

An Integrated Groundwater Model using Multicomponent Multiphase Theory (I) - Theoretical Developments -

Joon-Hyun Kim* and Michael K. Stenstrom**

* Environmental Engineering Department, Kangwon National University

** Civil and Environmental Eng. Dept., University of California, Los Angeles

ABSTRACT

A general comprehensive theory is presented to describe underground flow and mass transport, using a multicomponent multiphase approach. Two sets of comprehensive governing equations are derived considering mass and force balances of chemical species over four phases (water, oil, air, and soil) in a schematic elementary volume. The first approach is based upon the solution of the multicomponent multiphase continuity and momentum equation, which eliminates the necessity of capillary pressure-saturation relationship. The second approach is based upon the modified Darcy's velocity, and capillary pressure-saturation. The resulting primary unknown variables are saturation, pressure of each phase, and mass fraction of each component. Compact and systematic notations of relevant variables and equations are introduced to facilitate the inclusion of complex migration and transformation processes, and variable spatial dimensions. It is shown that the former governing equations for groundwater flow and pollutant migration can be obtained from the integrated transport equation by parameter substitution. The resulting system of nonlinear governing and constitutive equations are solved using a multidimensional finite element model described in a companion paper.

INTRODUCTION

Groundwater contamination proceeds through complicated physical, chemical and biological mechanisms, which requires flow and pollutant transport to be studied simultaneously. Groundwater models have evolved to simulate the problems from simple groundwater flow to composite multiphase flow. The enhanced capability of models requires an increased number of parameters. The objectives of this study are: 1) to develop an integrated model to explain several groundwater systems, ranging from simple saturated flow to composite multiphase flow using multicomponent multiphase theory; and 2) to present a systematic expression of the groundwater systems which is suitable for modeling and has reasonable parameter evaluation requirements.

MATHEMATICAL FORMULATION

1. Mass Balance Equation

The derivation of multicomponent multiphase flow theory started with the application of continuous partial differential equations over the discontinuous subsurface domain using traditional averaging concepts in continuum mechanics. All possible phases and migration patterns are shown in the localized problem domain and detailed view of the representative elementary volume [Bear, 1979; Bachmat and Bear, 1986] depicted in Figure 1. Averaged macroscopic balance equations of mass, momentum, heat, and energy were obtained from microscopic balances by defining averaging parameters, such as volume fraction [Hassanizadeh and Gray, 1979a,b]. Celia et al. [1993] presented a multi-scale computational model to overcome the lengthscale problem in the volume averaging concept. They suggested a hierarchic sequence with output from smaller-scale models serving as input to larger-scale models. In this study, the representative elementary volume was expressed as a schematic control volume to derive mass and force balance equations. As shown in Figure 2, the schematic control volume is a multicomponent multiphase system expressed by the volumetric fraction of each phase and by the mass fraction of each species.

A microscopic mass balance is represented in equation (1), considering convective, diffusive flux, and generation rate of component i in α phase.

$$\frac{\partial C_{\alpha}^i}{\partial t} + \nabla \cdot \left(C_{\alpha}^i \vec{V}_{\alpha} \right) = \nabla D_{m,\alpha}^i \nabla C_{\alpha}^i + g_{\alpha}^i \quad (1)$$

Where, C_α^i is concentration, \vec{v}_α^i is microscopic velocity, $D_{m,\alpha}^i$ is microscopic molecular diffusion tensor coefficient, g_α^i is generation rate of species i in α phase for recharge, discharge, radioactive decay, chemical and biological reactions.

The microscopic convective flux is expanded to macroscopic convective and dispersive flux as follows:

$$C_\alpha^i \vec{v}_\alpha^i = C_\alpha^i \vec{v}_\alpha + C_\alpha^i \left(\vec{v}_\alpha^i - \vec{v}_\alpha \right) = C_\alpha^i \vec{v}_\alpha - D_{h,\alpha}^i \nabla C_\alpha^i \quad (2)$$

where, \vec{v}_α is macroscopic velocity of the α phase, and $D_{h,\alpha}^i$ is mechanical dispersive coefficient tensor of species i in the α phase.

Equilibrium interfacial mass transfers among the different α phases can be summed to zero [Corapcioglu and Baehr, 1987]. Macroscopic mass balance equation of species i in the α phase is expressed as follows for nonequilibrium conditions :

$$\frac{\partial C_\alpha^i}{\partial t} + \nabla \left(C_\alpha^i \vec{v}_\alpha \right) = \nabla \left(D_\alpha^i \nabla C_\alpha^i \right) + I_\alpha^i + g_\alpha^i \quad (3)$$

where, $D_\alpha^i = (D_{h,\alpha}^i + D_{m,\alpha}^i)$ is dispersive coefficient tensor, and I_α^i is the interfacial mass transfer rate for mass exchange through the interface by means of dissolution, sorption, volatilization, ion exchange, and diffusion.

The overall migration process of the four phases depends upon the migration process of each phase. Thus, total migration of species i is summation of equation (3) over all phases. To include the effects of volumetric fraction, density, and mass fraction of each phase, equation (3) is multiplied by volumetric fraction. The final form of multiphase mass balance equation of species i is as follows :

$$\sum_{\alpha=1}^4 \left[\frac{\partial (\theta_\alpha \rho_\alpha w_\alpha^i)}{\partial t} + \nabla \left(\theta_\alpha \rho_\alpha w_\alpha^i \vec{v}_\alpha \right) \right] = \nabla \left(\theta_\alpha D_\alpha^i \nabla (\rho_\alpha w_\alpha^i) \right) + \theta_\alpha I_\alpha^i + \theta_\alpha g_\alpha^i \quad (4)$$

where, $\theta_\alpha (= U_\alpha / U = \phi S_\alpha)$ is the volumetric fraction of the α phase, $S_\alpha (U_\alpha / U v = U_\alpha / (\phi U) = \theta_\alpha / \phi)$ is the saturation of the α phase, U_α is the volume of the α phase, U is the schematic control volume, ϕ is the aquifer porosity, $\rho_\alpha (= M_\alpha / U_\alpha)$ is the density of α phase, M_α is the mass of the α phase, $w_\alpha^i (= M_\alpha^i / M_\alpha)$ is the mass fraction of species i in the α phase, and M_α^i is the mass of species i in the α phase.

The concentration of species i over the schematic control volume, C^i , is expressed as follows :

$$C^i = \frac{M_\alpha^i}{U} = \frac{U_\alpha M_\alpha^i}{U U_\alpha} = \theta_\alpha C_\alpha^i = \frac{U_\alpha M_\alpha M_\alpha^i}{U U_\alpha M_\alpha} = \theta_\alpha \rho_\alpha w_\alpha^i = m_\alpha w_\alpha^i \quad (5)$$

where, m_α is the unit mass of the α phase over the schematic control volume.

2. Force Balance

Lin and Gray [1971] presented one of the earliest studies related to multiphase force balance. They derived a steady state momentum equation for laminar flow in capillary tube in which head difference, capillary pressure, and surface tension were included. The theoretical equations were verified against experimental tests of capillary tubes. Hassanizadeh and Gray [1979a, 1979b], Allen [1984], and Abriola [1984] have rigorously derived the modified Darcy's velocity from the momentum equation. Kueper and Frind [1988] examined the effects of density, viscosity, surface tension on interfacial immiscible displacements when reviewing immiscible fingering, based upon a force balance of pressure, gravity force, viscous friction, and interfacial surface tension. Gray and Hassanizadeh [1991a, b, 1993] showed the paradox, if the modified Darcy's velocity is used in a variably saturated region, which requires false negative water phase pressure in capillary-saturation relations. To overcome the problem, they developed a multiphase momentum equation including interfacial dynamics based on conservation of mass, momentum, and energy, and the second law of thermodynamics. Application of their technique required experimental data to ascertain the constitutive coefficients. Beckie et al. [1993] presented a mixed formulation of the continuity and momentum equations for simple saturated groundwater flow, and performed large-scale finite element simulation using a multigrid, accelerated domain decomposition technique. Considering all the studies mentioned above, one can solve the multiphase momentum equation or use the modified Darcy's equation to describe a multiphase velocity problem.

1) Solution of multiphase momentum equation

Applying the momentum balance to one species of each phase of the schematic elementary volume, microscopic multiphase momentum equation is presented as a form similar to the Navier-Stokes equation.

$$\rho_{\alpha}^i \frac{D\vec{V}_{\alpha}^i}{Dt} = -\nabla(P_{\alpha}^i + \rho_{\alpha}^i g y) + \mu_{\alpha} \nabla^2 \vec{V}_{\alpha}^i \quad (6)$$

Where, ρ_{α}^i is the density of species i in the α phase, P_{α}^i is pressure acting on the species i , and μ_{α} is the dynamic viscosity of the α phase.

Including the interfacial momentum exchange, a macroscopic momentum equation is derived by the extension of the density and pressure of each species to all species in each phase.

$$\sum_{i=1}^{ns} \left[\theta_{\alpha} \rho_{\alpha}^i w_{\alpha}^i \frac{D\vec{V}_{\alpha}^i}{Dt} = -\nabla(P_{\alpha}^i + \theta_{\alpha} \rho_{\alpha}^i w_{\alpha}^i g y) + \mu_{\alpha} \nabla^2 \vec{V}_{\alpha}^i + \vec{R}_{\alpha} \right] \quad (7)$$

Where, ns is the total number of species in the α phase, P_{α} is the pressure of the α phase, \vec{R}_{α} is the momentum exchange in the form of an isotropic Stokes' drag force [Allen, 1984], which denotes the resistance to motion of the α fluid phase by a slowly moving or immovable soil particle, acting in a direction opposite to fluid phase velocity.

Applying the constitutive concept for mobility tensor, the momentum exchange between the soil particle and fluid phase is expressed as:

$$\vec{R}_{\alpha} = \theta_{\alpha} M_{\alpha}^{-1} \left(\vec{V}_s - \vec{V}_{\alpha} \right) \quad (8)$$

where, $M_{\alpha} (= K_{\alpha} / \mu_{\alpha})$ is the mobility tensor, K_{α} is the effective permeability tensor, \vec{V}_s is the velocity of the mobile solid phase, and \vec{V}_{α} is the velocity of the α fluid phase.

If viscous effects within each phase can be neglected, then the interfacial frictional force $\mu \nabla^2 \vec{V}_{\alpha}$ becomes $-\nabla \tau$, τ is the frictional stress. The interfacial frictional stress depends upon the surface tension, contact angle, and interfacial surface area of the two phases.

We can solve the problem of multicomponent multiphase flow and transport using the continuity equation (4) and the momentum equation (7). The primary variables are pressure, velocity, saturation, and mass fraction. The parameters are density, friction factor, mobility tensor, interfacial mass transfer rate and generation rate. The equation (4) and (7) should be arranged in terms of primary variables to solve, and because of the momentum transfer term, a coupling scheme is required. This method does not require Darcy's velocity and capillary pressure-saturation relationships. However, still several parameters such as the mobility tensor must be evaluated experimentally.

2) Derivation of modified Darcy's velocity

It is possible to neglect the inertia term of the momentum equation due to the slow velocity of fluid phase. After neglecting the viscous effects within each phase and between phases, the momentum equation becomes :

$$\nabla(P_{\alpha} + \rho_{\alpha} g y) = \theta_{\alpha} M_{\alpha}^{-1} \left(\vec{V}_s - \vec{V}_{\alpha} \right) \quad (9)$$

The velocity of the α phase in a deformable porous media becomes:

$$\vec{V}_{\alpha} = -\frac{K_{\alpha}}{\theta_{\alpha} \mu_{\alpha}} \nabla(P_{\alpha} + \rho_{\alpha} g y) + \vec{V}_s = -K \frac{k_{r\alpha}}{\theta_{\alpha} \mu_{\alpha}} \left(\nabla P_{\alpha} - \rho_{\alpha} \vec{g} \right) = \vec{V}_D + \vec{V}_s \quad (10)$$

where, k is the intrinsic permeability tensor, $k_{r\alpha}$ is the relative permeability of the α phase, \vec{g} is the downward vector of gravity force, and \vec{V}_D is the modified Darcy's velocity.

Assuming the density of the water phase is spatially unchanged, the Darcy's velocity can be written as follows. The pressure terms are expressed in equivalent water height :

$$\begin{aligned}\vec{V}_D &= -k \frac{k_{r\alpha}}{\theta_\alpha \mu_\alpha} (\nabla P_\alpha - \rho_\alpha \vec{g}) = -k \frac{k_{r\alpha}}{\theta_\alpha \mu_\alpha} (\nabla P_\alpha + \rho_\alpha \vec{g}) = -k \frac{k_{r\alpha} \rho_w \vec{g}}{\theta_\alpha \mu_\alpha} \left(\nabla \frac{P_\alpha}{\rho_w \vec{g}} + \frac{\rho_\alpha}{\rho_w} \vec{j} \right) \\ &= -\frac{K_\alpha}{\theta_\alpha} \left(\nabla h_\alpha + \frac{\rho_\alpha}{\rho_w} \vec{j} \right) = -\frac{K_\alpha}{\theta_\alpha} \nabla \left(h_\alpha + \frac{\rho_\alpha}{\rho_w} y \right) = -\frac{K_\alpha}{\theta_\alpha} \nabla H_\alpha\end{aligned}\quad (11)$$

where, $h_\alpha (= P_\alpha / (\rho_w \vec{g}))$ is the fluid pressure head in equivalent water height, $H_\alpha (= h_\alpha + y(\rho_\alpha / \rho_w))$ is the total piezometric head in equivalent water height, $K_\alpha (= K k_{r\alpha} + (\rho_w \vec{g}) / \mu_\alpha)$ is the fluid conductivity tensor of the α phase, and \vec{j} is the upward vector of the y direction. The fluid conductivity of β phase, K_β is expressed as $K_\beta (= K_\alpha (\mu_\alpha k_{r\beta}) / (\mu_\beta k_{r\alpha}))$.

3. Storage Capacity of Porous

The compressibility of porous media can be related to the movement of soil particle or solid species by deriving the solid transport equation from the multicomponent multiphase transport equation [Abriola et al., 1985a,b]. By solving this solid transport equation, the displacement of porous media and velocity of each soil particle can be calculated at each nodal point or in each element. Thus, the multicomponent multiphase model can be used for the problems of soil mechanics, such as land subsidence. The main difference from the traditional model of soil mechanics (e.g., land consolidation) is that the multicomponent multiphase model considers not only the intergranular stress or effective stress, but also the highly variant fluid pressure in the pore space, which occurs in the consolidation problems in a multiphase domain.

Solid species exist only in the solid phase and have no dispersive movement. If the available constituent species are soil and adsorbed species, then $w_s^* + w_s^0 = 1$. If the amount of adsorbed species is so small that it can be neglected, $w_s^w \cong 1$. Therefore, the transport equation of solid phase in multiphase domain becomes :

$$\frac{\partial(\theta_s \rho_s)}{\partial t} + \nabla \cdot (\theta_s \rho_s \vec{V}_s) = 0 \quad (12)$$

Solving for the derivative, equation (12) becomes the continuity equation of property $\theta_s (= 1 - \phi)$ as follows :

$$\theta_s \frac{D\rho_s}{Dt} + \rho_s \left[\frac{\partial \theta_s}{\partial t} + \nabla \cdot (\theta_s \vec{V}_s) \right] = 0 \quad (13)$$

Because the soil particles are incompressible, $(d\rho_s)/(dt) = 0$. Thus, equation (13) becomes a consolidation equation describing the time rate of change of void fraction or the magnitude of consolidation as follows :

$$-\frac{\partial \phi}{\partial t} + \nabla \cdot \left[(1 - \phi) \vec{V}_s \right] = 0 \quad (14)$$

The total stress loading is the summation of the effective stress and the pore pressure ($\sigma = \sigma' + p$). The time derivative of porosity can be expanded with respect to fluid pressure and total stress.

$$\frac{\partial \phi}{\partial t} = \sum_{\beta=1}^3 \frac{\partial \phi}{\partial (\sigma - h_\beta)} \frac{\partial (\sigma - h_\beta)}{\partial t} \quad (15)$$

If there is no change of total stress or overburden load, and the compressibility of the porosity by pressure head is defined as $\phi_\beta = (\partial \phi) / (\partial h_\beta)$, then solid transport equation is expressed in terms of compressible porosity, phase head, and solid velocity.

$$\sum_{\beta=1}^3 \left(\phi_\beta \frac{\partial h_\beta}{\partial t} \right) = \nabla \cdot \left[(1 - \phi) \vec{V}_s \right] \quad (16)$$

The compressibility ϕ_β is obtained experimentally from the constitutive equation. The fluid pressure h_β is computed from the whole multicomponent multiphase system. The velocity of the solid phase and the time rate change of porosity are computed from equation (16). For an elastic soil matrix, the parameter ϕ_β is constant; for a nonelastic soil, it is dependent upon pressure and properties of soil matrix, and the system becomes highly nonlinear. For contaminant migration problems, the elastic deformation assumption is usually accepted.

ϕ_β is incorporated into the fluid equation by specific storativity $S_{\alpha\beta}$ as follows :

$$S_{\alpha\beta} = \phi_\beta + \phi_{\alpha\beta} \quad (17)$$

where, $\phi_\beta = (\partial\phi)/(\partial h_\beta)$ is the compressibility of the porosity by the β pressure head, $\alpha_\beta = (\partial\alpha)/(\rho_\alpha \partial h_\beta)$ is the compressibility of the α phase by the β pressure head, and $S_{\alpha\beta}$ is the specific storativity of the porous matrix and fluid. α_β and ϕ_β always have negative values.

To combine the storage capacity of the porous media into the governing equation, the time derivative of mass balance equation is expanded as follows:

$$\frac{\partial(\phi S_{\alpha\beta} \rho_\alpha w_\alpha^i)}{\partial t} = w_\alpha^i S_{\alpha\beta} \frac{\partial(\rho_\alpha)}{\partial t} + \rho_\alpha S_{\alpha\beta} \frac{\partial w_\alpha^i}{\partial t} + \phi_\alpha w_\alpha^i \frac{\partial S_{\alpha\beta}}{\partial t} \quad (18)$$

The first term of equation (18) describes the storage capacity of the given system. The density of the liquid mixture is a function of temperature, pressure and concentration. The model is restricted to isothermal cases. By assuming isothermal conditions and neglecting the density change due to concentration, the storage capacity of the system can be expressed as follows :

$$w_\alpha^i S_{\alpha\beta} \frac{\partial(\rho_\alpha)}{\partial t} = w_\alpha^i S_{\alpha\beta} \left(\rho_\alpha \frac{\partial\phi}{\partial t} + \phi \frac{\partial\rho_\alpha}{\partial t} \right) = \rho_\alpha w_\alpha^i S_{\alpha\beta} \sum_{\beta=1}^3 \left(\frac{\partial\phi}{\partial h_\beta} + \frac{\phi}{\rho_\alpha} \frac{\partial\rho_\alpha}{\partial h_\beta} \right) \frac{\partial h_\beta}{\partial t} = \rho_\alpha w_\alpha^i S_{\alpha\beta} \sum_{\beta=1}^3 S_{\alpha\beta} \quad (19)$$

4. Integrated Transport Equation

By separating the solid phase from the time derivative, including the Darcy and solid velocity, and storage capacity of groundwater system, the integrated transport equation is expressed as follows :

$$\begin{aligned} & \sum_{\alpha=1}^3 \left[\sum_{\beta=1}^3 (\rho_\beta w_\beta^i S_{\beta\alpha}) \frac{\partial h_\alpha}{\partial t} + \rho_\alpha w_\alpha^i \frac{\partial S_{\alpha\beta}}{\partial t} + \phi_\alpha w_\alpha^i \frac{\partial S_{\alpha\beta}}{\partial t} \right] + \frac{\partial((1-\phi)\rho_s w_s^i)}{\partial t} \\ & = \sum_{\alpha=1}^3 \left[\nabla \left(\rho_\alpha w_\alpha^i K_\alpha \left(\nabla h_\alpha + \frac{\rho_\alpha}{\rho_w} \vec{j} \right) \right) + \nabla(\phi S_{\alpha\beta} D_\alpha^i \nabla(\rho_\alpha w_\alpha^i)) \right] - \nabla \left((1-\phi)\rho_s w_s^i \vec{V} \right) + \sum_{\alpha=1}^4 [\theta_\alpha (I_\alpha^i + \xi_\alpha^i)] \quad (20) \end{aligned}$$

The second term of the time derivative is the saturation change which depends upon the convective flux and capillary pressure. The expansion of this term can be implemented in one of two ways, depending upon conditions.

The first case, often called a Buckley-Leverett problem [Buckley and Leverett, 1942], occurs when the dominant driving force of the system is the convective flux of the fluid phase, as found in oil recovery problems. In this case, even though there is no capillary pressure, the saturation is changed by the flux of each phase, and the saturation can not be expanded with respect to the capillary pressure. The saturation becomes a primary variable of the system which should be solved simultaneously with the pressure.

The second case occurs when the dominant driving force is the pressure difference of each fluid phase. This condition typically occurs during contaminant migration in a groundwater basin. The time derivative of saturation can be expanded with respect to the capillary pressure, and simultaneous solution of the equation about the saturation term is not required. This assures convergence of the nonlinearity and short computation time. The saturation and its derivative are determined by the constitutive relation of the saturation and capillary pressure. Even when there is no actual capillary phenomena in the regions where there is only one phase, a hypothetical saturation derivative is required to avoid a singularity in the system of equations. This hypothetical value does not precisely match a real field problem and increases parameter requirements. The governing equation of convective dominant system is expressed as follows :

$$\begin{aligned} & \sum_{\alpha=1}^3 \left(\sum_{\beta=1}^3 (\rho_\beta w_\beta^i S_{\beta\alpha}) \frac{\partial h_\alpha}{\partial t} + \rho_\alpha w_\alpha^i \frac{\partial S_{\alpha\beta}}{\partial t} + \phi_\alpha w_\alpha^i \frac{\partial S_{\alpha\beta}}{\partial t} \right) + \frac{\partial((1-\phi)\rho_s w_s^i)}{\partial t} \\ & = \sum_{\alpha=1}^3 \left(\nabla \left(\rho_\alpha w_\alpha^i K_\alpha \left(\nabla h_\alpha + \frac{\rho_\alpha}{\rho_w} \vec{j} \right) \right) + \nabla(\rho_\alpha w_\alpha^i K_\alpha \nabla h_{\beta\alpha}) + \nabla(\phi S_{\alpha\beta} D_\alpha^i \nabla(\rho_\alpha w_\alpha^i)) \right) \\ & \quad - \nabla((1-\phi)\rho_s w_s^i \vec{V}) + \sum_{\alpha=1}^4 [\theta_\alpha (I_\alpha^i + \xi_\alpha^i)] \quad (21) \end{aligned}$$

where, $h_{\beta\alpha} = h_\beta - n_\alpha = f(S_{\alpha\beta})$ is capillary pressure between β and α phase.

In the capillary dominant system, the governing equation becomes :

$$\sum_{\alpha=1}^3 \left[\sum_{\beta=1}^3 \left(\rho_{\beta} w_{\beta}^i S_{\beta\alpha} + \phi \rho_{\beta} w_{\beta}^i \frac{\partial S_{\beta}}{\partial h_{\alpha}} \right) \frac{\partial h_{\alpha}}{\partial t} + \phi \rho_{\alpha} S_{\alpha} \frac{\partial w_{\alpha}^i}{\partial t} \right] + \frac{\partial(1-\phi)\rho_s w_s^i}{\partial t} \\ = \sum_{\alpha=1}^3 \left(\nabla \left(\rho_{\alpha} w_{\alpha}^i K_{\alpha} \left(\nabla h_{\alpha} + \frac{\rho_{\alpha}}{\rho_w} j \right) \right) + \nabla (\phi S_{\alpha} D_{\alpha}^i \nabla (\rho_{\alpha} w_{\alpha}^i)) \right) - \nabla((1-\phi)\rho_s w_s^i j_s) + \sum_{\alpha=1}^4 [\phi S_{\alpha} (I_{\alpha}^i + g_{\alpha}^i)] \quad (22)$$

As we can see in equations (21) and (22), the primary variables are pressure head, mass fraction and saturation. Even in the second case, there are at least two sets of primary variables. To solve for these primary variables we need additional constitutive equations, as well as boundary and initial conditions for each variable. In the case of the saturation variable, the resulting governing equation will be of the hyperbolic type with respect to saturation, and the characteristic method will produce the best result [Huyakorn and Pinder, 1983]. Alternatively, one of the upstream weighted finite difference, finite element, Eulerian-Lagrangian methods can be used [Kim and Stenstrom, this issue]. The principal parameters required to solve the governing equation are ρ_{α} (α phase density), $S_{\beta\alpha}$ (storage coefficient), K_{α} (fluid conductivity), D_{α}^i (dispersion coefficient of species i in α phase), I_{α}^i (interfacial mass transfer rate of species i), and g_{α}^i (internal production rate). Some of the evaluation techniques for several of these parameters mentioned here, detailed review of parameter studies will be implemented in the companion paper [Kim et al., 1994].

Saturation and relative permeability are computed from the effective saturation of each phase. The effective saturation is calculated from the constitutive relation between the saturation and capillary pressure [Parker et al., 1987]. The relative permeability of each phase is defined from the effective saturation.

The dispersive flux is caused by the microscopic velocity fluctuation, as well as chemical concentration gradient. In the derivation of macroscopically averaged transport equation, the character of dispersive flux appears as the difference between the microscopic species phase velocity. The dispersion coefficient has the directional property of the velocity of each phase and can be different for each species. The traditional formulation of dispersive coefficient tensor [Bear, 1979; Voss, 1984] was expanded for this species dependency [Kim, 1989]. Although studies have been implemented for the dispersive coefficient, no generally accepted procedure exists, due to the problems of the tortuosity of the geometry, evaluation of the microscopic phase velocity, and scale effect of heterogeneous porous media. The only method used heretofore relies on soil sample tests and the tracer tests. These results can be combined with parameter estimation techniques using deterministic or stochastic models. Often only approximate results can be obtained, and additional research is required to better estimate this parameter.

The mass fraction of the species i in the α phase is computed by $w_{\alpha}^i = w_{\beta}^i \times H_{\alpha\beta}^i$ for known mass fraction of the species i in the β phase (w_{β}^i). Equilibrium constant of the species i between the α and β phases is expressed as $H_{\alpha\beta}^i$. In the case of trichloroethylene, the solubility of TCE into water phase is approximately 1100 mg/L, which is the maximum possible mass fraction of TCE in water phase. The partition coefficient of dissolution is $H_{wo}^o = w_w^o / w_o^o$. Assuming no water species in oil phase ($w_o^o = 1$), mass dissolution constant becomes $H_{wo}^o = 1.1 \times 10^{-3}$.

Henry's law is applied to express the equilibrium rate of volatilization of volatile species in the liquid phase, which is defined as the ratio of the partial pressure of species in gas phase to concentration of species in liquid phase, expressed as $H_{av}^o = P_{vp}^o / S_w^o = 10^4 \text{ atm} / (\text{mole} / \text{cm}^3)$. Here, P_{vp}^o is vapor pressure of TCE in the air phase ($= 0.0837 \text{ atm}$), S_w^o is the solubility limit of TCE in the water phase ($= 0.0837 \times 10^{-4} \text{ mole} / \text{cm}^3$), and $P_{vp}^o / P_a = m_a^o / m_{\alpha} \times 28.9 / 131.4$, where 28.9, 131.4 are molecular weights of air and TCE phase. Thus, $w_{\alpha}^o = 0.0837 \times 131.4 / 28.9 = 0.38$.

Sorption process depends upon the solute, sorbent, solution condition (pH, temperature, ionic strength, specific species, organic and inorganic solute, colloids, etc.), and time. The partition coefficient of sorption is expressed as $H_{sw}^o = w_s^o / w_w^o$. Sorption is often correlated with the organic carbon of soil, for organic species, as expressed in $H_{sw}^o = f_{oc} \times H_{oc}$. Here f_{oc} is fraction of organic carbon measured from field data, H_{oc} is partition coefficient based on organic carbon ($\log H_{oc} = a \times \log(H_{ow}, S, BCF, \dots) + b$), H_{ow} is octanol water partition coefficient, S is solubility, and BCF is bioconcentration factor [Karickhoff, 1984]. However, such correlations are not generally applicable, and, in many cases, H_{sw}^o is measured experimentally.

Sorption is greatly influenced by the soil characteristics and the cosolvent, requiring the above equation to be modified. When sorptive reactions occur slowly, a kinetic model should be used. The sorption process is especially important in the case of the solute transport (when the chemical substance is totally dissolved in water phase). Traditionally, solvent "holdup" has been calculated through an empirical "retardation factor", which is calculated from the sorption coefficient. The velocity of the water flow is divided by the value of the retardation factor. In saturated flow, retardation by the adsorption process is the cause for the difference between the advancing concentration and the groundwater fronts.

The chemical and biological reactions are consolidated with the whole process by internal production rate g'_α . The estimation of reaction rates is complicated by the effect of buffer catalysis, dissolved metals, dissolved organic materials and cosolvents. To quantify the reaction terms, the reaction orders must first be confirmed, and then the parameter values such as reaction rate constant k'_α must be estimated.

In the subsurface domain, most of the microorganisms are attached to the surface of the solids making the biofilm. So, sloughing and endogenous effects should be considered for biological reactions. Monod-type kinetics are most commonly used for the substrate decay with the modification for electron acceptor such as oxygen.

CONCLUSIONS

In this study, the integrated groundwater model is developed from the mass and force balance of a multicomponent multiphase system. The model encompasses the migration processes of convection, dispersion, dynamic interfacial mass transfer, and biochemical generation, and the forces of pressure, gravity, interfacial friction, and interfacial momentum transfer.

Conventional groundwater flow and contaminant transport equations were derived from the integrated transport equation, and solved numerically in the companion paper [Kim and Stenstrom, this issue] by parameter substitution. Parameter evaluation techniques were improved for the fluid conductivity tensor, storage coefficient, dispersion and partition coefficients to facilitate coding. The developed numerical model will be verified for a broad range of system parameters and constitutive relations [Kim et al., 1994].

Acknowledgments

This work was supported in part by National Science Foundation Engineering Research Center for Hazardous Substances Control, the UCLA Center for Risk and System Analysis for the Control of Toxics, and an environmental fellowship from BP-SOH10. The authors would like to acknowledge the helpful suggestions and comments of Thomas C. Harmon (Civil and Environmental Engineering Dept., University of California, Los Angeles).

REFERENCES

- Abriola, L. M., *Multiphase Migration of Organic Compounds in A Porous Medium*, Lecture Notes in Engineering, Springer-Verlag, 1984.
- Abriola, L. M., and G. F. Pinder, A multiphase approach to the modeling of porous media contamination by organic compounds : 1. Equation development, *Water Resour. Res.*, 21(1), 11-18, 1985a.
- Abriola, L. M., and G. F. Pinder, A multiphase approach to the modeling of porous media contamination by organic compounds : 2. Numerical simulation, *Water Resour. Res.*, 21(1), 19-26, 1985b.
- Allen, M. B., *Collocation Techniques for Modeling Compositional Flows in Oil Reservoirs*, Lecture Notes in Engineering, Springer-Verlag, 1984.
- Bachmat, Y., and J. Bear, On the concept and size of a representative elementary volume(REV), *NATO ASI Series*, 5-20, 1986.
- Bear, J., *Hydraulics of Groundwater*, McGraw-Hill, Ind., New York, 1979.
- Beckie, R., E. F. Wood, and A. A. Aldama, Mixed finite element simulation of saturated groundwater flow using a multigrid accelerated domain decomposition technique, *Water Resour. Res.*, 29(9), 3145-3157, 1993.
- Buckley, S. E., and M. C. Leverett, Mechanism of fluid displacement in sands, *AIME*, 146, 107-116, 1942.
- Celia, M. A., H. Rajaram, and L. A. Ferrand, A multi-scale computational model for multiphase flow in porous media, *Adv. in Water Res.*, 16, 81-92, 1993.
- Corapcioglu, M. Y., and A. L. Baehr, A compositional multiphase model for groundwater contamination by petroleum products, *Water Resour. Res.*, 23(1), 191-213, 1987.

- Faust, C. R., Transport of immiscible fluids within and below the unsaturated zone: a numerical model, *Water Resour. Res.*, 21(4), 587-596, 1985.
- Gray, W.G., and S.M. Hassanizadeh, Paradoxes and realities in unsaturated flow theory, *Water Resour. Res.*, 27(8), 1847-1854, 1991.
- Gray, W.G., and S.M. Hassanizadeh, Unsaturated flow theory including interfacial phenomena, *Water Resour. Res.*, 27(8), 1855-1863, 1991.
- Hassanizadeh, S. M., and W. G. Gray, General conservation equations for multiphase systems: 1. Averaging procedure, *Adv. in Water Resour.*, 2, Sept., 131-144, 1979a.
- Hassanizadeh, S. M., and W. G. Gray, General conservation equations for multiphase systems: 1. Mass, momentum, energy, and entropy equations", *Adv. in Water Resour.*, 2, Dec., 191-203, 1979b.
- Hassanizadeh, S. M., and W.G. Gray, Toward an improved description of the physics of two-phase flow, *Adv. in Water Resour.*, 16, 53-67, 1993.
- Huyakorn, P. S., and G. F. Pinder, *Computational Methods in Subsurface Flow*, Academic Press, New York., 1983.
- Kaluvarachchi, J. J., and J. C. Parker, An efficient finite element method for modeling multiphase flow, *Water Resour. Res.*, 25(1), 43-54, 1989.
- Karickhoff, S. W., Organic pollutant sorption in aquatic systems, *J. of Hydraulic Engineering*, 110(6), 707-735, 1984.
- Kim, J.-H., Composite Multiphase Groundwater Model, Ph.D. dissertation, University of California, Los Angeles, 1989.
- Kim, J.-H., and M. K. Stenstrom, An integrated groundwater model using multicomponent multiphase theory : 2. Numerical analysis and model applications", *This Issue.*, 1995.
- Kim, J.-H., T. C. Harmon, and M. K. Stenstrom, An integrated groundwater model using multicomponent multiphase theory : 3. Parameter Studies in Multiphase Flow and Transport of Organic Contaminants", *This Issue*, 1995.
- Kueper, B. H., and E. O. Frind, An overview of immiscible fingering in porous media, *J. of Contam. Hydrol.*, 2, 95-110, 1988.
- Lin, C., G. F. Pinder, and E. F. Wood, Water and trichloroethylene as immiscible fluids in porous media, *Water Resour. Program*, 83-WR-2, Princeton University, 1982.
- Lin, W., and D. M. Gray, Physical simulation of infiltration equations, *Water Resour. Res.*, 7(5), 1234-1240, 1971.
- Pinder, G. F., and L. M. Abriola, On the simulation of nonaqueous phase organic compounds in the subsurface", *Water Resour. Res.*, 22(9), 109S-119S, 1986.
- Voss I. C., A Finite-element Simulation Model for Saturated-Unsaturated, Fluid-Density Dependent Groundwater Flow with Energy Transport or Chemically Reactive Single-Species Solute Transport, U.S. Geological Survey, *Water Resources Investigations Report* 84-4369, 1984.

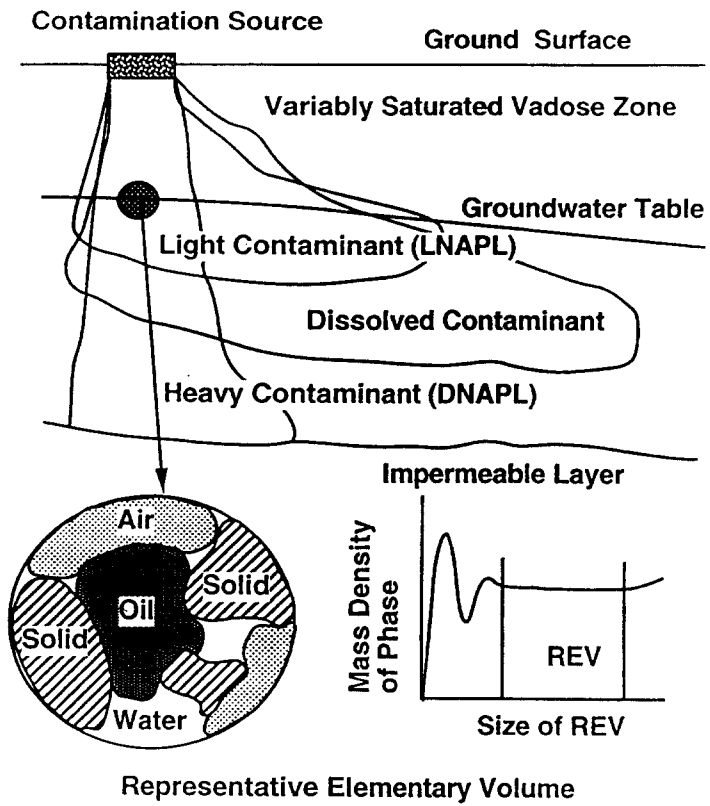


Figure 1. Idealized migration profile and REV of multicomponent multiphase flow

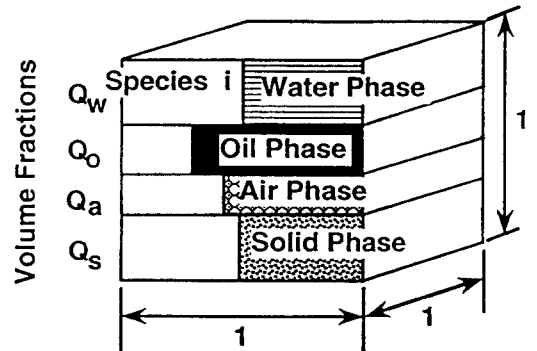


Figure 2. Schematic control volume.