6.9 Geochemical Transport

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6.9.1 Introduction

Chemicals migrating from industrial and municipal waste disposal sites, or intentionally applied to agricultural lands, are often subjected to a large number of simultaneous physical, chemical, and biological processes, including sorption–desorption, volatilization, precipitation–dissolution, complexation, and biodegradation. Sections 6.2 through 6.5 considered the transport of only one chemical species and assumed that the behavior of this solute is independent of that of other species that may be present in the soil solution. In reality, the soil solution is always a mixture of many ions that may interact, create complexed species, precipitate, dissolve, and/or compete with each other for sorption sites (van Genuchten & Šimůnek, 1996). Many important environmental problems require analysis of the coupled transport and reaction of multiple chemical species; a few examples include acid mine drainage (Walter et al., 1994; Lichtner, 1996), radionuclide transport (Viswanathan et al., 1998), fate of metal-organic mixed waste (Rittmann & VanBriesen, 1996; VanBriesen, 1998), analysis of redox zone formation in organic-contaminated aquifers (Abrams et al., 1998; Essaid et al., 1995), and reactive permeable barriers for aquifer remediation (Fryar & Schwartz, 1994). There are also important soil science applications that require consideration of multiple chemical species, for example, evaluation of water management practices and irrigation techniques under arid and semiarid conditions, evaluation of water suitability for irrigation, and reclamation of sodic soils (Rhoades, 1997, Šimůnek & Suarez, 1997). This section considers such complex problems that lead to multicomponent transport.

While many models have been developed to quantify solute transport in soils, they usually consider only one solute and thus severely simplify the different chemical interactions. For example, the complex processes of adsorption and cation exchange are often accounted for by invoking simplified linear (Huyakorn et al., 1991) or nonlinear Freundlich isotherms (Yeh & Huff, 1985; Šimůnek & van Genuchten, 1994; Liu & Narasimhan, 1989a, b) that lump all reactions between the solid and liquid phases into a single distribution coefficient K_D, either with or without a Freundlich type exponent. Other processes, such as precipitation, biodegradation, or volatilization, are frequently simulated by means of simple first- or zero-order rate equations. While several other models have been developed to simulate

multiple solutes, they focus primarily upon sequential first-order decay reactions (Gureghian, 1981; Wagenet & Hutson, 1987; Šimůnek & van Genuchten, 1994).

Aqueous equilibrium chemistry models, such as WATEQ (Truesdell & Jones, 1974), MINEQL (Westall et al., 1976), GEOCHEM (Sposito & Mattigod, 1980), FITEQL (Westall, 1982), PHREEQE (Parkhurst et al., 1980; Parkhurst & Appelo, 1999), MINTEQ (Felmy et al., 1984), GMIN (Felmy, 1990), MINTEQA2 (Allison et al., 1991), EQ3NR (Wolery, 1992), and The Geochemist's Workbench (Bethke, 1994, 1996), which solve for solution equilibrium without consideration of transport, were originally developed independently of models for water flow and solute transport. The most widely used equilibrium models have been recently reviewed by Mattigod and Zachara (1996). Only during the last two decades has there been a significant effort to couple these models with transport models.

Recent reviews of the development of hydrogeochemical transport models involving reactive multiple components are given by Kirkner and Reeves (1988), Yeh and Tripathi (1989), Mangold and Chin-Fu Tsang (1991), Lichtner (1996), and Steefel and MacQuarrie (1996). Kirkner and Reeves (1988) and Rubin (1983) presented an analysis of several methods for approximate solution of multicomponent transport with homogeneous and heterogeneous chemical reactions, and discussed how the nature of the chemistry may affect the choice of the numerical formulation and solution algorithm. Yeh and Tripathi (1989) provided a critical review of many computational methods that have been presented in the hydrologic literature for solving multicomponent, equilibrium-controlled transport.

Most modeling efforts involving multicomponent transport have thus far focused on the saturated zone, where changes in the water flow velocity, temperature, and pH are often much more gradual, and hence less important, than in the unsaturated zone. Consequently, most multicomponent transport models assume one- or two-dimensional steady-state saturated water flow with a fixed value of the flow velocity, temperature, and pH (Valocchi et al., 1981; Walsh et al., 1984; Cederberg et al., 1985; Bryant et al., 1986; among many others). Only recently have several multicomponent transport models been published which also consider variably saturated flow; these include DYNAMIX (Liu & Narasimhan, 1989a, b), HYDROGEOCHEM (Yeh & Tripathi, 1990), UNSATCHEM-2D (Šimůnek & Suarez, 1994), FEHM (Zyvoloski et al., 1997), MULTIFLO (Lichtner & Seth, 1996), HYDROBIOGEOCHEM (Yeh et al., 1998), and FLOTRAN (Lichtner, 2000). For example, the model DYNAMIX of Narasimhan et al. (1986) and Liu and Narasimhan (1989a) couples the chemical equilibrium submodel PHREEQE with an integrated finite difference model for fluid flow in variably saturated porous media. Yeh and Tripathi (1991) developed and demonstrated a two-dimensional finite element hydrogeochemical transport model, HYDROGEOCHEM, for simulating transport of reactive multispecies chemicals. Yeh et al. (1998) have recently developed the more general model HYDROBIOGEOCHEM that includes microbiological reactions, in addition to geochemical reactions.

Geochemical models can be divided into two major groups: those with specific chemistry and general models. Models with specific chemistry are limited in the number of species they can handle, and their application is quite restricted to problems having a prescribed chemical system. They are, however, much easier to use and can be more computationally efficient than general models. Typical ex-

amples of models with specified chemistry are those simulating the transport of major ions, such as LEACHM (Wagenet & Hutson, 1987) and UNSATCHEM (Šimůnek & Suarez, 1994; Šimůnek et al., 1996), or reclamation models (Dutt et al., 1972; Tanji et al., 1972) (see Section 6.9.5). Models with generalized chemistry (DYNAMIX, HYDROGEOCHEM, MULTIFLO, FLOTRAN, and OS3D/GIMRT [Steefel & Yabusaki, 1996]) provide users with much more freedom in designing their particular chemical systems; possible applications of these models are also much wider.

In the following sections we will give an overview of the mathematical equations representing the major chemical reactions and governing transport processes, briefly discuss how these equations can be implemented in reaction multispecies transport models, and describe several possible applications relevant to soil scientists.

6.9.2 Geochemical Reaction Equations

Reversible chemical reactions may be described conceptually using either a kinetic or equilibrium approach. The kinetic approach entails describing the temporal progress of the reaction and is usually based upon some model of the elementary reaction mechanisms. Mathematically this leads to a system of ordinary differential equations. On the other hand, the equilibrium approach uses thermodynamic principles to describe the equilibrium state of the reaction; this approach does not require a model for the reaction mechanism and mathematically leads to a system of nonlinear algebraic equations. Since groundwater and soil water are open systems that are subject to fluxes of mass and energy, it is more appropriate to adopt the concepts of "partial" and "local" equilibrium where thermodynamic equilibrium applies to certain subsets of reactions (Knapp, 1989; Bethke, 1996; Lichtner, 1996). Several investigators have studied the question of when local equilibrium conditions apply in a dynamic transport system. For example, Valocchi (1985, 1988) and Jennings (1987) studied adsorption processes. General reactions, including mineral precipitation and dissolution, were studied by Knapp (1989), Bahr (1990). and Lichtner (1996). Dissolution of nonaqueous phase liquids was studied by Miller et al. (1990) and Powers et al. (1991). In general, these studies show that local equilibrium conditions apply when the chemical reaction rates are much faster than the rates of advection and dispersion processes. Lichtner (1993) demonstrated that local equilibrium applies asymptotically, that is, after the system has evolved for a long (infinite) time, regardless of the values of the kinetic rate constants.

The term *component* is generally used when dealing with chemical equilibrium systems, while the term *primary species* is used for systems in partial equilibrium. Following Westall et al. (1976), components may be defined as a set of linearly independent chemical entities such that every species in the system can be uniquely represented as the product of a reaction involving only these components. No component can be represented as the product of a reaction involving only the other components. As a typical example, the chemical species $CaCO_3^0$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^0 \qquad [6.9–1]$$

consists of the two components Ca^{2+} and CO_3^{2-}. However, from the definition of a component it follows that any other combination of two species selected from the above system as basis components, such as $CaCO_3^0$ and Ca^{2+}, or $CaCO_3^0$ and CO_3^{2-}, may be used also, since the third species can always be represented by a linear combination of the two selected components.

Reversible chemical reaction processes are generally represented mathematically using mass action laws that relate thermodynamic equilibrium constants to activities (the thermodynamic effective concentration) of the reactants and products (Mangold & Tsang, 1991; Bethke, 1996; Appelo & Postma, 1993). For example, the reaction

$$bB + cC \rightleftharpoons dD + eE \qquad [6.9–2]$$

where b and c are the number of moles of substances B and C that react to yield d and e moles of products D and E, is represented at equilibrium by the law of mass action

$$K = (a_D^d a_E^e)/(a_B^b a_C^c) \qquad [6.9–3]$$

where K is a temperature-dependent thermodynamic equilibrium constant, and a_i is the ion activity, being defined as the product of the activity coefficient (γ_i) and the ion molality (m_i), that is, $a_i = \gamma_i m_i$. Single-ion activity coefficients may be calculated using either the Davies equation, an extended version of the Debye–Hückel equation (Truesdell & Jones, 1974), or by means of Pitzer expressions (Pitzer, 1979) (see Section 6.9.2.6). Equation [6.9–3] can be used to describe all of the major chemical processes, such as aqueous complexation, sorption, precipitation–dissolution, and acid–base and redox reactions, provided that the local chemical equilibrium assumption is valid. When Eq. [6.9–3] is used to describe heterogeneous reactions involving solids and/or gases, then appropriate definitions for activities of solid or gas phases are used rather than ion activities. However, mineral reactions involving precipitation–dissolution are extremely slow, as discussed below, and usually require a kinetic formulation. Acid–base reactions are usually formulated by using the hydrogen ion H^+ as a component (Yeh & Tripathi, 1989; Mangold & Tsang, 1991). The essential difference between the proton and other components lies in the meaning of the total aqueous concentration, which is defined with respect to a user-defined reference level. Different choices of the reference level can lead to an electroneutrality condition (Yeh & Tripathi, 1989; Šimůnek & Suarez, 1994) or a proton condition (Yeh & Tripathi, 1989; Rittmann & VanBriesen, 1996; Steefle & MacQuarrie, 1996; Tebes-Stevens et al., 1998). Redox reactions are often slow, as exhibited by redox disequilibria in natural systems. Nevertheless, several models treat redox equilibria by including the electron e^- as a component. Since the electron doesn't exist as a separate entity, these models invoke the notion of the "operational electron" as a conservative property that defines the redox state of the system (Yeh & Tripathi, 1989; Engesgaard & Kipp, 1992; Liu & Narasimhan, 1989a; Keating & Bahr, 1998). A more detailed analysis of the role of the electron is given by Lichtner (1998).

6.9.2.1 Complexation

Equations for the aqueous complexation reaction [6.9–1] can be obtained using the law of mass action as follows:

$$K_{CaCO_3^0} = \frac{a_{CaCO_3^0}}{a_{Ca^{2+}}\, a_{CO_3^{2-}}}$$

or

$$x_{\,CaCO_3^0} = \frac{K_{CaCO_3^0}}{\gamma_{CaCO_3^0}}\; c_{Ca^{2+}}\gamma_{Ca^{2+}}c_{CO_3^{2-}}\gamma_{CO_3^{2-}} \qquad [6.9–4]$$

Equations for general aqueous complexation (i.e., speciation) reactions are then obtained similarly (e.g., Lichtner, 1985; Yeh & Tripathi, 1989):

$$x_i = (K_i^x/\gamma_i^x)\prod_{k=1}^{N_a}(\gamma_k^a c_k)^{a_{ik}^x} \qquad i = 1,2,3,...,M_x \qquad [6.9–5]$$

where x_i is the concentration of the ith complexed species, K_i^x is the thermodynamic equilibrium constant of the ith complexed species, γ_i^x is the activity coefficient of the ith complexed species, N_a is the number of aqueous components (or primary species for systems in partial equilibrium), c_k is the concentration of the kth aqueous component, γ_k^a is the activity coefficient of the kth aqueous component species, a_{ik}^x is the stoichiometric coefficient of the kth aqueous component in the ith complexed species, M_x is the number of complexed species, and the subscripts and superscripts "x" and "a" refer to complexed species and aqueous components, respectively. The chemical equilibrium assumption often applies to most aqueous complexation reactions since they do not involve any interphase mass transfer and thus are generally considered "fast". Exceptions are oxidation–reduction reactions that involve the transfer of one or more electrons for which disequilibrium is the rule rather than the exception. These reactions must be treated kinetically (Lichtner, 1996). Aqueous speciation reactions can exert an important indirect effect upon species mobility and fate, since sorption and degradation processes can depend strongly upon the particular complexed form of a chemical.

6.9.2.2 Cation Exchange Reactions

Solute transport through soil is significantly affected by cation exchange reactions. These reactions govern the distribution of dissolved nutrients and other chemical species between the soil solution and solid exchange phase, and thus influence the rate of movement of chemicals in soils. These reactions are particularly important in practical problems of sodic soils reclamation (see example in Section 6.9.6).

Partitioning between the solid exchange phase and the solution phase can be described by the general exchange equation (White & Zelazny, 1986)

$$z_j A^{z_i+} X_{z_i} + z_i B^{z_j+} \rightleftharpoons z_i B^{z_j+} X_{z_j} + z_i A^{z_j+} \qquad [6.9–6]$$

or by the widely used Gapon equation

$$A_{1/z_i}^{z_i+}X + (1/z_j)B^{z_j+} \rightleftharpoons B_{1/z_j}^{z_j+}X + (1/z_i)A^{z_i+} \qquad [6.9–7]$$

where A and B are chemical formulas for particular cations, X refers to an "exchanger" site on the soil, and z_i and z_j are the valences of species A and B, respectively. The mass action equation resulting from the exchange reaction (Eq. [6.9–6]) is

$$K_{ij} = \left[\frac{\overline{c}_j^{z_j+}}{\gamma_j^a c_j^{z_j+}}\right]^{z_i} \left[\frac{\gamma_i^a c_i^{z_i+}}{\overline{c}_i^{z_i+}}\right]^{z_j} \qquad [6.9–8]$$

while the mass action expression resulting from the Gapon exchange equation (Eq. [6.9–7]) is

$$K_{ij} = \left(\frac{\overline{c}_j^{z_j+}}{\overline{c}_i^{z_i+}}\right)\frac{(\gamma_i^a c_i^{z_i+})^{1/z_i}}{(\gamma_j^a c_j^{z_j+})^{1/z_j}} \qquad [6.9–9]$$

K_{ij} is the selectivity coefficient, and $\overline{c}_i$ is the exchanger-phase concentration of the ith component (expressed in moles and equivalents per mass of solid in Eq. [6.9–8] and [6.9–9], respectively). In the above equations all concentration quantities are molar except for the adsorbed concentrations in Gapon equations, which are expressed as equivalents. As an example, for the case of exchange of the cations Ca^{2+} and Na^+,

$$2\,\overline{c}_{Na}^{+} + c_{Ca}^{2+} \rightleftharpoons \overline{c}_{Ca}^{2+} + 2c_{Na}^{+} \qquad [6.9–10]$$

we obtain the following Gapon equation

$$K_{Ca/Na} = \left(\frac{\overline{c}_{Ca}^{2+}}{\overline{c}_{Na}^{+}}\right)\frac{\gamma_{Na}c_{Na}^{+}}{(\gamma_{Ca}c_{Ca}^{2+})^{1/2}} \qquad [6.9–11]$$

White and Zelazny (1986) provide a review of other general forms for cation selectivity coefficients. It is often assumed that the cation exchange capacity $\overline{c}_T$ is constant and independent of pH. When exchanger-phase concentration is expressed in equivalents per mass of solid, then

$$\overline{c}_T = \sum_{i=1}^{M_z} \overline{c}_i \qquad [6.9–12]$$

where M_z is the number of ion exchange species.

Cation exchange reactions, recognized early by soil scientists and hydrologists to significantly regulate soil solution composition, have been implemented in many models with both generalized and specific chemistry (e.g., Dutt et al., 1972; Jury et al., 1978; Robins et al., 1980; Valocchi et al., 1981; Wagenet & Hutson, 1987; Šimůnek et al., 1996). Most of these models assume that equilibrium conditions apply to the cation exchange reactions. Although the actual ion exchange reactions written above are generally fast, in complex porous media (e.g., unsaturated soils) the reaction rates may be limited by mass transfer from the flowing fluid to the exchange sites. A few transport models presented in the recent hydrology literature

include such kinetic effects for chemical species that undergo ion exchange reactions (e.g., Andre et al., 1998).

6.9.2.3 Adsorption Reactions

In addition to the ion exchange processes discussed above, dissolved chemical species may adsorb onto solid surfaces as a result of a variety of physical and chemical processes (Sposito, 1984; Brusseau & Rao, 1989; van der Zee & Destouni, 1992; van der Zee & Riemsdijk, 1994). Although the presentation here will focus on equilibrium models, in many practical situations the time scales required for transfer of the dissolved chemical to the active sorption sites are large enough to require use of nonequilibrium models. This is especially true for unsaturated soils when there are dynamic changes in water and solute flux. These models are often based upon diffusion and mass transfer concepts. Further elaboration of nonequilibrium sorption modeling is widely available in the literature (e.g., see Selim et al., 1976; Cameron & Klute, 1977; Sparks, 1989; Sardin et al., 1991; Harmon et al., 1989; van Genuchten & Wagenet, 1989; and Section 6.3).

There are two approaches to describe equilibrium sorption reactions: isotherm equations (leading to a K_D approach for a linear case), and surface complexation models. These are summarized briefly in the next two sections.

6.9.2.3.a Sorption Isotherms

Isotherms relate the adsorbed concentration of a particular species to its solution concentration. In the past, a linear equilibrium isotherm, $s = K_D c$, where s is the concentration in the adsorbed phase and K_D is the distribution or partition coefficient, has been often used to describe solute interactions between the liquid and solid phases of the soil. This leads to a constant retardation factor R_f in the governing solute transport equation. While the use of a linear isotherm can greatly simplify the mathematics of a transport problem, sorption and exchange reactions are generally nonlinear and usually depend also on the presence of competing species in the soil solution. The solute retardation factor for nonlinear adsorption is not constant, as is the case for linear adsorption, but changes as a function of the slope of the adsorption isotherm:

$$R_f = 1 + (\rho_b/\theta)[ds(c)/dc] \qquad [6.9–13]$$

where ρ_b is the bulk density and θ is the volumetric water content. It should also be noted that the isotherm approach can be applied to equilibrium ion exchange reactions, in which case the multicomponent isotherm may be a nonlinear function of all aqueous species that participate in the reactions (e.g., Valocchi et al., 1981; Rubin & James, 1973).

A variety of models have been used in the past to describe the nonlinear nature of adsorption–desorption process. Van Genuchten and Šimůnek (1996) listed some of the most commonly used sorption models relating the adsorbed concentration, s, to the total concentration, c, of an ion in solution. Although several of these equations (e.g., the Langmuir and Freundlich equations) can be derived rigorously, such as for the adsorption of gases onto solids, the expressions are generally used

only in a purely empirical fashion. Of the equations listed by van Genuchten and Šimůnek (1996), the most popular sorption models are the Langmuir, Freundlich, and Temkin equations.

A general classification of adsorption as reflected by different features of the adsorption isotherm, such as the initial slope, the presence or absence of a plateau, or the presence of a maximum, was proposed by Giles et al. (1960). They divided possible adsorption processes into four main classes—S, L (Langmuir), H (high affinity), and C (constant partitioning) isotherms—and discussed mechanisms explaining the different types of isotherms. Increasing solution concentrations result in increasing or decreasing adsorption rates for the S and L isotherms, respectively. An H isotherm is characterized by extremely high affinities of the exchanger for exchangeable ions, whereas a C isotherm results from constant partitioning of the solute between the solution and adsorbed phases. The shape of an isotherm can have significant effects on transport predictions. For example, S and L isotherms lead to so-called unfavorable and favorable exchange situations, respectively (e.g., Valocchi et al., 1981). The latter (favorable) condition (e.g., for a Freundlich isotherm with exponent $\ll 1$) produces a sharp constant-shape concentration front during transport in a soil profile, while the former (unfavorable) conditions produces a front that continues to spread during transport (Reiniger & Bolt, 1972; van Genuchten & Cleary, 1979; Valocchi et al., 1981; van der Zee & van Riemsdijk, 1994).

Although many adsorption processes are more accurately described with the more sophisticated surface complexation models described below, isotherm models have been successfully applied to the environmentally significant class of neutral, relatively nonpolar organic compounds, such as chlorinated hydrocarbons and pesticides. In fact, for low solution concentration, the simple linear isotherm often applies. In soils with significant fractions of organic carbon these compounds adsorb primarily to solid-phase organic matter as a result of hydrophobic interactions, and the K_D of these compounds is often found to correlate directly with the fractional organic C content of the soil. Further details about hydrophobic sorption by soils can be found in a number of references, including Karickhoff et al. (1979), Hassett and Banwart (1989), Pignatello (1989), and Weber et al. (1991).

6.9.2.3.b Surface Complexation Models

Models based on the sorption isotherms are not sufficiently general to account for variations in sorption with pH, multiple oxidation states, electrostatic forces, and other factors. Surface complexation models, such as the constant capacitance, diffuse double layer, and triple layer models (Mattigod & Zachara, 1996), must be used for these more complex conditions. These models were developed for adsorption onto oxide surfaces, which are modeled as functional groups that undergo acid–base, metal binding, ligand exchange, and other reactions (Dzombak & Morel, 1990; Stumm and Morgan, 1996). This enables a quantitative description of the impact of pH upon adsorption and the development of surface charge. The various surface complexation models differ in their depiction of the interfacial region surrounding an adsorbent, that is, the number of considered planes and the charge-potential relationships. The constant capacitance model includes only one plane, the diffuse double layer model considers two planes, and the Stern and triple layer models con-

sider three planes. Detailed descriptions of different surface complexation models are beyond the scope of this discussion, but are provided by several authors, including Papelis et al. (1988), Dzombak and Morel (1990), and Stumm and Morgan (1996).

6.9.2.4 Precipitation–Dissolution

Equations describing precipitation–dissolution reactions are also obtained using the law of mass action, but contrary to the other processes are represented by inequalities rather than equalities, as follows:

$$K_i^{\mathrm{p}} \geq Q_i^{\mathrm{p}} = \prod_{k=1}^{N_{\mathrm{a}}} (\gamma_k^{\mathrm{a}} c_k)^{a_{ik}^{\mathrm{p}}} \qquad i = 1,2,...,M_{\mathrm{p}} \qquad [6.9\text{–}14]$$

where M_{p} is the number of precipitated species, K_i^{p} is the thermodynamic equilibrium constant of the ith precipitated species (i.e., the solubility product equilibrium constant), Q_i^{p} is the ion activity product of the ith precipitated species, and a_{ik}^{p} is the stoichiometric coefficient of the kth aqueous component in the ith precipitated species. The inequality in Eq. [6.9–14] means that a particular precipitate is formed only when the solution is supersaturated with respect to its aqueous components; if the solution is undersaturated then the precipitated species (if it exists) will dissolve in order to reach equilibrium conditions. Equation [6.9–14] assumes that the activity of the precipitated species is equal to unity.

Precipitation–dissolution reactions are often orders of magnitude slower than other chemical reactions, while rates of dissolution of different minerals can also differ by orders of magnitude. Therefore, precipitation–dissolution reactions usually have to be considered as kinetic, rather than equilibrium, reactions. Dissolution of dolomite or silicate minerals, such as feldspar, kaolinite, gibbsite, anorthite, and others, are typical examples of kinetic reactions. The precipitation–dissolution reaction equations are often written with the rate depending on the difference between Q_i^{p} and K_i^{p}, that is, on the disequilibrium driving force (see, e.g., Inskeep & Bloom, 1985, for calcite precipitation). Different mechanistic (Plummer et al., 1978) and empirical models can be used as well. For a more elaborate discussion of kinetics and related issues (the surface area, a moving boundary problem, a boundary layer, quasistationary states, and so on) see the excellent paper by Lichtner (1996).

6.9.2.5 Reactions with Organic Matter and Effects of Bacteria

There is increasing evidence that microorganisms, present throughout the subsurface, can catalyze many chemical reactions and thus affect the fate of organic and inorganic contaminants (Zysset et al., 1994b; Rittmann & VanBriesen, 1996). Transport and biodegradation of anthropogenically introduced chemical contaminants such as hydrocarbons are mediated by subsurface aerobic or anaerobic bacteria. Bacteria catalyze redox reactions in which organic compounds act as the electron donor and inorganic substances (oxygen, nitrate, sulfate, or metal oxides) serve as the electron acceptor. Bacteria, by catalyzing such reactions, gain energy and organic C to build up new biomass (Zysset et al., 1994b). The transport of bacteria is more complex than that of solutes, since it is affected by various additional

mechanisms, such as filtration, straining, sedimentation, adsorption, and desorption, growth, and decay and death of bacteria (see Section 6.7).

The effect of bacterial growth and microbiological reactions on geochemical transport in the subsurface has been recently incorporated into the biogeochemical transport models HYDROBIOGEOCHEM (Yeh et al., 1998), FEREACT (Tebes-Stevens et al., 1998), BIORXNTRN (Hunter et al., 1998), and FLOTRAN (Lichtner, 2000). As an interesting illustration of the coupling between biochemical and geochemical processes, an example from Tebes-Stevens and Valocchi (1998) is presented. The example considers the fate of nitrilotriacetate ($C_6H_6NO_6^{3-}$ or simply NTA), an organic chelating agent that has been detected along with metals and radionuclides in some contaminated groundwater. Although NTA is biodegradable, there is some uncertainty regarding the specifics of the degradation process (VanBriesen, 1998). For illustration purposes, it is assumed that only the single protonated form is biodegradable, which leads to the following overall stoichiometry under aerobic conditions (Tebes-Stevens & Valocchi, 1998):

$$HNTA^{2-} + 1.62O_2 + 1.272H_2O + 2.424H^+ \rightarrow 0.576C_5H_7O_2N + 3.12H_2CO_3^* + 0.424NH_4^+ \qquad [6.9\text{–}15]$$

where $C_5H_7O_2N$ is the simple elemental formula for biomass (Rittmann & VanBriesen, 1996) and $H_2CO_3^*$ represents both aqueous CO_2 and H_2CO_3. In the above equation, electrons are transferred from the donor substrate, $HNTA^{2-}$, to the acceptor, O_2, in order to produce the energy required for synthesis of new biomass. The overall rate of the above biological reaction is often described using a Monod-type kinetic model (Yeh et al., 1998; Rittmann & VanBriesen, 1996; Lichtner, 1998):

$$r = r_r[S/(K_S + S)][A/(K_A + A) \qquad [6.9\text{–}16]$$

where r and r_r are the actual and maximum reaction rates, S and A are the concentrations of the electron donor substrate and the electron acceptor, respectively, and K_S and K_A are the half saturation constants for the substrate and the electron acceptor, respectively, that is, the concentrations at which the rate is reduced by 50%. In systems with dynamically growing biomass, the maximum reaction rate is normally assumed directly proportional to the amount of biomass. The overall stoichiometry above clearly shows that biodegradation of NTA is coupled with other potentially important chemical changes; specifically, the increase in the pH and production of carbonic acid may exert significant influence over other reactions (e.g., precipitation–dissolution). In the example considered by Tebes-Stevens and Valocchi (1998), which also included metal species that complex NTA, the change in pH also affected the biodegradation rate by changing the fraction of NTA that was in the form of $HNTA^{2-}$.

The production of carbon dioxide and consumption of oxygen represent important effects of microbiological activity in the soil environment in the unsaturated zone. Microbiological respiration, combined with the plant root respiration and high water contents, can change CO_2 concentrations several orders of magnitude from values that are at equilibrium with the CO_2 content in the atmosphere (0.035%), up

to extreme values of about 20%. The solubility of many solid phases, such as carbonates and oxihydroxides, significantly changes within this range of CO_2, primarily because changes in soil CO_2 produce changes in soil pH for all but acid soils (Šimůnek & Suarez, 1994). The UNSATCHEM models (Šimůnek & Suarez, 1993a, b; Šimůnek et al., 1996) consider the effects of CO_2 producing microbiological activity and CO_2 transport in the soil environment on geochemical transport. Suarez and Šimůnek (1993) gave several examples of the seasonal simulations of the CO_2 concentrations in the soil and the CO_2 fluxes to the atmosphere for different crops and compared their results with published field data.

6.9.2.6 Activity Coefficients and Thermodynamic Equilibrium Constants

6.9.2.6.a Thermodynamic Equilibrium Constants

Large databases of thermodynamic equilibrium constants for hundreds of reactions, that is, equilibrium constants for aqueous complexed species, solubility products for solid phases, and the redox potentials for various oxidation–reduction reactions, are usually available as part of general geochemical equilibrium models (Mattigod & Zachara, 1996). These constants are normally valid at reference temperature (25°C) and for zero ionic strength. Since soil solutions involve different temperatures, and have finite ionic strength, the thermodynamic constants must be corrected to reflect these factors.

6.9.2.6.b Activity Coefficients

The solute activity coefficients are formally defined as (Stokes, 1979)

$$a_i = \gamma_i(m_i/m_0) \qquad [6.9\text{–}17]$$

where a_i is the activity, m_i is the molality (mol kg^{-1}), m^0 is the standard state unit molality (i.e., 1 mol kg^{-1}), and γ_i is the activity coefficient of the ith ion. Single-ion activity coefficients may be calculated either using the Davies equation and an extended version of the Debye–Hückel equation (Truesdell & Jones, 1974) for dilute to moderately saline solutions, or by use of the Pitzer expressions (Pitzer, 1979), which are considered more accurate for solutions having very high ionic strength down to solutions having infinite dilution. The Davies equation has the following form:

$$\ln\gamma = -Az^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right] \qquad [6.9\text{–}18]$$

The extended version of the Debye–Hückel equation (Truesdell & Jones, 1974) is given by

$$\ln\gamma = -\frac{Az^2\sqrt{I}}{1+Ba\sqrt{I}} + bI \qquad [6.9\text{–}19]$$

where A and B are constants depending only upon the dielectric constant, density, and temperature; z is the ionic charge (valence); a and b are two adjustable pa-

rameters accounting for the hydrated ionic radius of a species and for ion pair interactions, respectively (Lichtner, 1996), and I is the ionic strength

$$I = 0.5 \sum_{i=1}^{M} z_i^2 m_i \qquad [6.9–20]$$

where M is the number of species in the solution mixture. The activities of neutral species are calculated as (Sposito, 1981)

$$\ln\gamma = a' I \qquad [6.9–21]$$

where a' is an empirical parameter.

At high ionic strength (solutions at high concentrations, such as in brines or in soils in arid regions), activity coefficients are no longer universal functions of ionic strength, but depend on the relative concentration of the various ions present in solution (Felmy & Weare, 1986). The activity coefficients can then be expressed in terms of a virial-type expansion of the form (Pitzer, 1979)

$$\ln\gamma_i = \ln\gamma_i^{DH} + \sum_j B_{ij}(I) m_j + \sum_j \sum_k C_{ijk} m_j m_k + ... \qquad [6.9–22]$$

where γ_i^{DH} is a modified Debye–Hückel activity coefficient, which is a universal function of ionic strength, and B_{ij} and C_{ijk} are specific coefficients for each ion interaction. The disadvantage of using Pitzer's equations is their extensive demand on computer power.

6.9.2.6.c Temperature Dependence

Most thermodynamic equilibrium constants depend on the temperature and pressure of the system. The temperature dependence of the thermodynamic equilibrium constants is often expressed as a power function of the absolute temperature (Truesdell & Jones, 1974; Plummer & Busenberg, 1982)

$$\log K = a_1 + a_2/T + a_3 T + a_4 \log T + a_5/T^2 \qquad [6.9–23]$$

where T is absolute temperature, and a_1 through a_5 are empirical constants. The pressure dependence is usually neglected for near soil-surface conditions. The temperature dependence of the equilibrium constants for which the constants of Eq. [6.9–23] are not known is estimated with the enthalphy of reaction and the Van't Hoff expression (Truesdell & Jones, 1974)

$$\ln K = \ln K_r - (\Delta H_r/R)[(1/T) - (1/T_r)] \qquad [6.9–24]$$

where T_r is the reference temperature (298.15 K), R is the universal gas constant, K_r is the equilibrium constant at the reference temperature, and ΔH_r is the enthalpy change of the reaction.

6.9.3 Mass-Balance Transport Equations

Mass balance equations for N_a aqueous components are written in terms of the total analytical dissolved concentration C_j, the total precipitated concentration

P_j, the total sorbed (adsorbed and ion-exchanged) concentration S_j, and the total analytical concentration T_j, of the jth aqueous component (Yeh & Tripathi, 1989):

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i \qquad j = 1,2,...,N_a \qquad [6.9–25]$$

where the variables are as defined above when Eq. [6.9–5] was introduced, that is, x_i is the concentration of the ith complexed species, a_{ij}^x is the stoichiometric coefficient of the jth aqueous component in the ith complexed species (this is contrary to a_i which is the activity of the ith species), and c_j is the concentration of the jth aqueous component.

$$S_j = \sum_{i=1}^{M_y} a_{ij}^s s_i + \sum_{i=1}^{M_z} a_{ij}^z \overline{c}_i \qquad j = 1,2,...,N_a \qquad [6.9–26]$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^p p_i \qquad j = 1,2,...,N_a \qquad [6.9–27]$$

$$T_j = C_j + S_j + P_j \qquad j = 1,2,...,N_a \qquad [6.9–28]$$

where p_i is the concentration of the ith precipitated species, s_i is the concentration of the ith sorbed species, and a_{ij}^z and a_{ij}^s are the stochiometric coefficient of the jth aqueous component in the ith ion-exchange and sorbed species, respectively. All concentrations in the above equations are expresses in units of moles per unit volume of water in the system. When neglecting source terms, decay, and biodegradation reactions, we obtain the governing mass balance equations:

$$\frac{\partial \theta T_j}{\partial t} = \frac{\partial \theta (C_j + S_j + P_j)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ik} \frac{\partial C_j}{\partial x_k}\right) - \frac{\partial v_i C_j}{\partial x_i} \qquad j = 1,2,...,N_a \qquad [6.9–29]$$

where θ is the water content, v_i are components of Darcy's velocity, D_{ik} are coefficients of the dispersion tensor $\mathbf{D}$, t is time, and x_i are spatial coordinates. Since the water content can change rapidly in the soil environment, the total precipitated concentration, P_j, and the total sorbed concentration, S_j, are often expressed not on a volume, but on a mass basis (P_j^*, S_j^*) (Šimůnek & Suarez, 1994):

$$\frac{\partial \theta C_j}{\partial t} + \rho \frac{\partial (S_j^* + P_j^*)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ik} \frac{\partial C_j}{\partial x_k}\right) - \frac{\partial v_i C_j}{\partial x_i} \qquad j = 1,2,...,N_a \qquad [6.9–30]$$

The second term on the left side of Eq. [6.9–30] is zero for components that do not undergo sorption, ion exchange, or precipitation–dissolution. Transport Eq. [6.9–29] or [6.9–30] have to be coupled with a numerical solution of the Richards equation (or even better with the two-phase flow of gas and water equations) for spatially and temporally variable water contents and fluxes. If the reactions are assumed to be equilibrium controlled, then the transport Eq. [6.9–29] or [6.9–30] are also coupled with a geochemical speciation model that essentially solves Eq. [6.9–25] through [6.9–28] (along with the mass action equations) for the individual aqueous, sorbed, and precipitated species (i.e., c_i, s_i, p_i); this step is needed to compute the mass balance for the sorbed, ion exchange, and precipitated species (Yeh & Tripathi, 1991; Engesgaard & Kipp, 1992).

The governing equations given above assume that all reactions are equilibrium-controlled. The more general case with mixed kinetic and equilibrium reactions is presented by many investigators, including Chilakapati (1995), Lichtner (1996, 1998), Tebes-Stevens et al. (1998), Yeh et al. (1998), and Chilakapati et al. (1998). This more general formulation includes kinetic source–sink terms in the transport Eq. [6.9–30], plus separate mass balance equations for immobile species (e.g., sorbed, precipitated, and biomass species) governed by kinetically controlled reactions.

6.9.4 Numerical Implementation

The governing equations consist of partial differential equations for transport (i.e., Eq. [6.9–29] or [6.9–30]) plus a set of nonlinear algebraic and ordinary differential equations describing the equilibrium and kinetic reactions. Since the reaction of one species depends upon the concentration of many other species, these equation sets are coupled. For complex geochemical systems, consisting of many components and multidimensional transport, numerical solution of these coupled equations is challenging.

The chemical equilibrium reactions can be formulated and solved mathematically by means of two different but thermodynamically equivalent approaches, that is, (i) by minimizing the Gibbs free energy of the system subject to the constraints of mass balance, or (ii) by using equilibrium constants. For the approach based on the Gibbs free energy, the same mass is maintained throughout the iteration process, while equilibrium is iteratively reached by transferring mass from one species to another (Felmy, 1990). The solution procedure for the second approach begins with an initial guess for a set of components from which the minimum Gibbs free energy composition can be readily calculated using equilibrium constants, after which the mass balance equations are solved by iteration (Westall et al., 1976). Although the first approach tends to be more robust (Steefel & MacQuarrie, 1996), the second approach is a more popular method when dealing with chemical equilibrium systems (Truesdell & Jones, 1974; Westall et al., 1976). A Newton–Raphson method is usually employed to solve the final set of nonlinear algebraic equations. Steefel and MacQuarrie (1996) list several packages that are available for solving sets of ordinary differential and differential algebraic equations that can be used to solve systems of both kinetic and equilibrium reactions.

In a review, Yeh and Tripathi (1989) identified three different approaches for mathematically solving multicomponent transport problems: (i) a mixed differential and algebraic approach, (ii) a direct substitution approach, and (iii) a sequential iteration approach. In the first approach, the sets of differential and algebraic equations describing the transport processes and chemical reactions, respectively, are treated simultaneously (Miller & Benson, 1983; Lichtner, 1985). In the second approach, the algebraic reactions representing the nonlinear chemical reactions are substituted directly into the differential mass balance transport equations (Rubin & James, 1973; Valocchi et al., 1981; Jennings et al., 1982). The third approach (the iterative two-step method) divides the numerical solution into two independent steps that are solved separately. The first step provides solutions of the partial-differential equations governing convective–dispersive transport, whereas the second step

involves algebraic equations describing the different chemical equilibrium reactions, as well as ordinary differential equations describing kinetic reactions. The two steps are solved sequentially and iteratively (Walsh et al., 1984; Cederberg et al., 1985; Bryant et al., 1986; Yeh & Tripathi, 1991; Šimůnek & Suarez, 1994; Tebes-Stevens et al., 1998). Based on a study of computer resource requirements, Yeh and Tripathi (1989) suggested that only the third method (sequential iteration) is feasible for realistic multidimensional applications. In order to speed up the calculations, the iteration part between the chemical and transport steps is often avoided, which leads to a sequential noniterative approach. This is also called the *operator-splitting method*, and it has many advantages in terms of computational speed and programming flexibility (Steefel & Yabusaki, 1996; Steefel & MacQuarrie, 1996). There are, however, numerical errors associated with this noniterative approach, particularly for fast reactions. These errors can be reduced somewhat by selecting higher-order time splitting approaches (Valocchi and Malmstead, 1992; Zysset et al., 1994a; Steefel & MacQuarrie, 1996).

6.9.5 Effects of Solution Composition on Hydraulic Properties and Reclamation Models

High concentration of soluble salts accumulated in the soil can significantly decrease agricultural productivity by imposing osmotic stress on growing crops, resulting in decreased crop yields and possibly even crop failure (Šimůnek & Suarez, 1997). Moreover, accumulation of monovalent cations, particularly Na, may lead to clay dispersion, swelling, and overall poor soil physical properties. These processes have an adverse effect on the hydraulic properties of a soil, including hydraulic conductivity, infiltration rates, and soil water retention (Dane & Klute, 1977; Shainberg & Levy, 1992). These negative effects are usually explained on the basis of the diffuse double layer theory. Monovalent cations satisfy the negative charge of clays at a greater distance away from the surface than divalent cations, thus leading to a more extensive diffuse double layer for monovalent cations. The same is true for a dilute as compared with a high-electrolyte soil solution. A consequence of the greater extension of the diffuse double layer associated with monovalent ions is the greater repulsion force or swelling pressure between neighboring clay platelets, a situation that results in swelling and also dispersion.

The hydraulic conductivity can be reduced several orders of magnitude by soil swelling, while the effect upon water content is much smaller (Russo, 1988). Models that describe the effects of sodicity and salinity on the hydraulic conductivity can be divided into two broad groups, (i) theoretical models based on double layer theory (Lagerwerff et al., 1969; Russo & Bresler, 1977; Russo, 1988) and (ii) semiempirical models (Yaron & Thomas, 1968; McNeal, 1968, 1974; Dane, 1977). McNeal's work is based on a simple clay-swelling model, where clay swelling is related to decreases in soil hydraulic conductivity.

Initial attempts to describe and quantify the reclamation processes (i.e., removal of excessive salts from the soil profile and exchanging Na for Ca in the sorbed complex) were based mostly on chromatographic models (Dutt et al., 1972; Tanji et al., 1972). Models of this type assume that the soil profile is stratified chemically and physically into a series of horizontal layers, with water moving from one layer

to another by piston flow. Chemical processes between the solution, exchanger, and soil mineral phase within a particular layer are assumed to be instantaneous equilibrium processes. The models by Dutt et al. (1972) and Tanji et al. (1972) both consider major ion species, several complexation reactions, cation exchange, and dissolution of gypsum and calcite. Since these two models did not consider explicitly the soil hydraulic conductivity and water flow velocities, they cannot predict whether an amendment is concentrated enough to significantly improve the infiltration rate. Hence, they cannot accurately predict the time required for completing the reclamation process. More advanced models, such as LEACHM (Wagenet & Hutson, 1987) or UNSATCHEM (Šimůnek & Suarez, 1993a; Šimůnek et al., 1996), couple major ion chemistry with variably saturated water flow and solute transport. These models are powerful tools for quantitative predictions of the amount of water and amendment required in order to reclaim soil profiles to desired levels of salinity and ESP (exchangeable Na percentage). Of the reclamation models, only the UNSATCHEM model considers dynamic changes in CO_2 concentrations that can significantly alter pH and the solubility of $CaCO_3$, while also accounting for kinetic dissolution and precipitation processes for calcite and dissolution of dolomite (Šimůnek et al., 1996; Šimůnek & Suarez, 1997). The UNSATCHEM model also takes into account effects of solution composition on hydraulic properties. Example results using this model for sodic soil reclamation will be presented in the next section.

6.9.6 Applications

There are a large number of possible applications of reactive multispecies solute transport models in the soil environmental sciences. For example, Yeh and Tripathi (1991) used the HYDROGEOCHEM model to simulate the release of trace metals and acidity from an acidic uranium mill tailings pile. Water leaching from uranium mills tailing piles often contains, in addition to U, many trace metals including Mo, Se, As, and Cr (Brookins, 1984). Using the DYNAMIX model, Narasimhan et al. (1986) also studied groundwater contamination from an inactive uranium mill tailings pile. Similar studies were carried out by Walter et al. (1994) and Gerke et al. (1998).

Abandoned mines and mine tailing piles represent significant environmental problems. Water, rich with O_2, infiltrates through these structures, which often contain pyrite. Pyrite oxidation leads to the precipitation of iron oxide and the formation of acid that, in turn, mobilizes heavy metals with consequent pollution of environment (Lichtner, 1998). Multicomponent transport models are crucial tools in analyzing the potential environmental hazard of these sites.

Alkaline floods, that is, the process of oil recovery by the subsurface injection of high pH solutions that involve both precipitation–dissolution and cation exchange, were simulated by Bryant et al. (1986) using a multicomponent model. The injected alkaline solution neutralizes organic acids in the oil, thereby mobilizing the oil by a variety of mechanisms.

Safe disposal and long-term isolation of radioactive waste, especially high-level nuclear waste, represents another significant challenge. Since prediction has

to be done over geological times, numerical models of reactive transport are indispensable tools to handle such complex problems. For example, Viswanathan et al. (1998) used a multicomponent model to study the migration of Np between the repository and the groundwater table after a hypothetical repository breach at the potential high-level nuclear waste repository at Yucca Mountain, Nevada.

Sodic soil reclamation (i.e., removal of excessive salts from the soil profile and replacement of exchangeable Na^+ with Ca^{2+}) represents a typical application for geochemical transport models in agriculture and soil science. This complex problem involves variably saturated water flow, solute transport, dissolution of solid phases (i.e., reclamation amendments, such as gypsum or calcite), cation exchange (replacement of Na^+ with Ca^{2+}), complexation reactions, effects of solution composition on hydraulic conductivities and infiltration rates, and effects of elevated CO_2 on pH and consequently calcite dissolution. We will briefly summarize here results of the study of sodic soil reclamation by Šimůnek and Suarez (1997).

Šimůnek and Suarez (1997) considered six different reclamation strategies. In the first two cases, high-quality (i.e., low ion concentrations) and gypsum-saturated waters were applied to the soil without additional amendments. In the third example, high-quality water was applied to soil where gypsum was incorporated into the top 20 cm of the soil profile. In the next three cases, high-quality water and waters at two different acid concentrations were applied to the surface of a calcareous soil. The solution composition of the water initially present in the soil profile was assigned to be that of the following highly sodic soil water system: $Ca_T = 0.2$, $Mg_T = 0.2$, $Na_T = 4.8$, $Cl_T = 4.8$, alkalinity = 0.4 $mmol_c L^{-1}$ (alkalinity is defined as $2CO_{3T} + HCO_{3T} + OH – H$; for high H concentrations, alkalinity can be negative). The cation exchange capacity was set at 200 $mmol_c kg^{-1}$ and the ESP (exchangeable Na percentage) at 60 (Ca = 40.0, Mg = 40.0, Na = 120.0 $mmol_c kg^{-1}$). Four irrigation waters were used for infiltration: high-quality dilute water ($Ca_T = 1.5$ $mmol_c L^{-1}$, $Mg_T = 0.5$, $Na_T = 2.0$, $Cl_T = 1.0$, $SO_{4T} = 2.5$, Alkalinity = 0.5), water high in Ca^{2+} and SO_4^{2-} (almost gypsum saturated, $Ca_T = 32.0$, $Mg_T = 0.5$, $Na_T = 2.0$, $Cl_T = 1.0$, $SO_{4T} = 33.0$, Alkalinity = 0.5), and two acidified waters, one at pH = 2.05 ($Ca_T = 1.5$, $Mg_T = 0.5$, $Na_T = 2.0$, $Cl_T = 3.0$, $SO_{4T} = 11.0$, Alkalinity = −10.0) and the other at pH = 1.09 ($Ca_T = 1.5$, $Mg_T = 0.5$, $Na_T = 2.0$, Cl_T=93.0, $SO_{4T} = 11.0$, Alkalinity = −100.0). Model-predicted CO_2 concentrations were used for the last three cases, where CO_2 has an important effect on calcite dissolution. The hydraulic conductivity reduction due to solution composition (see Section 6.9.5) was considered for all calculations. The examples assume that the soil surface was flooded with water, with the water kept at a constant level of 1 cm above the soil surface. Šimůnek and Suarez (1997) give additional information about all relevant input parameters and the different reclamation strategies. Figure 6.9–1 shows Na adsorption ratio, SAR [= Na/{(Ca+Mg)/2}$^{0.5}$], profiles for all six reclamation strategies. Reclamation strategies were evaluated based on the considerations of the time required for reclamation to be completed and the quantity of water needed. Times to profile saturation for six strategies for selected conditions were calculated to be 358, 15.3, 2.0, 10, 6.4, and 3.2 d, respectively; times to profile reclamation were 86,870, 195.6, 116.5, 91, 64, and 15.5 d, respectively; and amounts of infiltrated water needed for reclamation were 7230, 559, 470, 600, 485, and 197 cm, respectively (Šimůnek & Suarez, 1997).

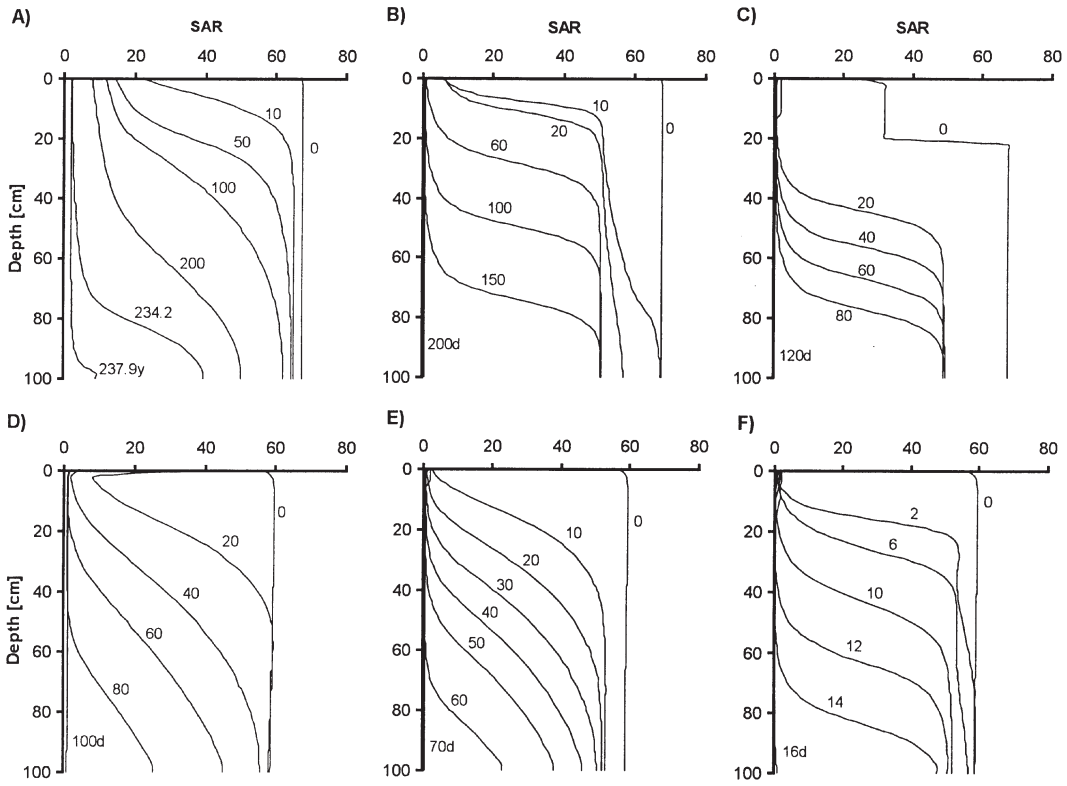

Fig. 6.9–1. Sodium adsorption profiles for six reclamation strategies: (A) irrigation with high quality water and no amendments, (B) irrigation with gypsum-saturated water, (C) irrigation with high quality water and gypsum incorporated in the top 20 cm, (D) irrigation with high quality water and calcite throughout the soil profile, (E) irrigation with acid water at pH = 2.05 and calcite throughout the soil profile, and (F) irrigation with acid water at pH = 1.09 and calcite throughout the soil profile.

Reclamation simulations using the UNSATCHEM model demonstrated the critical importance of including the effects of solution composition on soil hydraulic parameters in the model predictions (Šimůnek & Suarez, 1997). Only models with this feature can successfully estimate the time required for the reclamation process. This information is critical to decisions about choice of strategy to be employed, and its economic viability. Šimůnek and Suarez (1997) also showed using the multicomponent transport model that parameters, such as quantities of water, as well as the amounts of reclamation materials (and depth of incorporation), are dependent upon the CO_2 concentration, thus requiring a model capable of predicting CO_2 concentrations under dynamic field conditions. Flooding, combined with CO_2 production, elevates CO_2 concentrations in the root zone and results in a very effective reclamation practice. Application of acid or dilute water to calcareous soil with elevated CO_2 concentrations, incorporating gypsum into the top of the soil profile, and application of gypsum-saturated water were shown to be decreasingly less effective reclamation strategies. All these conclusions were consistent with previously reported field experiments.

Since sodic soil reclamation is a very complex process, only a model that quantitatively addresses and integrates all the involved processes can help in exploring issues that were impossible to be studied earlier and in drawing conclusions that could not be obtained using simpler models.

6.9.7 Use of Geochemical Transport Models

In recent decades, much of the research in the fields of soil science and groundwater hydrology has focused on understanding the fundamentals of pollutant fate and transport processes. The ultimate practical goal is to utilize such fundamental knowledge to develop cost-effective, technically sound strategies for resource management and pollution remediation and prevention. As society continues its technological development, and as our scientific understanding matures, the types of pollution problems that pose the more significant environmental threats become increasingly complex. Problems such as radioactive waste disposal, acid mine pollution, heavy metal transport, bioremediation of organic contaminants, and reclamation of saline soils all require understanding the coupling of multiple hydrogeological, geochemical, and microbiological processes. These are the problems that have motivated development of the class of sophisticated multicomponent reactive transport models presented here. It is the continually increasing speed and power of modern computers that has enabled such models to become a convenient tool for analysis of complex geochemical systems.

It is an open question whether we can expect to achieve the practical goal of using multicomponent reactive transport models as true predictive tools that can be used with confidence to make the quantitative forecasts necessary for remediation design. At present, there is even controversy regarding the predictive capability of simpler models of saturated water flow and single component transport (see, e.g., Konikow & Bredehoeft, 1992; de Marsily et al., 1992; Oreskes et al., 1994). The precision of the obtained predictions depends to a large extent upon the accuracy of available model input parameters and upon a proper conceptualization of soil heterogeneity and other system complexities. As discussed in Chapter 3, it is techni-

cally difficult to accurately determine the soil hydraulic function parameters characterizing soil water retention and permeability properties, which are the most important input variables for models based on the numerical solution of the variably saturated flow (Richards) equation. Adding multicomponent geochemical and microbiological processes only confounds the problem further. There may exist uncertainty about some of the equilibrium constants contained in thermodynamic data sets, and also about the composition of mixed solid phases that are present in natural soils. Many kinetic rate laws have parameters related to pore-scale diffusion length scales or reactive mineral surface area; such parameters may never be known with precision for realistic spatially heterogeneous soils. The impact of reaction parameter uncertainty upon predictions of multicomponent transport models has been studied recently by Tebes-Stevens and Valocchi (1998). Bethke (1996) presents a general discussion of sources of uncertainty in geochemical modeling.

In spite of the reservations noted above, multicomponent transport models are useful and valuable tools for analyzing complex environmental pollution problems and developing practical management strategies. The proper role of reactive transport modeling was assessed by Steefel and Van Cappellen (1998) who stated, "While reactive transport modeling is a fundamentally quantitative approach, it can be used to test the full range of implications of qualitative or conceptual models. It can help guide field observations by identifying which parameters and processes actually control the system behavior." Elaborating upon the assessment by Steefel and Van Cappellen (1998), we can identify several specific key ways that such models can be used:

Process Coupling and Interactions. While laboratory experimentation is the best tool for conducting fundamental studies of geochemical and microbiological processes under controlled conditions, mathematical models are the best tools for investigating the impacts of multiple coupled biogeochemical reactions in the presence of complex flow fields and spatial heterogeneity. These models also enable extrapolation to environmentally relevant temporal and spatial scales.

Interpretation of Laboratory and Field Data. Multicomponent transport models provide a useful framework for interpreting experimental results. The model serves as a tool for understanding qualitative and quantitative trends and relationships present in the data. In many cases properly applied modeling will identify specific hypothesis-driven experiments that will lead to more effective quantitative understanding of underlying biogeochemical processes.

Sensitivity Analysis. One of the most powerful uses of multicomponent transport models is conducting sensitivity analyses. These analyses permit the systematic evaluation of the impact of model parameters (both reactive and hydrogeological), initial conditions, and boundary conditions on the model output. The results of a sensitivity analysis provide insight into the relative importance of individual reactions within a complex biogeochemical system; thus, these results can help identify the most important parameters and processes and thereby help guide allocation of resources for laboratory and field investigations.

Integration and Synthesis. The transport model is a tool for integrating all of the knowledge obtained from simulation, sensitivity analyses, and laboratory and

field experimentation. This integration will lead to more coherent and rigorous conceptual models for the underlying coupled transport and reactions processes, and to models that are validated through their agreement with this diverse body of knowledge. As multicomponent transport models become increasingly capable of describing a broad range of natural phenomena, they become increasingly powerful tools in the fields of environmental and soil science.

6.9.8 References

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