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Transport in the Subsurface**

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Introduction and Scope

This review addresses modeling of subsurface hydrological systems in which contaminants are transported in more than one fluid phase. The primary focus is on problems involving nonaqueous-phase liquids (NAPLs), a dynamic gas phase, or both, so that the unsaturated and saturated zones are both discussed. Basic research in simpler settings is included if it develops concepts that could be applied in modeling of such problems.

Recent developments in practical models are reviewed, along with experimental work and theoretical issues related to the formulation of mathematical models. It will be seen that the extent of validity of the local equilibrium assumption (LEA) for component partitioning among phases is a major question influencing the direction of these formulations. Also emphasized are upscaling to macroscopic and grid lengths, and the choice and coupling of primary variables in multicomponent systems. Relations to and possible use of developments in petroleum reservoir simulation are discussed.

The significance of the type of modeling reviewed here is growing, as the last several years have seen increased awareness of the complexity and difficulty of groundwater contamination problems that involve multiphase flow. For example, emplacement of NAPLs, such as gasoline or trichloroethylene, in the subsurface typically entails downward migration through the vadose zone, leaving some (or all) NAPL mass trapped behind by capillary forces in globules of widely varying shape and size. Depending on the NAPL density and other factors, the remaining mass will float at the water table or continue down into the saturated zone. Some contamination can occur via transport of the NAPL phase itself, but even when this phase reaches immobile residual saturation, its components can dissolve in groundwater in concentrations well above environmental thresholds. These components can then be transported in the water phase to contaminate water far from the NAPL source. Many such components, known as volatile organic compounds (VOCs), will also vaporize into the air phase in the unsaturated zone and can then be transported in that phase.

Conventional pump-and-treat techniques will not readily remove immobile NAPL from the subsurface, where it may persist for decades as a source of contamination. Other mechanisms, such as interphase mass transfer, must be exploited. One example of such a process is vapor extraction, pumping air through the contaminated zone and relying on volatility to partition some mass of the offending components into the air, which is then extracted from the subsurface. This technique may be enhanced by injection of steam, if the chemicals are such that a higher temperature will yield a more favorable partitioning. Partitioning can be quite sensitive to the multicontaminant compositions of the phases present. This discussion is merely illustrative, not exhaustive; for the purpose of this review, it suffices to realize that the whole range of mechanisms of multiphase multicomponent flow in porous media, including viscous, capillary, and gravity forces, diffusion, dispersion, and component partitioning, and reactive processes, are expected to be important in the remediation strategies of the future.

To keep within reasonable bounds, the scope of this review is limited, perhaps somewhat arbitrarily. Exhaustive literature surveys of this and other areas were compiled by *Mayer et al.* [1992, 1993, 1994]. Important topics not discussed here, except as they surface in papers within the scope delineated at the outset, include geostatistics, stochastic hydrology, flow and transport in fractured media, pore-scale models, unsaturated-zone modeling (based on Richards' approximation), and bioremediation modeling. Except for the last, these topics are addressed by other reviews in the present U.S. National Report. Microbial bioremediation is coupled to multiphase models, but is considered here to be more specialized than the subjects under review and so is not emphasized. "Multiphase" is taken to refer to multiple fluid phases, so that sorption by itself is not reviewed here, though it may appear in a wider context or in papers considered relevant to multiphase modeling. Unsaturated-zone modeling that allows for an air-pressure gradient is within the scope.

The review is organized as follows. The next section outlines some major issues in multiphase multicontaminant transport modeling to lay the groundwork for what follows. Further sections deal with physical processes, theoretical upscaling, and formulation of equation systems, primarily at the level of basic research, after which recent published models and their numerical methods are discussed. Finally, developments are summarized and directions for future research are suggested.

Major Issues

The opinion here is that the question that will have the greatest impact on the practice of multiphase multicon-taminant modeling is the extent of suitability of the LEA. If component partitioning is sufficiently rapid that it can be considered instantaneous on transport time scales, then the approaches of compositional petroleum reservoir simulation, appropriately modified and enhanced for groundwater applications, should be very promising. If not, the formulation of models may be quite different, and the computational burdens may be such as to require new approaches. This question heavily influences the level of detail of problems that can be solved within available computing resources.

Another important issue relates to fundamental understanding of multiphase flow: the form of constitutive relations, and in particular the manner in which they can be upscaled to the order of simulation grid sizes, especially in heterogeneous media. This ties in with the LEA question, because the important matter for modeling is whether LEA can be invoked at the grid scale. When state variables change substantially on smaller scales, use of LEA in averaged equations at grid scale may be invalid even when LEA is a reasonable approximation at the smaller scales.

These issues set the context for the question of choice of primary variables and how they are coupled in a multicomponent model. Numerical concerns include calculation of phase equilibria (needed whether LEA is invoked or not); types of spatial and temporal discretization, in particular the extent to which unknowns are treated implicitly or explicitly in time; linearization of nonlinear discrete equations; solution of linear equations; and efficiency in a variety of computing environments (scalar, vector, parallel).

Physical Processes

As noted above, knowledge of relevant physical processes will be crucial in modeling practice. It is beyond the scope of the present modeling review to analyze such research critically; rather, appropriate recent work will be summarized in detail.

NAPL Dissolution

The principal questions are whether LEA is valid, and if not, how to define dynamic mass-transfer relations between NAPL and water.

Earlier work. In work before 1991, the papers of *Hunt et al.* [1988a,b] suggested that mass-transfer limitations would render groundwater extraction ineffective in removing NAPL trapped at residual saturation by capillary forces, recommending steam injection to remedy the situation. Analysis, supported by sand-tank experiments, predicted that a low fraction of solubility would be achieved under typical pump-and-treat conditions. *Parker* [1989] and *Sleep and Sykes* [1989] postulated that LEA could fail to be satisfied at field scale even if it held at pore scale, because heterogeneity could cause phases to be out of contact at many locations. *Miller et al.* [1990] experimentally studied conceptual mass-transfer models based on a driving force (the difference between a component's concentration in a phase and its equilibrium concentration in that phase) and the interfacial area between phases. The models correlated the Sherwood number (mass-transfer coefficient times square of flow diameter, divided by molecular diffusivity) to the Reynolds number (water velocity times water density times flow diameter, divided by water viscosity), the saturation of NAPL, and the Schmidt number (water viscosity divided by product of water density and molecular diffusivity). In homogeneous glass-bead columns, they observed fairly high transfer rates and suggested that LEA could be valid.

Potential causes of nonequilibrium behavior. *Powers et al.* [1991] observed through one-dimensional numerical work that larger NAPL blobs or higher water velocity would lead to greater departures from LEA. Subsequent experimental work [*Powers et al.*, 1992] with laboratory columns confirmed these tendencies and also found that small NAPL saturation or small dissolved NAPL concentration favored nonequilibrium. Soil grain size was found to affect patterns of NAPL distribution, which in turn affected dissolution rates. The authors developed a correlation of the Sherwood number to the Reynolds number, the median grain size, and a "uniformity index" indicative of grain-size distribution. It was suggested that differences in correlations could be due to different

techniques of NAPL placement that resulted in different specific surface areas, and speculated that water flushing of layered or lenticular media over extended periods would favor nonequilibrium by reducing NAPL surface area. Simulations of stochastically generated media by *Mayer and Miller* [1992] found nonequilibrium concentrations at greater distances from a NAPL source than in homogeneous cases. Based on one-dimensional simulations matching a conceptual model to a breakthrough curve, *Brusseau* [1992a] found that contaminant removal could be strongly rate-limited even with a high mass-transfer rate, with nonequilibrium liquid-liquid transfer and medium heterogeneity being more important than nonequilibrium sorption in causing field-scale nonideality.

NAPL blob shapes and sizes. In glass-bead experiments, *Mayer and Miller* [1993] reported discontinuous irregular NAPL blobs at residual saturation, with a few large ones containing more than half of the NAPL mass and many more small blobs with lengths spanning two orders of magnitude. The average dimensionless ratio of volume to surface area (1 for a sphere) was 0.6. This suggests the degree of departure from reality in the models of *Geller and Hunt* [1993] and *Powers et al.* [1994a], which both assume that blobs are spherical. The former study performed mechanistic analysis and glass-bead experiments to derive a model of nonequilibrium dissolution in homogeneous saturated media. It was pointed out that chemical heterogeneity can develop as more-soluble components dissolve, raising the equilibrium concentration of other components and creating nonequilibrium due to aqueous diffusion. The model developed a parameter called the mass-transfer zone, representing the minimum flow-direction length of a contaminated region in order for NAPL-water equilibrium to be achieved. For typical situations, the mass-transfer zone was predicted by the model to range from millimeters to meters, and it proved to be on the order of 10 cm in the experiments. *Powers et al.* [1994a] measured mass-transfer coefficients and specific surface areas independently, then assumed NAPL blobs with a range of sphere sizes and developed a model that could be calibrated to sufficiently rich experimental data. For surfactant-enhanced solubility of NAPLs, *Abriola et al.* [1993] compared calibrated simulations, assuming that trapped residual organics formed spherical globules, to laboratory experiments. Mass-transfer limitations were found to have a large effect on NAPL recovery in both simulations and experiments.

The assumption of spherical blobs was questioned in flow-visualization experiments with etched glass micromodels and short sand columns by *Conrad et al.* [1992]. Much of the NAPL in the saturated zone was in microscopic blobs, whose size, shape, and distribution affected dissolution rates. Spherical single-pore blobs were observed, but most of the NAPL mass in the residual-saturation zone (i.e., where NAPL was trapped by capillary forces) was contained in complex branching multipore blobs. After passing uncontaminated water through this zone, LEA would dictate that blobs at the upstream end should dissolve completely, leaving a sharp front at the point where the solubility limit was reached. This was not always the case, as mass-transfer rates were limited by diffusion through film surfaces of branched blobs, only the "heads" of which were exposed to flowing water.

Powers et al. [1994b] extended their earlier correlation by introducing a parameter corresponding to specific surface area. Previously this had been lumped into the mass-transfer coefficient, as in the correlation of *Imhoff et al.* [1994], where it could be separated out for a particular sand. *Powers et al.* [1994b] sought to generalize the separation with the new parameter, dependent on blob geometry and correlated to grain-size distribution. This was limited to homogeneous media and was verified by comparing experiments to numerical simulations incorporating it.

Heterogeneity and LEA validity. Simulations by *Mayer and Miller* [The influence of mass transfer characteristics and porous medium heterogeneity on nonaqueous phase dissolution, *Water Resour. Res.*, submitted, 1994] considered the effects of heterogeneity along with mass-transfer models and residual NAPL distribution. Distinctions were drawn between the above one-dimensional column experiments and field results, which tended toward greater nonequilibrium [e.g., *Mercer and Cohen*, 1990] due to low NAPL saturation, heterogeneity, and aqueous-phase bypassing. Simulations of stratified aquifers differed from homogeneous cases significantly more than did runs using correlated low-variance data from the Borden site. Mass-transfer correlations were compared for homogeneous media, with the one of *Powers et al.* [1992] showing the only significant deviation from equilibrium. The simulations neglected NAPL dissolution while NAPL was mobile, relying on the brevity of this period, and found that it was important to reduce water relative permeability to account for residual NAPL.

Bypassing was also addressed in three-dimensional laboratory experiments by *Anderson et al.* [1992a], with water flowing partially around a zone of solvent at stable residual saturation. Because there was little reduction of

dissolution due to low permeability in the solvent zone at a flow velocity of 1 meter per day, the authors proposed that below-solubility concentrations in field observations were caused by preferential formation of thin solvent pools, dispersion during transport, and dilution by uncontaminated well water. Another study [Anderson *et al.*, 1992b] noted that chlorinated hydrocarbon (CHC) solvents, which dissolve quickly in the laboratory, have concentrations far below solubility in field measurements. Using analytical transport models, the paper explained the difference through the accumulation of CHC below the water table in stagnant pools atop a low-permeability layer or aquitard, resulting in control of dissolution by vertical dispersion. Voudrias and Yeh [1994] flowed water horizontally under a light NAPL (toluene) pool and observed large vertical concentration gradients. Borden and Pivoni [1992] and Ptacek and Gillham [1992] compared laboratory-column data and column data from the Borden site, respectively, to simulations with equilibrium and nonequilibrium models; in both cases, the nonequilibrium model produced a better match.

Tailing. Two views of tailing in pump-and-treat systems, which can significantly increase remediation time, were put forth by Malone *et al.* [1993] and Wise *et al.* [1992]. The former paper, based on the failure of LEA to predict tailing and the desire to predict dissolution rates observed in long-term studies, split NAPL into two phases in a model, one with fast mass exchange with water and the other slow. The latter contended that the inability of LEA to explain tailing had been based on linear partitioning relationships, and that this could be remedied within LEA by use of favorable nonlinear ones. The study was based on chromatographic analysis of published laboratory data on leaching of NAPLs into a flushing water phase.

LEA summary. The range of validity for NAPL dissolution is unresolved at this time and is an area of active research. There does appear to be a trend toward greater departure from LEA in heterogeneous media. One can therefore speculate that models of NAPL remediation in realistic field formations, with a hierarchy of scales of heterogeneity, will often require nonequilibrium partitioning. As discussed below, the implications of this for practical modeling can be profound.

Equilibrium data. Because rate-limited partitioning models generally depend on a driving force, the difference between ambient and equilibrium concentration, equilibrium data are important whether LEA is invoked or not. Kerfoot [1991] derived equations for the dependence of gas-water-solid concentrations of contaminants on temperature and pore-water content, assuming an ideal gas, isobaric conditions, and complete mixing. Cline *et al.* [1991] studied the effects of complex composition on gasoline-water partitioning coefficients and found that an ideal mixture (Raoult's law) offered good predictions. Lane and Loehr [1992] contaminated field soils with 16 polycyclic aromatic hydrocarbon (PAH) solvents, obtaining aqueous concentrations independently by direct measurements, predictions from Raoult's law, and predictions with organic cosolvents. Good agreement among these three methods suggested that Raoult's law was valid, and strong dependence of solubility on organic composition was observed. PAH experiments of Lee *et al.* [1992a,b] also suggested that nonideality was sufficiently small to allow use of Raoult's law in most field-scale applications. However, the work on tailing by Wise *et al.* [1992] suggests that limitations exist.

Additionally, multiphase equilibria have been studied in the petroleum industry for decades, and a state-of-the-art summary of the best correlations, obtained by comparing published correlations to a Core Laboratories data base, is available [McCain, 1991]. Because components (e.g., refined as opposed to crude), phases (NAPL and water instead of liquid and vapor hydrocarbon), and conditions (e.g., much lower pressures) are different in groundwater modeling, these equilibria cannot be applied directly, but an analogue would be desirable.

Approximations to dissolution kinetics. Assuming that nonequilibrium models are needed in many applications, it may be important to assess approximations. Zaidel and Russo [1993] presented one- and two-dimensional analytical solutions for steady-state flow and transport in a homogeneous vadose zone with kinetic volatility and dissolution of immobile NAPL. An advection-diffusion-reaction equation was solved for concentration. LEA was found to hold if the Damkohler number (mass-transfer coefficient times vertical extent of NAPL, divided by advective velocity of water), or an analogue in diffusion-dominated flows, was sufficiently large. The rather specialized results could be useful for verification of numerical models. Also in homogeneous media, assuming LEA, Mackay *et al.* [1991] analyzed mathematically the time evolution of NAPL concentration as clean water flowed by, with later water receiving less NAPL than earlier because of reduced component NAPL concentration. Then they modified

the transfer for nonequilibrium by multiplying the flow rate by an efficiency factor less than unity, effectively exposing the NAPL to less water. For multiple components with distinct solubilities, the approximation became more complicated as dissolution of one component would affect NAPL concentrations of others. To compute the transfer of a component, the authors grouped the remaining ones into those of greater solubility, which were assumed to be rapidly lost from the NAPL phase, and those of lesser solubility, which were assumed to remain fully in the NAPL phase. Column experiments were consistent with the theory. As will be addressed below, approximate kinetics may be an important tool in future efficient modeling of nonequilibrium systems.

VOC Mass Transfer

Before 1991, *Baehr et al.* [1989] had measured liquid-vapor mass-transfer rates for gasoline in homogeneous media. Even for a fairly high air-phase velocity, the experiments were matched well by an equilibrium transport model. It was indicated that contact of the flowing air phase with the contaminant would be important in a heterogeneous medium. The authors speculated that equilibrium might not hold for a pure liquid in place of gasoline. Comparing simulations to laboratory experiments, *Gierke et al.* [1992] found that vapor extraction was affected by nonequilibrium transport in moist soils in which soil particles and immobile water were aggregated. The nonequilibrium effects were attributed to diffusion within aggregates, a more complicated mechanism than first-order kinetic mass transfer that has not been included in models. Another complication in mass transfer was reported by *Brusseau* [1992b], observing that the sorption rate constant depended on gas velocity, so that the validity of LEA could not be simply pegged to the reciprocal of velocity. *Cho et al.* [1993] measured gas-water transfer rates in the laboratory and the field for low gas-flow velocities in the unsaturated zone. They found that simulation of the dynamics of VOCs during infiltration required kinetic transfer. As with NAPL dissolution, the range of validity of LEA for VOC mass transfer is uncertain at this time, but it appears that nonequilibrium phenomena will be important in at least some applications.

Capillarity and Hysteresis

Several experimental studies revealed multiphase behavior that is not accounted for in standard models. In heterogeneous oil-water laboratory experiments, *Illangasekare et al.* [1992] observed lateral spreading of a plume when it reached the boundary between finer and coarser layers. The plume would not penetrate the fine layer until it attained a sufficient ponded depth, an apparent result of different capillary pressure-saturation relationships in the two sands. The oil preferentially filled the coarse lens and developed a sharp interface with the fine sand, in contrast to simulations with constitutive models used in typical numerical codes, which would show it diffusing through. *Oldenburg and Pruess* [1993] developed a numerical model using harmonic-average relative conductivities at capillary interfaces to avoid this type of diffusion caused by standard upstream weighting. With detailed cross-sectional characterization of saturations in an oil body floating on the water table at a spill site, *Essaid et al.* [1993] similarly found that migration of oil at the capillary fringe was not reproduced in simulations. To match the observed asymmetrical oil body with high saturation at its center, it was necessary to include hysteresis with oil entrapment in the model used, as well as heterogeneity to account for observed fingering. *Lenhard et al.* [1991] used an empirical correlation to obtain trapped saturation from imbibition residual nonwetting-phase saturation and other standard data, developing a hysteretic model that compared better to experiments than did a nonhysteretic model. This model included contact angles and irregular pore geometry to incorporate entrapment. Subsequent three-phase experiments [*Lenhard*, 1992; *Lenhard et al.*, 1993] extended the case for inclusion of hysteresis in models.

Kaluarachchi and Parker [1992] modeled effects of oil entrapment on three-phase relative permeability-saturation-capillary pressure relations. A non-hysteretic model, using data on air-water saturation-capillary pressure, residual oil saturation, and ratios of water surface tension to oil surface tension and to water-oil interfacial tension, proved to be more efficient than a full hysteretic model.

Seeking to predict capillary pressure-saturation curves from interfacial tensions, *Demond and Roberts* [1991] surprisingly found that residual water saturation increased as interfacial tension decreased. They explained this on the basis of the range of pore sizes, with decreasing interfacial tension leading to an increased drainage rate and hence to increased channeling and bypassing of pores. The authors found that capillary pressure had to be defined as a function of effective saturation, potentially a difficult matter without possibly unjustified assumptions about

residual water saturation.

Accurate representation of these capillarity-related phenomena is important for modeling in appropriate situations, as evidence mounts that models should account for hysteresis in particular. As a practical matter, these phenomena introduce additional model complications of a modular nature involving evaluation of coefficients in equations. Unlike nonequilibrium phase behavior, they do not affect the basic structure, such as the set of primary variables.

Theoretical Upscaling

Theoretical advances in the upscaling of multiphase-flow models were reported using several fundamentally different approaches. *Gray and Hassanizadeh* [1991a,b] and *Hassanizadeh and Gray* [1993a,b] derived an improved macroscopic physical description of two-phase flow from conservation of mass, momentum, and energy, and the second law of thermodynamics. Among the aims were to avoid the usual questionable extension of the single-phase Darcy law via relative permeability, and to obtain equations defined entirely in terms of macroscopic state variables, thereby averting confusion between scales. Theoretical and experimental paradoxes arising from traditional assumptions of capillary-gravity equilibrium were discussed. The complete two-phase model was quite complicated, but with quasi-equilibrium assumptions its variables were reduced to the standard ones along with macroscopic capillary pressure, P_c , and the specific interfacial area, a_{wn} , between the phases. P_c was a function of a_{wn} as well as wetting-phase saturation and was not in general equal to the difference between macroscopic nonwetting- and wetting-phase pressures; this held only at equilibrium, and the difference yielded a dynamic capillary equation. The model also added an interfacial-area equation to the usual set and a saturation-gradient term to the Darcy potential gradient in the momentum equation, and a nonempirical flow-coefficient tensor was derived to replace relative hydraulic conductivity. The inclusion of interfacial-area dependence of capillary pressure was expected to eliminate the need for hysteresis. The model required more data than a standard one, but its physical basis made the data potentially easier to describe and measure without having to rely on complex empirical functional dependencies.

Wang and Beckermann [1993] applied a two-step process, dual-scale volume averaging, to multiphase flow. They proved general dual-scale averaging theorems applicable to a variety of transport processes, avoiding the need to rederive the averaging for each equation set. Representative elementary volumes were allowed to change with time. If one physical phase flowed on both characteristic length scales, it was represented by two phases, one at each scale, with a time-varying imaginary interface between the scales.

King et al. [1993] extended real-space renormalization, based on an analogy with a network of resistors, to two-phase flow. In a numerical implementation, they found it to be 100 times faster than traditional petroleum-industry methods, which generate pseudo-relative permeabilities by successively moving from finer to coarser grids.

For upscaling of capillary pressure, *Kueper and McWhorter* [1992] used a macroscopic percolation theory. Each point of the percolation lattice, instead of being a pore, was a local-scale porous medium with given porosity, permeability, and saturation-capillary pressure relation. The result was a hysteretic large-scale capillary pressure as a function of large-scale saturation. This assumed capillary-dominated flow in which a static capillary-pressure curve could model dynamic conditions and gravity could be ignored. Macroscopic trapping could be modeled by the order in which lattice points were invaded, and in contrast to microscopic percolation, both phases could be continuous via local-scale relations.

Research on upscaling, in its infancy for multiphase flow, is of considerable future significance because it could determine the impact of other fundamental research on the practice of modeling. For example, with regard to phase partitioning, the real issue is the form that a model should have after averaging up to simulation grid scale. This may be quite different from the models being derived at laboratory scale from experiments. It is evident that much important fundamental work remains.

System Formulation

This section concerns basic matters of equation formulation, such as the choice of primary variables and the manner of coupling between them. Details of recent implementations are deferred to the section on recently

published models.

Richards' equation

This equation is relevant because of its influence on multiphase models. *Sudicky and Huyakorn* [1991] reviewed developments in this area through 1990. For present purposes, the paper of *Celia et al.* [1990] is recalled, which advocated the mixed formulation [*Milly*, 1985] of Richards' equation, in which storage and transport terms are expressed in terms of water content and head, respectively. This avoids mass-conservation errors of the traditional head-based form and problematic degeneracies that appear in the content-based form as saturated conditions are approached. A maximum principle, assuring absence of nonphysical oscillations in results, was enforced by lumping the finite-element storage matrix in analogy with finite-difference approximations at the cost of some artificial smearing of the solution. Based on this experience, *Celia and Binning* [1992a] extended the mixed form to a mass-conservative model of two mobile phases, each consisting of one component with no mass transfer. The nonlinear implicit equations were solved for two phase pressures (p - p formulation) by a modified Picard iteration. This can be viewed as a Newton-Raphson linearization with incomplete Jacobian, including primary-variable dependencies of spatial and temporal derivatives, but not of nonlinear coefficients. Time-step sizes were selected so as to expect 10 to 15 iterations for nonlinear convergence. Another study [*Celia and Binning*, 1992b] noted that, if an infiltrating moisture front is moving at near-constant speed, it is important to acknowledge the wave-like nature of the two-phase flow problem and base the model on one pressure and one saturation (p - s formulation) with a fractional-flow function of saturation. This permitted application of an Eulerian-Lagrangian approach [*Dahle et al.*, 1992] that approximates advection-dominated transport more accurately than standard Eulerian methods. *Kueper and Frind* [1991a,b] pointed out the ability of the p - s approach to handle infiltration into contaminant-free soil, avoid fictitious saturations, and specify boundary conditions in a straightforward way. Newton-Raphson linearization was used for their fully implicit equations.

The head- or pressure-based formulation was studied extensively by *Abriola and Rathfelder* [1993] for two mobile phases, seeking to control mass-balance errors in p - p formulations. With an unlumped finite-element storage matrix, they had difficulties because the chord-slope approximation of the capacitance coefficient [*Cooley*, 1983] would not conserve mass, and elaborate schemes were presented to attempt to eliminate the resulting errors. A further problem was the degeneration toward zero of the capacitance coefficient as capillary pressure became small.

The fundamental difficulties of the widely-used head-based and p - p formulations [e.g., *Osborne and Sykes*, 1986; *Kaluarachchi and Parker*, 1989] are avoided in a straightforward fashion by moving to mixed and p - s forms. From a conservation point of view, the transport terms are naturally expressed in terms of potential gradients or differences, while the storage terms naturally involve contents or saturations. Passing to a head-based formulation requires the unnatural conversion of a change in saturation into the product of a capacitance coefficient and a change in head. Evaluation of this coefficient by a chord-slope formula makes the product equal to the change in saturation, effectively returning to the mixed form, as long as the storage matrix is lumped so that distinct capacitances at adjacent nodes do not enter; thus, the approach of *Cooley* [1983] was equivalent to the mixed form.

Because pressure typically behaves in a diffusive manner, as represented by a parabolic partial differential equation, a p - p formulation hides the wave-like or hyperbolic parts of the overall behavior of multiphase flow. Essentially, this is an ill-conditioned choice of primary variables when the two pressures are closely related, i.e., when capillary effects are small relative to the system at hand. This manifests itself in the difficulties cited above, because the wave-like behavior is present but cannot be well represented. The p - s formulation does not suffer from this drawback. Presumably, the p - p approach grew out of the head-based form of Richards' equation. With one dynamic phase, capillary pressure, or equivalently head, can be an effective surrogate for saturation. With two, especially two liquid phases, ill-conditioning is likely. Petroleum reservoir simulation, based on the different tradition of Buckley-Leverett theory, has long used analogues of the mixed and p - s forms [*Peaceman*, 1977].

Single-Phase Solute Transport

Systems with several components were considered by *Yeh and Tripathi* [1989], focusing on the choice of primary variables and the coupling of transport equations to chemical reactions. With LEA, they recommended total analytical concentrations of aqueous components as primary variables, pointing out that these would describe any

possible state of the system. Under nonequilibrium reactions, appropriate phase concentrations would be primary also. To avoid excessive computational burdens and make inclusion of kinetics feasible, they recommended coupling by sequential iteration. This work on single-phase transport is cited here because multiphase analogues of these suggestions essentially coincide with the practice of state-of-the-art generalized compositional petroleum reservoir simulators [Young and Stephenson, 1983; Watts, 1986], where primary variables may be total component mole numbers rather than concentrations in order to simplify certain coefficient evaluations.

Time-Stepping Formulations

Compositional simulators have most often used the IMPES (implicit pressure, explicit saturation/concentration) formulation, due to the computational burden of generating and solving fully implicit multicomponent equations, though implicit codes also date back many years [Coats, 1980; Chien *et al.*, 1985]. With LEA, to our knowledge universally assumed in petroleum codes, the number of partial differential equations is the number of components, often 8 to 10 in applications. The IMPES pressure equation, with Newton-Raphson iteration, has averaged 1 to 1.5 iterations to converge to a solution [Young, 1992], and satisfactory results may often be obtained with one iteration per time step [Watts, 1986]. The principal limitation is numerical stability, with the time step constrained by some form of Courant condition.

Groundwater modeling has generally proceeded from an implicit perspective. Reeves and Abriola [1994] proposed a “set-iterative” two-phase compositional scheme that separated bulk-phase balances (two without LEA, one overall balance with LEA) from component balances in phases ($3(n - 1)$ without LEA, $n - 1$ with LEA for n components), with the two sets weakly coupled through composition-dependent fluid properties and mass-transfer terms. The equations were solved in a sequentially implicit fashion, passing from the most-volatile component to the least. A common difficulty with such formulations is the inconsistency that arises from the treatment of composition dependencies in transport terms: explicit in the phase balances, implicit in the component balances. The authors avoided a simultaneous fully implicit approach because of its computational requirements and considered an “adaptive IMPES” formulation impractical. This method, called “adaptive implicit” in the petroleum literature, adaptively treats some grid cells as IMPES and others implicitly as determined by an automatic switching criterion, ideally incurring the expense of implicitness only where stability demands it. The conclusion of impracticality was based on the difficulty of substituting primary variables with many components as phases appear and disappear, which the use of total concentrations or total mole numbers should avoid, and on the expensive need to make most cells implicit after mass transfer [Forsyth, 1988]. The latter need arose from switching criteria based solely on observed changes in primary variables; criteria that also incorporate numerical stability analysis in a Young-Stephenson code have required at most 15 to 20 percent of cells to be implicit, even in high-velocity near-well applications such as coning [Young and Russell, 1993]. These criteria allow a cell to switch from implicit to IMPES, which often happens after a front passes, and have proved useful in selecting time steps for efficient IMPES simulations.

Treatment of Nonequilibrium

As noted by Yeh and Tripathi [1989], Rathfelder *et al.* [1991], Reeves and Abriola [1994], and others, nonequilibrium significantly alters model formulation. With LEA, the phase concentrations that govern component fluxes are determined algebraically, locally in space, by component total concentrations. With kinetics, phase concentrations are history-dependent and differentially coupled to transport equations that contain spatial derivatives. Thus, in a system with n components and m phases, where every component can exist in every phase, LEA permits closure of the system with n partial differential equations, while a rigorous model for nonequilibrium requires mn . In groundwater modeling, historically n has been small, usually 3 or less, but increasing concerns with complex contaminants seem sure to stimulate interest in systems whose behavior demands many more components for accurate modeling. The petroleum industry has dealt successfully with systems of 10 or more components, but usually with IMPES techniques and always with LEA. It is highly unlikely that fully implicit treatment of mn equations, with n large and m around 3, will be practical in the foreseeable future. Hence, assuming that consideration of nonequilibrium is important, it will be critical to find simplifications that permit practical computations without unduly sacrificing accuracy.

If flux coefficients depend explicitly on phase concentrations, as in an IMPES procedure, it should be relatively straightforward in a Newton-Raphson iteration to set up and solve m flow equations implicitly in a manner analogous to *Young and Stephenson* [1983], using old values of phase concentrations, then solve $m(n - 1)$ transport equations explicitly, including kinetics. This decouples flow from chemistry, and caution may be called for in applying such an approach [*Valocchi and Malmstead*, 1992]. An intermediate possibility could be to somehow approximate flowing phase concentrations (e.g., via local transient ordinary differential equations, perhaps including data from adjacent cells), short of full differential coupling, given total component concentrations. The resulting n -equation model would then resemble an equilibrium model, but with modified flux coefficients and modified derivatives in the Newton-Raphson Jacobian. The approximate kinetic techniques of *Zaidel and Russo* [1993] and *Mackay et al.* [1991], or similar concepts, could be useful here. An adaptive implicit scheme could enhance accuracy by allowing finer grids and time steps within practical bounds; stability analysis would need to incorporate the kinetic relations.

Summary

System formulation, at a general, basic level as opposed to detailed application, appears to be the area in which the art of modeling of multiphase multicontaminant transport in groundwater could most benefit from experiences reported in the petroleum literature. Matters such as phase appearance and disappearance have been handled efficiently by generalized compositional models based on extensions of p - s formulations, total concentrations or analogues as primary variables, IMPES or partially implicit coupling, and Newton-Raphson iteration. The modularity of these codes allows for substitution of appropriate fluid-property calculations, inclusion of reactions, and so on. Nonequilibrium is the major phenomenon necessitating significant new concepts.

Recent Models

The review of *Sudicky and Huyakorn* [1991] includes a comprehensive summary of multiphase groundwater models through 1990. Related reviews were presented by *Abriola* [1987], *Parker* [1989], and *Mercer and Cohen* [1990]. Accordingly, this review concentrates on more recent developments. In an imprecise manner, discussion proceeds from more-specialized to more-general models.

VOC Movement

Rathfelder et al. [1991] modeled soil vapor extraction in two dimensions with a mobile gas phase, immobile oil and water phases, sorption, n components, and equilibrium or nonequilibrium versions. Citing *Baehr et al.* [1989], equilibrium modeling of field-scale venting seemed appropriate. Nonequilibrium was represented by source terms with a linear driving force. Implicit point-centered finite differences led to nonlinear equations solved sequentially by Newton-Raphson iteration, using a direct sparse linear-equation solver. *Benson et al.* [1993] also developed a two-dimensional n -component equilibrium model with a mobile gas phase. The flow equation was solved by block-centered finite differences, and the transport equations and phase equilibria were solved simultaneously. *Brusseau* [1991] modeled one-dimensional advective and dispersive gas transport with rate-limited sorption in the presence of an immobile liquid, emphasizing heterogeneity by considering advective and nonadvective regions in the soil and permitting equilibrium or nonequilibrium partitioning in each region. *Culver et al.* [1991] included mobile gas and water, surface volatilization, and vapor sorption in a two-dimensional finite-element LEA model. *Ong et al.* [1992] incorporated experimentally-derived vapor-sorption relationships into this model. *Armstrong et al.* [1994] extended the model of *Mendoza and Frind* [1990] to include nonequilibrium partitioning. The two-dimensional finite-element model also accounted for liquid sorption and gas advection and diffusion, with an immobile water phase.

Specialized Complex Models

In one dimension, *Ryan and Cohen* [1991] sequentially coupled two-phase (air and NAPL; immobile water) immiscible flow, with a NAPL phase in the unsaturated zone containing sparingly water-soluble organic compounds, to four-phase (air, water, NAPL, solid) nonequilibrium chemical transport. The model resulted in a flow equation for each phase and a transport equation for each solute in each phase. The numerical approach was notable for a front-tracking algorithm to locate the NAPL front as a function of penetration time without the front smearing

typical of standard methods, yielding a discontinuity in NAPL saturation at the front. *Abriola et al.* [1993] studied surfactant-enhanced solubility of NAPLs with a one-dimensional finite-element model. Residual NAPL was immobile, trapped in spherical globules, with transport of dissolved organic and surfactant in the water phase and nonequilibrium solubility with linear driving force.

Brusseau [1992a] considered an immobile NAPL with rate-limited exchange with air, water, and solid phases in one dimension. The usual first-order mass-transfer model, which assumed that exchange was constrained by one factor (usually transfer at the interface), was extended to include a second resistance to allow for additional constraints such as liquid diffusion rates. This led to two mass-transfer equations, one for each concentration coupled to the interface.

Chen et al. [1992] modeled one-dimensional biodegradation and transport of benzene and toluene, with equilibrium mass exchange between some combinations of solid, liquid, gas, and biomass. Components included the two substrates, two electron acceptors, one trace nutrient, and two microbe populations, resulting in five transport equations, five algebraic mass-transfer equations, and two ordinary differential equations describing microbe growth. The finite-element transport equations were solved by Picard iteration, with Newton-Raphson for mass partitioning. *Malone et al.* [1993] considered a similar one-dimensional problem, with solid, fast oil (in terms of rate of mass transfer with water), slow oil, and water phases and n hydrocarbon components. The physical difference between the two oils was in the size of trapped globules. Equilibrium linear sorption and rate-limited linear oil-water mass transfer were assumed. The model included equations corresponding to intermediate reaction compounds, oxygen, and oil saturation. The equations were solved sequentially, with upstream block-centered finite differences for transport and ordinary differential equations for reactions and partitioning. Numerical dispersion was controlled by reducing the physical dispersion coefficient to compensate for upstream weighting, which is feasible in one dimension.

Chemistry/Transport

With a single phase in two dimensions, *Yeh and Tripathi* [1991] presented a hydrogeochemical multisolute transport model based on the formulation that they had advocated earlier [*Yeh and Tripathi*, 1989]. Linear differential transport equations were solved sequentially, iterating between this module and one solving nonlinear algebraic equilibrium equations. Iterative coupling was found to be important, as results differed if only one iteration was taken. *Kalatzis et al.* [1993] used streamline directional splitting for transport in a two-dimensional LEA model that included sorption as well as reactions in solution. *Šimunek and Suarez* [1994] included transport of carbon dioxide in both the water and gas phases in the unsaturated zone, as well as solute transport in water. The model incorporated detailed chemistry, nonequilibrium kinetics, heat transport, and evapotranspiration. The conservative form [*Celia et al.*, 1990] of the flow-equation storage term was used, with fixed-point iteration between the transport and chemistry modules.

Limited NAPL Models

“Limited” refers to models that do not allow for at least three phases and three components. A mainly qualitative screening model of *Weaver et al.* [1994] simulated transport of a partitionable NAPL contaminant in the vadose zone, neglecting capillary-pressure gradients and reducing the problem to a first-order hyperbolic equation that could be solved by the method of characteristics. *Mayer and Miller* [1992] reported a two-dimensional two-phase two-component model allowing for nonequilibrium dissolution of NAPL into the aqueous phase, resulting in three equations solved for two pressures (p - p formulation) and one concentration. A Galerkin finite-element method with lumped storage terms was used for the two flow equations, which were solved simultaneously by Picard iteration. A Petrov-Galerkin scheme, again with Picard iteration, was sequentially applied to transport. Geostatistical heterogeneity was included. *Guarnaccia and Pinder* [1992] considered the same situation except that water was also allowed to dissolve in the NAPL phase, leading to four equations. Finite elements with orthogonal collocation and mass lumping yielded two flow equations, solved simultaneously for one pressure and one saturation (p - s formulation) by modified Picard iteration [*Celia et al.*, 1990], and two decoupled transport equations solved for two concentrations. The model simulated emplacement and removal of dense NAPL in a saturated system. *Kueper and Frind* [1991a] developed a finite-difference model for the same problem without mass transfer,

solving implicit p - s equations simultaneously by Newton-Raphson iteration with an Orthomin iterative linear-equation solver preconditioned by the Dupont-Kendall-Rachford (DKR) incomplete factorization. Heterogeneity was emphasized, with a grid aligned with geological bedding.

Essaid et al. [1993] developed a two-phase two-component upstream finite-difference p - p formulation. There was no mass transfer, and three-phase saturation-dependent properties were used in the unsaturated zone, where air pressure was constant. The implicit nonlinear equations were solved by Picard iteration. *Faust et al.* [1989] presented the only three-dimensional model in this group for the same type of problem, using a p - s formulation. The implicit nonlinear equations were solved simultaneously with Newton-Raphson iteration, using a slice successive overrelaxation (SOR) scheme for linear equations.

Parker et al. [1994] and *Wu et al.* [1994] described two-dimensional areal models of three-dimensional systems with local gravity-capillary vertical equilibrium. *Parker et al.* [1994], using the model of *Kaluarachchi et al.* [1990], simulated water and light-hydrocarbon components with no mass transfer, sequentially solving triangular or quadrilateral finite-element equations with preconditioned conjugate-gradient iteration. The model was derived from vertical integration of air, oil, and water phases. *Wu et al.* [1994] pointed out difficulties with such a vertical-equilibrium assumption in the vadose zone, such as inapplicability to descending NAPLs, and integrated only in the saturated zone. The two-phase two-component model allowed a nonzero residual NAPL saturation through history-dependent pseudo-functions, using the vertical distribution of NAPL as well as its vertically averaged saturation. The mass-conservative finite-element equations included fully implicit well terms based on the equivalent-radius formulation of *Peaceman* [1983] and were solved by Newton-Raphson iteration. A limitation of the model was that it required an immobile zone above the water table, even if the water table changed with time.

Three- and Four-Component Models

These models have three mobile phases and at least three components. In three dimensions, *Huyakorn et al.* [1994] developed a three-phase three-component dual-porosity model suitable for fractured or non-fractured media. There was one NAPL component and no mass transfer, which avoided the burden of compositional calculations but limited the applicability of the model. The primary variables were one pressure and two saturations, as in typical black-oil petroleum reservoir models. A fully implicit mass-lumped upstream-weighted finite-element discretization with hexahedral bricks allowed for 7-, 11-, and 27-point connectivities and implicit wells. The implicit equations were solved by Newton-Raphson iteration, treating linear algebraic equations with a block-Orthomin procedure preconditioned by incomplete factorization (ILU). Positive transmissivities were assured by the formulation. Building on an earlier model of *Forsyth and Shao* [1991], *Forsyth* [1993] presented a two-dimensional three-phase four-component model to handle two contaminant components and steam. NAPL could flow in all three phases, water in the water and gas phases, and air in the gas phase only, with equilibrium mass transfer governed by empirical fluid-property correlations. The gas phase was assumed to be always present, with a small fictitious saturation if necessary, and on this basis variable substitution was implemented to treat phase appearance and disappearance. This forces the substitution logic into the flow and transport equations, unlike generalized compositional petroleum reservoir models that confine this logic to a fluid-property module by using total component concentrations as primary variables. A fully implicit (except for some dispersion terms) mass-lumped upstream-weighted control-volume finite-element method generated nonlinear equations that were solved by Newton-Raphson iteration with an ILU-preconditioned conjugate-gradient algorithm for linear equations. A major point of the paper was a procedure for modifying some dispersion coefficients in order to avoid negative transmissivities and obtain a maximum principle, which prevents nonphysical oscillations.

Compositional Models

These formulations treat an arbitrary number of components. *Reeves and Abriola* [1994] proposed the set-iterative two-phase model described above. The mass-lumped finite-element method used variably-weighted time stepping, with linear kinetic mass exchange. Successive-substitution iteration solved the phase-equilibrium equations. *Adenekan et al.* [1993] (building on *Falta et al.* [1992]) and *Sleep and Sykes* [1993a] detailed three-dimensional three-phase n -component models that allowed every component to appear in every phase, with equilibrium mass transfer.

Adenekan et al. [1993] treated arbitrary phase appearance and disappearance by variable substitution without fictitious saturations. Gas properties were based on a Soave-Redlich-Kwong equation of state, ideal mixing in an incompressible oil phase was assumed, and water properties depended on pressure and temperature only. Advection by capillary, gravity, and viscous forces, diffusion, linear adsorption, and heat transfer were included. A fully implicit upstream-weighted integrated finite-difference discretization that allowed for implicit pressure-controlled wells yielded nonlinear equations solved by Newton-Raphson iteration, with a sparse direct or conjugate-gradient-based iterative linear-equation solver.

Sleep and Sykes [1993a,b] also used variable substitution in a complicated set of cases. Dispersion as well as diffusion was included. Products of phase saturations and dispersion coefficients were averaged harmonically, setting dispersive flux of a phase to zero if the phase did not exist on one side of a cell face. The nonlinear finite-difference equations were solved by Newton-Raphson iteration, with linear equations treated by Orthomin preconditioned by a D4-ordered ILU decomposition. Two numerical features of this model are notable. First, it allowed for fully implicit, IMPES, or adaptive implicit time stepping. The implicit/explicit switching criteria were based only on changes in state variables, so that implicit cells could not be allowed to become explicit. Stability-based criteria do not suffer from this drawback. Second, in explicit cells, second- and third-order upstream weighting schemes were offered as alternatives to the standard first-order approach. The goal was to reduce numerical dispersion, especially critical in NAPL applications because of the importance of the arrival time of low concentrations. It should be noted that the finite propagation speed of an IMPES formulation, advancing the leading edge of a front at most one cell per time step, can be helpful here. With 2 to 3 Newton-Raphson iterations for IMPES and 5 to 6 for fully implicit time steps, and with more-accurate weighting available in explicit cells, IMPES is likely to be more efficient in terms of overall accuracy per unit of processing time, an observation similar to that of *Young and Russell* [1993], where adaptive implicit in many cases was still more efficient.

Representative of the state of the art in compositional petroleum reservoir simulation is the report of *Young* [1992]. The three-dimensional generalized compositional formulation [*Young and Stephenson*, 1983] separates flow and transport computations from fluid-property calculations, simulating different types of systems by substituting different fluid-property modules that can allow any number of components to flow in any phase. The mass-conservative finite-difference equations, allowing for bordered matrices resulting from implicit wells, are solved by an IMPES or adaptive implicit procedure. With vectorization of 98 to 99 percent of the computations, overall speeds of over 500 MFLOPS (500 million floating-point operations per second) have been achieved on supercomputers. Particular attention has been paid to vectorization of equation-of-state equilibrium calculations, which typically occupy over half of the computing time [*Young*, 1991]. An IMPES run with 20,000 cells, 1,000 time steps, and 9 components was completed in 23 minutes on a Cray X-MP [*Young*, 1991], and black-oil simulations with over 1,000,000 cells have since been performed in minutes [*Young*, 1992]. As is typical for petroleum models, dispersion, sorption, reactions, and biodegradation are not included; the paper indicated how some of this could be done. *Hinkley and Killough* [1992] applied the Young-Stephenson formulation to three-phase groundwater flow and transport in the vadose zone, finding that gas-phase dynamics was important in their examples.

Recent innovations in compositional reservoir modeling primarily centered around more efficient or robust alternatives to traditional successive-substitution algorithms [e.g., *Mehra et al.*, 1982] for phase equilibria. *Litvak* [1993] proposed direct minimization of Gibbs free energy, as opposed to methods that find a state where its first partial derivatives vanish. *Sams et al.* [1993] used equations based on scaling theory from condensed-matter physics to obtain a more robust algorithm in near-critical regions.

Summary

The range of multiphase models has increased in the last 4 years in variety, complexity, and sophistication. Many more three-dimensional codes have been developed, some of the first n -component groundwater models have appeared, and specialized models are more intricate as well. There are clear trends toward p - s multiphase formulations, which should be more robust than p - p for general applications, less-restrictive assumptions (e.g., more mobile phases), Newton-Raphson iteration for nonlinear discrete equations, which should be more robust than Picard, and iterative linear-equation solvers of conjugate-gradient type with ILU-like preconditioners, which have been the solvers of choice in petroleum simulation for about a decade. Temporal discretizations are mostly fully implicit or sequentially implicit, with a wide range of essentially standard spatial finite-difference, finite-volume,

and finite-element schemes.

Nonequilibrium partitioning is included in some more-limited models, but not in those with many components and phases. Macroscopic multiphase relationships are of traditional forms, generally non-hysteretic, awaiting better fundamental understanding of the physical processes. Recent developments in discretization techniques, such as mixed finite-element methods, Lagrangian and Eulerian-Lagrangian schemes, local grid refinement, domain decomposition, and multigrid algorithms, generally have not been implemented in the practical arena represented by these models. These techniques offer greater efficiency and accuracy than standard schemes in scalar computing environments, with still greater advantages on vector and parallel machines. Currently, most codes appear to be designed for scalar machines, with little emphasis on vectorizability or parallelizability.

Summary and Future Directions

Development of accurate predictive models for multiphase multicontaminant transport in groundwater requires contemporaneous advances on a multitude of fronts. Fundamental physical understanding of upscaled macroscopic multiphase flow and of the validity of the local equilibrium assumption has progressed but is far from complete. Both of these are critical in determining the form and computational complexity of numerical models. Data describing partitioning behavior of multicontaminant systems, presently rather sparse, will need to be enhanced, with realistic assessments of the number of components necessary to represent a given compositional system adequately. Because a fully implicit nonequilibrium m -phase n -component model appears to be impractical, modelers have had to make compromises, and this can be expected to continue. With the local equilibrium assumption, generalized compositional formulations have been successful in the petroleum industry, and groundwater modeling is trending in some of the same directions. For nonequilibrium, analogous or alternative formulations will require new ideas, such as approximate couplings between kinetics and transport, to achieve effective compromises. Innovations in numerical methods, which will substantially reduce the computing effort for a given accuracy, especially on vector and parallel computers, will ease the need for compromises but cannot be expected to eliminate it.

It will be important to develop perspective on the balancing of various uncertainties and errors. Is the multiphase Darcy equation accurate enough to justify the expense of nonequilibrium? Nonequilibrium may greatly increase the computational burden of a simulation, necessitating a coarser grid. Is the error of assuming equilibrium, with a fine grid, greater than the discretization error of a coarser grid for nonequilibrium? Is it sensible to perform rigorous nonequilibrium calculations if the results are used in transport equations solved by numerically dispersive methods such as upstream finite differences? How effectively will improved numerical discretizations reduce numerical errors, making the effort of improving other modeling aspects appropriate? To make intelligent compromises, at least at an intuitive engineering level, modelers will need the answers, possibly different answers for different problems, to these types of questions. This will involve understanding of fundamental and upscaled physical processes, knowledge of properties of alternative mathematical formulations of multicomponent systems, and assessment of constraints imposed on accuracy by limited computational resources, even with efficient, accurate numerical techniques.

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