of considerably greater uniformity than the natural systems of most relevance. On the other hand, the actual systems of concern have length scales that are often on the order of 10^{1} to 10^{3} m for environmental applications and much larger for some petroleum applications. This observation, along with the previous discussion concerning the effects of heterogeneity on multiphase flow and transport phenomena, leads immediately to two conclusions: (1) natural multiphase systems cannot possibly be characterized at a scale that is consistent with the existing constitutive theory and should thus be considered in a stochastic framework; and (2) it is necessary to determine appropriate scaling relationships in order to develop meaningful constitutive relationships at the target scales of interest even if complete information of the system exists.

Natural systems are marked by uncertainty in media conditions and hence parameters in constitutive relations. Moreover, significant differences usually exist among scales at which constitutive relations were developed, parameters are measured, and important properties of a system vary. Given these observations, there seems to be no question that natural multiphase systems should be considered stochastic in nature. We treat this very important case in §5.

However, one can approach this problem from a different perspective. Consider the case in which variability exists in the media (and hence parameters in constitutive relations) and complete information is available for the system parameters; this case could correspond to a well-characterized laboratory system or a hypothetical case represented by a realization of a correlated random field(s). Further, assume that variability occurs at a scale that is finer than the discretization level that is possible to use with a numerical multiphase flow and transport model. In this case, it is necessary to develop and parameterize the constitutive relations at the grid block scale that adequately represent the effects of the smaller scale underlying system. We call this type of scaling "deterministic scaling" or "upscaling."

Expressing constitutive relations at scales larger than those for which they were developed is essential; it is not computationally feasible at this time to discretize a compositional multiphase model at a scale consistent with that at which the constitutive relations were developed. So, just as scaling relationships are required in order to move from the pore scale to a laboratory scale where constitutive theory is typically developed, it should be expected that such relationships are also required to move from the laboratory scale to larger scales. It is unreasonable to apply the constitutive theory developed at one scale for homogeneous systems to heterogeneous systems that are several orders of magnitude larger (e.g., [79,80]), yet it is common practice to do so for modeling multiphase systems. Further, consideration must be given to variations that exist among the scales of natural variability, parameter measurements, and model discretization [120,79].

While the need to bridge the gap between the scale at which constitutive relations are developed, parameters are measured, and models are discretized is clear, the solutions are not. In the sections that follow, we comment on approaches currently in use for p-S-k relations, and we demonstrate that scaling issues are of central importance for Nonaqueous-aqueous phase mass transfer, although these issues have not been considered to date. Indeed, scaling of mass transfer and reaction relations in general is an area with many open questions and abundant opportunities for advancements.

4.3 Pressure-saturation-permeability

4.3.1 Considerations

p-S-k relations are of central importance for modeling multiphase systems. These relations and their dependence on pore structure and media and fluid characteristics have been the topic of extensive investigations (e.g., [75,94]). It is also an area in which similarities and significant differences can be seen between the common approaches and needs of petroleum reservoir simulation and those of environmental applications. Similarities result from commonalities that exist in the operative physical and chemical phenomena and the parametric modeling approach used in both fields. Differences arise in large measure because of the need to consider lower values of NAPL saturation for many environmental applications, values that are too low to be of economic significance for most petroleum applications. Petroleum reservoir applications also focus primarily on the imbibition of the aqueous phase during oil removal, while changes in direction of fluid movement frequently occur in environmental applications.

With these general similarities and differences noted, we consider the following aspects of p-S-k relations: (1) modeling approaches, (2) experimental bases, (3) nonwetting phase (NWP) entrapment, (4) interfacial spreading and mixed wettability, (5) dynamics, (6) anisotropy, (7) mathematical inconsistencies, and (8) scaling.

4.3.2 Modeling approaches

Modeling of p-S-k relations may be subdivided into the following components: (1) pressure-saturation (p-S) models, (2) saturation-permeability (S-k) models, and (3) hysteresis models. We consider these three classes of models in turn, and we address differences for modeling two- and three-fluid-phase systems.

Table 3 presents three frequently used p-S models in environmental applications. Fundamentally, these models describe the capillarity of the system—the role that the curvature in the interfaces separating the various bulk phases plays in determining the physicochemical state of the system [94]. The Brooks-Corey (BC) [40] and van Genuchten (VG) [291] models are empirical relationships that relate the capillary pressure—the difference in pressure between two fluid phases in a porous medium—to the saturation of these phases. These models are functions of porous media and fluid properties, and thus the model parameters (e.g., ϵ and λ for BC) vary depending on the porous medium.

Fluid and solid properties affecting the system interfaces, in particular wettability and interfacial tension, will alter the BC and VG models and are discussed below. In addition, an important feature of the p-S relation that is frequently neglected in numerical simulators is the dependence of p-S on system history. This history dependence is not accounted for in the models in Table 3, but it has been incorporated in extensions to these basic models and is also discussed below.

While the VG and BC models were originally developed for systems with two fluid phases, Leverett [180] was the first to suggest that two-phase p-S relationships could be extended to three-phase systems. Leverett assumed that the total liquid saturation, $S_t = S_a + S_n$, was a function of the interfacial curvature at the gas-liquid interface, independent of the composition of fluids comprising the liquid in the multiphase system. Using this assumption and others, Parker et al. [224] extended the VG model to three fluid phases; this nonhysteretic model is also presented in Table 3.

The effective permeability is the permeability of the medium to the flow of a specific phase. It is defined as $k_\alpha = k k_{r\alpha}$, where k_α is the effective permeability

Table 3
p-S models

Work	Formulation	Comments
Two-phase p-S models.		
[291]	$\bar{S}_w = [1+(\alpha p_{nw-w})^n]^{-m} \quad p_{nw-w} > 0$ $\bar{S}_w = 1 \quad p_{nw-w} \leq 0$ where : $\bar{S}_w = \frac{S_w - S_{wr}}{S_{ws} - S_{wr}}$	van Genuchten model for main drainage p-S.
[40]	$\bar{S}_w = (\epsilon p_{nw-w})^{-\lambda} \quad \epsilon p_{nw-w} > 1$ $\bar{S}_w = 1 \quad \epsilon p_{nw-w} \leq 1$	Brooks and Corey model for main drainage p-S.
Three-phase p-S model for a, g, and n phases.		
[224]	$\bar{S}_a^{gna} = [1+(\alpha_{na} p_{n-a})^n]^{-m} \quad p_{n-a} > 0$ $\bar{S}_a^{gna} = 1 \quad p_{n-a} \leq 0$ $\bar{S}_t^{gna} = [1+(\alpha_{gn} p_{g-n})^n]^{-m} \quad p_{g-n} > 0$ $\bar{S}_t^{gna} = 1 \quad p_{g-n} \leq 0$ where : $\bar{S}_a^{gna} = \frac{S_a^{gna} - S_{ar}}{1 - S_{ar}}$ $\bar{S}_t^{gna} = \frac{S_t^{gna} - S_{ar}}{1 - S_{ar}}$ $S_t^{gna} = S_a^{gna} + S_n^{gna}$	Parker et al. model. Aqueous phase wetting.

S_w is the wetting phase saturation; S_{wr} is the irreducible, residual wetting phase saturation; S_{ws} is the wetting phase saturation at $p_{nw-w} = 0$; p_{nw-w} is the difference between the nonwetting and wetting phase pressures; α, ϵ, n, m, and λ are empirical model parameters; subsripts g, n, and a denote gas, NAPL, and aqueous phase quantities; superscripts g, n, and a denote gas, NAPL, and aqueous phases present in system.

for the α phase, k is the intrinsic permeability of the media, and $k_{r\alpha}$ is the relative permeability of the α phase. S-k relations are typically expressed in terms of $k_{r\alpha}$, and Table 4 presents a few representative models.

The Corey [74] two-phase S-k relations in Table 4 were determined from experiments with a variety of porous rocks. Similar empirical relations have been used frequently in petroleum reservoir simulators (e.g., [310]).

The Mualem [209] and Parker et al. [224] two-phase S-k relations in Table 4 are statistical models and were developed with the objective of including the physical properties of the porous medium, primarily pore-size distribution, through measured p-S relations. An example of this approach is the model by Brooks and Corey [40], which was obtained by coupling the Burdine statistical

Table 4
S-k models

Work	Formulation	Comments
Two-phase S-k models.		
[74]	$k_{rw} = \bar{S}_w^4$ $k_{rnw} = \left(1-\bar{S}_w\right)^2\left(1-\bar{S}_w^2\right)$	Corey model.
[40]	$k_{rw} = \bar{S}_w^{l+1+\frac{2}{\lambda}}$ $k_{rnw} = \left(1-\bar{S}_w\right)^l\left[1-\bar{S}_w^{1+\frac{2}{\lambda}}\right]$	Brooks and Corey model.
[209]	$k_{rw} = \bar{S}_w^u\left[\frac{\int_0^{\bar{S}_w}\frac{d\bar{S}_w}{p_{nw-w}(\bar{S}_w)}}{\int_0^1\frac{d\bar{S}_w}{p_{nw-w}(\bar{S}_w)}}\right]^2$	Mualem model.
[224]	$k_{rnw} = \bar{S}_{nw}^u\left[\frac{\int_{\bar{S}_w}^1\frac{d\bar{S}_w}{p_{nw-w}(\bar{S}_w)}}{\int_0^1\frac{d\bar{S}_w}{p_{nw-w}(\bar{S}_w)}}\right]^2$	Parker et al. model – Mualem model extended to NWP.
Three-phase S-k model.		
[152]	$k_{ra} = \bar{S}_a^v\left[1-\left(1-\bar{S}_a^{\frac{1}{m}}\right)^m\right]^2$ $k_{rn} = \left(\bar{S}_t-\hat{S}_a\right)^v\left[\left(1-\hat{S}_a^{\frac{1}{m}}\right)^m-\left(1-\bar{S}_t^{\frac{1}{m}}\right)^m\right]^2$ $k_{rg} = \left(1-\bar{S}_t\right)^v\left[\left(1-\bar{S}_t^{\frac{1}{m}}\right)^m\right]^2$ where : $\bar{S}_t = \frac{S_n+S_a-S_{ar}}{1-S_{ar}}$ $\hat{S}_a = \bar{S}_a + \frac{S_{ne}}{1-S_{ar}}$ $\bar{S}_a = \frac{S_a-S_{ar}}{1-S_{ar}}$	Kaluarachchi and Parker model. Trapped NAPL and no trapped gas.

k_{rw}, k_{rnw}, k_{ra}, k_{rn}, k_{rg} are the relative permeabilities to the wetting, nonwetting, aqueous, NAPL, and gas phases; $\bar{S}_w$ and $\bar{S}_a$ are the effective wetting phase and aqeuous phase saturations; S_{ar} is the irreducible, residual aqueous phase saturation; S_{ne} is the entrapped nonaqueous phase saturation; and l, m, u, v, and λ are model parameters.

model [50] with the BC p-S relation.

Because of the significant difficulty in measuring three-phase S-k relations, many investigators have proposed methods for predicting three-phase S-k val-

Table 5
Hysteretic p-S models

Work	Formulation	Comments
Two-phase. Separate VG model used for main drainage and main imbibition curves. The following relations are used for scanning curves in conjunction with the VG model.		
[253,161]	$S_w^* = \frac{S_{w\Delta} - S_{wr}[1-\bar{S}_w^d(p_{nw-w,\Delta})]}{\bar{S}_w^d(p_{nw-w,\Delta})}$ $S_{wr}^* = \frac{S_{w\Delta} - S_{ws}\bar{S}_w^i(p_{nw-w,\Delta})}{1-\bar{S}_w^i(p_{nw-w,\Delta})}$	Scott et al. model. S_w^* replaces S_{ws} in denominator for $\bar{S}_w$ for drainage scanning paths. S_{wr}^* replaces S_{wr} in denominator for $\bar{S}_w$ for imbibition scanning paths. No entrapped nonwetting phase.
[179]	$\tilde{S}_w\left(p_{nw-w}\right) =$ $\frac{\left(\tilde{S}_w^i(p_{nw-w}) - \tilde{S}_w^i\left(p_{nw-w,\Delta}^{id}\right)\right)\left(\tilde{S}_{w\Delta}^{di} - \tilde{S}_{w\Delta}^{id}\right)}{\tilde{S}_w^i\left(p_{nw-w,\Delta}^{di}\right) - \tilde{S}_w^i\left(p_{nw-w,\Delta}^{id}\right)} + \tilde{S}_{w\Delta}^{id}$	Lenhard et al. model. $\tilde{S}_w$ replaces $\bar{S}_w$ in VG model. This expression used for imbibition scanning curves with an analogous expression used for drainage scanning curves.
	where : $\tilde{S}_w = \bar{S}_w + \frac{S_{nwt}}{1-S_{wr}}$	

Δ indicates quantity evaluated at reversal point of flow direction; d indicates quantity evaluated on main drainage curve; i indicates quantity evaluated on main imbibition curve; di and id indicate quantity evaluated on drainage to imbibition or imbibition to drainage path; S_w is the wetting phase saturation; S_{wr} is the irreducible, residual wetting phase residual saturation; S_{nwt} is the total nonwetting phase saturation; S_{ws} is the wetting phase saturation at $p_{nw-w} = 0$; and p_{nw-w} is the difference between the nonwetting and wetting phase pressures.

ues from two-phase measurements [268,269,16]. Alternatively, two-phase S-k models have been extended to three phases; the model of Kaluarachchi and Parker [152] in Table 4 is one example and is based on the VG p-S relation and the Mualem S-k model.

Hysteresis in p-S and S-k relations arises because of (1) pore-scale effects associated with contact angle hysteresis and what has been termed the "ink-bottle" effect, and (2) nonwetting fluid entrapment during saturation path reversals [179]. Two hysteretic p-S models are shown in Table 5 for a two-phase system. The Scott et al. [253] model was combined with the VG model by Kool and Parker [161]: a set of VG model parameters is fitted to the main drainage curve and a second set of parameters to the main imbibition curve for the wetting fluid. For flow path reversals that occur between the endpoints of these curves, the VG model is used but with the wetting phase saturation at zero capillary pressure, S_{ws}, and the irreducible wetting phase saturation, S_{wr}, defined based on the system history. The model by Scott et al. does not account for NWP entrapment.

The model by Lenhard et al. [179] includes both pore-scale effects and NWP entrapment and is considerably more complicated. Incorporation of NWP entrapment requires a submodel (see §§4.3.4). .Here as well, the VG model is used for the main drainage and imbibition curves. Saturation paths that fall between these two curves are referred to as scanning curves, and alternative expressions are used: the equation given in Table 5 is for the situation where the wetting fluid imbibes into the porous medium along a scanning curve.

Just as for nonhysteretic models, three-phase hysteretic models for p-S have been extended from two-phase models [223,179]. Hysteretic S-k relations have also been developed, most notably by Lenhard and Parker [177]. By coupling hysteretic p-S relations with a generalization of the Mualem S-k model corrected for fluid entrapment effects, Lenhard and Parker [177] were able to account for both pore-scale effects and NWP entrapment. In addition to this work and those noted above, other investigators in hydrology [279,234,280,207,208,183,130] and petroleum reservoir engineering [211,172,263,251] have made noteworthy efforts to model hysteresis in p-S-k relations.

In both environmental restoration and petroleum reservoir engineering, nonhysteretic p-S and S-k relations are the norm because they are less computationally demanding and require fewer data. Neglecting hysteresis may be appropriate for many applications in petroleum reservoir engineering, because aqueous phase displacement of oil without flow reversal is a common scenario. However, multiple changes in flow direction occurs frequently in environmental restoration. Lenhard [174] showed that if hysteresis was neglected in algorithms to predict subsurface fluid saturation distributions before and after contamination by a NAPL, the resulting error in fluid saturation was as great as half of the pore volume. Errors of this magnitude would significantly affect predicted permeabilities and thus model-predicted fluid movement.

Many different modeling combinations can be developed by combining different p-S, S-k, and hysteresis modeling approaches. Because these p-S-k relations are often minimally calibrated, results produced using these models can only yield an approximate simulation of the process being modeled. Even if hysteretic p-S-k relations were measured extensively for a specific multiphase system, several aspects would warrant additional investigation: (1) experimental bases for developing p-S-k relations, (2) the treatment of NWP entrapment, (3) the effect of interfacial spreading and mixed wettability, (4) dynamics, (5) anisotropic media, (6) the mathematical inconsistency of the currently used relations, and (7) scaling. Because many papers have been published on p-S-k relations, our intent is not to provide an exhaustive review of these issues. Rather, we use the literature to highlight and support some of the major issues involving these constitutive relations.

4.3.3 Experimental bases

Laboratory scale p-S-k relations for homogeneous porous media are a common component of compositional simulators. Yet few multiphase experimental studies have characterized hysteretic p-S-k relations and used these relationships in a multiphase flow and transport simulator to predict and compare to results from well-characterized experiments. Rather, a minimal measurement approach is often used to define hysteretic p-S-k relations for a water-wet, three-fluid-phase system, typically consisting of the following:

(i) measuring the main gas-aqueous phase drainage p-S relation and the main gas-aqueous phase imbibition p-S relation, yielding the maximum initial-residual NWP saturation;
(ii) measuring the saturated aqueous phase conductivity and estimating the S-k relation from the p-S relation;
(iii) estimating other two-phase p-S relations by scaling according to interfacial tension and contact angle, or measuring gas-NAPL, NAPL-aqueous p-S relations;
(iv) extending two-phase p-S-k relations to three-phase p-S-k relations by using Leverett's assumption; and
(v) using a hysteretic model calibrated with only the main drainage and imbibition p-S relations.

The time and expense involved in measuring hysteretic p-S-k relations is prohibitive and as a result few published data sets exist. Efforts to date include (1) testing whether two-phase p-S-k relations for unconsolidated media conform to results for consolidated porous media presented in the petroleum literature [89,90,88], and (2) developing approaches that can yield shortcuts in obtaining hysteretic p-S-k relations [224,223,177,176,178,179].

The work of Parker and Lenhard [224,223,177,176,178,179] illustrates weaknesses in the supporting data that are used for the calibration of hysteretic p-S-k relations. Even with the sustained effort represented by their work, their supporting data primarily comprises two-phase p-S and the saturated conductivity of one phase. While Parker and Lenhard have made commendable efforts at confirming hysteretic two- and three-phase p-S relations, the two-phase and three-phase S-k relations are rarely measured. Also, the tendency in the laboratory is to use porous media (sands) with narrow grain size distribution to facilitate homogeneous packing. These media have steplike p-S-k relations, which are not representative of most natural materials.

Issues in the use of parametric models include parameter estimation and the validity of experiments that generate the data for such estimation. The most well-posed inverse problem is provided by fitting a p-S relation to static p-S data and a S-k relation to steady-state flow data. But simultaneously fitting p-S and S-k relations to transient flow data can represent an ill-posed inverse problem. For example, the one-step outflow method to determine parameter values inversely in specified p-S-k relations—initially proposed for a gas-aqueous phase system by Kool et al. [162,163]—can be regarded as an ill-posed inverse problem, requiring either the additional information of fluid pressure as a function of time [285] and/or a sparse p-S relation through a multistep approach [286].

As the range of fluid property values being considered in environmental multiphase problems expands, one should reexamine the adequacy of current measurement apparatuses in yielding the desired p-S-k data. For example, the current vertical dimension of the standard retention cell (2.0 to 3.0 cm) may yield p-S data that is affected significantly by buoyancy forces for some two-fluid systems [181]. This effect can be minimized by the use of local measurements in long vertical columns at static equilibrium, with a nondestructive means to quantify the fluid saturations [262,249,83]. This method has the advantages of avoiding end effects as well as reducing the time required for defining the hysteretic p-S relation; data from multiple scanning paths can be observed for each change in the elevation of the reference fluid-fluid interface.

4.3.4 Nonwetting phase entrapment

An issue of central importance for multiphase environmental systems is the mass of NAPL existing as entrapped residual in a NAPL-aqueous phase system. This trapped residual is the source of contamination, and accurate modeling of its formation is a prerequisite for realistic assessment, analysis, and remediation simulation.

The initial-residual NWP (often NAPL) saturation is the initial value of the residual NWP (at $p_{nw-w} = 0$) before NWP removal via mobilization or solubilization [290,152]. The initial-residual NWP saturation is not necessarily the value of the residual NWP saturation obtained from measuring the imbibition NWP-aqueous phase p-S relation, which yields rather the maximum initial-residual NWP saturation. The maximum initial-residual NWP saturation is a function of the geometry of the porous matrix; the fluid-solid properties, in particular wettability; fluid-fluid properties, including viscosity ratio, interfacial tension and density difference; and displacement rates [256]. While many of these effects have been explored in the petroleum literature [267,256,206], significant attention has not been given to the effect of displacement history on the initial-residual NWP saturation. One needs a macroscopic NWP-entrapment model capturing the displacement history to correctly predict the initial-residual NWP saturation [152,290]. The NWP entrapment model has been called the "residual-initial NWP relation" and is used as a submodel in hysteretic p-S-k relations. This relation describes the initial-residual NWP saturation as a function of the initial-funicular (connected) NWP saturation reached during displacement of the wetting phase. To avoid the potentially confusing use of "initial", we propose the term "residual-funicular NWP relation".

Figure 2 depicts various proposed residual-funicular NWP saturation relations. Some hysteretic p-S relations minimally describe the effect of displacement history by assuming that the initial-residual NWP saturation corresponds to the initial-funicular NWP saturation up to the maximum residual value and equals the maximum residual value thereafter [183,253,157]. Other residual-funicular NWP relations have been included in hysteretic p-S relations proposed by Mualem [208], Parker and Lenhard [223], and Tan [273]; they differ on the shape of the residual-funicular NWP relation, whether linear [223] or curvilinear [152,290]. In addition, data from Morrow [205], Schiegg [249], and our laboratory point to a threshold funicular NWP saturation above which no further entrapment is observed, at least for porous media having a narrow pore size distribution; Stonestrom and Rubin [271] also show such a relation for two other porous media.

4.3.5 Interfacial spreading and mixed wettability

Fundamental physical chemistry suggests [6], and experimental results show that interfacial tensions must be balanced between gas-aqueous, NAPL-aqueous, and gas-NAPL, which lead to either spreading or nonspreading of a NAPL on a gas-aqueous interface. Wilson et al. [303] has visually shown that at low NAPL saturations, a spreading NAPL exists as a thin film between gas and aqueous phases, while a nonspreading NAPL is manifested as discrete microlenses. With increasing NAPL saturation, these microlenses coalesce to form a layer between the gas and aqueous phases. If the nonspreading NAPL forms microlenses, Leverett's assumption is likely to be violated.

McBride et al. [195] found that the rate of advance of a NAPL imbibition front in a column of water-wetted glass bead medium was influenced by the spreading coefficient of the NAPL. Anderson [9] found a similar result for two-dimensional NAPL infiltration into a vadose zone, the spreading coefficient of

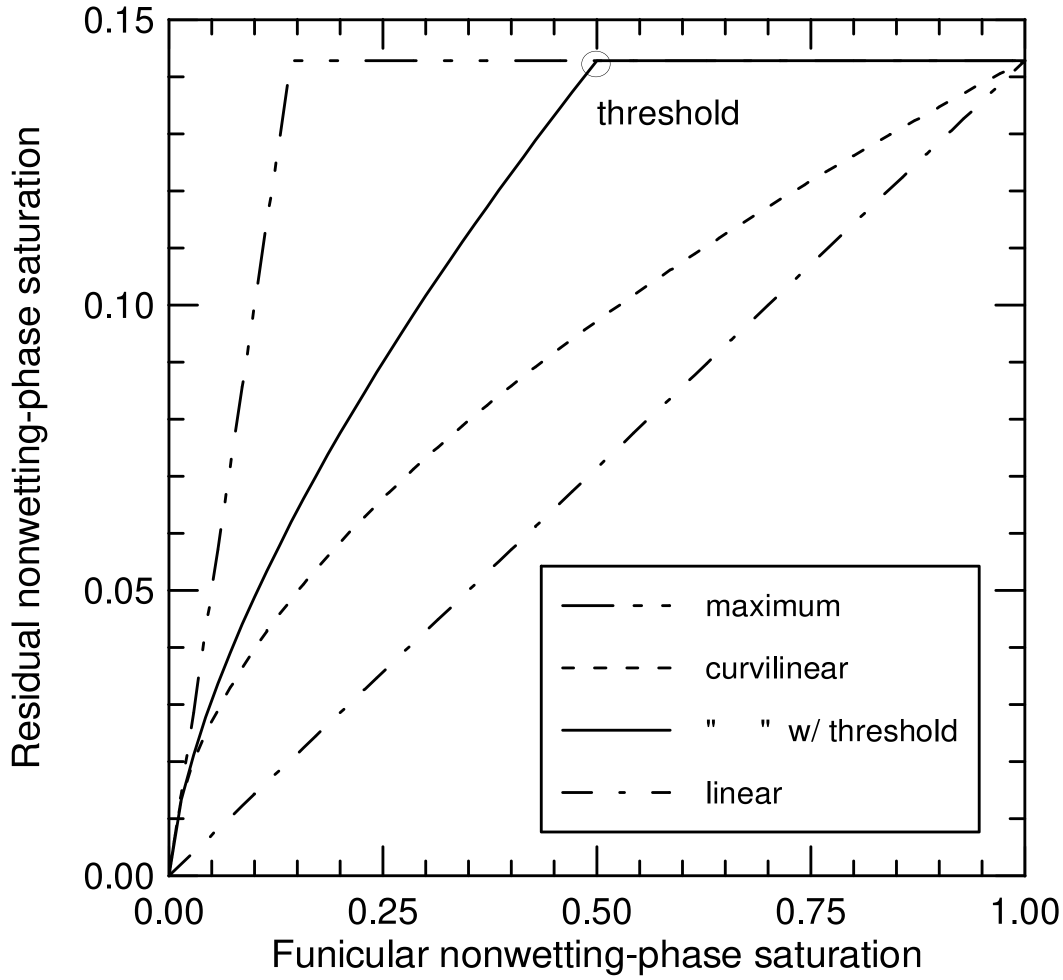


Fig. 2. NAPL residual comparisons for typical residual-funicular NWP relations.

the NAPL greatly influencing the extent of lateral migration in the vicinity of the water table. The contact angle of a nonspreading NAPL is reflected by a reduced capillary force, which can be modeled by current p-S relations. The additional driving force observed with spreading NAPLs has not been accounted for. The imbibition of nonspreading NAPLs over aqueous phase films in capillaries with angular cross section has recently been investigated [92]. When using NAPLs that have a nonzero spreading coefficient on a gas-aqueous interface, one should be alert for unexpected behavior.

Other manifestations of interfacial phenomena have been observed. Demond and Roberts [89] showed that the adhesion of the aqueous phase to water-wet solids decreased with decreasing NAPL-aqueous interfacial tension. This decrease led to an increase of the contact angle of the aqueous phase with respect to the solid. Solid wettability effects are important in mixed wettability porous media systems. Two-phase p-S to three-phase p-S scaling techniques have recently been found inadequate for artificial mixed-wettability porous media [37,38]. Last, poorly defined solid wettability may lead to the spreading of NAPL along solid surfaces, such as along a metal surface, in contact with the NAPL-aqueous porous media system [250, p. 131]; [299].

4.3.6 Dynamics

Mass balance and momentum equations, which are inherently dynamic, are closed by p-S-k relations. However, data are usually collected at pseudostatic equilibrium conditions. Theoretical considerations and experimental evidence demonstrate that this assumption should be tested at every opportunity, as an expanding range of buoyancies, viscosity ratios, and interfacial tensions are considered for two- and three-phase systems. For the relations to be unique and thus independent of dynamic effects, the relations must be unaffected by (1) the rate at which static equilibrium or steady state is reached, and (2) the number of intermediate points used to define the relation. The extent of dynamic effects is not well known and deserves further study.

Few studies exist on this topic, and the majority examine gas-aqueous p-S-k relations in relatively uniform, coarse porous media. The uniqueness of p-S relations has been tested in two ways. In one, the fluid saturation at a measured fluid pressure during steady-state or transient displacement experiments is compared to that at static equilibrium [281]. The most reliable experiments of this type use a nondestructive radiation attenuation instrument to measure fluid saturation at the same elevation as the location of a tensiometer, yet one must be very careful to avoid any time lag in the measurement of fluid saturation and pressure. In the other method, larger but fewer pressure steps are used to define the p-S relation, and the results are compared to the static p-S relation measured using a multitude of small pressure steps [84]. The equilibration time used for a large pressure step should be equal, at minimum, to the sum of the equilibration times used for the small pressure steps.

Evidence for dynamic effects comes from experiments where the use of large pressure steps during drainage resulted in more aqueous phase retained at a given pressure than when smaller pressure steps were used [84,262,284,266]. Topp et al.[281] found that more aqueous phase was retained during transient drainage than at static equilibrium. These results indicate that the use of large pressure steps can lead to the hydraulic isolation of saturated pores, which would otherwise drain with small pressure steps. Given these observations, the one-step outflow technique used to estimate parameters inversely in p-S-k relations is likely subject to dynamic effects. Even multistep outflow techniques that inversely estimate parameters in p-S-k relations and use as few as three or four steps are probably subject to dynamic effects but to a lesser extent.

In an extensive series of experiments, Schiegg and Schwille [250, p. 163] examined aqueous phase imbibition into a long vertical column of sand, initially at a uniform low water content. They found that at six different hydraulic gradients, the observed aqueous phase pressures and saturations during imbibition matched the static gas-aqueous imbibition p-S relation observed after 60-day equilibration for each of the six experiments. In the above studies that also examined dynamic imbibition p-S relations, only Davidson et al. [84] found that, because of greater NWP entrapment, the use of larger pressure steps yielded lower water contents than smaller pressure steps. In a two-dimensional experiment of LNAPL infiltration into a vadose zone, van Geel and Sykes [289] invoked dynamic effects to explain the lack of correspondence between static p-S relations and observed pressures at the light NAPL (LNAPL) front. Interestingly, they also considered whether interfacial spreading effects could account for the discrepancy. Displacement rate considerations examined for a pore doublet model show that dynamic effects should be expected during imbibition as well [264]. Given the possibility for dynamic effects, the effect of the displacement rate on the residual-funicular NWP relation should be examined.

Another dynamic effect identified in the literature is the change in the curvature of a meniscus within a capillary tube as a function of the velocity of the advancing or receding meniscus. The observed dynamic capillary pressure approaches that calculated using the capillary radius and Laplace's equation of capillarity but only at static equilibrium. For an example involving gas-aqueous, kerosene-aqueous, and cyclohexane-aqueous displacements in a straight capillary tube, please see Calvo et al. [52] and Dullien [93]. In porous media, we believe that any dynamic effect on p-S-k relations produced by this mechanism is secondary to the mechanisms that change the sequence in which pores fill or drain as a function of the macroscopic displacement rate.

4.3.7 Anisotropy

A number of studies have concluded that the relationship between phase saturation and effective permeability, k_α, depends on direction [210,307,308,185,197,26,198]. Mualem [210] computed the hydraulic conductivity for aqueous phase flow in a gas-aqueous phase system using a statistical model, showing that the anisotropy in the principal directions of hydraulic conductivity increases with decreasing aqueous-phase saturation. Yeh et al. [307,308] and Mantoglou and Gelhar [185] used a spectral perturbation approach to express effective, aqueous-phase conductivity for heterogeneous, spatially correlated media in a gas-aqueous phase system. They also found that anisotropy increases with decreasing aqueous-phase saturation.

McCord and Stephens [197] and McCord et al. [198] presented data from a field study designed to assess the magnitude of moisture-dependent anisotropy on solute transport for natural conditions. While field and laboratory measurements indicated sands that were nearly isotropic at complete aqueous phase saturation, the dune sands behaved as highly anisotropic porous media at in situ aqueous-phase pressure heads (-30 to -80 cm). The network modeling study of Bear et al. [26] supports these results.

Taken together, these investigations indicate that relative permeability is not scalar; rather, the effective media anisotropy varies with the state of the system (phase saturation). Bear et al. [26] suggest that relative permeability is well defined for isotropic porous media. However, extending this concept to anisotropic porous media, even those with small amounts of anisotropy, is not appropriate if relative permeability is assumed to be scalar.

4.3.8 Mathematical inconsistencies

It is common to develop empirical models for relative permeabilities without examining the mathematical implications of the models for dynamic behavior. For example, oil companies rely on various extrapolations of two-phase relative permeability data for three-phase systems [268,269]. Previous work has often failed to uncover that these extrapolations are ill posed for initial-value problems, because they inherently involve saturation regions where the flow equations change from hyperbolic to elliptic. This problem was first discovered by Bell et al. [28], who showed that innocuous relative permeability curves could have rather large elliptic regions and produce very interesting oscillatory behavior in initial value problems.

Shearer [257] further demonstrated that the problem was generic. He showed that all models for incompressible, immiscible three-phase flow using relative permeabilities must have at least one point in the interior of the saturation triangle where the characteristic speeds are equal; most models allow that “umbilic point” to open up into a region where the characteristic speeds are complex. Marchesin and Medeiros [187] showed that Corey-type relative permeabilities, in which the relative permeability of each phase is a function of its own phase saturation only, prevent the umbilic points from opening into elliptic regions, even when gravity is included in the model.

Trangenstein [282] showed that the Corey models are the only relative permeability models that are functions of the phase saturations only, which never produce elliptic regions in the presence of gravity. Thus, in terms of well-posed mathematical problems, the Corey relative permeabilities appear to be the only choice; however, they do not reproduce most two-phase experimental data sets exactly. Delshad and Pope [87] argue that the deviations of the Corey relative permeabilities from the available two-phase data are within acceptable experimental error.

4.3.9 Scaling

Scaling of p-S-k relations is a major concern in both the environmental and petroleum fields for the general reasons presented in §4.2, which apply to all constitutive relations. In this section, we focus on what we have previously termed deterministic scaling or upscaling, assuming that complete information exists regarding both the form and parameters of the p-S-k relation at some scale smaller than the model discretization level in a numerical simulator. This area is one of active research for both single and multiphase fluid flow and transport problems.

Considerable work has been directed at the problem of upscaling permeabilities for single-phase flow and has been reviewed recently [298]. Work accomplished to date has shown that while many approaches have been used to determine upscaled permeabilities, each has certain limitations. It is now understood that upscaled conductivities depend on the geometry and properties of the fine-scale permeabilities, the boundary conditions imposed on the region to be upscaled, and the discretization pattern used in the numerical flow model. Exact upscaling thus effectively requires solution of the embedded fine-scale problem simultaneously with the coarse-scale problem. Approximations based on assumptions such as structured heterogeneity and periodic boundary conditions lead to more general upscaling relations. For systems that differ from those for which the approximation was derived, these relations are of an approximate nature but are still quite useful. [95,298].

Upscaling of p-S-k relations for multiphase flow requires the scaling of inherently nonlinear constitutive relations, which is a significant difference between single- and multiphase flow. Of additional importance is the frequent practice in multiphase flow of reducing dimensionality as a part of the upscaling process. Reductions in dimensionality are often used for large-scale reservoir or spill simulations to yield a tractably sized problem.

Early approaches for determining effective relative permeability determined the effective volumetric flux by summing the fine-scale fluxes. Then, a multiplicative decomposition of the effective flux into a product of width (or area) times average velocity times average fractional flow was used to determine the effective relative permeability. This method, combined with certain assumptions about pressure drops, forms the basis for the Kyte/Berry/Stone models [240,270,131].

One of the obvious difficulties of this approach is that effective parameters depend on far-field properties, such as boundary conditions, causing the dynamic behavior of the upscaled equations to be inconsistent with those of the fine scale. For example, the effective fractional flow might be convex rather than concave in saturation and thus predict shocks rather than expansions for some injections. Other authors actually exploited this feature by artificially adjusting the shape of the effective fractional flow curve, correcting for nonphysical spreading of the fine-scale fluid fronts due to the large numerical viscosity of the upstream weighting method [156,159]. In this manner, a "physical" solution was sought to a numerical problem.

A homogenization approach has been developed for and applied to the case of two-phase, transient flow in periodically heterogeneous media [8]. The homogenization technique agreed reasonably well with the true solution for a set of test problems compared to a variety of averaging techniques, although the assumption of a constant shape p-S-k relation was assumed over the domain. Upscaling of the BC p-S relation for the case of capillary-gravity equilibrium has also been performed and shown to compare well with averaged point-scale measurements [91]. General approaches for upscaling p-S-k relations under dynamic conditions is an open area of research.

Recently, Blunt and Christie [31] have combined the Todd and Longstaff mixing model [277] with the Koval model of effective mobility [164] to determine effective relative permeabilities for viscous fingering. In this work, there is still a change of both scale and dimension, but the effective model is chosen so that it reproduces the average dynamics of the fine-scale simulations. For example, the approach is designed to replace the sharp fronts within the fingering zone with an appropriate expansion in the solution of the upscaled equations. These efforts generated effective equations that described the impact of a dynamic instability of fluid flow for a heterogeneous medium with small correlation lengths; for the case of correlation lengths that are not small when compared to the size of the scaled region, the solution of this problem is still an open question. These same authors have also averaged fine-scale flow for the case of random heterogeneity to determine the influence of heterogeneity on the dynamics of two-fluid front dynamics, using an effective fractional flow approach [67].

4.4 General mass transfer considerations

Characterization of any interphase mass transfer relation requires specification of the eventual thermodynamic equilibrium between phases, and a relation to represent the dynamics of the approach to that equilibrium. The order of wettability in the solid phase is usually assumed to begin with the aqueous phase, followed by NAPL and gas; the primary mass transfer processes of concern, then, are aqueous-solid, Nonaqueous-aqueous, NAPL-gas, and aqueous-gas. Of these processes, aqueous-solid and Nonaqueous-aqueous mass transfer have received the most attention in previous work, and while we focus our comments on these two processes, we consider the others briefly.

4.5 Aqueous-solid phase mass transfer

4.5.1 Overview

Aqueous-solid phase mass transfer, better known as sorption/desorption, has received a substantial amount of attention in the literature. Sorption processes for neutral organic species include adsorption to mineral surfaces as well as partitioning into the natural organic matter associated with the solid phase; we restrict our comments to these systems. Recent reviews are available in the literature by Brusseau and Rao [48] and Weber et al. [296]; our intent is to note recent developments, implications, and open questions. With this goal, we consider equilibrium models, rate models, multicomponent systems, and scaling issues.

4.5.2 Equilibrium models

All forms of sorption rate models require a description of the equilibrium distribution relationship of a solute between the aqueous and solid phases. The equilibrium distribution relationship for a solute/solid system is often experimentally determined in batch-type (well-mixed) systems. The time required for the sorption process to reach equilibrium in batch-type systems is dependent on the solute/solid system being studied. Reported equilibrium times have ranged from several minutes to years (e.g., [19]). For some systems, accurate experimental determination of the equilibrium distribution relationship is complicated by competing processes, including abiotic and biotic transformations, volatilization into headspace, adsorption to reactor walls, and diffusion through seals [48,19].

Particle size reduction via pulverization of the natural solid being investigated has been used to reduce the time required for sorption equilibrium to occur. Pulverization reduces the path length that a solute molecule must traverse during the sorption process, resulting in a reduced equilibration time. Ball and Roberts [20,21] demonstrated that sorption equilibrium was not measurably altered by pulverization in sorption experiments conducted with aquifer sands and nonionic hydrophobic organic solutes. Similar results may not hold true for sorption of ionic species, where the increase in mineral surface area from pulverization may lead to increased solute uptake.

The equilibrium distribution relationship of many solute/solid systems is often adequately described by a simple linear model, particularly for systems involving nonionic hydrophobic solutes sorbed by natural solids with appreciable organic carbon content. Karickhoff and co-workers [153] suggested that a linear equilibrium distribution relationship should be expected in systems where the aqueous phase solute concentration is below $10^{-5}M$ or less than one half of the aqueous phase solubility, whichever is lower. While many systems may be adequately described by a linear model, nonlinear sorption equilibrium is also frequently observed (e.g., [203,295,226]). The Freundlich model (a simple power law expression) is commonly used to describe nonlinear sorption equilibrium, the exponent being a measure of the degree of nonlinearity. Other nonlinear models, such as the Langmuir and Toth, have also been used to describe nonlinear sorption equilibrium. Kinniburgh [160] offers an extensive list of suitable nonlinear forms.

Figure 3 shows the results of an equilibrium experiment for γ-1,2,3,4,5,6-hexachlorocyclohexane (i.e., lindane) sorption by an aquifer sand in its native and pulverized form. We describe the materials and methods used for this experiment elsewhere [200,226]. The results obtained with the native sand indicate that sorption continued at a measurable rate between 26 and 84 days. The results obtained with the pulverized sand suggest that sorption by the native sand was far from equilibrium even after 84 days. Figure 3 is also an example of nonlinear sorption, each of the distributions being adequately described by the Toth model. These recent results and other supporting evidence collected to date show that sorption/desorption processes may require from months to years to approach an eventual nonlinear equilibrium. There are, then, significant implications for subsurface remediation of systems that are contaminated with solutes that exhibit such behavior.

4.5.3 Rate models

Notable contributions to the modeling of sorption/desorption rates are listed in Table 6. While several different models exist, the most common sorption rate model formulations assume that the sorption process is limited by diffusion within individual grains or aggregates. A first-order mass transfer approximation is often used to model this process but does not usually provide a good description of the process dynamics. When Fick's law is used to model the diffusion process, the sorbing media is usually assumed to be spherical. Most rate model formulations have implicitly assumed the sorbing media to be homogeneous with respect to their equilibrium and rate characteristics. However, extensive experimental evidence indicates otherwise (e.g., [153,20,297,22]). The simple first-order mass transfer models and Fick's law models have been extended in an attempt to address the experimentally observed heterogeneities. Some of these model extensions are noted below.

First-order mass transfer rate models are not able to describe accurately the rapid initial uptake observed in sorption rate experiments conducted in batch systems. The simplest extension of these models allows for a fraction of the sorption to occur instantaneously (e.g., [255]). These types of modeling approaches are sometimes referred to as bi-continuum models and are open to

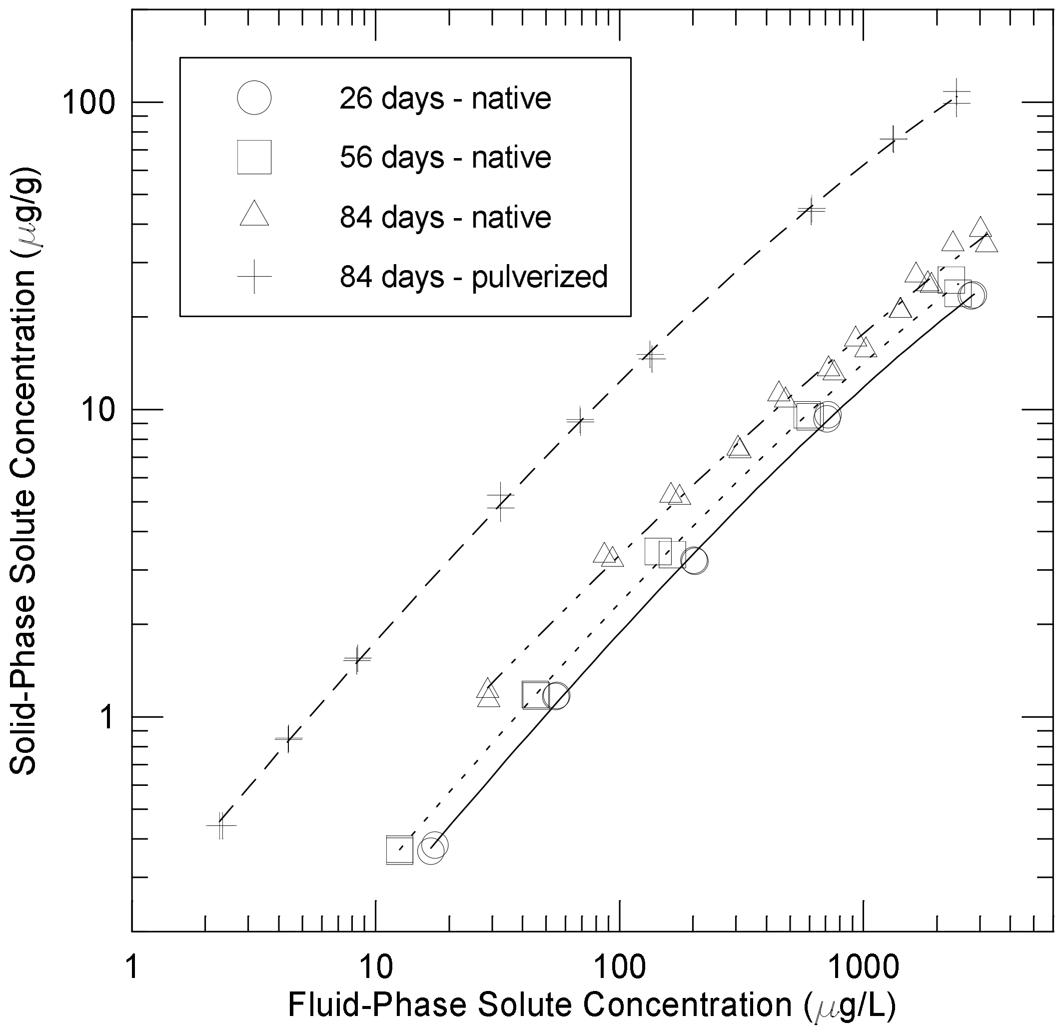


Fig. 3. Experimental data and Toth model fits for the distribution of lindane at various sorption times on unaltered and pulverized Wagner aquifer sand.

interpretation on either a chemical or physical basis. More recent extensions of the first-order mass transfer approach allow for the mass transfer coefficient to follow a statistical probability distribution, such as the gamma [72,226] or lognormal distributions [226].

Diffusion modeling approaches are also unable to describe accurately the rapid initial uptake observed in batch studies. An instantaneous fraction has been added to diffusion-based models to overcome this shortcoming (e.g., [21,232]). While this approach leads to better descriptions of the data, it does not address the underlying reasons why homogeneous models often fail to describe sorption rate data accurately. Models have been developed that account for variations in particle size and sorption equilibrium. The approaches that have proven successful at modeling sorption rate data are those that treat sorption

Table 6
Selected aqueous-solid phase mass transfer models

Work	Number of Sorption Classes	General Model Type
[216]	one	first order
[292]	continuous	first order
[255]	two	equilibrium and first order
[78]	one	pore/surface diffusion
[203]	one	surface diffusion
[304]	multiple	pore diffusion
[305]	multiple	first order
[46]	four	first order
[21]	two	equilibrium and pore diffusion
[309]	two in series	pore diffusion
[227]	continuous	pore diffusion

equilibrium variations within a bulk sample as following a lognormal distribution within the diffusion modeling framework [227].

Figure 4 shows the results of a sorption rate experiment conducted in a batch reactor for lindane and an aquifer sand in its native form. For this experiment, the initial aqueous-phase solute concentration was 1,898 μg/L, and the solid to solution ratio was 3 g to 30.04 mL. We modeled the results of the experiment by a simple first-order mass transfer model, a simple pore-diffusion model, and a pore-diffusion model that assumed sorption equilibrium within the bulk sample to be described by a lognormal distribution. The homogeneous models underpredict the rapid initial uptake and overpredict the uptake at later times. The distributed-equilibrium diffusion model accurately describes sorptive behavior throughout the experiment.

Effects of slow sorption rates in miscible displacement experiments are demonstrated in Figure 5. Influent aqueous-phase solute concentration was a step input of lindane at 2,942 μg/L for 73 bed volumes, and the pore velocity was 2.04 m/d. The effluent curve during the sorption period shows early breakthrough (compared to what would be expected if local equilibrium were operative) followed by a slow approach to equilibrium with the input concentration (which never occurs). The effluent curve demonstrates the so-called tailing effect, as solute continues to desorb even after 200 bed volumes of solute-free aqueous phase are passed through the system. This recent result is consistent with

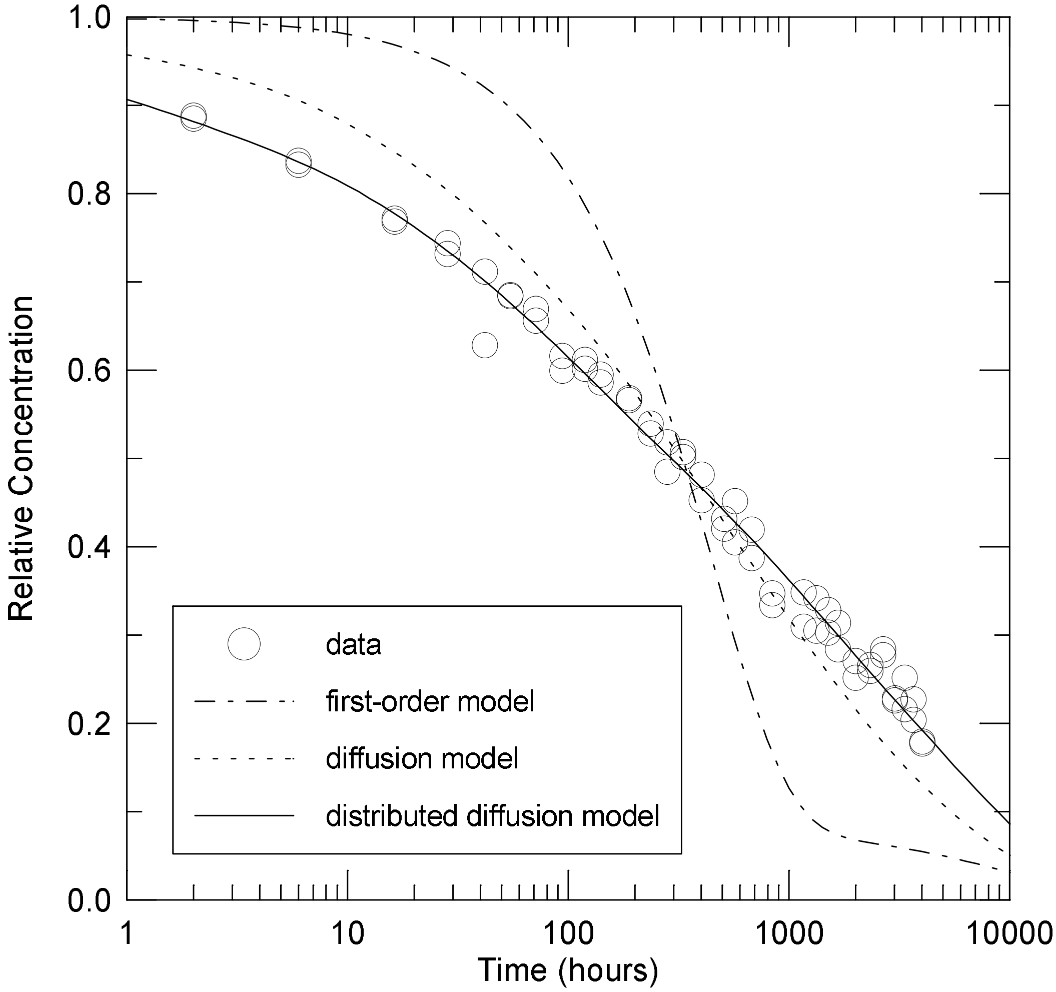


Fig. 4. Experimental data and rate model fits for lindane sorption and abiotic degradation on unaltered Wagner aquifer sand.

batch rate and equilibrium results presented from studies conducted with the same materials. The long time scale of sorption/desorption processes for these materials is indicative of the importance of nonequilibrium effects over a wide range of spatial and temporal scales of environmental relevance.

4.5.4 Multicomponent systems

Effects of multiple solutes on sorption equilibrium and rates have not been extensively researched. The commonly held view that sorption of nonionic hydrophobic organic chemicals by natural solids is a partitioninglike phenomenon suggests that the presence of multiple solutes would have no effect on the sorption equilibrium of each solute; such results have been observed by Chiou et al. [58] and Karickhoff et al. [153]. More recent experimental work demon-

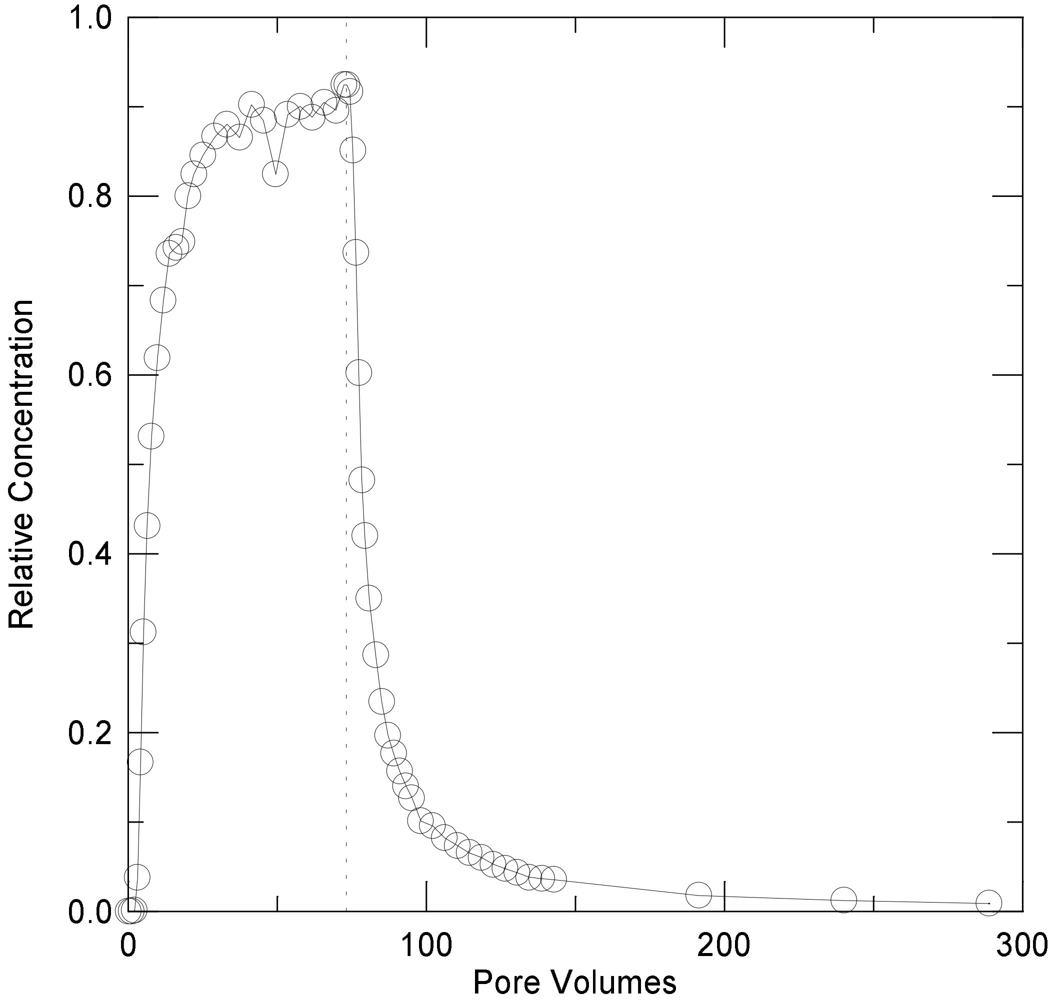


Fig. 5. Experimental data for lindane sorption and desorption from unaltered Wagner aquifer sand in a laboratory column.

strates that competitive sorption may occur [69,231,199], while others suggest the same about cooperative sorption [44,230]. While sorption equilibrium for multiple solute systems is poorly understood, even less is known about the effects that multiple solutes have on sorption rates.

4.5.5 Scaling issues

Natural systems display heterogeneities in their sorptive properties at scales ranging from the microscale of an individual solid grain to the megascale used to describe large natural systems. There have been numerous experimental investigations demonstrating that substantial equilibrium variations exist at many scales (see references cited in [226]). Relatively few studies have investigated how sorption rates vary within a bulk sample (several grams to several kilograms scale) and even fewer on how sorption rates vary at the field scale.

Sorption is often viewed as a diffusion-limited process. If the diffusion path length is related to particle size, then variations in particle size at the bulk sample scale would indicate that variations in sorption rates should also occur at the bulk sample scale. Brusseau and Rao [47] proposed an inverse relationship between sorption rates and sorption equilibrium based on experimental evidence gathered at the bulk sample scale. There are numerous studies demonstrating equilibrium variations within bulk samples [154,36,153,214,148,20,297,22]. It seems reasonable to expect that sorption rates at the bulk sample scale would be distributed because of equilibrium variations at that scale.

Even though particle size variations and equilibrium variations at the bulk sample scale are widely recognized, the traditional approaches (i.e., single-class models using first-order mass transfer, pore diffusion, or surface diffusion) that have been used to model sorption rates at the bulk sample scale do not explicitly account for these variations. The shortcomings of traditional modeling approaches have been clearly demonstrated in batch systems where these modeling approaches often fail to describe adequately the rapid initial uptake observed experimentally [226]. Extensions of traditional modeling approaches have been proposed which attempt to address heterogeneities in sorption rate and equilibrium properties [292,304,305,46,227,226,72,119]. These approaches have led to improvements in the ability to describe sorption phenomena in batch and column experiments. Improvements usually come at the expense of additional model parameters. Extensions of these modeling approaches to larger scales have been limited.

As the scale of interest increases (i.e., bulk sample to the field scale), spatial variations in sorptive properties at increasingly larger scales need to be addressed. There have been several theoretical investigations on the effects of heterogeneities at these larger scales. Many of these investigations have invoked the assumption of local equilibrium and examined the effects of uncorrelated and correlated variations between hydraulic conductivity and sorption equilibrium [150,241,121,287,278,29,35]. Some studies have examined the effects of single class rate-limited sorption when variations in hydraulic conductivity and sorption equilibrium exist [241,136,121,51].

While these studies have addressed large-scale heterogeneities, they have failed to address simultaneously the variabilities observed at the smaller scales (e.g., the bulk sample scale). The most important aspect of grain-scale sorption rate models is that there is a component of the sorption phenomena that takes extended periods (months to years) to reach equilibrium. As the time scales for sorption equilibrium increase, so does the importance of modeling rates in field-scale simulators. This effect has been demonstrated by Haggerty and Gorelick [119], who modeled remediation of spatially homogeneous aquifers that had small scale variations in sorption equilibrium and rate properties. They showed that the presence of a small fraction of aquifer material with slow rate properties may cause long remediation times.

Several scaling issues need to be addressed. Models developed to describe sorption rates accurately when grain scale heterogeneities exist may be too computationally demanding to be incorporated into field-scale simulators. Efficient methods need to be determined by which the important information from the small scale sorption rate models can be incorporated into field simulators. This method will likely involve a change in the form of the small scale sorption rate models rather than just a change in model parameters.

4.6 Nonaqueous-aqueous phase mass transfer

4.6.1 Overview

Nonaqueous-aqueous phase mass transfer is a process of central importance for multiphase environmental systems, because NAPLs are a frequent source of contamination, and groundwater concentrations are often the basis of health concerns and regulated cleanup levels. While this process is of major importance, our understanding of it is not well developed. While local equilibrium between phases has been a common assumption, field-scale observations do not usually support its validity (e.g., [184,238]). Considerable work has thus been aimed at developing an appropriate mass transfer rate model for Nonaqueous-aqueous phase mass transfer.

The current development of Nonaqueous-aqueous phase mass transfer constitutive relations is summarized in Table 7 and can be focused with the following observations:

(i) while other constitutive relations, such as p-S-k relations and aqueous-solid phase mass transfer, have a significant experimental basis and multiple models (see §§4.3 and 4.5), Nonaqueous-aqueous phase mass transfer does not;
(ii) to date, Nonaqueous-aqueous phase mass transfer rate modeling uses a first-order approach similar to aqueous-solid phase mass transfer models but differing in the expressions used to estimate the mass transfer rate coefficient in terms of system parameters;
(iii) based on dimensional analysis of this process [201], several nondimensional parameters may be required to describe the rate of mass transfer, but to date, only a few of these parameters have been experimentally investigated for a relatively small set of media properties and over a limited range of conditions;
(iv) experimental work to determine mass transfer rate coefficients correla-

tions has been performed almost entirely from homogeneous systems with a length scale of 10^{-3} to 10^{-2} m; and

(v) because of the length scale and heterogeneous nature of the systems of concern, significant unresolved scale issues remain for Nonaqueous-aqueous phase mass transfer.

Table 7
Empirical NAPL-aqueous phase mass transfer models

Work	Length Scale	Formulation	Model Type
[201]	cm	$Sh_{na} = 12(\phi - \theta_n) Re_a^{0.75} \theta_n^{0.60} Sc_a^{0.5}$	lumped domain
[237]	mm	$Sh_{na} = 4.13 Re_a^{0.598} \delta^{0.673} U_i^{0.369} (\frac{\theta_n}{\theta_{ni}})^\beta$ $\beta = 0.518 + 0.114\delta + 0.10U_i$	lumped domain
[144]	mm	$Sh_{na} = 340 Re_a^{0.71} \theta_n^{0.87} (\frac{x}{d_{50}})^{-0.31}$ [a]	lumped domain
[109]	mm	$Sh_{na} = 70.5 Re_a^{\frac{1}{3}} \theta_n^{\frac{4}{9}} S_{ni}^{\frac{5}{9}} \phi^{\frac{-2}{3}} (\frac{d_{50}}{d_{ni}})^{\frac{5}{3}}$ [b]	sphere model
[235]	mm	$Sh'_{na} = 36.8 Re_a^{0.654}$	multiple sphere
[45,127,128,34]	*ns*	none developed	two-site

[a] $\frac{x}{d_{50}} = 7$ for conditions without dissolution fingering

[b] estimated from published results

Sh_{na} = NAPL-aqueous phase Sherwood number; Sh'_{na} = modified NAPL-aqueous phase Sherwood number; ϕ = porosity; θ_n = NAPL volume fraction; Re_a = aqueous-phase Reynolds number; Sc_a = aqueous-phase Schmidt number; δ = normalized grain size; d_{50} = median grain size diameter; U_i uniformity index; θ_{ni}, S_{ni}, and d_{ni} are the initial-residual NAPL volume fraction, initial-residual NAPL saturation, and initial diameter of the NAPL spheres after NAPL entrapment but before NAPL dissolution. Dimensionless variables are defined in the Notation.

Given these observations, several issues involved in NAPL dissolution can be identified: low residual saturation dissolution, Schmidt number dependence, initial-residual condition observations, dissolution fingering, dissolution from pools, scaling issues, and computational inconsistencies.

4.6.2 Low residual dissolution

To investigate Nonaqueous-aqueous phase mass transfer behavior, most researchers pass water through columns of porous media contaminated with a single-species NAPL at residual saturation and model their results using empirical relations [201,171,144,237]. Results usually show effluent concentrations that are initially close to the solubility limit but which decrease steadily until most of the NAPL mass is removed.

A significant void in these results is the behavior of NAPL at low residual saturation. Are tiny amounts of residual NAPL left in isolated pores, resulting in low mass transfer rates, after most of the NAPL mass has been removed from the system. Lamarche [171] presented data from column experiments in which the NAPL was dissolved from the porous medium by water flushing. He observed severe tailing of effluent concentrations long after most of the mass in the system had been removed. He also formulated a bicontinuum model to account for his results and concluded that a multicontinuum approach was needed to model different regions of mass transfer. Powers [237] observed tailing only in nonuniform media but neglected to account for it in the predictive model, citing a lack of data in the low concentration region.

Our group recently performed a series of column experiments to evaluate dissolution characteristics of a NAPL as the saturation approached zero. The porous medium (a nonuniform sand) and the NAPL (trichloroethene, TCE) were the same as that used by Lamarche, and the experimental conditions were similar. In our experiments, the effect of column materials on effluent concentrations was minimized by careful attention to column design and experimental methods. In contrast to Lamarche's results, we found that TCE concentrations decreased below health-based standards without producing a tail. Figure 6 highlights these interesting results.

Although the two data sets are not directly comparable due to differences in column dimensions, the distinct difference in the shapes of the dissolution curves underscores the difficulties with assessing rate-limited mass transfer at low NAPL saturations.

4.6.3 Schmidt number dependence

Nonaqueous-aqueous phase mass transfer has been studied for a variety of contaminants, flow conditions, and porous media using a range of methods [107,252,201,171,222,11,33,236,109,128,237,235,144]. However, with the advent of enhanced flushing technologies (e.g., surfactant, alcohol, and hot water flushing), mass transfer processes may become different than observed to date because of the conditions under which these studies have been performed. All of these technologies alter the aqueous phase viscosity and diffusivity of

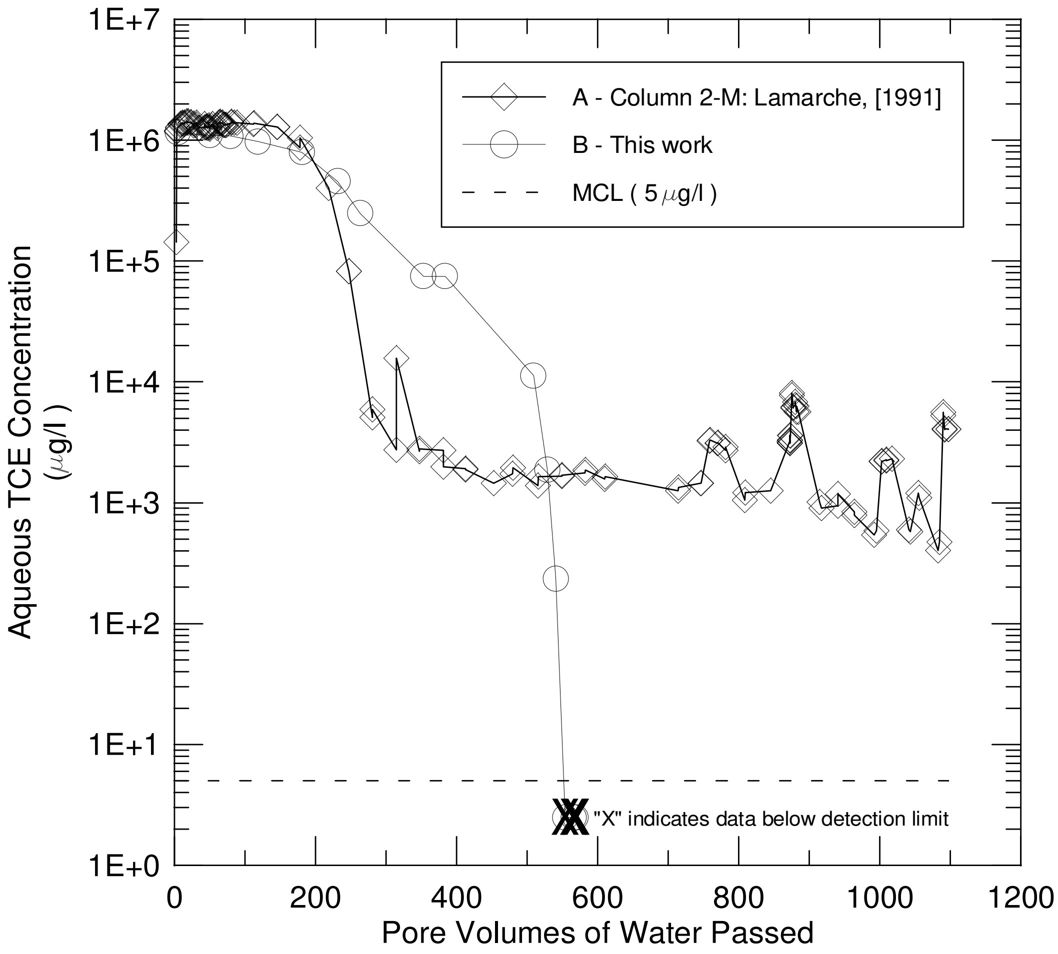


Fig. 6. Dissolution characteristics of TCE.

the NAPL species. Variations in these properties have not been examined in previous investigations of NAPL dissolution in porous media.

We have studied the effect of temperature, 5 ^{o}C to 40 ^{o}C, on the dissolution of PCE in a glass bead porous medium [142]. Over this range, the kinematic viscosity of the aqueous phase decreases by a factor of two, while the molecular diffusivity of PCE in the aqueous phase increases by a factor of five. Interfacial tension changes between PCE and the aqueous phase were minor over this temperature range and should have had an insignificant effect on interfacial areas for mass transfer.

Nonaqueous-aqueous phase mass transfer rate coefficients measured for this system were put in dimensionless form using the Sherwood number, Sh_{na}, and fitted to a power-law model, using dimensionless numbers suggested from an earlier analysis [201]. Sh_{na} was found to vary with the aqueous-phase Schmidt number, Sc_a, to the 0.5 power, which is the relationship suggested by Miller et al. [201] based on mass transfer studies in chemical engineering. This result is expected to apply to Nonaqueous-aqueous phase mass transfer in other systems where aqueous phase properties are altered by the addition of chemicals.

4.6.4 Initial-residual NAPL conditions

No systematic examination has been performed to assess the effect of the initial-residual NAPL volume fraction on the mass transfer rate coefficient. We investigated this dependence by performing experiments with the same glass-bead porous medium but different initial-residual NAPL saturation levels. In these experiments, the initially water-saturated porous medium was flushed with PCE to different initial, funicular PCE volume fractions. A water flush followed, displacing most of the PCE from the system. Residual PCE was left trapped in the glass beads according to the residual-funicular NWP relation (see §§4.3.4), and differed between the experiments. A 60% methanol 40% water solution was then flushed through the column dissolving the PCE from the system, and the mass transfer rate coefficient was measured. Details of these experiments can be found elsewhere [143].

The results shown in Figure 7 posit K_{na} as a function of NAPL volume fraction during dissolution for two methanol flushing experiments. The data from these experiments, conducted with the same medium, are systematically different: K_{na} are higher for experiment 3. These differences may have been due to differences in the initial-residual PCE volume fraction. Average initial-residual PCE volumetric fraction for experiment 2 was 0.11 but for experiment 3 was 0.21. The smaller initial-residual NAPL saturations in experiment 2 suggest that funicular NAPL invaded fewer smaller pores in this column. After NAPL displacement with a water flood, a larger fraction of the trapped NAPL ganglia may have occupied larger pores in experiment 2 than in experiment 3. Thus, for the same NAPL volumetric fraction during dissolution, NAPL dissolution in experiment 2 may have occurred from a smaller number of ganglia that were larger in size than in experiment 3. Fewer, larger ganglia would have a smaller total area for mass transfer and would result in smaller dissolution rates for the same NAPL volumetric fraction. While this observation is consistent with the mass transfer model of Geller and Hunt [109], it is inconsistent with that of Powers et al. [237] and has not been clearly identified in the literature.

4.6.5 Dissolution fingering

Most investigations of Nonaqueous-aqueous phase mass transfer have examined the dissolution of NAPL ganglia trapped at residual saturation in porous media [107,252,201,171,222,11,33,236,109,128,237,235,144]. With the exception of Anderson et al. [11] and Geller and Hunt [109], all were performed in columns where dissolution was assumed to occur uniformly across the col-

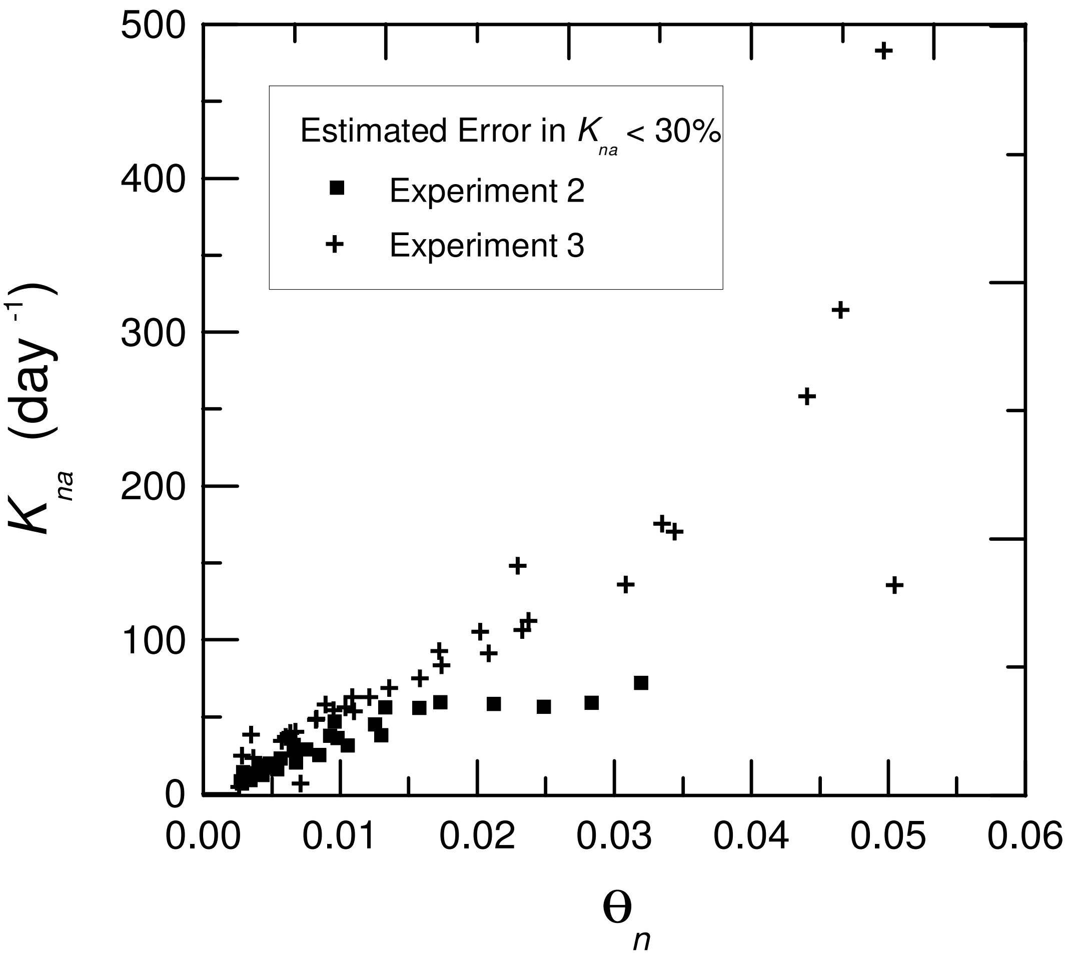


Fig. 7. Mass transfer rate coefficient K_{na} versus PCE volumetric fraction θ_n for data collected from two methanol flushing experiments in the same porous medium.

umn cross-section.

Imhoff et al. [144] performed detailed measurements of NAPL dissolution, which suggest that uniform dissolution within a NAPL-contaminated region may not always occur. In these experiments, gamma-attenuation measurements were used to determine nonaqueous-aqueous phase mass transfer rates for TCE dissolution at various positions along a column. Average mass transfer rates across the column diameter were observed to decrease with increasing distance into the region of NAPL residual. Imhoff [141] suggested that these observations were due to the development of preferential flow paths within the NAPL region: the aqueous phase may have interacted with dissolution-induced permeability changes leading to fingered patterns. Subsequent to these measurements, a linear stability analysis was performed on the nonlinear model describing the dissolution of NAPL ganglia, demonstrating that instabilities may develop from a planar dissolution front [145]. This analysis yielded the wavelengths of the fastest growing instabilities—wavelengths which are most likely in real systems.

The analysis was followed by experiments in two- and three-dimensional flow cells to visualize finger development, compare predictions from the linear stability analysis with experimental measurements, and assess the importance of dissolution fingering on NAPL removal in a three-dimensional, homogeneous porous medium. Details of these experiments can be found elsewhere [146]. Fingers were observed for a range of Darcy fluxes, porous media, and two different NAPLs, with finger wavelengths 0.5–3.5 cm, in agreement with predictions from the linear stability analysis.

In addition, locations of fingers were correlated with regions of low initial-residual NAPL saturation, S_{ni}. Figure 8 shows contours of initial-residual TCE saturation determined by x-ray attenuation at the start of a two-dimensional dissolution experiment. Measurements were made for every 5 mm $\times$ 5 mm block. The histogram indicates that smaller average S_{ni} occurred at locations $y = 0$ mm and $y = 120$ mm. Figure 9 shows the system at two later times; fingers formed at the two locations where S_{ni} were small.

Regions of small S_{ni} are likely correlated with porous medium structure. Sketches of finger development are shown for two other experiments in Figure 10. These experiments were conducted using the same porous medium and the same packing, with nearly identical initial conditions and flushing rates. Fingers developed in both experiments at the same locations and at nearly the same times. However, an experiment conducted with the same porous medium, similar initial conditions and flushing rates, but a *different* packing resulted in finger formation at different locations. Although the porous medium used in these experiments was a very uniform sand, $U_i = 1.0$ and $d_{50} = 0.036$ cm, subtle variations in packing likely resulted in systematic variations in S_{ni} that initiated finger development in a repeatable manner.

A single experiment conducted in a three-dimensional flow cell indicated that dissolution fingers in a homogeneous medium can grow as long as 30 cm [146]. Numerical simulations of NAPL removal from this column that neglected dissolution fingering resulted in significantly different distributions of NAPL residual and aqueous phase effluent concentrations.

Because of the number of experimental data sets in the literature on NAPL dissolution [107,252,201,171,222,11,33,236,109,128,237,235,144] and the possible influence of dissolution fingering on the results, it is important to assess whether dissolution fingering occurred in these experiments. Using criteria determined from the linear stability analysis and the experimental study, each of these investigations was examined to assess the likelihood of dissolution fingering [146]. It was concluded that dissolution fingering may have occurred in the work of Fried et al. [107], Lamarche [171], and Imhoff et al. [144]. A discussion of the possible effect of dissolution fingering on the reported data in these investigations is given by Imhoff et al. [146].

Natural porous media are usually more heterogeneous than the systems examined in the theoretical and experimental study described above. This heterogeneity may lead to spatial variations in the distribution of initial-residual NAPL and the aqueous phase permeability field that could dampen finger growth. Further investigation is required to assess the importance of dissolution fingering in more heterogeneous porous media.

4.6.6 Dissolution from pools

Relative to the number of references reporting on the dissolution of uniform maximum initial-residual NAPL from laboratory columns [201,236,144], little research has been reported on dissolution from dense NAPL (DNAPL) pools. A DNAPL pool is defined as a body of DNAPL with hydrostatic equilibrium saturations greater than the maximum initial-residual DNAPL saturation determined from the residual-funicular saturation relation of the porous media (see Figure 2). Given the greater DNAPL saturations, the aqueous phase permeability reduction in a DNAPL pool will likely create changes in the aqueous-phase flow field greater than the inconsequential changes reported by Anderson et al. [11] for a well-defined residual DNAPL zone.

Both substantial and subtle subsurface heterogeneities will encourage the formation of DNAPL pools [169]. Vertically thin DNAPL pools are likely to exist along the top of low-permeability layers (functioning as a capillary barrier because of their smaller mean pore size) and to collect within depressions along the top of these layers. More subtle porous media heterogeneities will also encourage the formation of DNAPL pools. Pools can exist in lenses of coarse porous media (larger mean pore size) because of capillary trapping caused by the surrounding finer porous medium [194]; they can also be found in the higher porosity zones of a nonuniformly packed porous medium [143]. DNAPL pools in coarse lenses, existing near the threshold of regaining continuity with DNAPL ganglia in the surrounding finer porous media, are very sensitive to redistribution caused by changes in the DNAPL-aqueous phase interfacial tension and aqueous-phase pressure [169,143].

Mathematical model-based estimates of mass transfer rates from DNAPL pools of simple geometry confirm that the pools persist longer in an aquifer than do residual DNAPL ganglia, because mass transfer from the DNAPL pool is limited by transverse dispersion [149,12]. A variety of pool geometries above aquitards have been considered in the mathematical models: (1) a uniformly thick pool across the bottom boundary [138,254], and (2) raised

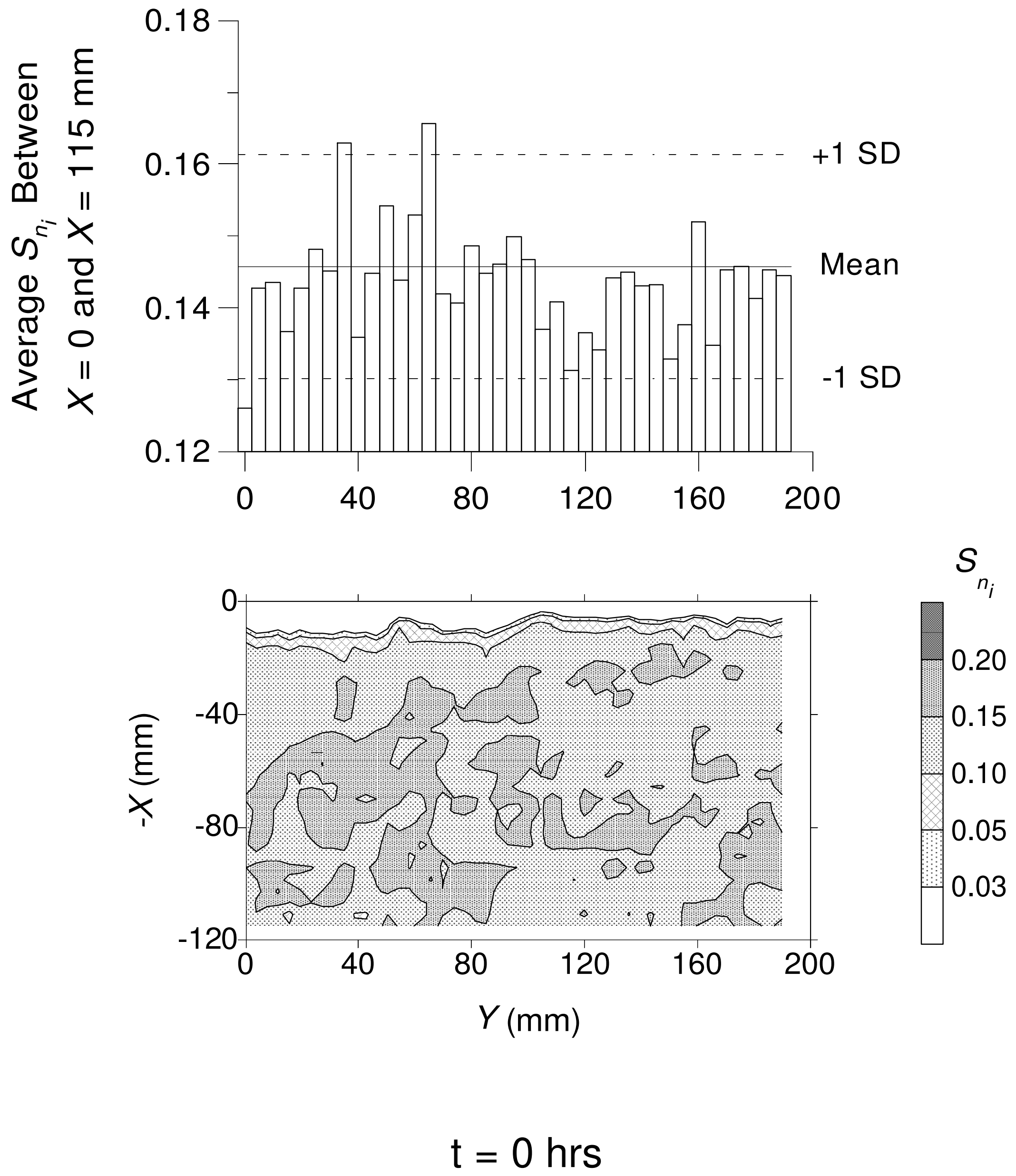


Fig. 8. Contours of initial-residual TCE saturation determined by x-ray attenuation at the start of a two-dimensional dissolution experiment.

rectangular, elliptic and circular pools [68]. Only one attempt has been reported comparing the mathematical model to laboratory-scale data [225]. At the scale of the aquifer, a sharp aqueous phase/DNAPL interface is assumed in the mathematical models, yet in laboratory-scale studies such an interface has proved difficult to obtain [299].

Since existing mass transfer models are all based on saturation levels less than or equivalent to the maximum initial-residual saturation level, existing rela-

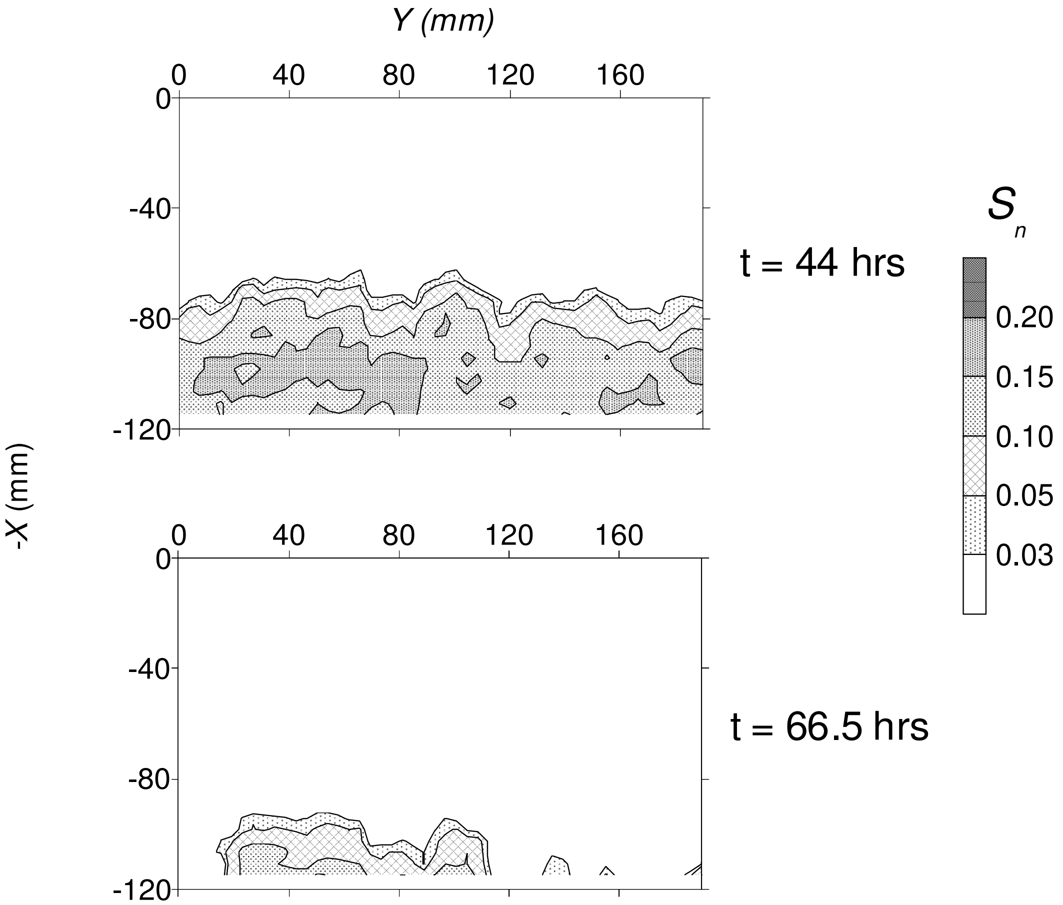


Fig. 9. Contours of TCE saturation at two times during the same dissolution experiment.

tions are inadequate to describe mass transfer in pooled regions. Yet these pools will be long-lived in the subsurface environment and hence of significant concern. In summary, the dynamics of DNAPL pool formation and mass transfer from DNAPL pools in markedly and subtly heterogeneous porous media are worthy of further investigation.

4.6.7 Scaling Issues

Mass transfer between a single-species residual NAPL and groundwater is commonly described with a first-order rate model $\mathcal{I}_a = K_{na}(C_a^S - C_a)$, where $\mathcal{I}_a$ is the flux of solute from the NAPL to the aqueous phase, K_{na} is the mass transfer rate coefficient, C_a^S is the aqueous-phase concentration corresponding to a condition of thermodynamic equilibrium when the NAPL phase is present, and C_a is the aqueous-phase solute concentration in the bulk fluid. In all models describing rate-limited mass transfer between residual NAPL and groundwater, the assumption is that K_{na} is a scalar, independent of flow

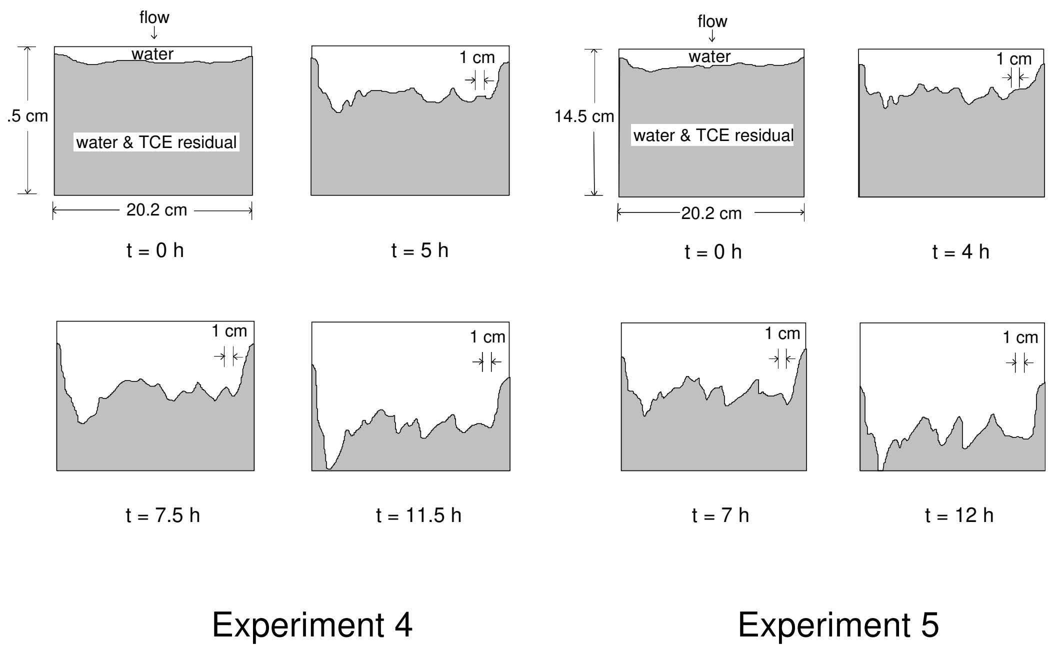


Fig. 10. Sketches of the zone of TCE contamination at four times during dissolution experiments conducted with the same porous medium and the same packing.

direction. While this assumption seems reasonable for small scales and homogeneous media, it may not hold true at larger scales for heterogeneous media.

To demonstrate this possibility, we examined NAPL dissolution in a heterogeneous porous medium. The porous medium was assumed to be scale-heterogeneous [245], with heterogeneity in k and K_{na} represented by a spatially distributed scaling function

$$k^*(\mathbf{x}) = k\gamma^2(\mathbf{x}) \tag{11}$$

$$K^*_{na}(\mathbf{x}) = K_{na}\mathrm{f}\left[d_{50}\gamma(\mathbf{x})\right] \tag{12}$$

where k and K_{na} are the field-averaged values of intrinsic permeability and mass transfer rate coefficient, and k^* and K^*_{na} are scaled values. Median particle size was scaled with γ, a dimensionless scaling function. k is related to the median particle diameter squared [24], and correlations for K_{na} explicitly contain median particle size. This type of scaling is referred to as Miller-similar [204,265] and was used by Mayer and Miller [194] to simulate multiphase flow and interphase mass transfer in heterogeneous systems. The mass transfer correlation of Powers et al. [237] was chosen to estimate K_{na}, since this correlation was developed for porous media with the widest range of properties.

The porous medium was expressed by a stochastic realization of the scaling function $\gamma(\mathbf{x})$. The spatial structure of $\gamma(\mathbf{x})$ was approximated by a log-normal distribution, as suggested by Warrick et al. [294], using a two-dimensional anisotropic covariance function

$$Cov(\mathbf{x}) = \sigma^2(\gamma)exp\{-s_x^2/[\eta_x(\gamma)]^2 - s_z^2/[\eta_x(\gamma)]^2)\} \tag{13}$$

where $\sigma^2(\gamma)$ is the variance, s_x and s_z are the spatial separation vectors, and $\eta_x(\gamma)$ and $\eta_z(\gamma)$ are the correlation lengths.

In this simulation, a 2-cm by 2-cm square domain was used with properties assigned to 16 0.5-cm by 0.5-cm blocks. The domain was discretized into a fine grid using square grid cells, each of which was 0.031 cm in the x- and z-directions. Statistics selected for this simulation were $\eta_x(\gamma) = 2.0$ cm, $\eta_z(\gamma) = 0.5$ cm, and $\sigma^2(\ln k) = 0.8$. Two aqueous-phase flow regimes were examined: (1) no flow boundaries at $x = 0$ cm and $x = 2$ cm with constant aqueous-phase pressure at $z = 0$ cm and $z = 2$ cm, and (2) no flow boundaries at $z = 0$ cm and $z = 2$ cm with constant aqueous-phase pressure at $x = 0$ cm and $x = 2$ cm. The NAPL was discontinuous and at residual saturation, and the boundary conditions were adjusted to give the same average aqueous-phase velocity in the x- and z-directions. Thus, NAPL dissolution and transport were examined in two orthogonal directions for the same physical system. TCE was selected as the NAPL, and a finite difference scheme was used to solve for TCE dissolution and transport with porosity $\phi = 0.35$ and initial-residual TCE saturation $S_{ni} = 0.13$ everywhere.

Average steady-state TCE concentrations leaving the effluent boundaries were computed for each flow configuration before TCE saturations decreased significantly in the system. These concentrations were then used to determine an average K_{na} for the 2-cm by 2-cm system using an analytical solution for TCE dissolution and transport [236]. For this simulation, K_{na} in the x direction was 1.22 times larger than K_{na} in the z direction. For simulations with homogeneous properties, K_{na} was independent of direction. Thus, small-scale heterogeneities, when averaged at a larger scale resulted in anisotropy at the large scale K_{na}. Because current multiphase simulators incorporating NAPL dissolution [116,194] for field-scale problems have used discretizations larger than the scale at which mass transfer correlations were developed (see Table 7), K_{na} will be a function of flow direction in these simulators. This effect is not accounted for in these simulators and has not to our knowledge been suggested in the literature. It is expected to be significantly greater for systems where S_{ni} is not uniform and as NAPL saturations decrease due to dissolution. The magnitude of $\gamma(\mathbf{x})$ and the correlation structure of the media are also expected to influence the anisotropy significantly in this relation. A great deal of work remains to be done to develop appropriate scaling relationships for nonaqueous-aqueous phase mass transfer.

4.7 Gas-phase mass transfer

Investigations of nonaqueous-aqueous and gas-aqueous phase mass transfer have concentrated on systems where rate limitations for mass transfer occur primarily within the aqueous phase. For this reason, mass transfer correlations for these systems take similar forms.

While there have been several experimental investigations examining mass transfer between gas and aqueous phases, only a few empirical models have been developed, which are shown in Table 8. The correlations in Table 8 were developed for porous media without significant intraparticle diffusional resistance [59,272] or selected from the chemical engineering literature and used for systems where intraparticle resistance was modeled separately [110,111]. Investigations have demonstrated mass transfer limitations within intraparticle pores that can dramatically reduce the overall rate of mass transfer between gas and aqueous phases [111,100,101]. This resistance may be dominant for many systems and is not included in the correlations in Table 8. Similarly, the rate-limiting step in sparging groundwater with air to remove contaminants in the saturated zone is likely not gas-aqueous phase mass transfer at the gas-aqueous phase interface but rate-limited transport within the bulk aqueous phase.

A few investigations have examined rate limitations for mass transfer between nonaqueous and gas phases in porous media. Of them, several indicated rapid equilibrium between the nonaqueous and gas phases [275,18]. To our knowledge, Wilkins et al. [302] have developed the only correlation for mass transfer from experimental data, shown in Table 8. Their correlation is for steady-state conditions, but more data are needed for a variety of conditions to predict nonaqueous-gas phase mass transfer rates, particularly as NAPL volumes become small.

4.7.1 Computational inconsistencies

In the process of simulating multiphase flow, discretization methods will need a model for phase behavior and interphase mass transfer. While the assumption of phase equilibrium does not hold on the field scale for any useful time scale, in fine-grid simulations it is a reasonable approximation on some time scale. The desire to develop complicated phase behavior models brings with it the need to insure that the model predictions are reasonable. The models must involve more than simple reproduction of quasi-steady laboratory data; modelers must also consider the mathematical implications of their model for dynamic flow simulations.

As an example, one of the authors has recently examined the mathematical

Table 8
Gas-aqueous and NAPL-gas phase mass transfer models

Work	Length Scale	Formulation	Model Type
[283]	cm	$Sh_{ga} = 16.8 d_{50}^2(\phi(FS_a))^{0.25}$ $Ga_a^{-0.22} Re_a^{0.25} Sc_a^{0.5}$	Gas-Aqueous mass transfer, lumped domain model.
[59]	cm	$Sh_{ga} = 0.94(\frac{d_{50}^2\phi(1-S_a)}{D_{m_a}})(\frac{\nu_a\phi S_a F}{d_{50}})^{0.151}$ $Re_a^{0.151}(1-S_f)^{22.9}(1-F)^{1.22}$ with $(\frac{d_{50}^2}{D_{m_a}})$ in units of cm h and $(\frac{\nu_a}{d_{50}})$ in units of cm h^{-1}	Gas-Aqueous mass transfer, lumped domain model.
[272]	cm	$Sh'_{ga} = d_{50} Sc_a^{0.5}(0.023$ $+0.849 Re_a^{0.861})$	Gas-Aqueous mass transfer, lumped domain model.
[302]	mm	$Sh'_{ng} = 10^{-2.79} Pe_g^{0.62} \delta^{1.82}$	NAPL-Gas mass transfer, lumped domain model.

Sh_{ga} = gas-aqueous phase Sherwood number; Sh'_{ga} = modified gas-aqueous phase Sherwood number; Sh'_{ng} = modified NAPL-gas phase Sherwood number; ϕ = porosity; F = mobile fraction of aqueous phase; S_a = saturation of aqueous phase; Ga_a = aqueous-phase Galileo number; Re_a = aqueous-phase Reynolds number; Sc_a = aqueous-phase Schmidt number; D_{m_a} = molecular diffusion coefficient in aqueous phase; d_{50} = median grain size diameter; ν_a = kinematic viscosity of aqueous phase; S_f = fraction of immobile aqueous phase contacting both the mobile aqueous phase and the gas phase; Pe_g = gas-phase Peclet number; and δ = normalized grain size. Dimensionless variables are defined in the Notation.

properties of a successful model for surfactant flooding [155]. The individual pieces of this model had been developed over a number of papers and theses [53,246–248,41,86]. Unfortunately, the individual contributions to this large project were not always consistent with each other. For example, phase compositions and relative permeabilities could change discontinuously when various conditional tests in the simulator were encountered. Such difficulties did not show up as significant modeling errors, because the quasi-static data was still being reproduced acceptably. However, in detailed simulations using numerical schemes with low numerical dissipation, these flux discontinuities showed up as undesirable behavior such as unphysical shocks. Once recognized, these unnecessary discontinuities were removed without changing the ability of the model to reproduce quasi-static data.

A more careful analysis of the same model showed that the model predicted an infinite characteristic speed as the NAPL concentration was being driven to its solubility limit in the aqueous phase by a surfactant concentration above the critical micelle concentration (CMC). Although numerical instability in explicit differencing resulted, it did not represent an essential physical feature of the model. The difficulty could be masked by sufficient physical dispersion or fully implicit treatment of the flow equations, but the model itself was still flawed. In fact, a slight change in the model to prevent infinite characteristic speeds allowed the revised numerical method to select explicit time steps roughly 100 times larger than the previous model. This experience shows that modelers should not rely on unconditionally stable numerical schemes to replace the development of mathematically stable and consistent models.

4.8 Experimental observations of multiphase systems

Various investigators have conducted intermediate scale experiments involving NAPLs, some of which are listed in Table 9. Most focused on fluid displacement processes, and almost all were conducted in homogeneous or layered media. Because natural porous media are most often heterogeneous, there is an obvious need for more experiments in heterogeneous media.

Limited experimental observations exist for many multiphase systems of concern. Such observations are lacking in enhanced remediation, for example, which we use to describe cosolvent, surfactant, and thermally motivated processes designed to reduce subsurface contamination by NAPLs. The observations typically progress from relatively simple phenomenological examples designed to observe important processes (e.g., macroemulsion transport noted above) to detailed experiments needed for developing appropriate physical and chemical models. Complex systems, such as enhanced remediation systems, require considerable time and effort to characterize due to the large number of properties known to affect transport phenomena. Well-characterized multidimensional experiments for such systems are especially rare, yet urgently needed as a foundation upon which to base appropriate models.

Table 9
NAPL transport in two- and three-dimensional laboratory experiments

Work	Length Scale	Fluid Phases	Dimensions	Porous Media	Processes
[252]	m	a, g, n	x, z	layered	displacement
[165]	m	a, n	x, z	heterogeneous	displacement
[249]	m	a, g, n	x, z	homogeneous	displacement
[222]	m	a, g, n	x, z	homogeneous	displacement
[132]	cm	a, n	x, z	layered	volatilization
[11]	m	a, g, n	x, y, z	homogeneous	dissolution
[133]	m	a, n	x, z	homogeneous	displacement
[293]	m	a, g, n	x, z	homogeneous	dissolution
[299]	m	a, n	x, z	homogeneous	dissolution
[225]	m	a, n	x, z	homogeneous	displacement
[289]	m	a, g, n	x, z	homogeneous	displacement
[140]	m	a, g, n	x, z	heterogeneous	displacement
[129]	m	a, n	x, y, z	homogeneous	displacement

4.9 Evolving Approaches

4.9.1 Overview

While laboratory experiments will continue to play a crucial role in the development and testing of constitutive relations, they are difficult, costly, and time-consuming—field-scale experiments even more so. We believe fundamental computational approaches will play an increasingly crucial role in the development and testing of constitutive relations.

If the conceptualization of constitutive relations is to project the essential information needed from a small scale to a larger scale system while ignoring unnecessary details, the presumption is that the phenomenon of concern can be understood on the small scale, which is simply not the case for many multiphase porous media systems. Not having this small-scale or fundamental understanding precludes the possibility of insuring that the essential features have been preserved, since it is impossible to evaluate experimentally but a small fraction of potentially important variables—usually for a limited set of media and fluids. We have given many examples throughout this section of the inconsistencies and deficiencies caused by this approach.

The rapid evolution of computational capabilities will afford new opportunities for the refinement of constitutive relations for multiphase systems by allowing the application of increasingly more fundamental approaches. However, even if the current rate of evolution in computational capabilities were projected a decade into the future, computational limitations would continue to be a concern.

We advocate an approach not unlike that suggested by Celia et al. [55] but differing in some significant respects. We believe that a two-scale approach is unlikely to be sufficient for understanding and simulating multiphase systems. While network modeling approaches are powerful and can lead to significant insights, there are many aspects of these models that warrant further investigation, especially for multiphase systems [182]: film flow of the wetting phase, active interfacial areas for mass transfer, adequacy of current lattice structures, the ability of pore body and throat idealizations to capture realistic flow and transport processes, and the role of spatial correlation. Another continuing problem is the difficulty and expense of obtaining accurate pore-scale morphology upon which to build a fundamental understanding.

We believe that constitutive theory for multiphase systems should be examined from a variety of fundamental perspectives, which may include statistical mechanics, cellular automata methods, discretization and solution of the pore-scale equations for flow and transport, and network models. Further, given computational limitations and the role of constitutive relations, a recursive application of computational methods at a variety of scales seems logical.

We are currently working along these lines and offer two brief examples of such approaches: NAPL entrapment morphology and NAPL dissolution dynamics. Both of these approaches use a Lattice Boltzmann (LB) method to simulate multiphase flow at the pore scale.

LB models have been used to simulate multiphase flow in porous media [117,49,190]. The fundamental objective in LB models is to construct a system with microscopic flow characteristics while its macroscopic properties obey the required macroscopic equations. This approach can accommodate complex geometries and can be easily implemented on parallel computing architectures.

The LB model may provide a powerful tool to investigate multiphase flow systems at a very fundamental scale. For example, the effect of the phase morphology and related variables, such as the interfacial area on the flow system, can be studied at the pore scale using the appropriate LB model; it provides an important link between pore-scale modeling and a macroscopic continuum approach.

It should be stressed that these two applications are only brief examples of some powerful methods; many fundamental questions that have not been resolved experimentally to date may be resolved using such approaches. We will report on such applications in future works.

4.9.2 NAPL entrapment morphology

In the first example, we consider the morphology of an entrapped NAPL. This has importance for evaluating interfacial areas, which are extremely difficult to measure for natural porous media; and for the more general problems of NAPL dissolution and mobilization.

Because of the difficulties with measuring pore morphology, we have developed an algorithm to pack spheres selected from a truncated log-normal distribution for both the case of spatially-correlated and uncorrelated conditions [306]. We used a code that implements this algorithm to produce the spherical packing shown in Figure 11, which is spatially uncorrelated and has a standard deviation of a log-normal distribution of 0.2.

A region of the sphere packing was discretized to obtain a lattice of $70 \times 70 \times 60$ nodes; a smoother rendering of the spheres would require a finer discretization. The lattice was initialized with a nonwetting fluid (NAPL). The wetting fluid completely wet the solid phase relative to the nonwetting phase and displaced a portion of the non-wetting phase yielding the distribution shown in Figure 12. Detailed examination of the resultant distribution shows that the initial-residual NAPL has a complex morphology that tends to occupy the large pores, which is consistent with the physics of the process. These results can be used to quantitatively examine interfacial areas and morphological descriptions. They can also be used as a starting point for an analysis of interphase mass transfer, such as the case shown in the next example.

4.9.3 Dissolution dynamics

Most models for NAPL dissolution use lumped-parameter descriptions to describe the mass transfer rate. Exceptions include those models that conceptualize the process as dissolution of NAPL ganglia of various shapes and sizes [239,235,109]. Interfacial areas for mass transfer are estimated from the geometrical shapes. The advantage of these models is that they recognize the difficulty in using a lumped parameter, such as NAPL volumetric content θ_n, to describe the interfacial area for mass transfer. Variations in pore structure may lead to small isolated regions of very large pores that create large NAPL ganglia—ganglia that are not well represented by an average θ_n over the region.

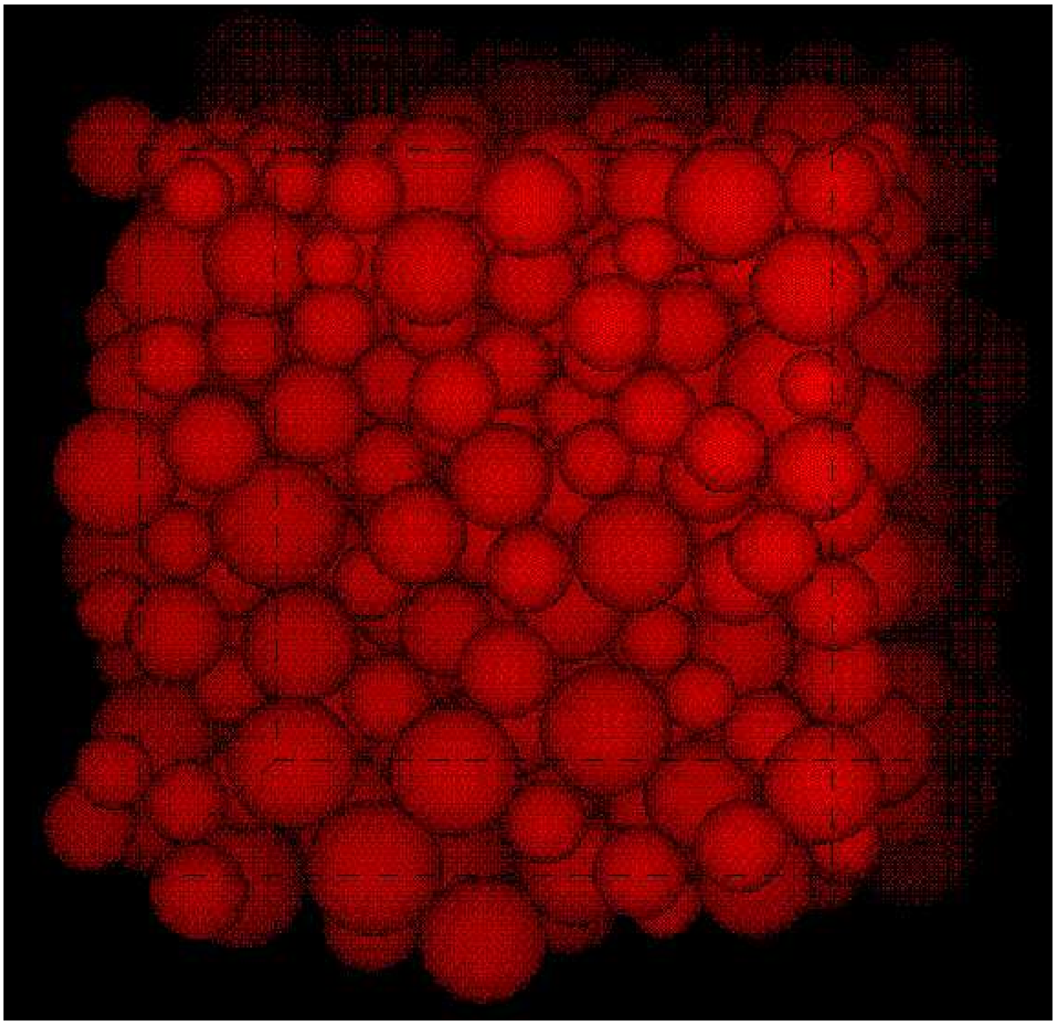


Fig. 11. Random sphere packing.

Existing models using geometrical configurations of NAPL ganglia assume these ganglia shrink in size during dissolution. However, we have performed experimental and numerical simulations that contradict this assumption. Figure 13 illustrates the dissolution of a TCE ganglion, dyed with Oil Red O, in a glass bead porous medium. The porous medium was uniform and homogeneous, $U_i = 1.0$ and $d_{50} = 0.078$ cm, and the Darcy flux was 8.44 m/day. Experimental details can be found elsewhere [276]. Photographs of one ganglion at 0 and 555 pore volumes are shown in Figure 13. Rather than shrinking in size, this amorphous ganglion breaks up into multiple ganglia as dissolution progresses.

In collaboration with N. S. Martys, we have simulated a similar case using LB methods [190], yielding the results shown in Figure 14. In this figure, the glass beads are shown in blue, NAPL is nonwetting and red, and the aqueous phase

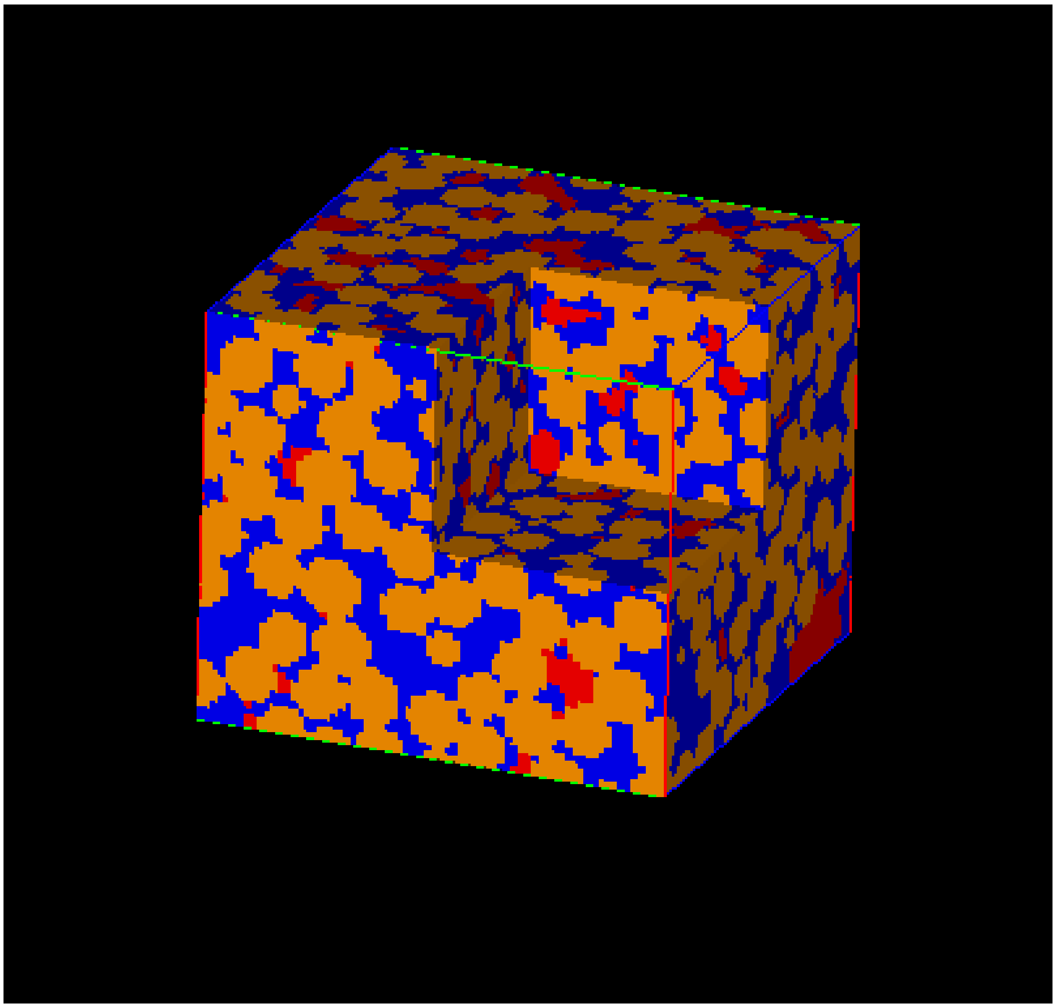


Fig. 12. Lattice Boltzmann simulation of multiphase flow. The red regions represent solids while the blue and green regions show the wetting phase and the NWP respectively.

is wetting and transparent. Boundary conditions are periodic in all directions. The NAPL was initially situated as a spherical ganglion in the center of the bead pack, after which it relaxed to the position shown in (a) and (b); it resides in the largest pores. In (b), the beads and aqueous phase are transparent. Once the NAPL reached a stable equilibrium, a body force was applied to produce flow in a direction out of the nearest plane. Although the NAPL is trapped within the bead pack by capillary forces, it slowly dissolves into the flowing fluid. Figure 14(c) shows an intermediate stage where the partially dissolved NAPL ganglion has broken into smaller ganglia.

Clearly, models for NAPL dissolution that model dissolving ganglia as shrinking spheres or other geometrical shapes are approximations of the actual processes. Whether this approach is adequate for estimating changing interfacial

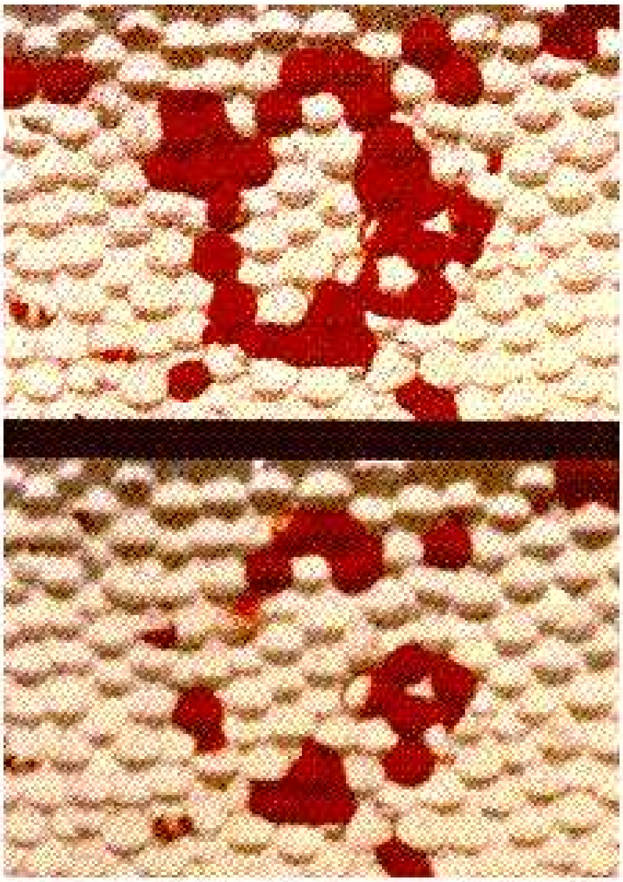


Fig. 13. TCE ganglion initially and after flushing with 555 pore volumes of water.

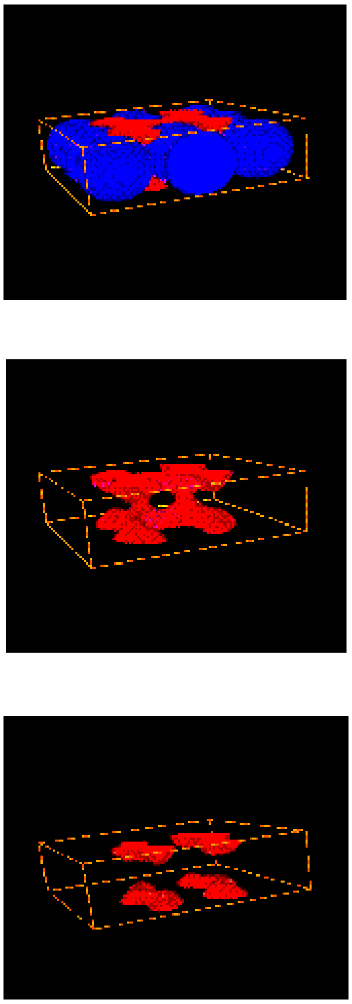
areas for mass transfer is an open question.

These examples show possible applications of pore-scale methods. Such approaches have significant potential for achieving a better understanding of fundamental transport phenomena and leading to improved constitutive relations.

5 STOCHASTIC ISSUES

5.1 Overview

Assuming that a sufficiently complete set of balance equations has been formulated and an appropriate constitutive theory used to close the system of balance equations, it is necessary to specify model parameters and solve the system of equations accordingly. For natural systems, the physical and chemi-



a

b

c

Fig. 14. Lattice Boltzmann simulation of NAPL dissolution in a bead pack: (a) initial conditions with spheres; (b) initial-residual NAPL distribution; and (c) intermediate state of dissolution. This work was performed in collaboration with N. S. Martys of the National Institute of Standards and Technology, Building Materials Division, Gaithersburg, Maryland, while he was on sabbatical at the University of North Carolina.

cal parameters that characterize them vary substantially in space and/or time [82,60,108,226]. Since the complexity of the underlying mechanisms make it impossible to characterize this variability in model parameters deterministically for any system of practical concern, a considerable uncertainty in model parameters must result. As a consequence, natural systems can be realistically modeled only by means of stochastic concepts and methods—multiphase porous media systems are no exception.

In light of this realization, we examine experimental evidence to support the important effects of heterogeneity on multiphase systems, the current understanding of stochastic analysis of flow and transport phenomena, stochastic scaling, and finally, evolving solution methods for stochastic modeling and solution of stochastic partial differential equations (PDE's).

5.2 Experimental observations

Mass transfer from a residual NAPL phase to a flowing aqueous phase is an important process for many environmental multiphase systems. We have commented on the homogeneous conditions under which constitutive relations to describe this phenomenon have been developed as well as on the complex ways in which these relationships scale for heterogeneous systems. In this section, we use recent experimental results to show that even slight heterogeneities significantly affect the distribution of residual NAPL in porous media systems and subsequent mobilization and mass transfer. These observations are used to document the stochastic nature of multiphase flow and transport phenomena in natural systems.

Using methods described elsewhere by Imhoff et al. [143], a residual distribution of PCE was established in an initially water-saturated porous medium, consisting of 70–140 mesh glass beads packed in a 2.5-cm diameter glass column. For this homogeneous system, the media were packed in one column in 3-cm lifts using a wet technique (Experiment 2); the other column was identical but was packed dry (Experiment 3). The distribution of porosity, initial-residual PCE saturation, and PCE saturation as a function of time were measured using x-ray attenuation methods. The difference in packing methods resulted in slightly different porosity distributions, shown in Figure 15. The mean porosity was 0.359 for Experiment 2 and 0.372 for Experiment 3. Experiment 2 showed slightly more variability (standard deviation in porosity = 0.01) than Experiment 3 (standard deviation in porosity = 0.005). Figure 15 shows the initial-residual PCE distribution, which varied markedly and showed much greater variability for Experiment 2 than Experiment 3. We attribute this difference to micropooling of the NAPL above regions of relatively smaller porosity. We also observed that approximately 12% of the total NAPL mass was mobilized when the column for Experiment 2 was flushed with a 60% methanol/40% water solution, while no significant mobilization occurred for Experiment 3 [143].

Clearly, in these experiments, which were performed with a very uniform porous media, small changes in porosity resulted in major changes in residual formation and mobilization. The effect of heterogeneities on NAPL movement has been noted in several two- and three-dimensional experiments [165,140,10,129]. Although infiltrating NAPL will often finger because of viscous instabilities [166,129], locations and diameters of fingers are unpredictable and are influ-

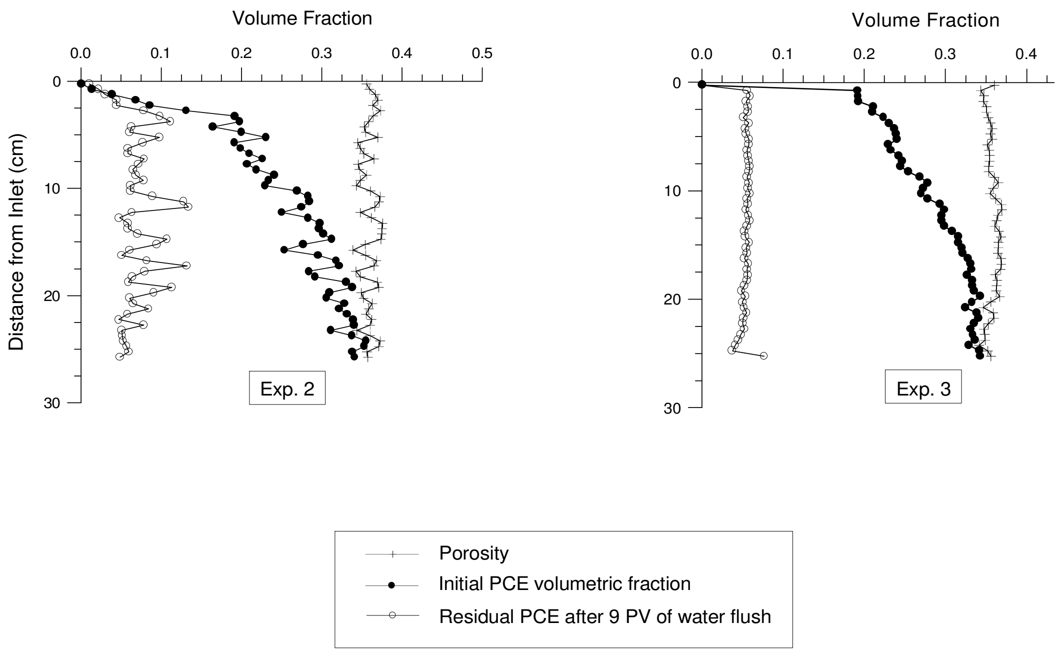


Fig. 15. Distribution of porosity, funicular PCE volume fraction, and initial-residual PCE volumetric fraction after flushing columns with about two pore volumes of water.

enced in part by small-scale heterogeneities [10]. Larger scale heterogeneities in media structure also result in the bypassing and trapping of NAPL [165,140].

In field experiments, geophysical measurements of PCE distribution during a spill in a relatively homogeneous aquifer have demonstrated the effect of natural heterogeneities on the horizontal spread of PCE [39]. Because two similar PCE releases in the same aquifer resulted in significantly different infiltration and migration rates, it was suggested that subtle changes in the distribution of intrinsic permeability and porous media structure led to unique PCE behavior [39]. Thus, natural variability, which may be impossible to characterize, is expected to affect multiphase flow and species transport significantly for all natural multiphase systems.

5.3 Current understanding

While considerable work has centered on the stochastic analysis of single-phase fluid flow and species transport, relatively little has been accomplished for multiphase systems. Yet spatial and/or temporal variability is a central concern for flow and transport in multiphase systems; it should profoundly influence the way in which multiphase systems are conceptualized, theoretically analyzed, experimentally investigated, and modeled.

Currently, the basic steps of the stochastic multiphase flow analysis and transport are similar to those of single-phase flow analysis. Typically, one seeks a description in terms of the low-order statistical moments of the flow and transport parameters involved. There are two standard groups of stochastic techniques for calculation of the low-order moments:

(i) analytical methods that are based on low-order perturbation expansions [57]; and
(ii) simulation methods that generate an ensemble of realizations representing spatially variable inputs [97].

There are unresolved problems with the application of both traditional groups of techniques in multiphase systems. Analytical approaches often rely on a number of simplifying assumptions: constant mean and variance (statistical homogeneity) of physical parameters; low-order truncation of the infinite hierarchy of statistical moment equations (closure problem); unjustifiable elimination of important fluctuation and correlation terms; restrictive and sometimes even unrealistic forms of constitutive relationships; and infinite domains or periodic boundaries [212,185,186,64,57,56,218]. Difficulties may also arise from singular Green's functions, complicated auxiliary conditions, and spatially variable inputs. In many applications, useful applications require combining both analytical and numerical techniques.

Numerical methods are inherently expensive, because they simulate the process with the aid of a discrete four-dimensional network (one time and three space dimensions) of nodes at which a very large number of equations must be solved simultaneously. Hence, simulating the hundreds or thousands of realizations needed for a complete numerical analysis of flow and transport phenomena is beyond the capabilities of even the most advanced existing supercomputers, if performed for realistic scales and finely discretized domains. Other complications arise because field-scale simulators require an averaging of fluid and media properties for grid blocks that are much larger and more heterogeneous than the conditions under which the constitutive theory was developed. For example, see §§4.2 and 4.3.9.

5.4 Stochastic scaling

One of the most fundamental questions of physical sciences is the problem of scales in nature and the description of phenomena over multiple scales. In physics, several scales are considered, giving rise to approaches that range from quantum mechanical approaches at the particle scale to thermodynamic approaches at the field scale. Within this context, scaling relationships are encountered in many situations and over a wide range of scales. These relationships are usually found empirically, since we often lack a theory allowing us to understand them from fundamental principles.

In the geosciences, scale laws have appeared in the form of upscaling. The procedure of upscaling arose from practical considerations: the need to generate representative hydraulic conductivity values for the grid blocks of a considerably larger numerical simulation scale than that where actual hydraulic conductivity measurements have been obtained.

Many computational upscaling techniques are based on the use of *ad hoc* numerical schemes and questionable simplifications to compensate for the limited information available and the lack of a well-established scale theory. Indeed, a realistic upscaling process is confronted with a series of theoretical and practical issues: unknown relationships connecting multiphase systems at different scale levels, limited number of hydraulic conductivity measurements, measurements obtained at various scale levels, boundary conditions, and the formulation and solution of inverse problems. Stochastic analysis can provide theoretical concepts and practical tools that can support computational upscaling techniques, such as those mentioned in §4.3.9.

The effective hydraulic conductivity, K_e, of a porous medium is an important concept in the stochastic study of scaling relationships for single-phase flow. K_e is assumed to be an intrinsic property that gives the mean Darcy velocity $\mathbf{V}$ through the medium in terms of the mean hydraulic gradient $\mathbf{J}$

$$\mathbf{V}(\mathbf{x}) = -K_e\mathbf{J} \tag{14}$$

For a constant K_e to exist, the conductivity random field must be statistically homogeneous and the mean hydraulic gradient uniform (which is equivalent to neglecting the effects of boundaries and sources). K_e may be either a deterministic or random quantity depending on assumptions and methods used in its derivation.

K_e can be calculated either analytically by calculations [158,215] or numerically by the renormalization method [159]. Analytical calculations assume that the conductivity field is log-normally distributed, and it can be shown [191] that K_e of one- and two-dimensional isotropic porous formations is given by the scalar expression

$$K_e = K_g \exp\left[\sigma^2(lnK_e)\left(\frac{1}{2} - \frac{1}{n\,d}\right)\right] \tag{15}$$

where K_g is the geometric mean conductivity, $\sigma^2(lnK_e)$ is the variance of the conductivity in log space, and n_d is the spatial dimensionality of the system.

The validity of equation (15) for three-dimensional porous media has been investigated by several researchers [118,274,215]. Using field theory techniques, Noettinger [215] has shown that this equation is actually an approximation obtained by a partial resummation of the series expansion for the mean flux, and that it fails to capture the effects of zero conductivity zones within the medium. A nonuniform mean gradient is obtained if the conductivity random field is nonhomogeneous, and in this case the mean flow is given by

$$\mathbf{V}(\mathbf{x}) = -\int d\mathbf{x}'\,\mathbf{K}_e(\mathbf{x},\mathbf{x}')\mathbf{J}(\mathbf{x}') \tag{16}$$

Note that due to the nonuniformity of the hydraulic gradient the effective conductivity in equation (16) is a tensor. The nonlocal kernel is a nonhomogeneous function that represents a partial sum of the mean flow series and depends purely on the statistical properties of the medium. The diagrams omitted in the calculation of equation (16) have the same topological structure as the omitted terms in the approximation of equation (15) for the effective conductivity of the homogeneous porous medium. A detailed diagrammtic analysis of this nonlocal approach is available [135].

There are certain things that a theoretically rigorous and physically meaningful stochastic upscaling analysis should do: (1) incorporate flow as well as transport processes; (2) account for the fact that permeability data and flow and transport variables are not always available at the same scale level; and (3) develop stochastic geometrical and stereological tools that provide an adequate description of the complex porous media geometry.

5.5 Evolving stochastic modeling methods

While natural multiphase systems are stochastic in nature, little work exists to characterize the stochastic features of these systems and to establish relationships between stochastic representations and physical modeling. This situation exists for a good reason—the difficulties of characterizing the stochastic nature of multiphase systems.

Lessons learned from single-fluid-phase modeling work on stochastic flow and transport can be used to foreshadow certain aspects of stochastic flow and transport in multiphase systems. These ideas can be applied to the appropriate form and locality of the momentum equations and the constitutive relations used to describe fluid flow and species transport in a stochastic medium.

The momentum equations typically used to model multiphase flow at a macroscopic scale through a heterogeneous porous medium are variations of the local

Darcy's law. However, the standard averaging process for deriving the single-phase form of Darcy's law from Navier-Stokes equations governing flow at a microscopic or pore-scale relies on the assumption that a significant correlation does not exist in the media properties over the scale in which the constitutive relation is derived. The continued averaging of reservoir and fluid properties necessary to use grid blocks of the size of 10^1 to 10^3 m in field-scale simulators further complicates the modeling process.

In last few years, hydrogeologists and petroleum engineers have acknowledged that the local laws of continuum mechanics do not always provide an adequate description of flow and transport phenomena in porous formations. Instead, recent research has given rise to nonlocal formulations of the basic phenomenological laws that generalize the local expressions in cases where the approximations and averages are not valid (e.g., a representative elementary volume [REV] cannot be defined). The nonlocal formulations for single-phase flow and transport equations appear in two forms:

(i) The solution of the local stochastic flow equations leads to macroscopic nonlocal expressions for the statistical moments [65,66,213,147]. The nonlocality of the equations of the statistical moments results from the correlation structure of the hydraulic conductivity and dispersivity random fields. Nonlocality can be expressed in either an analytical or diagrammatic form.

(ii) The local PDE are replaced by nonlocal integrodifferential equations [81,137]. The nonlocality is due to the nonuniformity of the local fields and the memory effect: the motion of the fluid particles within the porous medium under the influence of a force field establishes spatial correlations in the dynamic operators that represent the memory of the field within the medium. The correlations are partially destroyed due to the random scattering of the particles. Thus, the memory depends on the scattering mechanism. The system's evolution is represented by a first-order differential equation in time with a forcing term, the solution of which includes a nonlocal kernel.

While these results have been derived for single-fluid-phase systems, nonlocal equations and relations will be needed to characterize the stochastic nature of multiphase systems as well. p-S-k and interphase mass transfer relations may be included.

5.6 Evolving stochastic solution methods

While serious problems confront current analytical and numerical approaches to the solution of stochastic multiphase flow and transport systems, certain evolving approaches promise to resolve some of these difficulties, based on single-phase work accomplished to date. Such approaches include the diagrammatic and space-transformation methods.

5.6.1 Diagrammatic methods

The stochastic diagrammatic perturbation approach to the solution of stochastic flow and transport systems [65,66,219,63] has been developed as an alternative to standard analytical methods. The approach has certain important advantages over conventional stochastic methods and has been applied with considerable success in the stochastic analysis of single-phase-flow systems. Diagrammatic representations provide solutions to tenacious problems in stochastic theories of flow. For example, the problem of closure of the moment equations can be overcome by formulating closed-form diagrammatic equations that very accurately approximate the exact solutions for the moments. Also, the problem of low-order truncation of the perturbation series can be solved by including an infinite class of diagrams in the equations (i.e., terms from all perturbation orders). Another advantage of this method is that the effects of the boundaries are incorporated explicitly in the solution. Hence, the idealistic assumption of an infinitely extended domain is not necessary, and realistic cases of flow in bounded domains can be studied [219,218]. The diagrammatic formulation is particularly suitable for nonlinear problems.

The considerable advantages of the diagrammatic approach, as compared to the ordinary perturbation techniques, motivate its use for solving the stochastic PDE's of multiphase flow and transport in porous formations with spatially variable properties. This method establishes an exact correspondence between the multidimensional integrals of the Neumann series solution of the multiphase flow equations and provides a graphic representation that offers a more compact and intuitive framework for calculations than cumbersome analytical formulations. Diagrammatic analysis provides a visual language that is valuable to the understanding and prediction of flow and transport of multiphase or multicomponent fluids through porous formations that are strongly influenced by heterogeneities—either large-scale lithological discontinuities or quite localized phenomena.

While many of the abstract diagrammatic representations of the multiphase systems are very similar to those for single-phase systems, considerable challenges arise in the diagrammatic formulation of the constitutive relationships. These relationships lead to a number of diagrammatic terms in the multiphase system's mean and covariance equations, including second and third order statistical moments of the multiphase system's flow parameters. Evaluating the relative importance of these terms, based on a deeper understanding of the physics of the situation, will greatly simplify the subsequent diagrammatic calculations.

The solution of the diagrammatic multiphase flow systems can be obtained by a decomposition of the stochastic equations into a deterministic part that can be solved by a combination of analytical and numerical techniques and a random part that includes the fluctuation effects. The random part is viewed as a random source, and the stochastic solution is therefore expressed as a series of deterministic Green's functions that propagate the effects of fluctuations. Diagrammatic analysis also provides the means for studying coupled fluid-fluid interactions that are highly nonlinear and complex.

5.6.2 Space transformation methods

As an alternative to standard numerical simulation methods, the intuitively attractive space transformation method can provide realizations for multidimensional groundwater flow and transport problems [61,62,134]. The method is based on Radon-type operators and generalized function representations. Space transformations of stochastic PDE's lead to one-dimensional stochastic ordinary differential equations (ODE's) by compressing information in spatial averages along lines or over planes. The set of one-dimensional stochastic ODE's contains sufficient information to permit reconstruction of the full multidimensional PDE solution. The method avoids the simultaneous numerical solution of very large systems of equations in three dimensions, which is both extremely costly and frequently impossible [105]. This technique shows promise but requires further research and development.

6 COMPUTATIONAL ISSUES

6.1 Challenges

The focus of this work is on issues involved with multiphase model formulation and not on numerical approximation methods, solution algorithms, or computational considerations. These neglected topics are important aspects of multiphase flow modeling as well and are deserving of comprehensive works that focus on each of them. However, we comment briefly in this section on some computational issues, since these considerations are important in deciding on an appropriate model formulation, and we expect to see considerable work in this area in the coming years.

It is clear that further development in compositional modeling of multiphase systems will continue to demand the most powerful computers available for the foreseeable future. This assertion follows directly from the desire to explore more complete formulations, treat many component systems, use more complex constitutive relations, and improve the resolution of phenomena that evolve over multiple time and length scales in heterogeneous media. In many cases, the interesting features in the flow are highly localized: DNAPL pools, contaminant plumes, NAPL motion at the top of the water table, and remediation techniques involving chemical injection. For such problems, it is desirable to concentrate the computational effort in the region of interest; dynamically, adpative mesh refinement (AMR) and domain decomposition techniques are natural approaches. These approaches generate significant programming complications, such as dynamically changing data structures, communication problems, and complicated iterative techniques for linear systems.

Current compositional multiphase models are complex, subject to frequent change in the underlying constitutive relationships and process submodels, time-consuming to develop, expensive to maintain, not usually used by a large community, and often poorly documented. This situation is inefficient, and new approaches are needed to increase the rate of evolution of multiphase flow and transport modeling. From a computational science perspective, the current situation for modeling multiphase systems presents a major challenge, especially considering the constraints of both computational efficiency and memory usage.

The most powerful computers will continue to be large vector and massively parallel machines. But even desktop machines are employing architecture that was previously developed for supercomputers, such as pipelining, memory caching, and multiprocessing. Because of these characteristics and the computational challenges facing compositional multiphase modeling, it will be necessary to continue developing parallel solution algorithms and to port the existing codes to parallel processing machines. There is a recent work which highlights some of the challenges in developing a parallel compositional simulator [?].

6.2 Approaches

We believe that object-oriented (OO) approaches will be helpful in responding to many of the challenges noted in the previous section, specifically in managing the complexity involved with simulating multiphase flow and transport phenomena and adaptive methods, and in reducing the effort needed to maintain and extend code as requirements change.

Powerful, comprehensive, and efficient OO libraries written in the C++ language have been developed and released, including Motif for graphical user interfaces, Iris Inventor for 3D graphics, and Lapack++ for linear algebra. For the numerical solution of PDE's, there are some interesting recent developments such as the AMR++ project at Los Alamos for parallel AMR. Another useful toolbox is Diffpack [173,43]. These OO approaches offer a means to increase code reusability, produce efficient codes [13], and greatly decrease development and maintenance time.

For example, given the Diffpack OO toolbox support classes for finite element methods and basic linear algebra functions, it is possible to develop and debug a code in one dimension and then extend it trivially to three dimensions—often the same day. Of course, this process assumes that the application uses nodal basis functions already resident in the library, and the available linear algebra is adequate to handle the particular application.

OO methods are still evolving. While the computer science community has developed target standards for OO languages—such as C++—years ago [96], the maturation of OO methods in general [32,189], and scientific computing using OO methods [23], has been relatively recent. In fact, the standard for C++ is still in draft form. Compiler vendors are working toward implementing features in the draft C++ standard that will allow for an expanded rate of use and development. The development of parallel C++ compilers and libraries is an area of active research that has important implications for modeling multiphase transport phenomena.

We believe that OO approaches represent a powerful new paradigm for scientific computing in general, including compositional multiphase flow and transport modeling. Our experience has been that OO approaches offer a means to respond to the issues of code complexity, need for frequent change, code reusability, and maintenance costs [13]. We expect complex scientific computing applications to benefit substantially from these approaches in the future.

7 CONCLUSIONS

We have critically considered the status of model formulation issues for multiphase flow and transport phenomena. The standard approach for modeling such phenomena relies on continuum balance equations written about a representative elementary volume and closed by supplementing these balance equations with empirical EOS and constitutive relations. These supplementary expressions include relations between pressure, saturation, and conductivity, and expressions for interphase mass transfer and reactions.

The standard approach for modeling multiphase flow and transport phenomena leaves many issues unresolved and leads to many inconsistencies, paradoxes, and questionable approximations. For example, while standard approaches primarily use volume balance equations for conservation of mass alone (and occasionally energy), and Darcy's law as a momentum balance equation, more complete formulations are possible. These formulations include balance equations for mass, momentum, energy, and entropy about volumes, interfacial areas, and three-phase contact lines. These so-called formal averaging approaches provide a means to guide and restrict the development of constitutive relations to thermodynamically consistent forms. These methods require more work to develop, evaluate, and perform enlightened simplifications of the original systems of equations, which are complicated and expensive to solve.

Constitutive relations are projection operators in theory and scaling relations in practice, used to hide unnecessary details while providing a useful description of a phenomenon in terms of accessible parameters. These relations are typically empirical in origin and often based on incomplete experimental data. They are also usually derived using small-scale, homogeneous systems, while the systems of interest are orders of magnitude larger and heterogeneous. The form and parameters of these constitutive relations are subject to change when applied to conditions that differ markedly from those under which they developed—the so-called scaling problem. Resolution of this scaling problem can be considered from either a deterministic or stochastic perspective. Nonlocal behavior is well documented for relations investigated in detail; similar documentation is expected for those relations not yet studied at this level.

Sorption/desorption of organic solutes to natural solids is an important mass transfer process, which is now understood to have time scales that may be on the order of years for attaining what is frequently a nonlinear equilibrium. Multiple-scale models that account for small-scale heterogeneity have been successful in describing the dynamics of this process, but the extension of these relations to field scales is considered an open issue.

Nonaqueous-aqueous mass transfer is a process that has been described using a first-order mass transfer approach, with the mass transfer coefficient usually correlated in terms of dimensionless parameters. Potentially important but only partially understood aspects of this process include dissolution at low levels of residual saturation, the dependence on saturation history, dissolution finger formation and growth, the formation and dissolution of pools, and scaling in heterogeneous media.

While experimental approaches have usually formed the basis for the development of constitutive relations for multiphase systems, multiple-method, multiple-scale computational approaches will significantly assist in the development and refinement of such relations in the future. Promising approaches include synthetic pore-space generation, lattice-gas, LB, pore-scale continuum, network, and multiple-scale continuum approaches.

Multiphase systems are stochastic in nature, and important processes, such as NAPL residual formation and mobilization, are significantly influenced by relatively minor changes in media properties. Stochastic solutions of multiphase flow and transport phenomena are few in number and limited by restrictive assumptions in model form, media properties, and importance of certain terms arising in low-order approaches. High-resolution, Monte Carlo approaches of fine-scale models are considered out of reach even with state-of-the-art methods and supercomputers. Evolving stochastic methods, namely diagrammatic and space-transform approaches, are promising tools for advancing the stochastic analysis of multiphase systems.

Multiphase flow and transport models will continue to demand the most advanced computational machinery available for the foreseeable future, and models for such systems are expected to grow in complexity. Because of this certainty, enlightened simplification of multiphase flow and transport models will be an essential objective to ensure that computational resources are used to resolve the most significant aspects of these models.

Modern computational science tools, such as parallel processing supercomputers and modern software methods will play an important role in the maturation of multiphase modeling. OO approaches are examples of modern software methods that can support a more rapid evolution of simulation models by increasing code reuse and improving both the flexibility and extensibility of simulation models. However, it will be important to continue the development of clever algorithms that both limit computational demands for a given formulation and take advantage of rapidly evolving modern computer architectures.

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