Documentation and Applications of the Reactive Geochemical Transport Model RATEQ

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March, 1, 2005

Prepared for the U. S. Nuclear Regulatory Commission
To be published in the NUREG Report series

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ABSTRACT

The computer program RATEQ implements a numerical method for simulating reactive transport in porous media. For RATEQ simulations, groundwater flow is simulated using MODFLOW-2000. The reactive transport simulations in RATEQ are built on MT3DMS. RATEQ is intended for a wide range of applications involving biogeochemical reactions governed by rate- or equilibrium-controlled reactions. This report documents the input requirements and the output capabilities of RATEQ. The report also presents a number of example simulations illustrating the capabilities of RATEQ. The example simulations include five benchmark simulations that compare results obtained with RATEQ with results obtained independently. Simulations of U(VI) transport at the UMTRA site near Naturita, CO, are also described. Finally, several addition simulations are included that illustrate the application of RATEQ to problems with immobile zones, redox-controlled reactive transport, and biogeochemical transport.

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1. INTRODUCTION

The fate and transport of chemicals such as radionuclides in groundwater aquifers is affected by both the flow of ground water and by geochemical reactions. Computer models are often used to simulate the reactive transport of radionuclides in groundwater in order to predict future concentrations and subsequently the dose. These computer models therefore must simulate the groundwater flow which accounts for fluid sources and sinks and changes of storage within the aquifer. In addition, the models must simulate the effects of advection, dispersion, diffusion and geochemical reactions on radionuclide transport.

MODFLOW-2000 (Harbaugh et al., 2000) is one of the most widely used models for simulating groundwater flow. This model is capable of simulating transient or steady state flow in three dimensional confined or unconfined aquifers. MODFLOW-2000 (Harbaugh et al., 2000) is applicable to many near-surface groundwater environments that have constant temperature and fluid density. MODFLOW-2000, however, does not have the capability to simulate solute transport, but the model MT3DMS (Zheng and Wang, 1999) provides an approach for using the groundwater flow simulation results obtained using MODFLOW-2000 to simulate transport of multiple species that can participate in simple rate or equilibrium controlled adsorption reactions.

The computer program RATEQ, which is described in this report, extends the capability of MT3DMS to simulate multi-component, reactive solute transport in three-dimensional ground-water flow systems. A wide variety of geochemical reactions can be simulated using RATEQ including aqueous complexation, precipitation-dissolution, surface complexation, ion exchange, oxidation/reduction and formation of separate gas phases. Any of the reactions can be specified as either rate or equilibrium controlled. The reaction rates can be represented by a wide array of reaction rate laws including variable order kinetics, mass action or 'Transition State Theory' kinetics, Monod kinetics, and user defined rate laws. Thus, RATEQ replaces the simple reaction package available in MT3DMS with a fairly general geochemical reactions package. A key advantage of RATEQ is that multicomponent geochemical reactions can by added to a groundwater flow model implemented using MODFLOW-2000. Simple one dimensional simulations can also be conducted independently of MODFLOW-2000.

1.1 Model Overview

This section briefly summarizes the input to the model, options for producing model output, and describes the applicability and limitations of the model.

In two- and three- dimensional simulations, RATEQ is intended to be used with MODFLOW 2000 which is used to simulate groundwater flow. After MODFLOW-2000 is run, RATEQ is used to simulate reactive transport. Because RATEQ is an extension of MT3DMS, all of the major processes that can be simulated with MT3DMS can be simulated using RATEQ. These processes include advection, dispersion, and exchange between mobile and immobile zones.

RATEQ is written in Fortran-90. All arrays are allocated dynamically and all calculations are conducted using double precision. Computational requirements for simulations conducted with RATEQ vary significantly with the dimensionality of the domain and with the number of chemical components. Simple one dimensional simulations with a few components may require substantially less than a minute whereas multidimensional simulations

involving 10^5 to 10^6 nodes and 10 or more components could require hundreds of hours or more to complete.

1.1.1 Model Input

The majority of the model input for a reactive transport simulation using RATEQ consists of multiple files that specify the model input for MODFLOW-2000 and MT3DMS. The files that are common between MT3DMS and RATEQ include those that describe, (1) the general properties of the domain and the initial conditions, (2) the input to the advection, dispersion and diffusion, and source-sink packages, and (3) the input for the generalized conjugate gradient solver. Two additional files are required for RATEQ. The first file contains a list of geochemical reactions which describes the reaction stoichiometry, the associated thermodynamic data and a description of any kinetic rate laws. This file is loosely based on the PHREEQC thermodynamic datafile format. The second additional file species the composition of each of various solutions that are used to represent the initial conditions and the composition of each of the various fluid sources and associated mineral phases and reactive surfaces. Finally, the last new input file specifies the three dimensional spatial distribution of each of the solutions in the initial conditions.

1.1.2 Model Output

The most important model output from RATEQ consists of (1) the results of speciation calculations that are conducted so that the concentrations in the reactive domain and in the fluid sources can be initialized, (2) concentration histories at a given location, (breakthrough curves) and (3) concentrations distributions at a given time (concentration snapshots). For these latter two output files, the output can be customized so that the output file is created at specific times and can contain the concentration of selected species or selected component concentrations. The breakthrough curves and concentration snapshots can be written using a user specified format, or they can be written using the MT3DMS list directed format. In this latter case, the simulated concentrations can be visualized using Model Viewer (Hsieh and Winston, 2002). Alternatively, on the windows platform, simulation results can be visualized using compiled Matlab® scripts provided with RATEQ.

1.1.3 Model Applicability and Limitations

RATEQ can simulate reactive geochemical transport in fully saturated confined or unconfined aquifers and in laboratory column studies. It is assumed that the flow is not impacted by variable temperature or variable fluid density. Changes in fluid flow because of variable porosity that results from the formation or dissolution of new solid or gaseous phases are not considered. Geochemical activity coefficients are computed using either the Davies equation or the extended Debye-Huckel equation and therefore the model is not appropriate for ionic strengths exceeding approximately 0.1M.

1.2 Purpose and Scope

This report first documents the RATEQ code which is derived from the MT3DMS model (Zheng and Wang (1999). MT3DMS and therefore RATEQ have been created to work with MODFLOW-2000 (Harbaugh et al., 2000). This report is intended only to serve as documentation of RATEQ and does not fully document MODFLOW-2000 or MT3DMS. The users are referred to Harbaugh et al. (2000) and Hill et al (2000) for more information on MODFLOW-2000, and to Zheng and Wang (1999) for more information on MT3DMS. However, this report does contain documentation for the MT3DMS packages used in RATEQ. Specifically, this report describes the input required for the basic transport, advection, dispersion, source-sink, and generalized conjugate gradient packages available in

both MT3DMS and RATEQ. The user is referred to Zheng and Wang (1999) for a description of the MT3DMS reactions package.

This report first describes the simulation setup and operational procedures for conducting reactive transport simulations using RATEQ. The report then presents results of several benchmark test problems where simulation results obtained with RATEQ are compared directly with results obtained with other geochemical or reactive transport codes. The remainder of the report presents simulation results for a wide variety of reactive transport scenarios.

2. MODEL EQUATIONS AND ASSUMPTIONS

2.1 Introduction

The first section of this chapter describes the approach used to simulate transport influenced by multiple interacting geochemical reactions. This is presented together with a description chemical equilibrium equations, surface complexation equations, ion exchange equations, and the rate laws applicable to the geochemical reactions. Subsequently, the relation between the advection, dispersion, reaction equation and the groundwater flow equation is described. Finally, the general principals of the numerical solution are outlined.

2.2 Reaction Stoichiometry

The transport of multiple reacting species in porous media is intricately related to the reaction stoichiometry. Chemical reactions can be written using several different approaches. In some approaches, a set of primary or master species is defined and all other species, termed the secondary species, are formed from the primary species. The approach used in RATEQ is simply to define stoichiometrically balanced reactions from which the required mass balance constraints are derived. This second approach has the advantage that primary species that have negligible concentrations over a wide range of chemical conditions can be ignored in some simulations. This can yield a slight improvement in numerical performance which could become significant if many simulations are conducted as in a Monte Carlo analysis.

In this report, the reactions are expressed in matrix form since this approach is quite general and yields equations that can be manipulated using linear algebra. All reactions treated here are written with all species on one side of the equation using the convention that products have positive stoichiometric coefficients. In the general case, the set of N_R interacting reactions involving N_T species can be written as

$$[\nu_c][A] = 0 \qquad (2\text{-}1)$$

where ν_c is a matrix of stoichiometric coefficients containing N_R rows and N_T columns and A is a column vector containing N_T chemical symbols [*Smith and Missen*, 1982]. The system of N_R reactions can consist of N_{Ra} aqueous reactions, N_{Rs} surface reactions and N_{Rp} precipitation-dissolution reactions. Similarly, the N_T species consists of N_a aqueous species, N_s surface species and N_p solid species. Writing the reactions in this form has several advantages: (1) the approach can be applied to all stoichiometrically balanced reactions; (2) the mass balance equations can be derived from ν_c as described below; (3) the mass action expressions are directly related to ν_c; and (4) the approach eliminates the need to express all reactions in terms of a primary species.

For example, the formation of $UO_2(CO_3)_3^{-2-}$ from UO_2^{+2} and CO_3^{2-} is

$$UO_2^{+2} + 3CO_3^{2--} = UO_2(CO_3)_3^{-4} \qquad (2\text{-}2)$$

This reaction can also be written in the standard form of equation 2-1:

$$-UO_2^{+2} - 3CO_3^{2--} + UO_2(CO_3)_3^{-4} = 0 \qquad (2\text{-}3)$$

where the convention that the stoichiometric coefficients of reactants are negative and the stoichiometric coefficients of products are positive is used. In matrix form, Equation 2-3 is

$$\begin{bmatrix} -1 & -3 & 1 \end{bmatrix} \begin{bmatrix} UO_2^{+2} \\ CO_3^{-2} \\ UO_2(CO_3)_3^{-4} \end{bmatrix} = 0 \qquad (2\text{-}4)$$

where the elements of the row vector [-1 -3 1] are the stoichiometric coefficients of the reactants and the column vector contains the symbols of the chemical species considered. The approach can be readily extended to consider pultple species. For example, the reactions for the formation of $UO_2(CO_3)_3^{-4}$, $UO_2(CO_3)_2^{-2}$, UO_2CO_3 and are

$$\begin{bmatrix} -1 & -3 & 1 & 0 & 0 \\ -1 & -2 & 0 & 1 & 0 \\ -1 & -1 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} UO_2^{+2} \\ CO_3^{-2} \\ UO_2(CO_3)_3^{-4} \\ UO_2(CO_3)_2^{-2} \\ UO_2CO_3 \end{bmatrix} = 0 \tag{2-5}$$

The purpose of the remaining part of this section is to illustrate the relation between stoichiometry matrix, ν_c and the reaction rates. The change in concentration of species i resulting from all reactions

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{N_R} \nu_{ij} R_j \tag{2-6}$$

where R_j is the rate of reaction j and N_R is the total number of reactions. Thus, for a system of reactions, the change in concentration in a closed system is given by

$$\frac{\partial \vec{C}}{\partial t} = [\nu_c]^T \vec{R} \tag{2-7}$$

where $\vec{C}$ is a vector of concentrations, $[\nu_c]^T$ is the transpose of the reaction stoichiometry matrix defined in equation 2-1 and $\vec{R}$ is a vector of reactions rates.

2.3 Transport Equation

The mass balance equation for each reacting species in a groundwater flow system is the advection-dispersion-reaction equation. This is a partial differential equation which can be written as follows for the fate and transport of species *k* in 3-D groundwater flow systems:

$$\frac{\partial(\theta C_m^k)}{\partial t} + \frac{\partial(\theta C_{im}^k)}{\partial t} = \delta^k \left(\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_m^k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left(\theta v_i C_m^k \right) + q_s C_s^k \right) + \sum_{r=1}^{N_R} \nu_{k,r} R_r \tag{2-8}$$

where the Einstein summation convention on the repeated indices i and j applies, and

C_m^k = dissolved concentration of species k in the mobile zone, (ML^{-3})

C_{im}^k = dissolved concentration of species k in the immobile zone, (ML^{-3})

θ_m= porosity of the mobile zone in the subsurface medium, (dimensionless)

θ_{im}= porosity of the immobile zone in the subsurface medium, (dimensionless)

x_i = distance along the respective Cartesian coordinate axis, (L)

δ_k = equals 1 if species k is mobile and 0 otherwise (dimensionless)

D_{ij} = hydrodynamic dispersion coefficient tensor, as described below (L^2T^{-1})

q_s= volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative), (T^{-1})

N_R = the number of reactions in the geochemical network, (dimensionless)

R_r^k = the rate of production of the k'th species by the rth reaction ($ML^{-3}T^{-1}$).

t = time, (T)

When the solute transport is simulated using the dual porosity domain approach, Equation 2-8 must be coupled with an equation that that describes the rate of mass transfer into the immobile zone:

$$\frac{\partial(\theta_{im}C_{im}^{k})}{\partial t} = k_{la}(C_{m}^{k} - C_{im}^{k}) \qquad (2\text{-}9)$$

where

k_{la} = first-order mass transfer rate between the mobile and immobile domains (T^{-1}). Equation 2-9 applies to the diffusive exchange of a solute between two fluid compartments and therefore only applies to dissolved species.

Hydrodynamic dispersion in porous media, which is included in Equation 2-10, refers to the spreading of contaminants that results from deviations of actual velocity on a microscale from the average groundwater velocity, and from molecular diffusion driven by concentration gradients. Molecular diffusion is often negligible compared with the effects of mechanical dispersion, and is only important when groundwater velocity is very small.

The hydrodynamic dispersion tensor, D_{ij}, for an isotropic porous medium, is defined as (Bear, 1979)

$$D_{ij} = \left(D_m + \alpha_T|v|\right)\delta_{ij} + (\alpha_L - \alpha_T)\frac{v_i v_j}{|v|} \qquad (2\text{-}10)$$

where

D_{ij} = a component of the dispersion tensor (LT^{-1}),

D_m = molecular diffusion coefficient (L^2T^{-1}),

α_L = the longitudinal dispersivity (L),

α_T = the transverse dispersivity (L),

δ_{ij} = Kronecker delta that equals 1 if i=j, and zero otherwise (dimensionless),

v_k= groundwater velocity in the k'th direction (k=i,j) (LT^{-1}), and

$|v|$ = the magnitude of the velocity (LT^{-1}).

It is has been observed in several field studies that transverse spreading in the vertical direction is much smaller that transverse spreading in the horizontal direction. To simulate this effect, Burnett and Frind (1987) made an *ad hoc* modification to equation 2-10 to allow different dispersivities in the horizontal and vertical directions. These modifications are included in MT3DMS and therefore RATEQ and can be written explicitly as

$$D_{xx} = \alpha_L \frac{v_x^2}{|v|} + \alpha_{TH}\frac{v_y^2}{|v|} + \alpha_{TV}\frac{v_z^2}{|v|} + D_m \qquad (2\text{-}11)$$

$$D_{yy} = \alpha_L \frac{v_y^2}{|v|} + \alpha_{TH}\frac{v_x^2}{|v|} + \alpha_{TV}\frac{v_z^2}{|v|} + D_m \qquad (2\text{-}12)$$

$$D_{zz} = \alpha_L \frac{v_z^2}{|v|} + \alpha_{TV}\frac{v_x^2}{|v|} + \alpha_{TV}\frac{v_y^2}{|v|} + D_m \qquad (2\text{-}13)$$

$$D_{xy} = D_{yx} = (\alpha_L - \alpha_{TH})\frac{v_x v_y}{|v|} \qquad (2\text{-}14)$$

$$D_{xz} = D_{zx} = (\alpha_L - \alpha_{TV})\frac{v_x v_z}{|v|} \qquad (2\text{-}15)$$

$$D_{yz} = D_{zy} = (\alpha_L - \alpha_{TV})\frac{v_y v_y}{|v|} \qquad (2\text{-}16)$$

where α_{TH} is the transverse dispersivity in the horizontal direction and α_{TV} is the transverse dispersivity in the vertical direction. Equations 2-12 through 2-16 reduce to equation 2-11 for the case where α_{TH} equals α_{TV}.

2.4 Multicomponent Transport

Equations 2-8 describes the transport of a single species in a porous medium. The purpose of this section is to consider all of the species in the reacting system and then develop the set of transport equations solved in RATEQ. First, it is useful to rewrite equation 2-8 for the complete set of species as

$$\frac{\partial}{\partial t}\left(\theta_m \vec{C}_m + \theta_{im}\vec{C}_{im}\right) = L'\left(\vec{C}\right) + \nu_c^T \vec{R} \qquad (2\text{-}17)$$

where

$$L' = \left(\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_m^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(\theta v_i C_m^k\right) + q_s C_s^k\right)$$

as described in equation 2-8 if species m is mobile and $L' = 0$ if species m is immobile.

Equation 2-17 is a system of equations representing the transport and reaction of each species. This system of equations is not typically solved in a reactive transport simulation because, in part, the reaction rates are not known for each of the reactions; many reactions are assumed to proceed sufficiently fast that the reactions can be approximated as an equilibrium process.

Equation 2-17 can be transformed using linear algebraic methods to yield a new set of equations that isolate reaction rates into separate equations. Approaches for accomplishing this transformation are described in Appendix 1. The result of these transformations is a set of equations with the following form:

$$\frac{\partial}{\partial t}\left(\theta_m \vec{V}_m + \theta_{im}\vec{V}_{im}\right) = L'\left(\vec{V}\right) + \begin{bmatrix} I_{N_R} \\ 0 \end{bmatrix}\vec{R} \qquad (2\text{-}18)$$

where

$\vec{V}$ = a vector of primary dependent variables for the transport PDEs, and

I_{N_R} = a N_R x N_R identity matrix .

Because linear transformations are used in developing equation 2-18, the primary dependent variables are linear combinations of the species concenctrations:

$$\vec{V} = [S]\vec{C} \qquad (2\text{-}19)$$

where

S = a matrix resulting from the linear transformations and

$\vec{C}$ = of the concentration of each of the species. A key assumption made in formulation equation 2-19 is that a single dispersion coefficient applies to all dissolved species. If species-dependent diffusion must be considered, then the full set of equations in 2-18 needs to be retained.

Equation 2-18 is a set of equations that consists of N_R equations that each containing one reaction rate term in each equation and N_T-N_R equations that do not contain any reaction rates. These latter equations that do not contain rate terms can be interpreted as mass balance equations for a set of primary or basis species.

Equation 2-18 consists of N_T equations for the N_T unknown concentrations. In RATEQ, if a rate law is specified in the input as described in chapter 3, then the corresponding equation in 2-18 is retained and used in the numerical solution. Conversely, if the rate law is not specified, then the transport equation for the reaction in 2-18 is replaced by the corresponding equilibrium expression.

2.5 Equilibrium Equations

The mass action expressions for the equilibrium controlled reactions depend on the type of reaction because chemical activities are treated differently depending on whether a species is dissolved in an electrolyte, present as a separate phase, or adsorbed to a surface.

This section summarizes the kinds of mass action expressions used in RATEQ for the different types of reactions.

2.5.1 Dissolved species and precipitated phases.

For dissolved species the mass action expression is

$$K_i = \prod_{j=1}^{N_a} a_j^{\nu_{M(i,j)}} \qquad (2\text{-}20)$$

where

N_a = the number of aqueous species,

K_i = the equilibrium constant of the ith reaction,

a_j = the activity of species j and

$\nu_{M(i,j)}$ = the stoichiometric coefficient of species j in reaction i. ν_M is a subset ν_C that represents the equilibrium controlled aqueous speciation reactions.

In RATEQ, the activities of solid phases are assumed to equal unity. The activities of solution species are related to the concentrations by

$$a_i = \gamma_i C_i \qquad (2\text{-}21)$$

where

γ_i is the activity coefficient [*Stumm and Morgan, 1996*].

The activity coefficient can be computed from one of several approaches available in RATEQ. In the first approach, the activity coefficients of species in electrolyte solutions can be represented by the Debye-Hückel relation

$$\ln \gamma_i = -\frac{z_i^2 A\sqrt{I}}{1 + a_i^o B\sqrt{I}} - bI \qquad (2\text{-}22)$$

where,

γ_i = the activity coefficient of the ith species,

A, B = Debye-Hückel parameters,

a_i^o = the hydrated ionic radius, and

b = ion pair interaction parameter.

The variable I in equation 2-22 is the ionic strength defined by

$$I = \frac{1}{2}\sum_{i=1}^{N_a} z_i^2 C_i \qquad (2\text{-}23)$$

where z_i is the charge of the ith species.

In addition to the Debye-Hückel relation, other methods for computing activity coefficients include the Davies equation defined as

$$\ln \gamma_i = -\frac{z_i^2\sqrt{I}}{1 + \sqrt{I}} - 0.2I \qquad (2\text{-}24)$$

and the extended Debye-Hückel

$$\ln \gamma_i = -\frac{z_i^2\sqrt{I}}{1 + aB\sqrt{I}} \qquad (2\text{-}25)$$

where a and B are extended- Debye-Hückel parameters.

RATEQ only simulates isothermal conditions, but the temperature the fixed temperature can be set in the input file. When a simulation is conducted at temperatures other than 25C, the equilibrium constant can be computed using one of two approaches. In the first approach,

the equilibrium constant at a given temperature can be computed from

$$\ln K_T = \ln K_{298} \frac{\Delta H_o}{R}\left(\frac{1}{298} - \frac{1}{T}\right) \qquad (2\text{-}26)$$

where

K_T is the equilibrium constant at temperature T,

ΔH_o = the standard enthalpy of reaction,

T is the temperature in Kelvin, and

Alternatively, the equilibrium constant can be computed from

$$\log K_T = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log T + \frac{A_5}{T^2}$$

2-27

where

K_T is the equilibrium constant at temperature T,

A_1 to A_5 are empirical coefficients,

T is the temperature in Kelvin, and

Log refers to base 10 logarithms

2.5.2 Surface complexation

The surface complexation modeling approach for simulating the adsorption of ions is based on the premise that adsorbed ions form coordinative bonds with specific functional groups present on the adsorbing surface. In surface complexation models, the surface charge varies as a result of both the accumulation of ions at the surface and the dissociation of surface functional groups. In addition, the surface ions alter the electrical potential at the adsorbing surface.

Although several approaches have been described to account for the relation between surface charge and potential, all approaches share two common attributes; (1) the Gibbs free energy of adsorption is partitioned into chemical and electrostatic components and (2) and the properties of electrical double layer (EDL) adjacent to the surface are described by a model that relates surface potential and surface charge.

Although many models have been proposed to simulate the EDL, the only EDL model supported by RATEQ is the diffuse layer model (DLM). In the diffuse layer model, mass action expressions for the adsorption of an ion are modified by an electrostatic potential term as described by

$$K_j^{int} = \prod_{i=1}^{N_a} a_i^{\nu_{ij}} \exp\left(-\Delta z_j F \Psi_s / RT\right) \qquad (2\text{-}28)$$

where

K_j^{int} is the intrinsic equilibrium constant,

Δz_j is the change in the change of the surface resulting from the jth reaction,

F is Faraday's constant,

Ψ_S is the surface potential,

R is the gas constant, and

T is the absolute temperature

The relation between Ψ_S and σ, the surface charge resulting from the charged surface species, also varies for different EDL models. In the DLM, the Ψ_S and σ are related by

$$\sigma = \left(8x10^3 RT\varepsilon\varepsilon_o c\right)^{1/2} \sinh\left(Z\psi_o F / RT\right)$$

(2-29)

where

R = gas constant,

T = absolute temperature,

ε = the dielectric constant of water,

ε_o = the permittivity of free space

c = the molar electrolyte concentration,

Z = the ionic charge for the symmetrical electrolyte,

Ψ_o = the surface potential, and

F = Faraday's constant.

Although adsorption reactions generally result in the accumulation of charge at mineral/water interfaces (Davis and Kent, 1990), quantifying the effects of this surface charge is often difficult for sediments and aquifer materials because the surfaces of these materials are inherently complex. The non-electrostatic, semi-empirical surface complexation model (SCM) neglects that actual accumulated surface charge should be balanced by a counter ion in the diffuse layer to maintain electroneutrality at the surface.

If the surface charge that forms because of the adsorption reaction is large enough, errors in major ion chemistry could result because the surface cation is immobile while the counter ions that actually balance the surface charge that are present in the diffuse layer are mobile. For example, the surface charge resulting from the formation of a surface cation could be balanced by accumulation anions such as HCO_3^- and CO_3^{-2} anions in the diffuse layer. This could cause calcite to dissolve if present and possibly change the solution pH.

A direct approach of simulating counter ions in the diffuse layer by integrating the charge-potential versus distance equations, [Parkhurst and Appelo, 1999] is not possible in the semi-empirical approach because the electrical double layer is not included. Alternatively, adsorbed surface charge can be balanced empirically by removing ions from bulk solution to exactly balance the surface charge.

This surface charge balance can be expressed as

$$\sum_{j=1}^{N_S} z_j^s S_j + \sum_{i=1}^{N_A} z_i C_i^e = 0 \qquad (2\text{-}30)$$

where

N_S is the number of surface species,

z_j^s is the charge of the jth surface species,

S_j is the concentration of the jth surface species,

N_A is the number of the aqueous species,

z_i is the charge of the ith species, and

C_i^e is the surface excess concentration of the ith species. The excess concentration of each ion is assumed to be given by

$$C_i^e = f|z_i|\delta_i C_i \qquad (2\text{-}31)$$

where

f is a proportionality constant that applies to all ions,

z_i is the charge of ith ion,

δ_i is 1 if the charge z_i is opposite that of the surface charge and is 0 otherwise, and

C_i is the concentration of the ion in bulk aqueous solution.

The approach of using the charge to weight the immobilized concentrations is empirical in this instance but is analogous to ion association models for dilute solutions. Equations 2-30 and 2-31 can be combined to give

$$f = \frac{\sum_{j=1}^{N_S} z_j^s S_j}{\sum_{i=1}^{N_A} \delta_i z_i^2 C_i} \qquad (2\text{-}32)$$

Given this definition of f, the immobilized surface concentrations (C_i^e) can be calculated from Equation 2-31. The combination of equations 2-30 to 2-32 together with mass balance equations modified to account for immobilized counter ions can be used approximate the sensitivity of model simulations to the development of surface charge.

2.5.3 Ion Exchange

Ion exchange reactions are similar to a nonelectrostatic SCM in that the electrical field at the mineral water interface is not explicitly considered. The two primary differences between the nonelectrostatic SCM and the ion-exchange approach are; (1) reactive site in the ion exchange model is always assumed to be occupied by an ion whereas in the SCM approach the surface complex can dissociate to yield a surface ion and (2) there are several commonly used conventions for approximating the activities of exchanged species in an ion exchange model whereas in the nonelectrostatic and DLM SCM the activity coefficients of the surface species are assumed to equal unity.

In RATEQ, ion exchange simulations are solved using the same computational routines as used for the surface complexation reactions. Two approaches for approximating the activities of exchanged complexes in RATEQ are the Gapon convention and the Gaines-Thomas convention. In the Gapon approach, ion exchange reactions are written as

$$Na^+ + \tfrac{1}{z} MX_z = \tfrac{1}{z} M^{z+} + NaX \qquad (2\text{-}33)$$

The equilibrium constant for this reaction is

$$K_{Na\backslash M} = \frac{\beta_{Na}\{M\}^{1/z}}{\beta_M^{1/z}\{Na\}} \qquad (2\text{-}34)$$

where β is the equivalent fraction which is assumed to represent the activity of the exchanged ion on the exchanger. RATEQ converts equivalent fractions to concentrations and used the modified equilibrium constants in the nonelectrostatic SCM

$$zNa^+ + MX_z = M^{z+} + zNaX \qquad (2\text{-}35)$$

and the corresponding equililbrium constant is

$$K_{Na\backslash M} = \frac{(\beta_{Na})^z\{M\}}{\beta_M\{Na\}^z} \qquad (2\text{-}36)$$

where the symbols are as described above.

2.6 Rate Expressions

Three types of rate laws are available include: (1) simple stoichiometric rates laws, (2) mass action kinetics, and (3) multiple Monod kinetics.

The first option in RATEQ for simulating a reaction rate considers separate terms for the forward and backward rates of reaction as illustrated by

$$R_k = k_{f(k)} \prod_{i=1}^{N_T} C_i^{\upsilon_{i,k}^f} - k_{b(k)} \prod_{i=1}^{N_T} C_i^{\upsilon_{i,k}^r} \qquad (2\text{-}37)$$

where

R_k is the rate of the kth reaction,

$k_{f(k)}$ is the forward rate constant of the k'^{th} reaction,

C_i is the concentration of the ith species,

$\upsilon_{i,k}^f$ is the coefficient for the ith species in forward rate term,

$k_{r(k)}$ is the backward rate constant of the k'th reaction,

$\upsilon^{r}_{i,k}$ is the coefficient for the ith species in backward rate term.

The coefficients $\upsilon^{f}_{i,k}$ and $\upsilon^{r}_{i,k}$ in 2-37 are not required to equal the stoichiometric coefficients of the reaction. However, the the coefficients equal the stoichiometric values and if the values of k_f and k_b are related to the thermodynamic equilibrium constant by

$$K = \frac{k_f}{k_b} \tag{2-38}$$

then this approach can be used to approximate transport controlled by the local equilibrium approximation which can be achieved if the value of k_f is sufficiently large.

An alternative rate law usually applied to the precipitation and dissolution of mineral phases that is supported in RATEQ is

$$r_k = A_{sp(k)} k_{f(k)} \prod_{i=1}^{N_T} a_i^{\upsilon^{a}_{i,k}} \left(\frac{(1 - Q_{(k)} / K_{(k)})}{1 + \left(1 / f_{m(k)}\right) Q_{(k)} / K_{(k)}} \right)^{m} \delta_{(k)} \tag{2-39}$$

where

$A_{sp(k)}$ is the specific surface area of the reacting phase,

$k_{f(k)}$ is a forward rate constant,

$Q_{(k)}$ is the ion activity product,

$K_{(k)}$ is the equilibrium constant,

m is an empirical coefficient,

f_m is an empirical coefficient that limits the reaction rate for reactions that are far from equilibrium and thus empirically accounts for the fact that reaction rates are inherently limited by pore scale diffusion (Lichtner and Felmy, 2003).

$\delta_{(k)}$ is unity if the solid is present and zero otherwise and is used to assure that a phase can not dissolve if it is not present.

The final rate law embedded in RATEQ allows the rate of reaction to be simulated using the so-called Multiple Monod Kinetics and this approach is commonly used to simulate microbially mediated reactions (Kindred and Celia, 1988; Essaid et al., 1995). In this model, the rate of reaction is given by

$$r_k = k_f \prod_{i=1}^{N_T} a_i^{\upsilon^{a}_{i,k}} f\left(\Delta G_{RXN}\right) \prod_{j=1}^{N_{m(k)}} \frac{v_{max(k,j)} C_{k,j}}{\left(K_{M(k,j)} + C_{k,j}\right)} \prod_{p=1}^{N_{p(k)}} \frac{K_{I(k,p)} + C_{k,p}}{\left(K_{I(k,p)}\right)} \tag{2-40}$$

where

k_f is a forward rate constant,

$\prod_{i=1}^{N_T} a_i^{\upsilon^a_{i,k}}$ is a term that permits the specific catalysis by one or more species,

$N_{m(k)}$ is the number of Monod terms included in the kth rate law,

$v_{max(k,j)}$ is the maximum rate of substrate utilization,

$C_{k,j}$ is the concentration of the substrate considered in the Monod rate law,

$K_{M(k,j)}$ is the Monod half velocity coefficient,

$N_{p(k)}$ is the number of inhibition terms included in the kth rate law,

$C_{k,p}$ is the concentration of the pth inhibiting species,

$K_{I(k,j)}$ is the inhibition constant of the pth inhibiting substance in the jth rate, and

$f(\Delta G_{RXN})$ is a function of the Gibbs free that insures that the rate of irreversible reaction simulated by the Monod rate law equals zero when the reaction is energetically unfavored:

$$f(\Delta G_{RXN}) = \begin{cases} 1 & \text{if} \quad \Delta G_{RXN} < \Delta G_{THR} \\ 0 & \text{if} \quad \Delta G_{RXN} \geq \Delta G_{THR} \end{cases}$$

where ΔG_{RXN} is the Gibbs free energy of reaction and ΔG_{THR} is at threshold free energy of reaction and must be less than or equal to zero (Curtis, 2003).

2.7 Ground Water Flow Equation

MODFLOW-2000 simulates steady and nonsteady flow in an irregularly shaped flow system in which aquifer layers can be confined, unconfined, or a combination of confined and unconfined. Flow from external stresses, such as flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through river beds, can be simulated. Hydraulic conductivities or transmissivities for any layer may differ spatially and be anisotropic (restricted to having the principal directions aligned with the grid axes), and the storage coefficient may be heterogeneous. Specified head and specified flux boundaries can be simulated as can a head-dependent flux across the outer boundary of the system being modeled. Such head-dependent fluxes allow water to be supplied to a boundary block in the modeled area at a rate proportional to the head difference between a "source" of water outside the modeled region and the boundary block.

MODFLOW 2000 simulates constant density groundwater flow in aquifers under the assumption that the principal components of the hydraulic conductivity tensor are aligned with coordinate axes of the model grid so that all of the nonprincipal components equal zero. Under these assumptions, the groundwater flow partial-differential equation used in MODFLOW is (McDonald and Harbaugh,1988)

$$\frac{\partial}{\partial x_i}\left(K_i \frac{\partial h}{\partial x_i}\right) + q_S = S_S \frac{\partial h}{\partial t} \qquad (2\text{-}41)$$

where

K_i = the principal component of the hydraulic conductivity tensor, (LT^{-1});

h = the potentiometric head (L);

q_S = the volumetric flux per unit volume representing sources and/or sinks of water, with q_S <0.0 for flow out of the groundwater system, and q_S >0.0 for flow into the groundwater system (T^{-1});

S_S = the specific storage of the porous material (L_{-1}); and

t = time (T)

and it is assumed that the Einstein summation convention applies in Equation 2-41.

The groundwater flow equation is solved in MODFLOW-2000 using the block-centered finite-difference approximation. The flow region is subdivided into blocks in which the medium properties are assumed to be uniform. In plan view the blocks are made from a grid of

mutually perpendicular lines that may be variably spaced. Model layers can have varying thickness. A flow equation is written for each block, called a cell. Several solvers are provided for solving the resulting matrix problem; the user can choose the best solver for the particular problem being simulated. Flow-rate and cumulative-volume balances from each type of inflow and outflow are computed for each time step.

The MODFLOW-2000 software includes the capability to simulate several kinds of fluid sources and sinks including flow to and from wells, recharge, evapotranspiration, rivers, streams, constant-head boundaries, drains, and lakes. However, as described below, not all of these fluid sources can be simulated using MT3DMS and therefore they cannot be simulated using RATEQ.

Equation 2-42, when combined with boundary and initial conditions, describes transient three-dimensional ground-water flow in a heterogeneous and anisotropic medium, provided that the principal axes of hydraulic conductivity are aligned with the coordinate directions. Solution of this equation gives the groundwater head and water fluxes for each of the fluid sources but the solution does not directly yield groundwater velocities.

2.8 Darcy's Law

The groundwater velocity is related to the flow equation through Darcy's Law

$$v_i = \frac{q_i}{\theta_m} = -\frac{K_i}{\theta_m}\frac{\partial h}{\partial x_i} \qquad (2\text{-}43)$$

where

v_i = seepage or linear pore water velocity, (LT^{-1}),

q_i = groundwater flux (flow rate per unit area) of aquifer representing fluid; (LT^{-1}),

θ_m = porosity of the subsurface medium containing flowing groundwater, dimensionless

K_i = principal component of the hydraulic conductivity tensor along Cartesian axis i, LT^{-1}

h = hydraulic head, L

x_i = distance along the respective Cartesian coordinate axis, L

The linear groundwater velocities are computed in RATEQ using Darcy's Law and the volumetric fluxes that are computed in MODFLOW-2000.

2.9 Overview of the Numerical Solution

MT3DMS is designed to be independent of MODFLOW-2000 and although MT3DMS is most often used with MODFLOW, it can be used with any flow code that stores flow related output as defined by the LINK-MT3DMS package for MODFLOW-2000. MT3DMS independently reads the unformatted files created by the LINK-MT3DMS package. The unformatted file contains the MODFLOW-2000 output required for conducting a transport simulation. This output consists of model geometry, groundwater fluxes, the magnitude of all fluid sources and other miscellaneous information as described elsewhere (Zhang et al., 2002). By using an unformatted file to save the intermediate results the MODFLOW-2000 results are stored without loss of accuracy. However, because different compilers use different formats for the creating unformatted files, it is usually necessary that both MODFLOW-2000 and MT3DMS or RATEQ be compiled using the same Fortran-90 compiler. MT3DMS supports many, but not all of the packages that have been developed for MODFLOW-2000.

The set of transport (mass balance) equations and mass action equations can be solved using the method of operator splitting. In the operator splitting method, the temporal derivatives are

split so that different processes are solved separately. MT3DMS uses operator splitting to separately solve for the processes of advection and dispersion. For example, for the ith transport equation, first advection is simulated by solving

$$\theta_m \frac{V_i^* - V_i^n}{\Delta t} + \nabla \bullet (vV_i) = 0 \qquad (2\text{-}43)$$

and then dispersion simulated by solving

$$\theta_m \frac{V_i^{**} - V_i^*}{\Delta t} + \nabla \bullet (-D\nabla V_i) = 0 \qquad (2\text{-}44)$$

Finally, the

$$\theta_m \frac{V_i^{n+1} - V_i^{**}}{\Delta t} - R_i = 0 \qquad (2\text{-}45)$$

and

$$\prod_{i=1}^{N_R} (\gamma_i C_i)^{\upsilon_{ij}} = K_j \qquad (2\text{-}46)$$

are solved simultaneously.

3 COMPUTER PROGRAM STRUCTURE AND INPUT

3.1 Introduction

This section describes the model input that is required to conduct a reactive transport simulation using RATEQ. Following the approach used in MODFLOW-2000, input for individual processes is supplied in separate files. This approach is used in RATEQ.

3.2 Groundwater Flow

MODFLOW-2000 is a comprehensive model for simulating groundwater flow subject to many kinds of stresses (fluid sources and sinks). Individual packages are typically developed for each kind of stress. Table 3-1 lists the packages that are available in MODFLOW-2000 and whether or not that particular package is supported in MT3DMS, and therefore whether or not the package is supported in RATEQ.

Each of the packages listed in Table 3-1 requires a separate input file. In addition, input files are also required to define the computational grid, specify what simulation results to save to output, and to control numerical methods used in the simulation. A full description of all of this output is beyond the scope of this report and has been presented elsewhere (Harbaugh et al., 2000; see also citations listed in Table 3-1).

In addition to the packages listed in Table 3.1, MODFLOW-2000 can be used with the 'Link MT3DMS' (LMT) package. This package causes the MODFLOW-2000 code to save flow related simulation results in an unformatted Fortran file. This file contains discretization information, fluxes between cells, and source and sink fluxes. The LMT package is described in detail in Zheng et al., (2001).

The LMT package is activated by including an entry in the MODFLOW-2000 name file. Specifically, the name file must contain the line:

```
lmt6     66        filename.lmt
```

which activates the LMT package (version 6) in MODFLOW-2000, attaches unit 66 to the LMT input, and defines 'filename.lmt' as the existing input file containing the user-specified options for controlling how to save the flow-transport link file from MODFLOW-2000.

Input to the Link-MT3DMS Package is read from the file that has the file type "LMT6" in the name file. The LMT input file has the format illustrated in Table 3-2. All input records are preceded by a case-insensitive keyword. The underscore character must not be skipped. The following paragraphs describe the input records of Table 3.2 in more detail.

Record 1. FNAME is the name of the flow-transport link file produced by MODFLOW-2000 through the LMT6 Package for use by the MT3DMS transport model. Directory path names may be specified as part of Fname as in D:\ MF2K\ DATA\ TWRI\ TWRI . The convention for the file extension of the LMT6 Package produced output file is designated as 'FTL' for 'Flow-Transport Link'. If Fname is not specified (left blank) after the keyword 'OUTPUT_FILE_NAME', or if the entire record including the keyword is missing, the output file is assigned the default name, "RootName.FTL", where "RootName" is whatever file name is assigned to the LMT6 Package input file. For example, if the input file to the LMT6 Package is named "TEST1. LMT", then the name for the LMT6 Package produced output file is "TEST1. FTL" by default.

Record 2. INFTL is the unit number on which the LMT6 Package produced output file will be saved. A positive, unique integer must be used that has not been associated with any other file. If an invalid input is entered, an error message is written to the MODFLOW-2000 LIST output file, and the program execution is terminated. If INFTL is not specified by the user, or if the

Table 3-1. MODFLOW Packages and Support Status by Link-MT3DMS and RATEQ

MODFLOW package name (Harbaugh et al., 2000; or as noted)	MT3DMS Support	RATEQ Example[1]
Block-Centered Flow	Yes	5.3, 5.4, 6.2
Layer Property Flow	Yes	NT[2]
Horizontal Flow Barrier	Yes	NT[2]
River	Yes	5.3, 5.4
Recharge	Yes	5.3, 5.4
Well	Yes	
Drain	Yes	5.3
Evapotranspiration	Yes	NT
General-Head Boundary	Yes	6.2, 6.3
Time-Variant Constant Head Boundary	Yes	
Hydrogeologic Unit Flow (Anderman and Hill, 2000)	Yes	NT
Streamflow-Routing	Yes	NT
Reservoir	Yes	NT
Specified Flow and Head Boundary	Yes	NA[3]
Interbed Storage	No	NA
Transient Leakage	No	NA
Lake (Merritt and Konikow, 2000)	No	NA
Drain with Return Flow (Banta, 2000)	No	NA
Evapotranspiration with a Segmented Function (Banta, 2000)	No	NA

[1] Numbers refer to sections in this report
[2] Flow package not tested with RATEQ
[3] Flow package not available in RATEQ

Table 3.2 Format of LMT Input File

Record	Keyword	Description
1	OUTPUT_FILE _NAME	FNAME
2	OUTPUT_FILE_UNIT	INFTL
3	OUTPUT_FILE_HEADER	FHEADER
4	OUTPUT_FILE_FORMAT	FFORMAT

entire record including the keyword is missing, the output file will be saved on the default unit number of 333.

Record 3. FHEADER is a string that specifies the header structure of the LMT6 Package produced flow-transport link file. In MT3DMS, FHEADER can be either STANDARD or EXTENDED and the default value is STANDARD.

For the STANDARD option, the Well, Drain, River, General Head Boundary, Recharge, Evapotranspiration packages are supported. Note that the Time-Variant Specified Head (CHD) Package (Leake and Prudic, 1991) is automatically supported since its functionality is implemented through an internal flow package, such as the Block-Centered Flow (BCF) Package. In addition, the Stream-Routing (STR) Package (Prudic, 1989) is supported if it is not

used concurrently with the River Package in the same simulation.

For the EXTENDED option, the flow-transport link file supports most of the sink/source packages that have been added to MODFLOW-96 and MODFLOW-2000, such as the Specified Flow and Head Boundary (FHB) Package (Leake and Lilly, 1997) and the Reservoir (RES) Package (Fenske et al., 1996). In addition, the Stream-Routing (STR) Package can be supported along with the River Package in the same simulation. However, these packages have not been tested with RATEQ.

Record 4. FFORMAT can be either formatted by UNFORMATTED or FORMATTED. The unformatted file is preferable because it is much smaller in size than an equivalent ASCII text file. The FORMATTED file should be used only when the user needs to check the contents of the file or when MODFLOW-2000 and MT3DMS use different unformatted file formats.

3.3 RATEQ model input

RATEQ is capable of conducting a several types of geochemical calculations including simple batch speciation calculations, batch kinetic calculations, simple one dimensional (1D) transport simulations that have no external fluid or solute sources and relatively complex simulations in that can external sources of solute and possibly multiple dimensions. The number of input files required for a RATEQ simulation varies with the complexity of the problem being simulated. In addition, because RATEQ is closely related to MT3DMS, several RATEQ input files are identical to those used by MT3DMS or have very small differences.

Table 3.3 summarizes the input files that may be required for a RATEQ simulation. The first six files in the table are identical or very closely related to files used by MT3DMS. Specifically, these files provide input for the basic transport, advection, dispersion, generalized conjugate gradient and source sink packages in MT3DMS and therefore also RATEQ. The input required in these files is described below and the descriptions include a discussion of the minor difference between the RATEQ and M3DMS input files. RATEQ also requires the geochemical solver (GSR) file. This file is used to specify the input required to setup and solve the geochemical calculations. The geochemical solver file provides the option of specifying the geochemical reactions. While it is possible to specifying all of the geochemical reactions in the geochemical solver input file, this is not recommended because this list of reaction is usually very long. Instead, the recommended practice is to include all or most of the geochemical reactions in the geochemical reaction database file. Reactions that are included in the geochemical solver file are the used to add reactions that are not contained in the database, or are used to override reaction parameters contained in the database file.

For batch and simple 1D calculations, RATEQ can be executed using only the geochemical solver file and, in most instances, the reaction database file. For these simple 1D calculations, the following conditions must be met: (1) there are no fluid sources along the 1D domain except for the fluid that enters at the end of the column, (2) the computational grid must be uniform, and (3) the flow is a steady state. Conversely, flow and transport in complex geometries and possibly involving 2 or 3 spatial dimension and multiple fluid source

3.3.1 Name File

RATEQ reads a Name File when execution is started. The Name file is nearly identical to that used by MT3DMS and an example is shown in Table 3.4. The Name file contains a list of the packages that will be used in a simulation and the name of the input file for each package. The input for each package is contained on a single line, and each line contains the package name, the unit used for input, and the name of the input file. The package name can be LIST, BTN, ADV, SSM, GCG, RCT, FTL, RDB, and GSR. These abbreviations correspond to MT3DMS/RATEQ packages as follows: LIST for the standard MT3DMS output file, BTN for the MT3DMS Basic Transport Package, ADV

Table 3.3 Summary of Input files Required for a RATEQ Simulation

INPUT	Description of File	Batch/ Simple 1D Simulations	Complex 1D/2D/3D	MT3DMS – RATEQ Differences
Name File	Lists the names of the input files and the basic output file	Optional	Yes	Yes (see section 3.3.1)
Basic Transport	Sets problem dimensions, spatially distributed concentrations, output, and discretization	No	Yes	Minor (see section 3.3.2)
Advection	Sets the advection package options	No	Yes	None
Dispersion	Input for dispersivities and molecular diffusion coefficient	No	Yes	None
Generalized Conjugate Gradient	Sets options for the generalized conjugate gradient solver	No	Yes	None
Source Sink	Describes the location and composition of fluid sources	No	Yes	Minor (see section 3.3.6)
Geochemical Solver	Sets up geochemical reactions; can be used to set up 1D transport simulations	Yes	Yes	RATEQ GSR replaces MT3DMS RCT
Reactions Database	A database of reactions including thermodynamic and kinetic properties	Recommended	Recommended	Not Used in MT3DMS

for the MT3DMS Advection Package, DSP for the MT3DMS Dispersion Package, SSM for the MT3DMS Sink-Source Mixing Package, RCT for the MT3DMS Reaction Package, GCG for the MT3DMS Generalized Conjugate-Gradient Solver Package, FTL for the flow model produced flow-transport link file, RDB for the reaction database file name, and GSR for the Geochemical Reaction package. Unit numbers can be specified after the package name, but it is recommended that the default units be used for input. The default units are selected when the unit number is zero in the Name File. Comments are indicated by the # character in column 1 and can be located anywhere in the file. Any text characters can follow the # character. All comment records after the first item-1 record are written in the listing file.

The following list is an example Name File required to start a RATEQ simulation.

Table 3.4 Example of the Namefile

# Standard output file		
List	**0**	**naturita.lst**
# Input files		
BTN	**0**	**naturita.btn**
ADV	**0**	**naturita.adv**
DSP	**0**	**naturita.dsp**
GCG	**0**	**naturita.gcg**
GSR	**0**	**naturita.gsr**
RDB	**0**	**reactions.dat**

3.3.2 Array Reader

MODFLOW-2000 and MT3DMS both use an array reader package to read input for spatially dependent properties, such as hydraulic conductivity, porosity, recharge rates or concentrations. The array reader reads data files which either specifies constant or cell associated values. However, the array reader does not allow for the spatially dependent properties to be dependent on the physical dimensions of the problem; instead the array reader reads values for individual finite difference cells. This limitation can be a great disadvantage if the model discretization is changed because all of the input files containing spatially variable data would need to be redefined. This can be time consuming if a pre-processeor or a graphical user interface in not available. Consequently, a new routine was developed for the array reader supplied with MT3DMS that allows spatial data to be dependent on the physical dimensions of the problem and therefore be completely independent of the finite difference discretization. Property values for the finite difference cells are determined from the physical dimensions for each layer using bilinear interpolation if the real values are being read and by using the nearest neighbor if integer values are being read. To use this new addition to the array reader, the variable IREAD should be set to either 170 or 180 as described below.

The general format of the data read by the array reader is listed in Table 3.5. The first variable read, IREAD, determines how the spatial data is read. The first record must have one of the following 3 formats:

Record 1: IREAD CNSTNT FMTIN IPRN

or

Record 1: 170 input_option Species_name Species_type Species_value or filename

Or

Record 1: 180 input_option Value.

IREAD determines how array values are read.

If IREAD = 0, every element in array will be set equal to the value CNSTNT.

If IREAD = 100, an array of input values follows the control record. The array values are read in the format specified in the third field of the array-control record (FMTIN) from the same unit used for reading the array-control record.

If IREAD = 101, an array of values organized in “block” format follows the array-control record. The block format consists of a record specifying the number of blocks, NBLOCK, followed by NBLOCK records of input values (all in free format), specifying the first row (I1), last row (I2), first column (J 1), and last column (J2) of each block as well as the value for each cell within the block. If a subsequent block overlaps any preceding blocks, the subsequent block overrides the preceding blocks. It is recommended that the first block cover the entire grid to insure that each cell is initialized.

If IREAD = 102, an array of values organized in “zonal” format follows the array-control record. Each zone represents one value of the input variable, and each zone is identified by a zone number -- an integer which may actually be thought of as a code for the corresponding value of the input variable. The zonal format consists of a record specifying the number of zones, NZONE, followed by an array of values for the input variables, ZV(NZONE) which are listed in sequence according to zone numbers (1, 2, 3, ..., etc.); Following ZV is the zone indicator array A(NCOL,NROW)/IA(NCOL,NROW) specifying the zone number assigned to each node (cell) in a given layer of the model. The input vales are read using free format.

If IREAD = 103, an array of values follows the array-control record. The array values are read using list-directed or free format.

If IREAD = any value other than 0, 100, 101, 102, 103, 170 and 180 array values are read from a separate file.

Table 3.5 Alternative Input Formats for the Array Reader

Record	
1	0 CNSTNT FMTIN IPRN
1	100 CNSTNT FMTIN IPRN
2	Table of values read with format FMTIN
1	101 CNSTNT FMTIN IPRN
2	NBLOCK
3	I1 I2 J1 J2 Value (Repeated NBLOCK Times)
1	102 CNSTNT FMTIN IPRN
2	NZONE
3	ZONE_VALUES(NZONE)
4	ZONE_INDEX(NCOL,NROW)
1	103 CNSTNT FMTIN IPRN
2	Table of values read with using free format
1	170 input_option Species_name Species_type Species_value or filename
2	xmin:dx:xmax ymin:dy:ymax
3	Table of values
1	180 input_option value or filename
2	xmin:dx:xmax ymin:dy:ymax
3	Table of values

If IREAD = 103, an array of values follows the array-control record. The array values are read using list-directed or free format.

If IREAD = any value other than 0, 100, 101, 102, 103, and 170, array values are read from a separate file.

If IREAD > 0, it is the unit number on which the external file is read using the format specified in FMTIN.

If IREAD < 0, the absolute value of IREAD gives the unit number on which the array values are read from an external unformatted file. The unformatted file contains one record of header, followed by an unformatted record of NCOL*NROW values.

b. CNSTNT is a constant. Its use depends on the value of IREAD and can be either a real value or an integer value, depending on the array being read.

If IREAD = 0, every element in the array is set equal to CNSTNT/ICONST.

If IREAD ≠ 0, and CNSTNT/ICONST ≠ 0, elements in the array are multiplied by CNSTNT/ICONST.

FMTIN is the user-specified format to read array values or the zonal indicator array. The format must be enclosed in parentheses; for example, (15F5.0) for real values and (15I5) for integer input values.

IPRN is a flag indicating whether or not the array being read should be printed out for checking, and it also serves as a code indicating the format that should be used in printing. It is used only if IREAD is not equal to zero. IPRN is set to zero if the specified value exceeds those defined in Table 3.6 If IPRN is less than zero, the array will not be printed.

Table 3.6 Printing Formats Corresponding to the IPRN Code (after McDonald and Harbaugh 1988)

PRN	RARRAY	IARRAY
0	10G11.4	10I11
1	11 G10.3	60I1
2	9G 13.6	40I2
3	15F7.1	30I3
4	15F7.2	25I4
5	15F7.3	20I5
6	15F7.4	
7	20F5.0	
8	20F5.1	
9	20F5.2	
10	20F5.3	
11	20F5.4	
12	10G11.4	

If IREAD = 170, then record 1 has the format

IREAD input_option Species_name Species_type Value.

If the array reader is used to set the initial geochemical conditions in the simulations and if the initial conditions are specified as species concentrations instead of solution numbers as described in the input for the geochemical reactions package, then the values of Species_name Species_type Species_value are optional character strings that are required in some uses of the array reader The variables Species_name and Species_type are described in secation 3.3.5.

Record 2: xmin:dx:xmax ymin:dy:ymax. These entries are used to define the x and y dimensions for the spatial array of data read in Record 3. If Xmin is the minimum distance in the x direction, dx is the distance between values in the x direction, and xmax is the maximum distance in the x direction. Ymin, dy and ymax have similar meanings for the y direction. The values of xmin, xmax, ymin and ymax define physical dimensions characterized by a possibly spatially variable physical property. The value of the property is contained in record 3 as defined below.

Record 3: Record 3 contains the input data in free format.

If input_option is 'file', then the string contains the name of the file and the file must have the same structure as defined by Records 2 and 3.

Input_option is a case insensitive string and can equal either 'const', 'file' or 'next'

If input_option is 'const', the Value contains a numerical value and each cell in the array is set equal to that value.

If IREAD = 180 then the input is structure of the remaining input is the same as when IREAD = 170 except that the variables Species_name and Species_type are not read.

3.3.3 Transport and Reaction

MT3DMS requires input for 6 different packages; for RATEQ, the input for the ADV, DSP, and GCG packages are identical to that for MT3DMS. However, the input for the ADVECTION package is restricted to the third order TVD package. The CHEMICAL REACTION PACKAGE, which was designed for simulating simple reactions such as first order reactions and nonlinear isotherms, is replaced by a new GEOCHEMICAL SOLVER (GSR) PACKAGE. The input in the BTN and SSM packages were slightly modified, to include capabilities to provide input for simulating geochemical reactions.

3.3.3.1 Basic Transport File

Table 3.7 summarizes the information format of the basic transport file. This file consist of 23

records that mainly control the model discretization, set the initial conditions in the model, control selected model output, and define the time steps used in the model. Table 3.7 also indicates whether the input records were changed relative to the initial MT3DMS code. When the input is changed, the changes are limited to the meaning of the input rather than the number of variables. The changes in the meaning of the input only activate new options; in this way traditional MT3DMS input files can still be used in RATEQ. However, the simulations cannot be conducted simultaneously, because the MT3DMS Reaction package cannot be used in the same simulation as the Geochemical Reaction Package. One other important change is that the input for RATEQ was converted to free format. This change sacrifices backward compatibility because MT3DMS requires formatted input, but the free formatted input greatly simplifies input and reduces the chances for input errors.

Record 1 is the first line of any title or heading for the simulation run. The line should not be longer than 80 characters.

Record 2: Heading(2) is the second line of any title or heading for the simulation run. The line should not be longer than 80 characters.

Record 3: NLAY, NROW, NCOL, NPER, NCOMP, MCOMP

NLAY is the total number of layers,

NROW is the total number of rows,

NCOL is the total number of columns,

NPER is the total number of stress periods, and NCOMP determines how the initial conditions will be input.

MCOMP is read for consistency with MT3DMS, but it is not used in RATEQ.

Record 4: TUNIT, LUNIT, MUNIT

TUNIT is the name of unit for time, such as DAY or HOUR,

LUNIT is the name of unit for length, such as FT or M, and,

MUNIT is the name of unit for mass, such as LB or KG.

Note that these names are used for identification purposes only and do not affect the model outcome.

Record 5: TRNOP(10)

Each value in TRNOP is a logical flags for major transport and solution options. TRNOP (1) through (6) correspond to Advection, Dispersion, Sink & Source Mixing, Chemical Reaction, and Generalized Conjugate Gradient Solver packages and Geochemical Reactions, respectively. If any of these options is used, enter its corresponding TRNOP element as T, otherwise as F. TRNOP (7) through (10) are reserved for add-on packages.

Record 6: LAYCON(NLAY)

LAYCON is a 1-D integer array indicating the type of model layers. Each value in the array corresponds to one model layer. Enter LAYCON in as many lines as necessary if NLAY > 40.

If LAYCON = 0, the model layer is confined. The layer thickness, DZ, to be entered in a subsequent record will be used as the saturated thickness of the layer.

If LAYCON ≠ 0, the model layer is either unconfined or convertible between confined and unconfined. The saturated thickness, as calculated by the flow model and saved in the flow-transport link file, will be read and used by the transport model.

Table 3.7 Summary of Input Required for the BTN Package

Record	Modified	Array	Input	Description
1	N	N	HEADING1	Descriptive title
2	N	N	HEADING2	Descriptive title
3	Y	N	NLAY, NROW, NCOL, NPER, NCOMP, MCOMP	Problem dimensions
4	N	N	TUNIT, LUNIT, MUNIT	Units labels
5	N	N	TRNOP	Packages
6	N	N	LAYCON(NLAY)	Layer type
7	N	Y	DELR(NCOL)	Row-wise grid
8	N	Y	DELC(NROW)	Column-wise grid
9	N	Y	HTOP(NCOL,NROW)	Top of aquifer
10	N	Y	DZ(NCOL,NROW)	Layer
11	N	Y	PRSITY(NCOL,NROW)	Porosity
12	N	Y	ICBUND(NCOL,NROW)	Ibound array
13	Y	Y	SCONC(NCOL,NROW)	Initial concentration or solution number used to give initial concentration
14	N	N	CINACT, THKMIN	
15	N	N	IFMTCN, IFMTNP, IFMTRF, IFMTDP, SAVUCN	
16	N	N	NPRS	Number of periods
17	N	N	TIMPRS(NPRS)	
18	N	N	NOBS, NPROBS	
19	N	N	KOBS, IOBS, JOBS	
20	N	N	CHKMAS, NPRMAS	
21	N	N	PERLEN, NSTP, TSMULT	
22	N	N	TSLNGH(NSTP)	
23	N	N	DT0, MXSTRN, TTSMULT, TTSMAX	

Record 7: DELR(NCOL)

DELR is a 1-D real array of the cell width along rows (x) in the direction of increasing column indices (j). Specify one value for each column of the grid.

Record 8: DELC(NROW)

DELC is a 1-D real array representing the cell width along columns (~y) in the direction of increasing row indices (i).

Record 9: HTOP(NCOL,NROW)

HTOP is a 2-D array defining the top elevation of all cells in the first (top) model layer, relative to the same datum as the hydraulic heads.

If the first model layer is unconfined, HTOP can be set most conveniently to a uniform elevation above the water table. Note that the difference between HTOP and the bottom elevation of the first layer must be equal to the layer thickness, DZ, to be defined in the next record.

If the first model layer is confined, HTOP is equal to the bottom elevation of the confining unit overlying the first model layer.

Record 10: DZ(NCOL,NROW) (one array for each layer in the grid)

DZ is the thickness of all cells in each model layer. DZ is a 3-D array. The input to 3-D arrays is handled as a series of 2-D arrays with one array for each layer, entered in the sequence of layer 1, 2, ..., NLAY. The thickness of the first layer must be equal to the difference between HTOP and its bottom elevation. When the grid is discretized into horizontal layers, HTOP for the first layer and DZ within each layer are uniform. However, if a vertically distorted grid is used, both HTOP and DZ may be variable for cells within the same layer.

Record 11: PRSITY(NCOL,NROW) (one array for each layer)

PRSITY is the effective porosity of the porous medium in a single porosity system and it equals the mobile porosity as described in Section 2.2 when a dual porosity simulation is conducted. Note that if a dual-porosity system is simulated, PRSITY should be specified as the "mobile" porosity (i.e., the ratio of interconnected pore spaces filled with mobile water over the bulk volume of the porous medium); the "immobile" porosity is defined through the Chemical Reaction Package.

Record 12: ICBUND(NCOL,NROW) (one integer array for each layer)

ICBUND is an integer array specifying the boundary condition type (inactive, constant-concentration, or active) for every model cell.

If ICBUND = 0, the cell is an inactive concentration cell for all species. Note that no-flow or "dry" cells are automatically converted into inactive concentration cells. Furthermore, active cells in terms of flow can be treated as inactive concentration cells to minimize the area needed for transport simulations, as long as the solute transport is insignificant near those cells.

If ICBUND > 0, the cell is an active (variable) concentration cell where the concentration value will be calculated.

ICBUND values less than 0, which indicates constant concentration cells in MT3DMS, are not allowed with geochemical reactions.

Record 13: Array: SCONC(NCOL,NROW) (one array for each layer)

SCONC is the initial concentration for the simulation (unit, ML^{-3}). For RATEQ, if NCOMP equals one, then SRCONC equals the solution number specified in the Geochemical Reaction package. If SRCONC is greater than one, then NCOMP must equal then number of components, and SCONC must be specified

NCOMP times for each layer. In addition, the SCONC array must be entered using the array reader using the options described for IREAD=170 as described in `Section 3.3.2)

Record 14: CINACT, THKMIN

CINACT is the value for indicating an inactive concentration cell (ICBUND = 0). Even if inactive cells are not anticipated in the model, a value for CINACT still must be submitted. THKMIN is the minimum saturated thickness in a cell, expressed as the decimal fraction of the model layer thickness, DZ, below which the cell is considered inactive. The default value is 0.01 (i.e., 1 percent of the model layer thickness).

Record 15: IFMTCN, IFMTNP, IFMTRF, IFMTDP, SAVUCN Format: 4I10, L10

IFMTCN is a flag indicating whether the calculated concentration should be printed to the standard output text file and also serves as a printing-format code if it is printed. The codes for print-formats are the same as those listed in Table 3.7.

If IFMTCN > 0, concentration is printed in the wrap form (80 columns of output) or if IFMTCN< 0, concentration is printed with an unlimited number of columns.

If IFMTCN = 0, concentration is not printed.

IFMTNP, IFMTRF, and IFMTDP are not used in RATEQ but these input variables are retained for compatibility with MT3DMS, and therefore values must be provided.

SAVUCN is a logical flag indicating whether the concentration solution should be saved in a default unformatted file named MT3Dnnn.UCN, where nnn is the species index number, for post-processing purposes or for use as the initial condition in a continuation run.

If SAVUCN = T, the concentration of each species will be saved in the default file MT3Dnnn.UCN. In addition, the model spatial discretization information will be saved in another default file named MT3D.CNF to be used in conjunction with MT3Dnnn.UCN for postprocessing purposes.

If SAVUCN = F, neither MT3Dnnn.UCN nor MT3D.CNF is created.

The concentrations saved in these files will equal the total dissolved concentration of the primary dependent variables (PDVs) that were used in solving the partial differential equations (transport equations). In some instances, the PDVs equal easily recognized values, such as total dissolved concentrations, but this is always true. The Geochemical Reaction package has additional options for creating output files with specific species concentrations or functions of the species concentrations, such as pH, total dissolved concentrations, total adsorbed concentrations, reaction rates, and free energies of reaction for rate controlled reactions.

Record 16: NPRS

NPRS is a flag indicating the frequency of the output and also indicating whether the output frequency is specified in terms of total elapsed simulation time or the transport step number. Note that what is actually printed or saved is controlled by the input values entered in the preceding record (Record 15).

If NPRS > 0, simulation results will be printed to the standard output text file or saved to the unformatted concentration file at times as specified in record TIMPRS(NPRS), to be entered in the next record.

If NPRS = 0, simulation results will not be printed or saved except at the end of the simulation.

If NPRS < 0, simulation results will be printed or saved whenever the number of transport steps is an even multiple of NPRS.

Record 17: TIMPRS(NPRS)

TIMPRS is only entered if NPRS>0 and equals the total elapsed time at which the simulation

results are printed to the standard output text file or saved in the default unformatted (binary) concentration file MT3Dnnn.UCN. Note that if NPRS > 8, enter TIMPRS in as many lines as necessary.

Record 18: NOBS, NPROBS, LOCATION_TYPE

NOBS is the number of observation points at which the concentration of each species will be saved at the specified frequency in the default file, MT3Dnnn.OBS, where nnn is the species index number.

NPROBS is an integer indicating how frequently the concentration at the specified observation points should be saved in the observation file, MT3Dnnn.OBS. Concentrations are saved every NPROBS step.

LOCATION_TYPE is optional input that affects how the values in record 19 are read. If LOCATION_TYPE is omitted or is a text string 'kij', then the input in record 19 is interpreted as cell indices. Alternatively, if LOCATION_TYPE is 'xyz' or 'zyx', then the input in record 19 is interpreted as cell distances.

Record 19: KOBS, IOBS, JOBS (Enter NOBS times if NOBS > 0)

KOBS, IOBS, and JOBS are the cell indices (layer, row, column) or cell distances (z, x, y), as determined in record 18, in which the observation point or monitoring well is located, and for which the concentration is to be printed at every transport step in file MT3Dnnn.OBS. Enter one set of KOBS, IOBS, and JOBS for each observation point.

Record 20: CHKMAS, NPRMAS

CHKMAS is a logical flag indicating whether a one-line summary of mass balance information should be printed, for checking and post-processing purposes, in the default file MT3Dnnn.MAS, where nnn is the species index number.

If CHKMAS = T, the mass balance information for each transport step will be saved in file MT3Dnnn.MAS.

If CHKMAS = F, file MT3Dnnn.MAS is not created.

NPRMAS is an integer indicating how frequently the mass budget information should be saved in the mass balance summary file MT3Dnnn.MAS. Mass budget information is saved every NPRMAS step.

Record 21: PERLEN, NSTP, TSMULT

Record 21 is entered once for each stress period.

PERLEN is the length of the current stress period. If the flow solution is transient, PERLEN specified here must be equal to that specified for the flow model. If the flow solution is steady-state, PERLEN can be set to any desired length.

NSTP is the number of time-steps for the transient flow solution in the current stress period. If the flow solution is steady-state, NSTP = 1.

TSMULT is the multiplier for the length of successive time steps used in the transient flow solution; it is used only if NSTP > 1.

If TSMULT > 0, the value of each flow time-step within the current stress period is calculated using the geometric progression as in MODFLOW. Note that both NSTP and TSMULT specified here must be identical to those specified in the flow model if the flow model is transient.

If TSMULT ≠ 0, the value of each flow time-step within the current stress period is read from the record TSLNGH (see record 22). This option is needed in case the value of time steps for the flow solution is not based on a geometric progression in a flow model, unlike MODFLOW.

Record 22: TSLNGH(NSTP) (Enter if TSMULT ≠ 0)

TSLNGH provides the length of time steps for the flow solution in the current stress period. This record is needed only if the value of time steps for the flow solution is not based on a geometric progression. Enter TSLNGH in as many lines as necessary

Record 23: DT0, MXSTRN, TTSMULT, TTSMAX

DT0 is the user-specified transport step size within each time step of the flow solution. DT0 is interpreted differently depending on whether the solution option chosen is explicit or implicit.

For explicit solutions (i.e., the GCG solver is not used), the program will always calculate a maximum transport step size that meets the various stability criteria. Setting DT0 to zero causes the model-calculated transport step size to be used in the simulation. However, the model-calculated DT0 may not always be optimal. In this situation, DT0 should be adjusted to find a value that leads to the best results. If DT0 is given a value greater than the model-calculated step size, the model-calculated step size will be used in the simulation instead of the user-specified value.

For implicit solutions (i.e., the GCG solver is used), DT0 is the initial transport step size. If it is specified as zero, the model-calculated value of DT0, based on the user specified Courant number in the Advection Package, will be used. The subsequent transport step size may increase or remain constant depending on the user-specified transport step size multiplier, TTSMULT, and the solution scheme for the advection term.

MXSTRN is the maximum number of transport steps allowed within one time step of the flow solution. If the number of transport steps within a flow time step exceeds MXSTRN, the simulation is terminated.

TTSMULT is the multiplier for successive transport steps within a flow time step if the GCG solver is used and the solution option for the advection term is the standard finite-difference method. TTSMULT is not used when the third order TVD method is used and therefore TTSMULT is not applicable to RATEQ. It is listed for compatibility with MT3DMS.

3.3.3.2 Advection

The advection package simulates advection as described in section 2.3. The input to the advection package is relatively simple for RATEQ because only the third order TVD method is supported. Aside from this limitation, no changes were made. The input is summarized in Table 3.8.

Record 1: MIXELM, PERCEL

MIXELM must equal –1 for RATEQ, indicating that the TVD solver will be used,

PERCEL is the grid Peclet number that is used to limit the maximum time step used in the simulations. PERCEL must be greater than 0 and less than or equal to 1.

3.3.3.3 Dispersion

Table 3.9 summarizes the input required for the dispersion package which simulates dispersion and molecular diffusion as described in Section 2.3. The dispersion package is used to define the dispersivities and the molecular diffusion coefficients. The dispersion equations are solved numerically, either explicitly or. implicitly, depending on whether or not the GCG package is used. The GCG package also provides the option of including all of the cross terms of the dispersion tensor The input to the dispersion package was not changed for RATEQ

Table 3.8 Summary of Input Required for the ADV Package

Record	Modified	Array	Input
1	N	N	MIXELM, PERCEL

Table 3.9 Summary of Input Required for the DSP Package

Record	Modified	Array	Input	Description
1	N	Y	AL	Longitudinal dispersivity
2	N	Y	TRPT	Ratio of transverse to longitudinal dispersivity
3	N	Y	TRPV	Ratio of vertical to longitudinal dispersivity
4	N	Y	DMCOEF	Molecular diffusion coefficient

implicitly, depending on whether or not the GCG package is used. The GCG package also provides the option of including all of the cross terms of the dispersion tensor The input to the dispersion package was not changed for RATEQ

Record 1: AL(NCOL,NROW) (one array for each layer)

AL is the longitudinal dispersivity, ~L , for every cell of the model grid (unit, L).

Record 2: Array: TRPT(NLAY)

TRPT is a 1-D real array defining the ratio of the horizontal transverse dispersivity, ~TH , to the longitudinal dispersivity, ~AL . Each value in the array corresponds to one model layer. Some recent field studies suggest that TRPT is generally not greater than 0.1.

Record 3: TRPV(NLAY)

TRPV is the ratio of the vertical transverse dispersivity, ~TV , to the longitudinal dispersivity, ~AL . Each value in the array corresponds to one model layer. Some recent field studies suggest that TRPT is generally not greater than 0.01.

Set TRPV equal to TRPT to use the standard isotropic dispersion model.

Record 4: DMCOEF(NLAY)

MCOEF is the effective molecular diffusion coefficient (unit, L^2T^{-1}). Set DMCOEF = 0 if the effect of molecular diffusion is considered unimportant. Each value in the array corresponds to all species in one model layer.

3.3.3.4 Source/Sink

The source-sink package is used to define the chemical composition of all fluid sources or sinks.

Table 3.10 Summary of Input Required for the Source-Sink Package

Record	Modified	Array	Input	Description
1	N	N	FWEL, FDRN, FRCH, FEVT, FRIV, FGHB	Logical Flags indicating source type
2	N	N	MXSS	Maximum number of point sources
3	N	N	INCRCH	Flag indicating recharge
4	N	Y	CRCH	Solution numbers for recharge
5	N	N	INCEVT	Flag indicating evapotranspiration
6	N	Y	CEVT	Solution numbers for evapotranspiration
7	N	N	NSS, LOCATION_TYPE	Total number of source/sink terms, location_type
8	N	N	KSS, ISS, JSS, CSS, ITYPE, SOLN	Location, type and solution number of sources

The input for this package is summarized in Table 3.10. The source sink package in RATEQ is identical to that in MT3DMS, excepthat the locations of the point sources can be specified as either cell indices as in MT3DMS, or also as cell location (x, y, z) values. This latter option greatly simplifies the process of solving a simulation on a finer or coarser numerical grid. As with other packages, all input is free format. One limitation of the source-sink package when used with the Geochemical Reaction package is that the composition of sources and sinks must be specified as solutions and not specified as component concentrations.

Record 1: FWEL, FDRN, FRCH, FEVT, FRIV, FGHB, (FNEW(n), n=1,4)FWEL is a logical flag for the Well option,

FDRN is a logical flag for the Drain option,

FRCH is a logical flag for the Recharge option,

FEVT is a logical flag for the Evapotranspiration option,

FRIV is a logical flag for the River option, and,

FGHB is a logical flag for General-Head-Dependent Boundary option.

FNEW are logical flags reserved for additional sink/source options. If any of these options is used in the flow model, its respective flag must be set to T (True), otherwise, set to F (False).

Note that when MODFLOW is used to obtain flow solutions for MT3DMS, the LKMT package (Version 2 and later) of MODFLOW will store appropriate values for these flags in the unformatted flow-transport link file. If these flags are not specified correctly here, MT3DMS will issue a warning, reset the flags to correct values, and proceed with the simulation. Also note that a commonly used add-on package to MODFLOW, the Streamflow-Routing (STR) package is supported through the River option. This is done by associating the River option in MT3DMS with the STR package instead of the RIV package in MODFLOW. For this reason, the RIV and STR packages cannot be used concurrently in the same MODFLOW simulation.

Record 2: MXSS is the maximum number of all point sinks and sources included in the flow model. Point sinks and sources include constant-head cells, wells, drains, rivers, and general-head-dependent boundary cells. Recharge and evapotranspiration are treated as areally distributed sinks and sources; thus, they should not be counted as point sinks and sources. MXSS should be set close to the actual number of total point sinks and sources in the flow model to minimize computer memory allocated to store sinks and sources.

Records 3 through 8 are entered once for each stress period.

Record 3: INCRCH is a flag indicating whether an array containing the concentration of recharge flux for each species will be read for the current stress period.

If INCRCH ~ 0, an array containing the concentration of recharge flux for each species will be read.

If INCRCH < 0, the concentration of recharge flux will be reused from the last stress period. If INCRCH < 0 is specified for the first stress period, then by default, the concentration of positive recharge flux (source) is set equal to zero and that of negative recharge flux (sink) is set equal to the aquifer concentration.

Record 4: CRCH(NCOL,NROW) (Enter Record 4 for each species if FRCH = T and INCRCH ~ 0)

CRCH is the solution number of recharge flux for a particular species. If the recharge flux is positive, it acts as a source whose concentration can be specified as desired. If the recharge flux is negative, it acts as a sink (discharge) whose concentration is always set equal to the concentration of groundwater at the cell where discharge occurs. Note that the location and flow rate of recharge/discharge are obtained from the

flow model directly through the unformatted flow-transport link file.

Record: 5: INCEVT (Enter only if FEVT = T)

INCEVT is a flag indicating whether an array containing the solution number of evapotranspiration flux for each species will be read for the current stress period.

If INCEVT ~ 0, an array containing the concentration of evapotranspiration flux for each species will be read. If INCEVT< 0, the concentration of evapotranspiration flux for each species will be reused from the last stress period. If INCEVT < 0 is specified for the first stress period, then by default, the concentration of negative evapotranspiration flux (sink) is set to the aquifer concentration, while the concentration of positive evapotranspiration flux (source) is set to zero.

Record 6: CEVT(NCOL,NROW) (Enter for each species if FEVT = T and INCEVT ~ 0)

CEVT is the solution number of evapotranspiration flux for a particular species. Evapotranspiration is the only type of sink whose concentration may be specified externally. Note that the concentration of a sink cannot be greater than that of the aquifer at the sink cell. Thus, if the sink concentration is specified greater than that of the aquifer, it is automatically set equal to the concentration of the aquifer. Also note that the location and flow rate of evapotranspiration are obtained from the flow model directly through the unformatted flow-transport link file.

Record 7: NSS, LOCATION_TYPE

NSS is the number of point sources whose concentrations need to be specified. By default, unspecified point sources are assumed to have zero concentration. (The concentration of point sinks is always set equal to the concentration of groundwater at the sink location.)

Note that in MT3DMS, point sources are generalized to include not only those associated with a flow rate in the flow model, but also those independent of the flow solution. This type of "mass-loading" source may be used to include contaminant sources that have minimal effects on the hydraulics of the flow field.

LOCATION_TYPE is optional input that affects how the values in record 8 are read. If LOCATION_TYPE is omitted or is a text string 'kij', then the input in record 8 is interpreted as cell indices. Alternatively, if LOCATION_TYPE is 'xyz', 'zyx', or 'zxy', then the input in record 8 is interpreted as cell distances.

Record 8: KSS, ISS, JSS, CSS, ITYPE, SOLN (Enter NSS times if NSS > 0)

KSS, ISS, JSS are the cell indices (layer, row, column) of the point source for which a concentration needs to be specified for each species.

CSS is not used, but a dummy value still needs to be entered here for compatibility with MT3DMS.

ITYPE is an integer indicating the type of the point source as listed below:

ITYPE = 1, constant-head cell;

= 2, well;
= 3, drain (note that in MODFLOW conventions, a drain is always a sink, thus, the concentration for drains cannot be specified if the flow solution is from MODFLOW);
= 4, river (or stream);
= 5, general-head-dependent boundary cell;
= 15, mass-loading source;
= -1, constant-concentration cell.
SOLN defines the solution number for a point source for multispecies simulation.

Several important notes on assigning concentration for the constant-concentration condition (ITYPE = -1) are listed below:

1) The constant-concentration condition defined in this input file takes precedence to that defined in the Basic Transport Package input file.

2) In a multiple stress period simulation, a constant concentration cell, once defined, will remain a constant concentration cell in the duration of the simulation, but its concentration value can be specified to vary in different stress periods.

3) In a multispecies simulation, if it is only necessary to define different constant-concentration conditions for selected species at the same cell location, to specify the desired concentrations for those species, and to assign a negative value for all other species. The negative value is a flag used by MT3DMS to skip assigning the constant-concentration condition for the designated species.

3.3.3.5 Generalized Conjugate Gradient Package

No changes were made the to Generalized Conjugate Gradient (GCG) Package. Input for the GCG package consists of two lines as shown in Table 3.11 and described below.

Input to the GCG package is read on unit INGCG = 9, which is preset in the main program. The input file is needed only if the GCG solver is used for implicit solution schemes. This package is a new addition in MT3DMS.

Record 1: MXITER, ITER1, ISOLVE, NCRS

MXITER is the maximum number of outer iterations; it should be set to an integer greater than one only when a nonlinear sorption isotherm is included in the simulation. ITER1 is the maximum number of inner iterations; a value of 30-50 should be adequate for most problems. ISOLVE is the type of preconditioners to be used with the Lanczos/ORTHOMIN acceleration scheme:

= 1, Jacobi
= 2, SSOR
= 3, Modified Incomplete Cholesky (MIC)

MIC usually converges faster, but it needs significantly more memory.
NCRS is an integer flag for treatment of dispersion tensor cross terms:

= 0, lump all dispersion cross terms to the right hand-side (approximate but highly efficient).
= 1, include full dispersion tensor (memory intensive).

Record 2: ACCL, CCLOSE, IPRGCG

ACCL is the relaxation factor for the SSOR option; a value of 1.0 is generally adequate.

CCLOSE is the convergence criterion in terms of relative concentration; a real value between 10^{-4} and 10^{-6} is generally adequate. IPRGCG is the interval for printing the maximum concentration changes of each iteration. Set IPRGCG to zero as default for printing at the end of each stress period.

3.3.4 Reaction Database file

The reaction database file is based on the format of the thermodynamic datafile used in the program,

Table 3.11 Summary of Input Required for the GCG Package

Record	Modified	Array	Input	Description
1	**N**	**N**	**MXITER, ITER1, ISOLVE, NCRS**	**Longitudinal dispersivity**
2	**N**	**N**	**TRPT**	**Ratio of transverse to longitudinal dispersivity**

PHREEQC (Parkhurst and Appelo, 1999). Although RATEQ can directly use a PHREEQC thermodynamic input file, there are additional options that can be included in the RATEQ reaction input file.

The most significant difference for the RATEQ input file is that the rate law associated with each geochemical reaction must be included in the reaction input file.

The general format of the reaction database file is illustrated in Table 312. The reaction database file specifies master species that are used to both formulate association reactions and to set up the reactive transport equations. There are three possible kinds of master species: solution master species, surface master species, and exchange master species. These master species are used in formulating reactions in solution, on an adsorbing surface, and on an ion exchanger.

Record 1: SOLUTION_MASTER_SPECIES is a keyword indicating that the following lines define the correspondence between element names and aqueous primary and secondary master species. As a keyword, SOLUTION_MASTER_SPECIES is the only entry read from the reaction database file.

Record 2: ELEMENT NAME, MASTER SPECIES, ALKALINITY, FORMULA WEIGHT or FORMULA, FORMULA WEIGHT OF ELEMENT

ELEMENT NAME is an element name or an element name followed by a valence state in parentheses. The element name must begin with a capital letter, followed by zero or more lower case letters or underscores ("_").

Record 2 is repeated once for each master species in the reaction database file.

.

Table 3.12 Summary of Input Information in the Reaction Database file

1	**SOLUTION_MASTER_SPECIES**						
2	**Element**	**Element name**	**master species**	**alkalinity**	**gram formula weight**	**formula**	**gram formula weight for element**
3	**SOLUTION_SPECIES**						
4a		**Solution Reaction**					
4b		**Reaction Properties**					
5	**PHASES**						
6a		**Phase Name**					
6b		**Phase Dissolution Reaction**					
6c		**Reaction Properties**					
7	**SURFACE_MASTER_SPECIES**						
8		**Surface Name, Surface Master Species**					
9	**SURFACE_SPECIES**						
10a		**Surface Reactions**					
10b		**Reaction Properties**					
11	**EXCHANGE_MASTER_SPECIES**						
12		**Exchange Master Species List**					
13	**EXCHANGE_REACTION**						
14a		**Surface Reactions**					
14b		**Reaction Properties**					

MASTER SPECIES is the formula for the master species, including its charge. The term MASTER SPECIES is taken from PHREEQC and is a species used to formulate other or secondary species. If the ELEMENT NAME does not contain a valence state in parentheses, the corresponding master species is a primary master species. If the ELEMENT NAME does contain a valence state in parentheses, the master species is a secondary master species. The MASTER SPECIES must be defined in the SOLUTION_SPECIES datablock.

ALKALINITY is the alkalinity contribution of the master species. The alkalinity contribution of aqueous non-master species will be calculated from the alkalinities assigned to the master species.

FORMULA WEIGHT is used to convert input data in mass units to mole units for the element or element valence. For alkalinity, the gram equivalent weight is entered. Either FORMULA WEIGHT or FORMULA is required, but only one of them can be specified.

FORMULA is the chemical formula used to calculate gram formula weight, which is used to convert input data from mass units to mole units for the element or element valence. For alkalinity, the formula for the gram equivalent weight is entered. Either FORMULA WEIGHT or FORMULA is required.

Examples

```
Ca       Ca+2   0.0   Ca   40.08
Fe(+2)   Fe+2   0.0   Fe
```

Record 3: SOLUTION_SPECIES is a keyword indicating that the following lines define the species that occur in solution. Solution species are usually defined via formation reactions involving master species, although this is not required in RATEQ.

Record 4: This entry is used to define a solution species by a chemical reaction that should be balanced with respect to both mass and charge. Note that unlike PHREEQC, RATEQ does not require that identity reactions (e.g. H+ = H+) be defined for each 'master species. Identity reactions are ignored in RATEQ.

Record 4a: These entries define specific properties that apply to the reaction listed in Record 4. These properties include the thermodynamic equilibrium constant and the enthalpy of reaction, among other reaction properties. A complete list of reaction properties is discussed below.

Example: (4 and 4a)

```
CO3-2 + H+ = HCO3-
    Log_K 10.329
```

Record 5: PHASES is a keyword indicating that the following lines define separate phases that can be included in a simulation.

Records 6a-6c: Generally, a minimum of 3 lines is required to define a geochemical phase. The first line defines the name of phase, which can be a common mineral name, the second line defines the dissociation reaction for the phase, and the last line defines the reaction properties.

Example:

```
Calcite
    CaCO3 = CO3-2 + Ca+2
    log_k      -8.480
```

Record 7: SURFACE_MASTER_SPECIES This keyword data block is used to define the correspondence between surface binding-site names and surface master species. The default databases contain master species for Hfo_s and Hfo_w, which represent the weak and strong binding sites of hydrous ferric oxides (Dzombak and Morel, 1990).

Record 8: This record defines: (1) the name of the surface binding site, and (2) the master species for the surface species. The name of a surface binding site must begin with a capital letter or a '>', followed by zero or more lower case letters. Multiple binding sites can be defined for each surface.

Example:

Surf1 >WOH
Surf1 >SOH

In this example data block, a surface named "Surf1" has a strong (>SOH) and a weak binding site (>WOH). In setting up the equations for a simulation that includes multiple binding sites, a mole-balance equation is created for both the >WOH site and the >SOH site, and one charge-balance equation is created for surface SURF1.

Record 9: SURFACE_SPECIES is a keyword indicating that the following lines define surface species that can be included in a simulation. This is a keyword and no other input is read from this line.

Records 10a-10b: A minimum of 2 lines is required to define an adsorption reaction. The first line defines a chemical balanced adsorption reaction, and the second or more defines the reaction properties.

Example:

```
>SOH + UO2+2 = >SOUO2+ + H+
    log_K = 1.234
```

Record 11: EXCHANGE_MASTER_SPECIES

This is a keyword for the data block and no other data are read from line.

Record 12: The exchanger name is a name for the exchange site. The exchanger master exchange species is a species used in writing ion exchange reactions.

Example:

```
X     X-
```

where X is the name of the exchanger and X- is the master species.

Record 13a,b: Exchange species are written as half-reactions for the master exchange species (e.g., X^-) and an ion to form the exchanged complex. Each exchange half-reaction must be mass and charge balanced. Multiple half reactions are combined internally to give a 'typical' ion exchange reaction.

Example:

```
K+ + X- = KX
        log_K      0.7
```

Each of the reactions that define solution species, phases, surface species and exchange species can have supplemental information which defines important reaction properties including the thermodynamic equilibrium constant, the enthalpy or reaction, activity coefficient parameters and rate law information.

Table 3-13 gives a summary of all of the possible reaction information that can be included for each reaction.

log_K option. Log_{10} K at 25°C for the reaction is given.

Examples:

```
log_k  10.
Log_K 1.0
Log_K = 2.0
```

delta_h option. Enthalpy of reaction at 25°C is given. The enthalpy of reaction is used in the van't Hoff equation to determine the temperature dependence of the equilibrium constant. The default units are kilojoules per mole. Units may be calories, kilocalories, joules, or kilojoules per mole. Only the energy unit is needed (per mole is assumed) and abbreviations of these units are acceptable. Explicit definition of units for all enthalpy values is recommended.

Examples:

```
delta_h 10.0 kj/mole
delta_h 3.0 kcal/mol
Delta_h = 12.1
```

gamma option, a_0,b_0. This option specifies that the Debye-Huckel 'Bdot' method will be used to calculate the activity coefficient for the species defined by the association reaction.

Example:

```
gamma 5.000   0.1650
```

analytical_expression option, A_1, A_2, A_3, A_4, A_5. Identifier for coefficients for an analytical expression for the temperature dependence of log

K. A_1, A_2, A_3, A_4, A_5 are five values defining log K as a function of temperature in equation 2-27.

Example:

analytical 107.8871 0.03252849
-5151.79 -38.92561 563713.9

no_check option. Indicates the reaction equation should not be checked for charge balance. Default is to always check charge balance

Example:

No_check

is_ignored option. Toggle to ignore a reaction for a simulation. Default is to always include each reaction if all of the components are present in a solution. This option is useful for easily turning off or on a reaction when conducting iterative modeling studies.

Example:

Is_ignored

force_eq option. Toggle to force the reaction to be equilibrium controlled even if a rate law is given. Default behavior is to use the rate law if one is provided and the equilibrium expression if no rate law is provided. This option is useful for easily converting a rate-controlled reaction to an equilibrium-controlled reaction when conducting iterative modeling studies.

Examples:

Force_eq
force_equilibrium

molar_dens option. Molar density of mineral phase (moles/L) is given. This option is used when changes in mineral concentration are printed as a volume fraction. Alternatively, the keyword density can be by given.

Examples:

Molar_dens 44.167
molar_density = 50.
density 62.5

K_stoic option. Sets an option so that the stoichiometric coefficient for surface species can be different in the mass balance equations and the mass action expressions. This approach is an empirical approach that is sometimes used to simulate adsorption of species that form bidentate surface species, but where it is believed that the mass action expression should not depend on the square of the site concentration (see Waite et al., 1994) .

Examples:

K_stoic >SOH 1.0
K_stoic >WOH 1.0

Convention option. Defines the convention used for simulating ion exchange equilibria. Methods for computing ion exchange equilibria vary in the approach used to approximate the activity of the exchanged species. Ion exchange reactions in RATEQ can be simulated using the Gapon or Gaines-Thomas conventions as described in section 2.5.3. All reactions involving a particular exchanger use the same convention and the default is the Gaines Thomas convention.

Examples:

Convention Gapon
convention gaines

rate_law option. Defines the rate law for each rate-controlled reaction. This can be any number of lines and must end with the phrase "End_rate_law". There methods for describing rate laws are described in greater detail below.

Table 3.13 Summary of Reaction Options for Geochemical Reactions in RATEQ

Species Type					
Solution	**Surface**	**Solid Phase**	**Exchange**	**Option[1]**	**Description**
x	x	x	x	log_k	Log_{10} of the thermodynamic equilibrium constant
x	x	x	x	delta_h	Enthalpy of reactions
X	x	x	x	delta_h_units	Units of enthalpy of reaction
X				Gamma	Debye-Huckel activity coefficient parameters.
X	x	x	x	analytical	Coefficients of an analytical expression used in adjusting the temperature dependence of the log K.
X	x	x	x	no_check	Toggle to suppress checking the reaction for charge balance
X	x	x	x	is_ignored[2]	Toggle to ignore a reaction for a simulation
X	x	x	x	force_eq[2]	Toggle to force the reaction to be equilibrium controlled even if a rate law is given
		x		min_dens[2]	molar density of mineral phase (moles/L)
	x		x	K_stoic[2]	Sets an option so that the stoichiometric coefficient for surface species can be different in the mass balance equations and the mass action expressions
			x	convention[2]	Defines the convention used for compute ion exchange equilibria
X	x	x	x	rate_law[2]	Defines the rate law for each rate controlled reaction. This can be multiple lines long and must end with the phrase "End_rate_law"

[1] Each option can be specified by any mixture of upper and lower case letters. In addition, each option can be written with a leading hyphen (e.g. –log_K) [2] Indicates an option in RATEQ but not PHREEQC

Example:

```
rate_law
 simple
 forward 0.01 (OH-)^2 (Fe+2) (O2)
end_rate_law
```

3.3.4.1 Description of Rate Laws Implemented in RATEQ

There are two options for including rate laws for a given reaction in the reaction file. These two options are referred to as the simple and general methods, and both of these approaches are described below. These different approaches are specified by including the name simple or general on the line immediately following the rate_law identifier.

Time units To guard against errors the could result from inconsistent units, the variable units t_units can be specified in the rate law. This is a case insensitive variable that is compared with the units given in the BTN file and if the units do not match, the simulation is stopped

The simple rate law. The format of the simple rate law is described in Section 2.6 (equation 2-37). The simple rate law includes a line for the forward reaction rate, the backward reaction rate, and an option to compute the backward rate constant from the log_K.

Forward: The first line of the simple rate law specifies the forward reaction rate. The line contains the forward rate constant followed by a list of species that are included in the forward rate term. No units are specified with the rate law, and it is assumed that the units are consistent with the time units used in the reactive transport model.

Example:

```
forward 2.2 UO2+2 CO3-2
```

Backward: The second line, which is optional, specifies the backward rate constant followed by a list of species that are included in the backward rate term.

Example:

```
backward 1.3 UO2CO3
```

Adjust_kb: The third line, which is also optional, contains the phrase 'adjust_kb', which indicates that the backward rate constant read on the second line will be replaced by a rate constant calculated from the forward rate constant and the equilibrium constant ($k_b=k_f/K$).

Examples:

```
Adjust_kb
adjust_kb
```

The simple rate law does not allow for species raised to non-integer powers, but these can be considered by using the general rate law. If a species concentration occurs in the rate law raised to an integer power, that species must be entered multiple times in the forward or backward reactions.

Additional Examples. The following rate law describes the irreversible oxidation of acetate by oxygen:

```
rate_law
    t_units seconds
    simple
    forward 1.0e-01 Ac- O2
end_rate_law
```

The rate law below describes the reversible rate of an adsorption reaction, where the backward rate constant is calculated from the equilibrium constant and the specified forward rate constant.

```
rate_law
    simple
    forward 1.0e-01 >SOH  UO2+2
    backward 2 >SOUO2+2 H+
    adjust_kb
end_rate_law
```

Finally, the following example specifies the irreversible oxidation of Fe^{+2} by O_2:

Example

```
rate_law
    simple
    forward 1.0e-01 Fe+2 O2 OH- OH-
end_rate_law
```

The general rate law. The general rate law includes the ability to simulate rate- controlled reactions that are governed by both equation 2-39 and 2-40. These rate laws are rather general rate laws that include Monod kinetics, mass action kinetics and other nonlinear processes. The general rate law is selected by including a line containing the word, general, on the line after rate law. After this specifier, the following lines can be included in specifying a general rate law.

k_forward K_FORW: This is the forward rate constant for the reaction. No units are specified with the rate law and it is assumed that the units

are consistent with the time units used in the reactive transport model.

Example:
K_forward 1.3e-2

k_backward K_BACK: This is the backward rate constant for the reaction. No units are specified with the rate law and it is assumed that the units are consistent with the time units used in the reactive transport model.

Example:
K_backward 1.3e-2

forward_stoic SPECIES COEFF: This option specifies the species to be included in a forward rate law and a coefficient for that species. The coefficient is a positive real value that is used as an exponent in the forward rate law. Forward_stoic may be repeated as many times as is necessary, and multiple species and coefficients may be specified on the same line.

Example:
Forward_stoic H+ 0.5

backward_stoic SPECIES COEFF: This option specifies the species to be included in a backward rate law and a coefficient for that species. The coefficient is a positive real value that is used as an exponent in the backward rate law. Backward_stoic may be repeated as many times as is necessary, and multiple species and coefficients may be specified on the same line

Example:
backward_stoic UO2OH 0.5

vmax: vmax: This is maximum rate of substrate utilization used in a Monod Rate law. No units are specified with the rate law and it is assumed that the units are consistent with the time units used in the reactive transport model.

Example:
vmax 1.3e-2

Mass_action_kinetics P: This option adds the terms (1-Q/K) to the rate law where K is the thermodynamic equilibrium constant, and Q is the ion activity quotient. The Q value is computed using activities, except as noted below, so that the term (1-Q/K) equals zero at equilibrium. If the variable P is included, then the rate thermodynamic driving term is raised to the P power, e.g., $(1-Q/K)^P$

Example:
Mass_action_kinetics 2.0

Monod Km SPECIES: This option specifies that a monod term of the form $\frac{C}{Km + C}$ is included in the forward rate term. Km is the half velocity coefficient of the Monod equation, and C is the concentration of the indicated species.

Example:
Monod Ac- 1.0e-03

Inhibition: This option specifies that a Monod term of the form $\frac{K_i + C}{K_i}$ is included in the forward rate term. K_i is the inhibition constant half velocity coefficient of the Monod equation, and C is the concentration of the indicated species.

Example:
Inhibition NO3- 1.0E-05

Gibbs: Specifying this option limits irreversible reactions to proceed only when the Gibbs free energy of reaction is less than a threshold value. If the Gibbs free energy of reaction is greater than the threshold, then the reaction rate is set to zero.

Example:
Gibbs

Threshold ΔG_{RXN}: This specifies ΔG_{RXN}, the threshold free energy of a reaction in units of kJ/mol. This option is included because, in some instances, biologically mediated reactions are believed to require a minimum free energy of reaction in order to sustain metabolism. Units

can be written after the threshold value, but they are not read.

Example:
Threshold –2.0

activation_energy EA: This option species the activation energy (EA) of a rate- controlled reaction. The units must be in kJ/mol. The activation energy is used in the Arrhenius equation to adjust the reaction rate for temperatures other than 25°C. Units can be written after the value of EA, but they are not read.

Example:
activation_energy 45 kJ/mol

rate_variable OPTION: By default, the rate law is computed using concentrations, except for the thermodynamic driving term (e.g., (1-Q/K)). If OPTION is 'conc', then concentrations are used in all calculations, and if OPTION is 'activity' then activities are used in all calculations.

Example:
Rate_variable activity
rate_variable conc

Each of the options available for describing the geochemical reactions is illustrated in a simulation presented in the following sections. Table 3.14 presents a list that identifies which simulation illustrates a particular geochemical reaction option.

3.3.5 Geochemical Solver File

The input file for the geochemical conditions consists of 6 data blocks, which are labeled SETUP, REACTIONS, CALCULATION, OUTPUT, INITIAL CONDITIONS, and TIMED EVENTS. The SETUP data block is optional. The INITIAL CONDITIONS and TIMED EVENTS blocks are only used when one-dimensional simulations are conducted without using MODFLOW-2000 to compute the flow field. Finally, the CALCULATION and OUTPUT blocks are not required if only a batch speciation calculation is conducted.

3.3.5.1 SETUP DATA BLOCK

Including the Setup data block in the geochemical reactions file is optional. All of the input in this data block are either not required, or have default values. The data that can be input into the setup block are summarized in Table 3.15

Record 1: SETUP is a keyword that indicates that this is the setup data block.

Example:
Setup

Record 2: TITLES is a keyword indicating that the following lines are titles that will be printed at the top of most output files.

Table 3.14 Summary of Reactions Options in Benchmark and Example Simulations

No	Option	Ex[1]
1	log_k	All
2	delta_h	6.1
3	delta_h_units	6.1
4	Gamma	All
6	no_check	4.3
7	is_ignored	
8	force_eq	6.3
10	min_dens	NS[2]
11	K_stoic	NS[2]
12	Convention	4.33
13	rate_law – simple	4.2
14	Rate_law – monod	4.2
15	Rate_law – general	5.2, 6.3
16	T_unit	6.3

[1] Numbers refer to sections in this report; [2] Not shown in an example, see database; [3] See database

Table 3.15 Summary of Input in the Setup Data Block

1	**SETUP**						
2	**TITLES**						
3		**Title lines**					
4	**ACTIVITY**						
5		**Activity Model**					
6		**Ionic_strength**					
7	**NUMERICS**						
8		**ITMAX, DT_STEPS, DT_FACTOR TOL_NONLIN**					
9	**END_SETUP**						

Example:

TITLES
Titles

Record 3: Title lines Each title line at most, 200 characters long. Titles are printed at the beginning of each output file. Up to 20 title lines can be input.

Example:

Simulation of U(VI) transport
using the Waite et al surface
complexation model

Record 4: ACTIVITY is a keyword indicating that the next line establishes the method for computing activity coefficients. The default method is the use the Davies equation.

Record 5: Activity method, A parameter, B parameter Three methods for computing activity coefficients are available are the Davies equation, the Debye-Huckel equation and the extended Debye-Huckel model, also known as the 'B-dot' model. The default is the extended Davies. The a and b values for each method can also be included.

Example:

Debye_Huckel 0.51 0.33
B_dot 3.5 0.0150

Record 6: FIXED_IONIC_STRENGTH, I indicates that the value entered as I will be used a constant ionic strength for computing activity coefficients regardless of what the simulated ionic strength is in any given iteration or location. If this line is omitted, the default behavior is to use the computed ionic strength in the simulations.

Examples:

Fixed_Ionic_Strgth .01
Fixed_I 0.02

Record 7: NUMERICS is keyword that indicates that the next input are parameters used in controlling the numerical solution of the geochemical calculations.

Example:

NUMERICS

Record 8: ITMAX, TOL_NONLIN, DT_STEPS, DT_FACTOR ITMAX is the maximum number of iterations that the nonlinear solver will attempt. The default is 200. TOL_NONLIN is the tolerance to be used in solving the nonlinear system of equations. The default value is 1.0E-09. DT_STEPS is the number of chemistry time steps that will be attempted if the solver does not solve a set of rate-controlled equations in one step. The default is 100. DT_FACTOR is the factor by which the time step will be reduced if the solver fails and attempts to restart itself.

Example:

20 1.0e-06 500

3.3.5.2 REACTIONS DATA BLOCK

The purpose of the reactions data block is to define the solutions that are used to initialize the reactive transport model and to set the boundary conditions. This data block is also used to identify certain reaction-specific calculation methods. For example, the electrical double layer parameters are included in this data block. Table 3.16 summarizes the data that can be included in the REACTIONS data block.

Record 1: REACTIONS is a keyword that indicates the beginning of the REACTIONS data block

Example:

REACTIONS

Table 3.16. Summary of Input in the Reactions Data Block

1	**REACTIONS**						
2	**File**						
3		**Database**					
4	**Ignore**						
5		**Ignored Species**					
6	**EDL**						
7		**EDL_Method**					
8		**EDL Surface Master Species**					
9	**Diffuse**						
10		**Diffuse Species**					
11	**Reaction_set No.**						
12		**Reaction Input**					
13	**Solution No.**						
14		**Species**	**Type**	**Conc**	**Guess**	**M2/g**	**G /l**
15	**End Solution No.**						
16	**Reaction_set No.**						
17		**Reaction input**					
18	**Solution No.**						
19		**Species**	**Type**	**Conc**	**Guess**	**M2/g**	**G /l**
20	**End Solution No.**						
21	**END_REACTIONS**						

Record 2: File This specifies the reaction database file that will be used for batch and 1-D calculations when MODFLOW-2000 is not used to compute the flow field.

Example:

File

Record 3: Filename. This specifies the name of the reaction database file that will be used for batch and 1-D calculations.

Example:
C:\RATEQ\DATA\RXNS.DAT

Record 4: Ignore This record indicates that the next line or lines contain a list of species that will not be included in the simulation.

Example:
Ignore

Record 5: Ignored_species is list of species that will be excluded from the simulations.

Example:
Aragonite Chalcedony e-

Record 6: EDL This keyword is used to identify the following lines as EDL properties.

Example:
EDL

Record 7: EDL_METHOD Defines the method for computing electrical double layer properties. Currently, only the diffuse layer model is supported.

Example:
diffuse

Record 8: EDL surface master species This is a list of the names of surfaces as defined in the SURFAE_MASTER_SPECIES block that are included in the electrical double layer calculations.

Example:
>SOH

Record 9: Diffuse This keyword is used to identify the selected species will be removed from solution and accumulated in the diffuse layer to maintain electroneutrality The default is to not remove any species from solution.

Example:
DIFFUSE

Record 10: Diffuse species This is a list of the names of species that are included in the diffuse layer calculations. If 'All' is entered, then every charged species in solution will be included in the calculations.

Examples:
Ca+2 Mg+2 Na+
All

Record 11: Reaction set No This keyword is used to identify that the following lines identify new master species, new reactions, or new reaction properties. The numerical value No is used to identify the reaction set. Multiple reaction sets (with related solutions) can be defined possibly containing a unique phase assemblage.

Example:
Reaction_set 1

Record 12: Reaction Input New reactions can be specified using the format described in section 3.3.4.

Example:

```
SOLUTIONS_SPECIES
Ac- + H+ = CH4 + CO2
Rate_law
    General
    Vmax 12.0
     Monod Ac- 0.01
End_rate_law
```

Record 13: Solution N This keyword is to indicate that the following lines identify the Nth solution. All solutions must be number so that they can be referenced in defining the initial and boundary conditions and source concentrations.

Example:
Solution 1

Record 12: Species, Type, Conc, Guess , m^2/g, g/l This input is defined as follows.

Species is the name of a master species, a surface master species, an exchange master species, a kinetically controlled species, a mineral phase, a gas phase or it may be 'alkalinity'. Type can be fixed, aqueous, total, pH if the species is H+, or gas if the species is a gas. If the species is fixed, the concentration of the given species will equal the specified concentration. If type is aqueous, then the concentration refers to total dissolved concentration and if the species type is total the concentration refers to the total aqueous, surface and exchanged concentration. The concentration is the pH value if the type of species is pH, the alkalinity if the species is 'alkalinity', the log of the partial pressure if the species is a gas, or the concentration in moles/L. Guess is an optional value that is used as an initial guess of the species concentration. M^2/g is the specific surface area and only applies to surface site. Similarly, g/l is the concentration of the adsorbing phase. Both m^2/g and g/l must have units after the value.

```
Example:
Solution 1
H2O        total     55.
UO2+2      total      1.0e-06
H+         pH         6.0
CO2(g)     gas       -2.0
Na+        aqueous   1.0e-2
>FeOHs     total      1.0e-5
>FeOHw     total   1.0e-3 600 m2/g 2 g/L
end_solution 1
```

Records 16-17: Reaction_set and input
These records are optional and if included are identical to Records 11 and 12. This is useful for defining a new set of reactions that will be used to compute the initial solutions that are used for initial and boundary conditions and source waters. Alternatively, new reactions can be defined that apply to the transport calculations. For example, it is possible to convert a reaction from being equilibrium-controlled for the purposes of computing the initial solution composition to a rate-controlled reaction for the purposes of transport simulations.

Records 18-20: Solution Input These records are optional and if included are identical to Records 16-17. Each new solution should have a unique solution number.

Record 21: END_REACTIONS is a keyword that indicates the end of the REACTIONS data block.

Example:

```
END_REACTIONS
```

3.3.5.3 Calculations Data Block

The calculations data block determines the type of calculation that is being conducted and certain species controls for each calculation type. There are four types of calculations that can be conducted, including batch kinetic simulations, batch range simulations (where the concentration of one variable is varied in a batch calculation), 1-D transport calculations, and MT3DMS calculations. The input for each of these calculation options varies as shown in Table 3.17.

Record 1: CALCULATION is a keyword that indicates the beginning of the CALCULATION data block.

Example:

```
CALCULATION
```

Record 2: Calculation_type defines the type of calculation to be conducted. Calculation type can be either kinetic, range, 1-D or MT3DMS.

Example:

```
kinetic
```

Records for kinetic calculations
Only one record is read for kinetic calculations

Record 3: tmax TIME This record is used to specify the maximum time of the batch calculation.

Example:

TMAX 10.

Records for range calculations
Only one record is read for range calculations

Record 3: Species Cmin:Cstep:Cmax Type
Species is the species whose concentration will be varied in the range calculations, **Cmin** is the minimum concentration of the species, **Cstep** is the change in concentration from one calculation to the next, **Cmax** is the maximum concentration of the species. **Type** is optional input that indicates that the input concentrations are logs of concentrations and Cstep is the log units.

Examples:
pH 5:.2:8
Fe+2 1E-04:1E-05:1E-06
Hg+2 –9:.1:-6 log

Records for MT3DMS or 1-D calculations
Only two records are read for MT3DMS calculations, and both are optional.

Record 3: Ignore This record indicates that the next line or lines contain a list of species that will not be included in the simulation

Example:
Ignore

Record 4: Ignored_species is list of species that will be excluded from the simulations.

Example:
Aragonite Dolomite e-

Record 5: Reaction set, No, Although multiple reaction sets can be used to define the solutions, only one reaction set can be used in the transport simulation. This record selects the desired reaction set. The default is to use reaction set 1.

Example:
Reaction_set 2

Table 3.17. Summary of Input in the Calculations Data Block

1	**CALCULATION**	
2	**Calculation Type**	
RECORDS FOR KINETIC CALCULATIONS		
3	**tmax**	
RECORDS FOR RANGE CALCULATIONS		
3	**Cmin:Cstep:Cmax type**	
RECORDS FOR MT3DMS or 1-D CALCULATIONS		
3	**Ignore**	
4	**Ignored species**	
5	**Reaction Set, No.**	
RECORDS ONLY FOR 1-D CALCULATIONS		
6	**Domain**	
7	**Value input_type**	
8	**1D Transport**	
9	**Value input_type**	
10	**Discretization**	
11	**Value input_type**	
12	**END_ CALCULATION**	

Records only for 1-D transport calculations
Several records are required to conduct 1-D transport simulations. These records are required to create the LMT file used in the simulations. All of these records are optional. These records are in addition to the optional input in Records 3-5.

Record 6: Domain This entry is used to indicate that the default values for the length of the 1- dimensional column and the total time for

the simulation will be changed. The default length is 1 and the default time is 2.

Example:
Domain

Record 7: Value, Input Type This record can be used to override the default values for the domain. The input type can be either 'xmax' or 'tmax' to override the total length of the column or the length of the simulation. Either one or both default values can be overridden

Example:
10 tmax

Record 8: Discretization This entry is used to indicate that the default values for the number of grid cells in the one-dimensional column and the length of the time step. The default number of grid cells is 10 and the default time is computed from a Courant number ($V*\Delta t/\Delta x$) equal to 0.5.

Example:
discretization

Record 9: Value, Input Type This record can be used to override the default values for the discretization. To change the grid spacing the input type can be either ndx for the number of grid cells, dx for the length of grid cells, or Pegrid to compute Δx from the grid Peclet number ($\Delta x^2/(D\Delta t)$. To change the time step the input type can be either dt for the length of steps, or Courant to compute Δt from the Courant number ($V*\Delta t/\Delta x$). When either Δx or the grid Peclet number is specified, the Δx may be decreased slightly to give a uniform grid throughout the column.

Examples:
ndx
0.8 Pegrid
0.02 dt
0.9 courant

Record 10: 1-D Transport This entry is used to indicate that the default values for the velocity, porosity, dispersivity, molecular diffusion coefficient, immobile porosity and mass transfer coefficient will be changed. The default velocity is 1, the default dispersivity is 0.01, the default porosity is 1, the default molecular diffusion coefficient, immobile porosity and mass transfer coefficient are all 0.

Example:
1-D Transport

Record 11: Value, Input Type This record can be used to override the default values for the 1-D transport properties. The input type must be either the initial velocity, dispersivity, diffusion, porosity, im_porosity or mass_transfer. Record 11 may be repeated as necessary. Units may be supplied and if they are present, they will be compared with the units given in the BTN file to check for consistency.

Examples:
velocity
0.3 porosity
0.02 im_porosity
0.2 mass_trans

Record 12: END_CALCULATION is a keyword that indicates the end of the CALCULATION data block.

Example:
END_CALCULATION

3.3.5.4 Output Data Block

The output DATABLOCK controls how the geochemical concentrations will be written to selected output files and the options for this data block are summarized in Table 3.18.

Record 1: OUTPUT is a keyword that indicates that this is the output data block.

Example:
OUTPUT

Record 2: Output Type indicates the type of output to be printed. The type can be 'breakthrough' for concentration histories, 'profile' or 'snapshot' for concentration distributions at all nodes at a selected time, 'kinetic' for batch kinetic simulations, or 'range' for range calculations.

Examples:

Breakthrough
snapshot

Record 3: file indicates that the next name will specify the file name

Example:

FILE
file

Record 4: filename indicates the name of the output file including the extension. Specifying the filename is optional. If the filename is not specified, then the output file will be created from the name of the geochemical reactions filename. The root of that filename (the characters up to the first dot) will be used and an extension of .brk, will be added to the name of breakthrough files, .prf will will be added to the name of profile files, .kin will be added to the name of kinetic output files, and .rng will be added to the name of range output files. In addition, if breakthrough curves are printed at more than one location, then a number will be appended to the filename root.

Example:

background.brk

Record 5: format indicates that the next record will specify the output format

Example:

Format

Table 3.18 Summary of Input in the Output Data Block

1	**OUTPUT**	
2	**Output Type**	
3		**file**
4		**File name**
5		**format**
6		**Format description**
7		**PV**
8		**species**
9		**Species list**
10		**locations**
11		**Location list**
12		**time**
13		**Time values**
14	**END_OUTPOUT**	

Record 5: format description indicates the format of the output. The file format can be either MT3 for a binary file in MT3DMS output format, or a legal fortran format string enclosed in parentheses.

Examples:

MT3
(1x,i5,3(2x,e12.4))

Record 7: PV indicates that the pore volumes will be included in the output file. This is only useful for 1-dimensional transport simulations

Example:

PV

Record 8: species indicates that the next record will specify a list of species.

Example:

species

Record 9: Species list is a list of species that will be written to the output file. The species can contain the names of individual species, pH or alkalinity. In addition, if a master species is immediately followed by (aqu) then the total concentration of that master species in solution will be printed. Similarly, if the master species is followed by (ads) the total adsorbed concentration is printed, and if the total concentration is followed by (s) the total solid phase concentration is printed.

Examples:

Ca+2(aqu) pH
UO2+2(aqu) UO2+2(ads)
Alkalinity, U(+4)(s)

Record 10: locations indicates that the next lines will specify the output locations. This option only applies to breakthrough curves

Example:

Locations

Record 11: location list indicates locations in the model domain where the breakthrough curves will be recorded and then printed. The locations are specified in physical dimensions as x,y,z values, and the concentration at the cell containing that location will be printed.

Example:

10 2
22 6.7

Record 12: time indicates that the next record will specify the when the output will be printed. This option only applies to breakthrough curves and concentration snapshots. In addition, specifying the time is optional. The default is to print 10 evenly spaced concentration snapshots and approximately 100 evenly distributed breakthrough values.

Example:

Time

Record 13: time list is a list of times when the output will be printed. The list of values must be in ascending order.

Example:

0.1 1 2 5 10 20

3.3.5.5 INITIAL CONDITIONS DATA BLOCK

The initial conditions block identifies the initial conditions for simple 1-D transport where flow velocities are specified in the Geochemical Solver filer rather than read from the LMT file created by MODFLOW-2000. Table 3.19 summarizes the input that can be included in the initial conditions data block.

Record 1: INITIAL_CONDITIONS is a keyword that indicates that this is the initial conditions data block.

Example:

INITIAL_CONDITIONS

Table 3.19. Summary of Input in the Initial Conditions Data Block

1	**INITIAL_CONDITIONS**	
	TYPE XMIN XMAX SOLUTION	
8	**END_INITIAL_CONDITIONS**	

Record 2: TYPE refers to the type of initial condition and is used to distinguish simulations that have immobile zones from those that do not have immobile zones. If type is 1-D, then the initial conditions defined on this line applies to all nodes. If TYPE is IMMOB, the initial conditions apply to only the immobile zones, and if TYPE is MOB, then the initial conditions apply to only the mobile zone. **XMIN** is the minimum distance along the column where the initial conditions will be defined**, XMAX,** is the maximum distance along the column where the initial conditions will be defined, and **SOLUTION** is the solution number used to identify the initial conditions. The following example defines a column that has solution 2 throughout the column, except in the immobile zone between distances of 2 and 3. If XMAX

exceeds the length of the column, the XMAX is maximum length of the column is used.

Example:

```
1D     0  10   2
IMMOB  2   3   1
```

Record 3: END_INITIAL_CONDITIONS is a keyword indicating the end of the initial conditions data block.

Example:

END_INITIAL_CONDITIONS

3.3.5.6 TIMED EVENTS DATA BLOCK

The timed events data block contains input that changes the boundary conditions or flow velocity at selected times. Table 3.17 contains a summary of the information that can be included in this data block. This data block is only used for simple 1D calculations. The parameter values are set and held constant until the simulation time reaches the value in Record 7.

Record 1: TIMED_EVENTS is a keyword that indicates that this is the timed events data block.

Example:

TIMED_EVENTS

Record 2: BOUNDARY_CONDITIONS is a keyword that the next input will change the boundary conditions.

Example:

Boundary conditions

Record 3: This option specifies the location of the boundary and the solution number for the boundary. The location is either left for x=0 or right for x=L

Example

Left 3

Record 4: Velocity is a keyword indicating the next input will change the velocity. Changing the velocity is optional and is useful for simulating flow interruption experiments.

Table 3.20. Summary of Input in the Timed Event Data Block

1	**TIMED EVENTS**	
2	**BOUNDARY_CONDITIONS**	
3		**Location, Solution 2**
4	**VELOCITY**	
5		**Flow_velocity**
6	**DURATION**	
7		**TIME**
8	**END_TIMED_EVENTS**	

Example:

Velocity

Record 5: This specifies the velocity in the column.

Example:

1.0E-09

Record 6: Duration is a keyword indicating the next input will specify the duration of the boundary conditions or flow velocity.

Example:

Duration

Record 7: This specifies the time the velocity or boundary condition are held constant.

Example:

2.9

Record 8: END_TIMED_EVENTS is a keyword indicating the end of the timed events data block.

Example:

END_TIMED_EVENTS

4 BENCHMARK SIMULATIONS

4.1 INTRODUCTION

Benchmark simulations were performed to test if the RATEQ code produces results that agree with other geochemical and reactive transport simulators that have been independently developed. It should be noted that these benchmark studies do not 'verify' a particular code for a particular application. These benchmark simulations also illustrate many of the features of RATEQ.

4.2 BATCH CALCULATIONS

In using RATEQ for a reactive transport simulation, it is first necessary to complete a speciation calculation so that the initial conditions in the transport domain can be defined. These speciation calculations are identical to the calculations conducted by many speciation codes, including PHREEQC, HYDRAQL (Papelis et al., 1988); MINTEQA2; and FITEQL. Two simulations are presented to demonstrate that batch calculations performed with RATEQ agree with other geochemical models. These simulations consider: (1) the speciation of U(VI) in Naturita groundwater, and (2) the sorption envelope for As(III) sorbed by ferrihydrite. A third simulation compares batch kinetic simulations conducted with RATEQ with results obtained with a commercially available numerical package.

4.2.1 Naturita Groundwater Speciation

In September 1999, well NAT26 at the Naturita Mill Tailings site (Davis and Curtis, 2003) was sampled, and the measured composition is listed in Table 4.1. The corresponding RATEQ input file is listed in Table 4.2. Table 4.2 lists the RATEQ input of each of the species in Table 4.1. The units for the dissolved species are moles/L (M) with the exception of pH. The RATEQ input file also contains an entry for water that must be explicitly stated in the input file. An initial concentration of calcite is given as 1M. Both water and calcite are listed as fixed species, which indicates that each species will have the specified concentration *after* the speciation is completed. Calcium is not included in the input file, but the calcium concentration was computed from calcite solubility. Similarly, the OH- concentration was computed from the equilibrium with water.

The RATEQ input file also contains entries for the surface sites >WOH, >SOH, and >ZOH. These sites can react with dissolved U(VI) to form adsorbed U(VI) complexes. However, because the concentration of UO_2^{+2} is specified as an 'aqueous' variable, the adsorption reactions do not reduce the total dissolved UO_2^{+2} concentration. Instead, the calculation computes the surface U(VI) species that are in equilibrium with the measured groundwater concentration. The adsorption reactions used in these simulations were taken from Davis et al. (2004a) and were included in the thermodynamic datafile.

Speciation calculations were also conducted with the geochemical equilibrium model FITEQL (Herbelin and Westall, 1999). The results obtained using the two models are shown in Figure 4.1, which illustrates the species concentration computed with each of the two models. The figure includes all of the U(VI) species as well as the concentrations of major ions. The results show an excellent agreement

Table 4.1 Composition of Groundwater at well NAT26 at the Naturita UMTRA Site

Species	Concentration (M)
UO_2^{+2}	1.00×10^{-5}
pH	7.15
Alkalinity	1.13×10^{-2}
K^+	1.49×10^{-4}
Ca^{+2}	4.64×10^{-3}
Mg^{+2}	3.18×10^{-3}
Na^+	4.44×10^{-2}
SO_4^{-2}	1.58×10^{-2}
Cl^-	1.64×10^{-2}

Table 4.2 RATEQ Input File for NAT26 Groundwater Speciation Calculation

```
Setup

  Titles
      Speciation Calculation for Naturita well NAT26
      Sampled on:  21-Sep-1999
      Assume equilibrium with calcite

End_Setup

Reaction Set 1              ! define geochemical reactions and solution compositions
   file
        ..\reaction_file\PHREEQC_nat.dat

   ignore          ! define species not considered in the solutions
       Jarosite-K S-2 HS- CH4 CH4(g)

   solution 1
      ! SPECIES    TYPE      CONCENTRATION  !Molar concentrations
      H2O          fixed     55.
      Calcite      fixed     1.
      UO2+2        aqueous    1.0042e-005
      H+           pH         7.15
      Alkalinity   aqueous    1.1260e-002
      K+           aqueous    1.4937e-004
      Mg+2         aqueous    3.1845e-003
      Na+          aqueous    4.4367e-002
      SO4-2        aqueous    1.5833e-002
      Cl-          aqueous    1.6360e-002
      >WOH         total      1.711E-05
      >SOH         total      2.079e-07
      >ZOH         total      1.732e-08
   end_solution 1

   end of solutions
End of reactions
```

between the two models for aqueous concentrations that vary over 20 orders of magnitude.

4.2.2 Simulation of Rate-Controlled Reactions in Batch

The purpose of this benchmark calculation was to demonstrate the ability of RATEQ to solve rate-controlled reactions in a batch system characterized by a stiff set of equations. Stiff differential equations are characterized by processes that occur on different time scales, which results in computed profiles that change abruptly with time. For this example, a complex organic was assumed to be transformed to a simple organic acid, acetate (Ac^-). Then the acetate reacts with two terminal electron acceptors in the system, namely O_2 and SO_4^{-2}. Acetate also formed CH_4 and CO_2 in the simulations. The initial degradation of the complex organic was described by:

Complex Organic = $Ac^- + H^+ + CO_2$

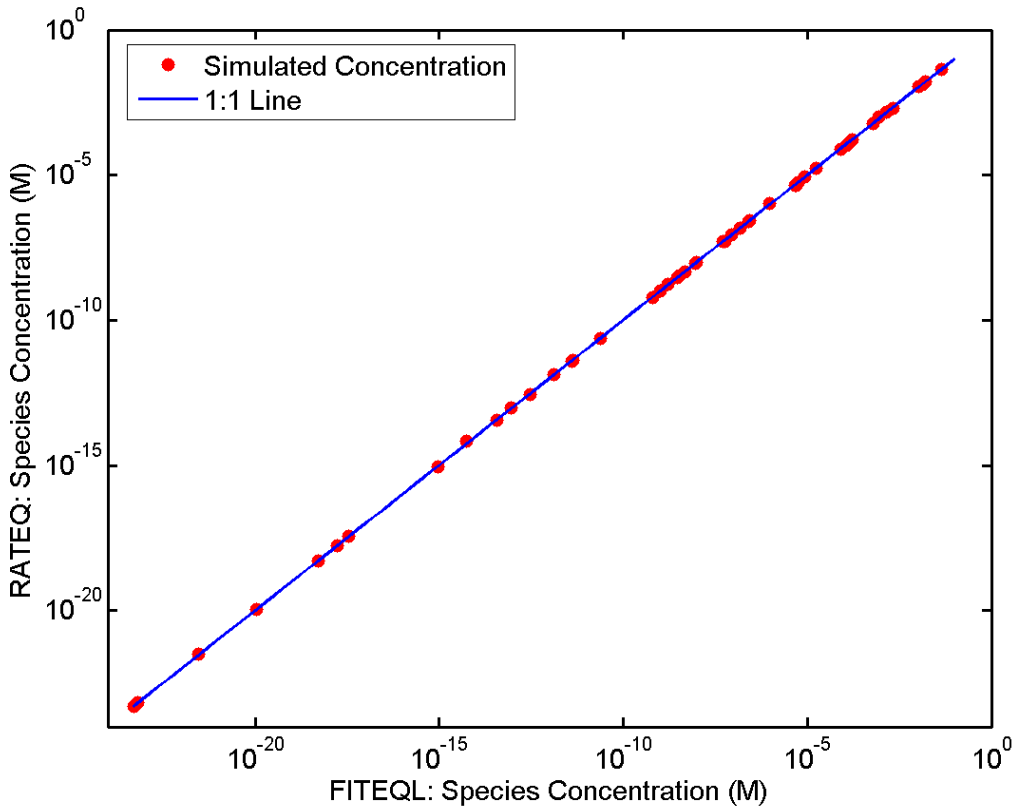

Figure 4.1. Comparison of simulated concentrations computed using RATEQ and FITEQL.

which was simulated using a simple first order decay rate law:

$$r_1 = -k_1 \text{ComplexOrganic}$$

The oxidation of acetate by O_2 is described by:

$$Ac^- + O_2 + H^+ = 2CO_2 + H_2O$$

The rate for this reaction was assumed to be governed by Monod kinetics:

$$r_2 = -v_{MAX_2}\left(\frac{C_{Ac^-}}{K_2 + C_{Ac^-}}\right)C_{O_2}$$

where where v_{MAX2} is the maximum rate of substrate utilization, K_2 is the Monod half velocity constants, The intermediate Ac^- was also oxidized by SO_4^{-2} in the simulations by the following reaction:

$$Ac^- + 2H^+ + SO_4^{-2} = 2CO_2 + 2H_2O + HS^-$$

This rate was also modeled by the Monod model, but this time a dual Monod formulation was used, and it was assumed that SO_4^{-2} reduction was inhibited by the presence of O_2. This gives a rate law:

$$r_3 = -v_{MAX3}\left(\frac{C_{Ac^-}}{K_{s3} + C_{Ac^-}}\right)\left(\frac{C_{SO_4}}{K_{a3} + C_{SO4}}\right)\left(\frac{K_{I3}}{K_{I3} + C_{O_2}}\right)$$

where v_{MAX3} is the maximum rate of substrate uitilization, K_{s3} and K_{a3} are Monod half velocity constants, K_{I3} is an inhibition constant, and the last term in brackets inhibits the reaction rate when $C_{O2} >> K_{I3}$. Finally, the cleavage of acetate,

$$Ac^- + H^+ = CH_4 + CO_2$$

was modeled using a Monod model that was inhibited by the presence of SO_4^{-2}.

$$r_4 = -v_{MAX4}\left(\frac{C_{Ac^-}}{K_{S4} + C_{Ac^-}}\right)\left(\frac{K_{I4}}{K_{I4} + C_{SO_4}}\right)$$

v_{MAX4} is the maximum rate of CH_4 formation, K_{S4} is the Monod half velocity constant for methanogenesis and K_{I4} causes the reaction to be inhibited by SO_4, The inhibition terms in the above rate laws are one of the reasons that the resulting set of equations becomes stiff. Table 4.3 contains a list of all of the parameters used in the simulation. These parameters have little physical or experimental basis but were selected to make the equations relatively stiff.

The RATEQ input file is listed in Table 4.4. This input file illustrates that the degradation reactions are listed in the RATEQ input file rather than in the thermodynamic datafile. This approach is often most convenient when conducting iterative modeling studies. The input file also illustrates how the Monod rate laws are described in the input file. Note that the species H_2S was ignored in the simulation so that

Table 4.3 Summary of Parameter Values in the Batch Kinetic Simulation

Parameter	Value
k_1	1.0×10^4 (d^{-1})
V_{max1}	1.0×10^5 (d^{-1})
V_{max2}	1.0×10^4 (d^{-1})
V_{max3}	1.0×10^3 (d^{-1})
K_{S1}	1.0×10^{-2} (M)
K_{S2}	2.0×10^{-3} (M)
K_{S3}	2.0×10^{-3} (M)
K_{A2}	2.0×10^{-3} (M)
K_{I2}	1.0×10^{-10} (M)
K_{I3}	1.0×10^{-8} (M)

comparisons could be easily made as described below. Finally, the CALCULATION block defines the time at which the output will be stored in the output file.

Comparisons were made with results obtained using MATLAB® to integrate the set of rate equations. The solution obtained using MATLAB® considered only the reactants included in the four degradation reactions listed above. Thus, the approach cannot easily consider other species, such as H_2S or H_2O. Nevertheless, MATLAB® includes several very stable numerical routines that can be used for solving stiff sets of differential equations, and therefore provides a good tool for conducting comparisons between two numerical approaches.

The simulated concentration histories obtained using RATEQ and MATLAB® are compared in Figure 4.2. The simulations show that O_2 is gradually consumed and once the O_2 is nearly completely consumed, then SO_4^{-2} is very rapidly consumed, followed immediately by the conversion of Ac^- to CH_4 and CO_2. For each of the six species considered, there is an excellent agreement between the two very different numerical approaches.

4.2.3 Adsorption of Cd^{+2} by Ferrihydrite

The purpose of this benchmark simulation is to illustrate how to set up electrical double layer calculations and to demonstrate that adsorption calculations performed with RATEQ using the diffuse double layer model agree with calculations obtained using a different numerical model. In addition, this simulation demonstrates how to conduct batch simulations where the concentration of one species is varied (in this case, pH) over a range of values, while keeping all other values constant.

The dominant reactions, which were included in the reaction file, consist of the adsorption of Cd^{+2} on ferrihydrite, and in one instance, complexation of Cd^{2+} by relatively high concentrations of Cl^- (Table 4.5).

Table 4.4 RATEQ Input File for Batch Kinetic Rate Law

```
Setup

  Titles
    Benchmark Simulation 2
    Demonstration of integration kinetics in RATEQ for a
    reaction set with a stiff set of equations

  Activity                  ! fixed to zero
    Fixed_I 0.

End_Setup

Reaction Set 1              ! define geochemical reactions and solution compositions
  file
    ..\reaction_file\PHREEQC_nat.dat

   ignore          ! define species not considered in the solutions
     e- H2S  CH4(g) O2(g) H2(g)  Hac

   Reaction    ! define new reactions not I the database

   SOLUTION_SPECIES

     Complex = Ac- + H+ + CO2
       log_K 1
       rate_law
         general
         kf 1.0e04
         linear Complex
       end_rate_law

     Ac- + O2 + H+ = 2CO2 + H2O
            log_K 1.0
       rate_law
         general
         vmax    1.0e+05
         monod   Ac- 1.0e-02
         linear  O2
       end_rate_law

      Ac- +  2 H+ +  SO4-2 =  2 CO2 +  2 H2O +  HS-
             log_K 6.0
             rate_law
```

Table 4.4 RATEQ Input File for Batch Kinetic Rate Law (continued)

```
            general
            vmax   1.0e04
            monod  Ac-    2.0e-03
            monod  SO4-2  2.0e-03
            inhib  O2     1.0e-10
      end_rate_law

     Ac- +  H+ =  CH4 +  CO2
           log_K 6.0
           rate_law
            general
            vmax   1.0e03
            monod  Ac-    1.0e-04
            inhib  SO4-2  1.0e-10
      end_rate_law

 end

  end

  solution 1
   ! SPECIES  TYPE   CONCENTRATION
   H2O        fixed     55.
   H+         pH        7.
   O2         fixed     2.0e-04
   Alkalinity  aqueous    1.0e-03
   Complex     fixed      8.0e-03
   Ac-        fixed     1.0e-10
   SO4-2      fixed     1.0e-03
   HS-        fixed     1.0e-50
   CH4        fixed     1.0e-50
  end_solution 1

end solutions
end of reactions

Calculation
  kinetic

  tmax 10.01
End_Calculation
```

Table 4.4 RATEQ Input File for Batch Kinetic Rate Law (continued)

Output
kinetic
time
1e-10 1e-09 1e-08
1e-07 2e-07 4e-07 6e-07 8e-07
1e-06 2e-06 4e-06 6e-06 8e-06
1e-05 2e-05 4e-05 6e-05 8e-05
1e-04 2e-04 4e-04 6e-04 8e-04
1e-03 2e-03 4e-03 6e-03 8e-03
1e-02 2e-02 4e-02 6e-02 8e-02
1e-01 2e-01 4e-01 6e-01 8e-01
1e-00 2e-00 4e-00 6e-00 8e-00
Species
Complex Ac- O2 SO4-2 HS- CH4
End
End

Table 4.5 Summary of Predominant Reactions for Adsorption of Cd^{+2} by Ferrihydrite

Reaction	Log K
$Hfo_sOH + Cd^{+2} = Hfo_sOCd^{+} + H^{+}$	**0.47**
$Hfo_wOH + Cd^{+2} = Hfo_wOCd^{+} + H^{+}$	**-2.91**
$Cd^{+2} + Cl^{-} = CdCl^{+}$	**1.98**
$Cd^{+2} + 2\ Cl^{-} = CdCl_2$	**2.60**
$Cd^{+2} + 3\ Cl^{-} = CdCl_3^{-}$	**2.40**

The percent of Cd^{+2} that was adsorbed by ferrihydrite was computed over the pH range from 5.5 to 8.0 for a batch system that contained 0.1 g/L of ferrihydrite. The calculations were repeated three times for the cases of total Cd^{2+} concentration 10^{-7}M, 10^{-5}M, and 10^{-5}M with 10^{-2}M Cl^{-} as the electrolyte anion, instead of NO_3^{-}.

Table 4.6 lists the RATEQ input file for this simulation. First, this file illustrates the 'edl' option in the REACTION data block. The following lines indicate that the diffuse double layer model will be used and the names of the surface master species included in the EDL calculations. The diffuse double layer model requires a value of the surface area concentration (m^2/L), and this value is computed from the supplemental information provided on the line specifying the total Hfo_wOH concentration. Finally, the CALCULATION block uses the RANGE option to vary the pH in the calculations from 5.5 to 8.0. The output from the RANGE calculation gives a simple table containing pH and total adsorbed Cd.

Simulations conducted with RATEQ are compared with results obtained with FITEQL in Figure 4.3. The simulations show that the percent of Cd adsorbed decreases with increasing Cd concentration and in the presence of Cl. For all 3 scenarios, the two models give an excellent agreement for the simulated percent of Cd adsorbed by the ferrihydrite.

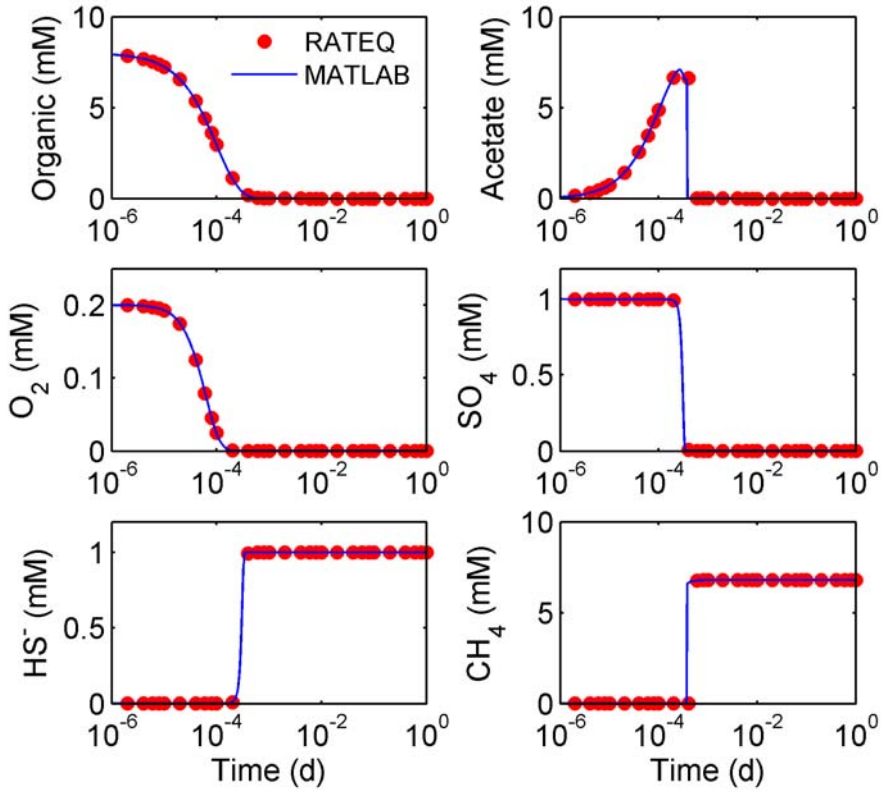

Figure 4.2. Comparison of simulated concentrations computed using RATEQ and MATLAB.

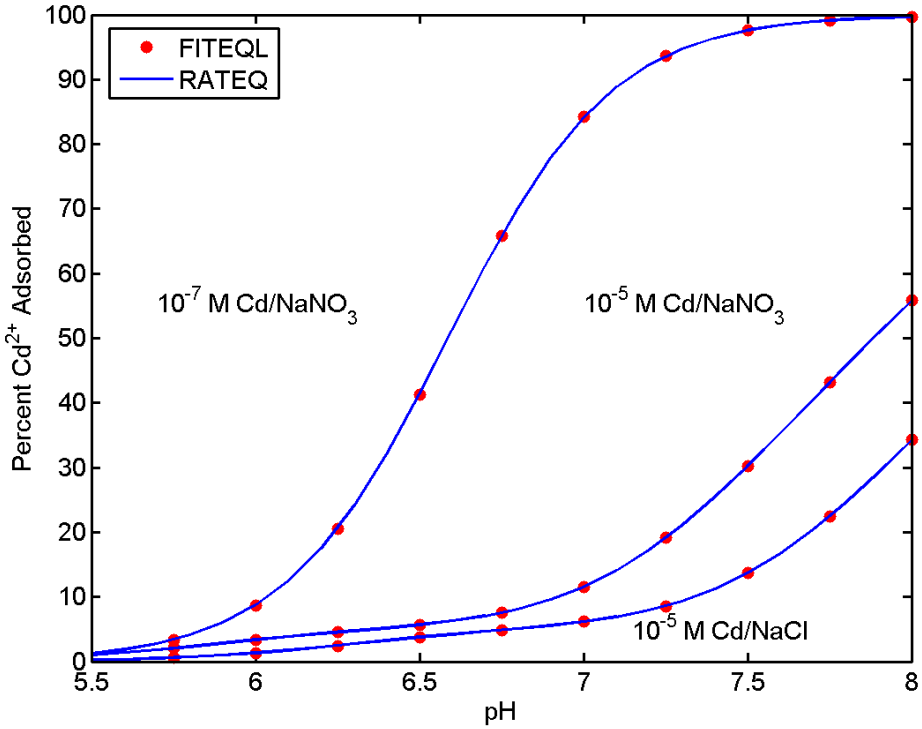

Figure 4.3. Comparison of simulated percent of Cd^{2+} adsorbed computed using RATEQ and FITEQL and the diffuse layer model.

Table 4.6 RATEQ Input File for Batch Adsorption of Cd^{+2} by Ferrihydrite Using the Diffuse Double Layer Model.

```
Setup

   Titles
     Benchmark Simulation 3
     Diffuse double layer model of Cd+2 adsorption on ferrihydrite

End_Setup

Reaction Set 1              ! define geochemical reactions and solution compositions
   file
       ..\reaction_file\PHREEQC_nat.dat

   edl                          ! use the diffuse layer model
     Diffuse
       Hfo_s Hfo_w

   end

   solution 1
     ! SPECIES    TYPE      CONCENTRATION
     H2O         fixed     55.
     H+          pH        5.5
     Cd+2        total     1.0e-07
     Na+         aqueous   1.0e-01
     NO3-        aqueous   1.0e-01
     Hfo_sOH     total     5.0e-06
     Hfo_wOH     total     2.0e-04   600. m^2/g   0.1 g/L
   end_solution 1

end solutions
end of reactions

Calculation
   Range

     H+ fix 5.5:0.1:8.01     ! Step pH from 5.5 to 8 in 0.1 pH units

End_Calculation
Output

   Range
     Species
       pH  Cd+2(ads)

   End

End
```

4.3 ONE DIMENSIONAL REACTIVE TRANSPORT SIMULATIONS

Benchmark calculations using one dimensional reactive transport scenarios were conducted to test the model in applications that couple transport and geochemical reactions. Two benchmark calculations were considered that included: (1) rate-limited sorption, aqueous speciation and biodegradation, and (2) equilibrium controlled transport with heterovalent ion exchange.

4.3.1 Rate-Limited Sorption, Aqueous Speciation and Biodegradation

This benchmark problem was originally proposed by Tebes-Stevens and Valocchi (1997). This simulation involves a reaction network that comprises: (1) complexation of Co^{+2} by various forms of NTA, (2) microbial oxidation of $HNTA^{-2}$ by oxygen, and (3) rate-limited sorption of Co^{+2} and $CoNTA^{-}$. This problem is also included as an example simulation in the PHREEQC documentation. The key reactions that dominate the reactive transport in this system are listed below.
For the conditions of the simulation, the dominant species of NTA in solution are $HNTA^{-2}$ and $CoNTA^{-}$. The dominant species of Co in solution are Co^{+2} and $CoNTA^{-}$. These species were related by the following equilibrium controlled reactions:

$NTA^{-3} + H^{+} = HNTA^{-2}$
$Co^{+2} + NTA^{-3} = CoNTA^{-}$

Several other reactions involving NTA and Co were considered, and these reactions are listed in the reaction file 'tebes-stevens.dat'. The adsorption of Co^{+2} was described by a simple linear isotherm. In addition, the sorption was assumed to be kinetically slow and the rate law was described by:

$Co^{+2} = >Co^{+2}$

$$r_1 = -k_1\left(C_{Co^{+2}} - \frac{C_{>Co^{+2}}}{K_{d1}}\right)$$

where k_1 is a first order sorption rate constant, and K_{d1} is the sorption K_d value for the Co^{+2} species. $CoNTA^{-}$ was assumed to sorb in similar fashion as Co^{+2}. The adsorption reaction was represented by:

$CoNTA^{-} = >CoNTA^{-}$

and the rate of sorption was represented by

$$r_2 = -k_2\left(C_{CoNTA^{-}} - \frac{C_{>CoNTA^{-}}}{K_{d2}}\right)$$

where k_2 is the first order sorption rate constant and K_{d2} is the sorption K_d value for the CoNTA- species.

$HNTA^{-2}$, was assumed to be biodegraded as described by:

$HNTA^{-2} + 1.62\ O_2 + 1.272\ H_2O + 2.42H^{+} =$
$0.576Biomass + 3.12CO_2 + 0.424NH_4^{+}$

where the term, Biomass, is used to represent active microbial cells in the simulation. The rate of the biodegradation reaction was represented by the multiple Monod approach:

$$r_3 = -v_{MAX}X_{BIO}\left(\frac{C_{HNTA^{-2}}}{K_s + C_{HNTA^{-2}}}\right)\left(\frac{C_{O_2}}{K_a + C_{O_2}}\right)$$

where v_{MAX}, K_s and K_a are Monod parameters and X_{BIO} is the biomass concentration. Finally, biomass produced by the $HNTA^{-2}$ oxidation was assumed to decay by a first order process:

$$r_4 = -bX_{BIO}$$

The specific values for the model parameters developed by Tebes-Stevens and Valocchi(1997) are listed in Table 4.7.
Often in modeling microbial systems, an equation for the growth and decay of the biomass is included in the set of equations, such as:

$$r_{BIO} = Yv_{MAX}X_{BIO}\left(\frac{C_{HNTA^{-2}}}{K_s + C_{HNTA^{-2}}}\right)\left(\frac{C_{O_2}}{K_a + C_{O_2}}\right) - bX_{BIO}$$

where Y is the cell yield (g cells/mol $HNTA^{-2}$). It is not necessary to include this equation in RATEQ because it is done implicitly by the stoichiometry of the $HNTA^{-2}$ oxidation reaction.

The benchmark simulation also specified a total distance of 10 m, a linear velocity of 1 m/hr, a solids concentration of 3750 g/L, a dispersivity of 0.5 m, and a total simulation time of 75 hr. Table 4-8 contains the RATEQ input file for the Tebes-Stevens benchmark problem.

Simulation results are presented in Figure 4-4, which shows the simulated pH value and concentrations of $CoNTA^-$, $HNTA^{-2}$, Co^{+2}, Biomass, and adsorbed Co^{+2}. The RATEQ simulations are compared with simulations obtained using the input file from the PHREEQC documentation (Parkhurst and Appelo, 1999) in Figure 4.4. For each species shown in the figure, there is an excellent agreement between the two model simulations.

Table 4.7 Model Parameters for the Tebes-Stevens Benchmark Simulation

Parameter	Value
Log K1	10.3
Log K2	11.7
k_1	1 hr^{-1}
k_2	1 hr^{-1}
K_{d1}	5.07×10^{-3} L/g
K_{d2}	5.33×10^{-4} L/g
V_{MAX}	0.1604 mol/hr
Ks	7.64×10^{-7} M
Ka	6.25×10^{-6} M
b	0.00208 hr^{-1}

Table 4.8 RATEQ Input File for the Tebes-Stevens Benchmark Simulation

```
Setup

  Activity
    Davies_Equation   .2        ! activity coeff method, b value
    Fixed_I  0.00               ! fixed ionic strength

End_Setup

Reaction Set 1              ! define geochemical reactions and solution compositions
  File
    tebes_stevens.dat           ! thermodynamic data file to use

  Ignore          ! define species not considered in the solutions
      CO2(g) e-

  !--DEFINE SOLUTION
  solution 1        ! Background concentration
    H2O           fixed      55
    HCO3-         fixed      1.513e-07
```

Table 4.8 RATEQ Input File for the Tebes-Stevens Benchmark Simulation (continued)

```
      NH4+          fixed       1.0e-20
      O2            fixed       3.125e-05
      NTA-3         aqueous     1.0e-56
      Co+2          aqueous     1.0e-56
      Na+           aqueous     1.0e-03
      Cl-           aqueous     1.E-03
      H+            pH          6.0
      Biomass       fixed       1.2035e-06
      Dead_Biomass  fixed       1.0e-20
      >WOH          total       1.0e-02
      >WOHCo+2      fixed       8.46e-26
      >WOHCoNTA-    fixed       8.46e-26
   end_solution 1

    solution 2        ! Background concentration
      H2O           fixed      55
      HCO3-         fixed      1.513e-07
      NH4+          fixed      1.0e-20
      O2            fixed      3.125e-05
      HNTA-2        fixed      0.4366e-06
      CoNTA-        fixed      4.793e-06
      Na+           aqueous    1.0e-02
      Cl-           aqueous    1.E-02
      H+            pH         6.0
      Biomass       fixed      1.0e-20
      Dead_Biomass  fixed      1.0e-20
   end_solution 2


   End of solutions

End of reactions

Calculation
   Transport                ! Options: Batch, Range, Transport, Mix

   ignore        ! define species not considered in the solutions
      CO2(g) e-

   Domain
      10.      xmax (meters)
      75.01    tmax (hours)

   Discretization
      80       ndx Pegrid Number
      .25      Courant Number
       8       PDE method
```

Table 4.8 RATEQ Input File for the Tebes-Stevens Benchmark Simulation (continued)

```
    1D-Flow
        1.0      velocity (m/year)
         0.05     dispersivity

End_Calculation

Output

    ! define the species for the breakthrough curves
      breakthru
        species
          Cl- pH  Co+2 CoNTA- HNTA-2 >WOH >WOHCo+2 >WOHCoNTA-
          Biomass Dead_Biomass O2 NH4+ H2 Na+


End output

Initial Conditions        ! Set the initial conditions on the grid

       1D  0.0   1.e19 1          ! dummy, xmin, xmax, soln_number

End Initial Conditions

Timed Events

    Boundary conditions
         left 0 10  2             ! location, ymin, ymax, soln_num

    Duration
         20

    Boundary conditions
                         left 0 10  1         ! location, ymin, ymax, soln_num

    Duration
       100000

End Timed Events
```

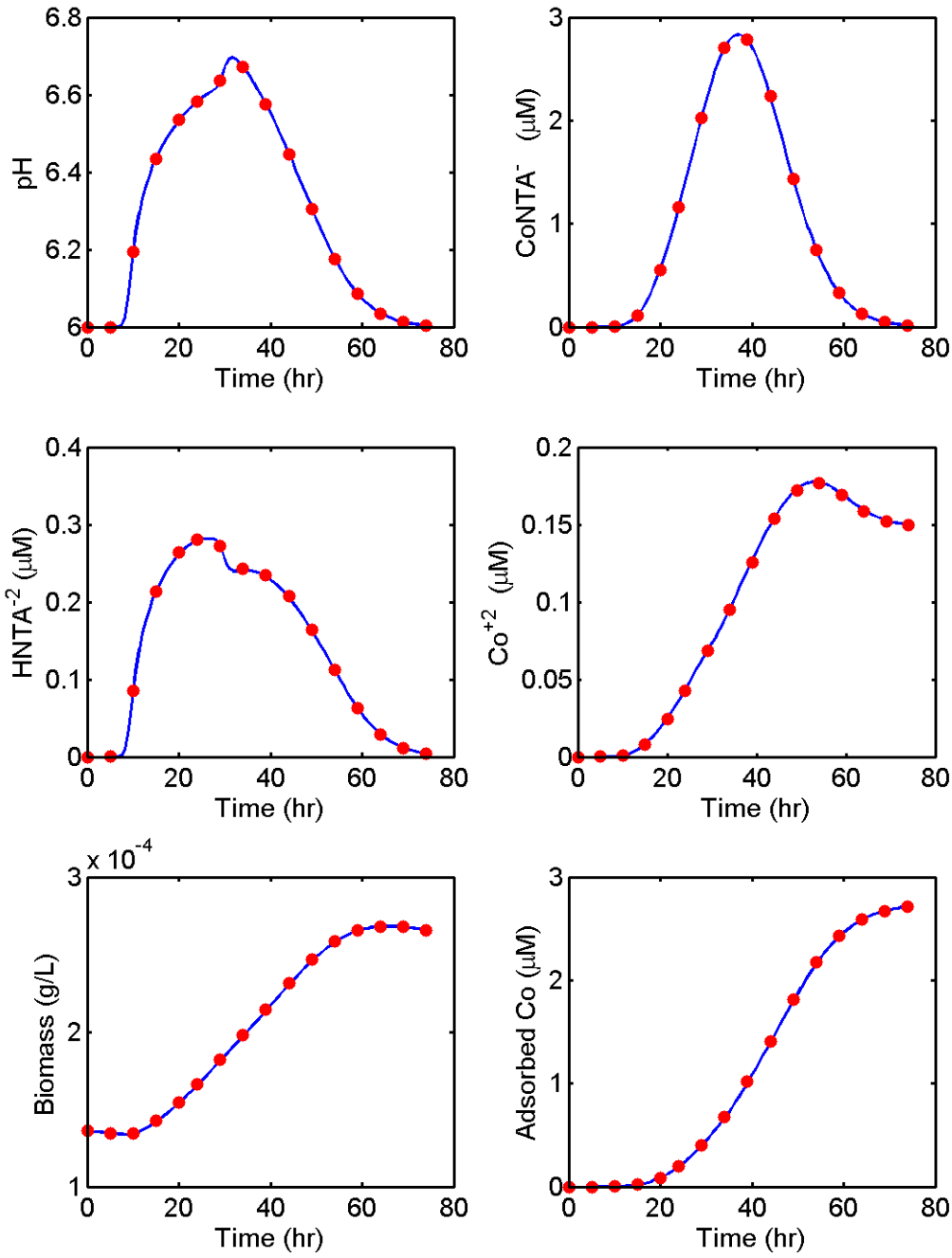

Figure 4.4. Comparison of RATEQ and PHREEQC simulation results for the Tebes-Stevens and Valocchi (1997) benchmark problem.

4.3.2 Equilibrium-Controlled Heterovalent Ion Exchange

This simulation is based loosely on the chemical conditions in the Cape Cod aquifer and examines the effect of injecting a 5 mM KBr tracer into a one-dimensional flow system. The assumed composition of the initial water is shown in Table 4.9. In addition, the porous media had an assumed total ion exchange capacity of 2.1 meq/L of groundwater. The simulation was conducted by adding 5 mM KBr to the water (composition shown in Table 4.9), and then injecting 1.8 pore volumes into a

hypothetical column. No dispersion was included in the model simulations. The increase in K concentration in the influent water caused release of Ca, Mg, Na and H from the exchanger surface. The ion exchange reactions considered in the simulation are listed in Table 4.10. Table 4.11 contains the RATEQ input file for the Heterovalent ion exchange benchmark problem.

Figure 4.5 illustrates the simulation results obtained using both RATEQ and PHREEQC. The agreement between the two simulations is very good. The results illustrate that the relatively high K concentrations displaced all of the other cations from the exchanger to varying extents. The increase in K concentration causes an initial sharp decrease in pH, because H^+ bound to the exchangers is released to solution. Subsequently, the pH increases because H^+ is readsorbed by the exchanger as the K concentration returns to the initial concentration. Similarly, Na, Ca, and Mg all show initial increases in aqueous concentration, followed by a decrease below the initial concentration as the K peak returns to the initial concentration.

The second example calculation repeated the first simulation except that ion exchange of H^+ was not included in the simulation. Again, the comparison between RATEQ and PHREEQC is excellent as shown in Figure 4.6. In addition, eliminating the H^+ exchange reaction from the reaction network has a negligible effect on the transport of K, Na, Ca, and Mg, but there was a significant effect on the simulated pH values. This small effect results because the H^+ concentration at pH values near 5 is approximately 100 times smaller than the concentration of the other ions. Thus, the proton concentration has a negligible effect on the transport of the major ions, Ca, Mg, K and Na. Conversely, when H^+ ion exchange is included, the major ions Ca, Mg, K and Na have a large effect on the exchanged H^+. In systems with negligible pH buffering, such as in the simulation considered here, the changes in exchanged H^+ cause large transients in pH in solution. This could be important for the transport scenarios that also include ions the exhibit strongly pH dependent adsorption.

Table 4.9 Assumed Groundwater Composition for Ion Exchange Benchmark Simulation

Species	Concentration
pH	5.2
Mg^{+2}	1.5e-04
Na^+	1.5e-03
Ca^{+2}	3.0e-05
Cl^-	2.41e-03
K^+	0.2e-03
Br^-	0.2e-03

Table 4.10 Ion Exchange Reactions and Equilibrium Constants

Exchange Reaction	Log K
$K^+ + >XNa = >XK + Na^+$	0.7
$Ca^{+2} + 2 >XNa = >X_2Ca + 2 Na^+$	0.8
$Mg^{+2} + 2 >XNa = >X_2Mg + 2 Na^+$	0.6
$H^+ + >XNa = >XH + Na^+$	1.0

Table 4.11 RATEQ Input File for the Ion Exchange Benchmark Simulation

```
Setup
    Titles
        Benchmark 5: Heterovalent ion exchange

End_Setup

! Geochemical Conditions
```

Table 4.11 RATEQ Input File for the Ion Exchange Benchmark Simulation (continued)

```
Reaction Set 1              ! define geochemical reactions and solution compositions
  File
    bench5_database.dat          ! thermodynamic data file to use

  !—DEFINE SOLUTION
  solution 1  -- The background solution
    H2O       fixed       55
    H+        pH          5.2E+00
    Mg+2      aqueous     1.5e-04
    Na+       aqueous     1.5e-03
    Ca+2      aqueous     3.0e-05
    Cl-       aqueous     1.95e-03
    K+        aqueous     0.2e-03
    Br-       aqueous     0.2e-03
    >X        total       2.1e-02
  end_solution

  solution 2 – The injectate
    H2O       fixed       55
    H+        pH          5.2E+00
    Mg+2      aqueous     1.5e-04
    Na+       aqueous     1.5e-03
    Ca+2      aqueous     3.0e-03
    Cl-       aqueous     1.95e-03
    K+        aqueous     5.0e-03
    Br-       aqueous     5.2e-03
    >X        total       2.1e-02
  end_solution

  End of solutions

End of reactions
Calculation
   Transport

   reactions  1

   Domain
      1      xmax
      13     tmax

   Discretization
      100    ndx
      .75    Courant Number      ! Cr = v*dt/dx
```

Table 4.11 RATEQ Input File for the Ion Exchange Benchmark Simulation (continued)

```
    1D-Flow
        1    velocity
        0.0  dispersivity

End_Calculation

Output

    breakthrough
        species
          pH  Cl- K+  Na+ Ca+2 Mg+2


End output

Initial Conditions                  ! Set the initial conditions on the grid

      1D  0.0   1.e19 1           ! type, xmin, xmax, soln_number

End Initial Conditions

Timed Events

    Boundary conditions
        left 0 10  2

    Duration
        1.8

    Boundary conditions
        left 0 10  1

    Duration
      100000

 End Timed Events
```

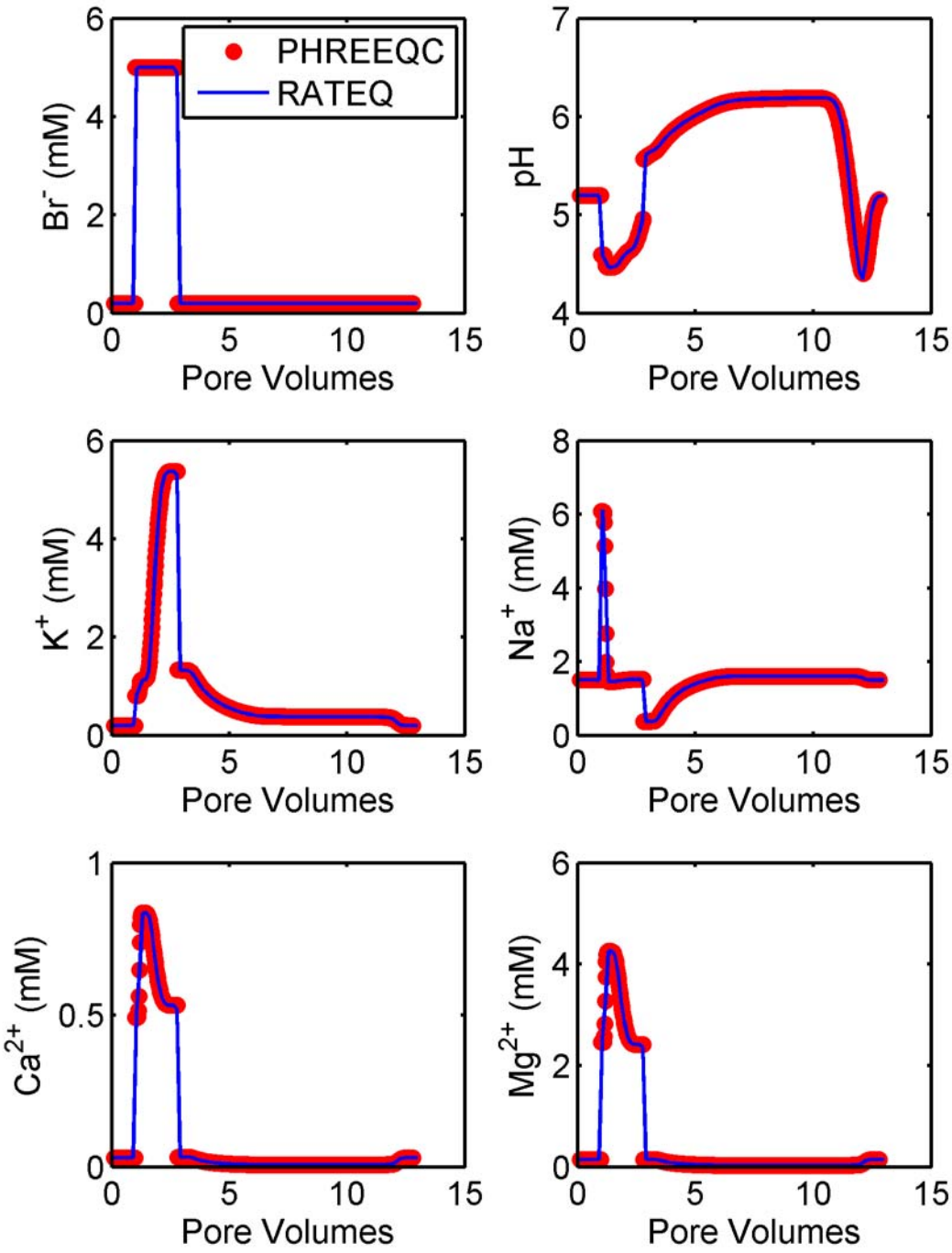

Figure 4.5. Comparison of RATEQ and PHREEQC simulation results for the heterovalent ion exchange benchmark problem.

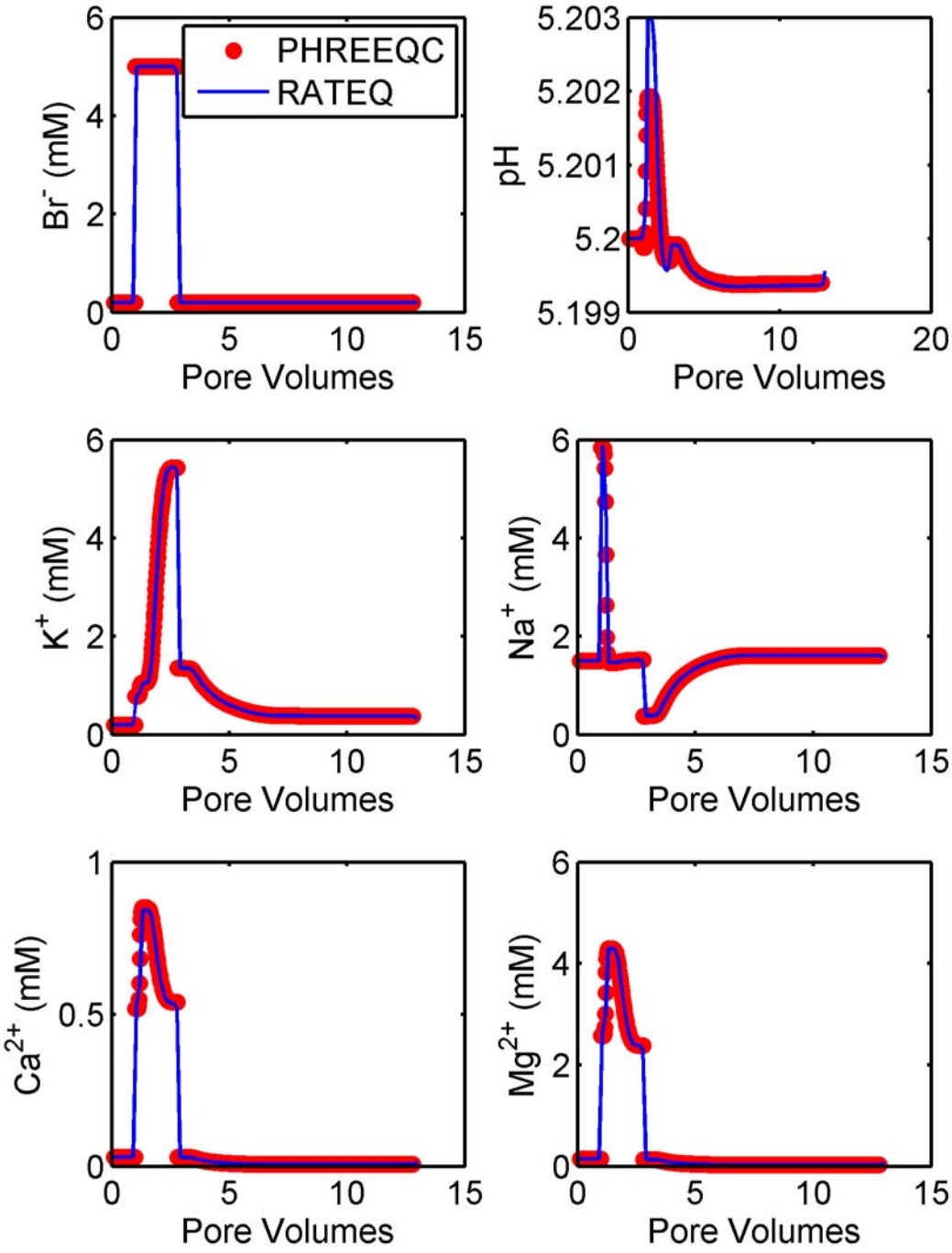

Figure 4.6. Comparison of RATEQ and PHREEQC simulation results for the heterovalent ion exchange benchmark problem for the case where H^+ exchange was not included.

5. REACTIVE TRANSPORT SIMULATIONS RELATED TO THE NATURITA UMTRA FIELD SITE

5.1 Introduction

Reactive transport simulations related to the Naturita field site were performed with the RATEQ code to simulate reactive transport in laboratory columns, at the field scale with uniform properties, and at the field scale with non-uniform properties. This section presents a discussion of these simulations, and in so doing, illustrates additional features of RATEQ.

5.2 Transport in Laboratory Columns with Kinetically Controlled Sorption Reactions

The first example related to the Naturita field study simulates uranium transport in laboratory columns. These simulations were based on experiments that were described previously (Davis and Curtis, 2003). The experiments used the flow interruption technique to evaluate the importance of possibly slow sorption and desorption kinetic effects. In this method, flow in the column is stopped for a period of time and then the original flow rate is resumed. If kinetic effects are important, the concentration measured in the column effluent changes during the flow interruption, because of slow sorption or desorption that continues even in the absence of flow. In the RATEQ simulations, the velocity can be set to zero at specific time intervals, and this causes the advection and mechanical dispersion to stop. Molecular diffusion can be simulated if a non-zero molecular diffusion coefficient is specified in either the DSP input file for in the 1-D calculation data block.

The input file for these example simulations is shown in Table 5.1. The rate laws included in the simulation were fit to batch data (Davis and Curtis, 2003). Two simulations were conducted. One simulation used rate constants derived from the batch data, and the second simulation used the same kinetic model except that the rate constants were all decreased by a factor of 2. For these simulations, it is convenient to print pore volumes instead of time, as shown in Table 5.1. Simulation results are shown in Figure 5.1. For the slow kinetics simulations, there were significant changes in the U(VI) concentration after 19, 28 and 38 pore volumes, when the flow in the column was interrupted for approximately 4 days. The changes are slightly smaller when the rates constants were not changed.

5.3 Two-Dimensional Reactive Transport at the Naturita Field Site

This section describes some of the assumptions made in constructing the flow and transport model, but for brevity, does not reproduce each of the input files required for the simulation.

The flow model was created using the Argus MODFLOW graphical user interface (Winston, 2000). All of the input files required for simulating 2-dimensional reactive transport at the Naturita site are available at the web site (http://wwwrcamnl.wr.usgs.gov/rtm). The site contains both the Argus1 input file and all of the MODFLOW-2000 input files that are created by the graphical user interface. Some of the details of the model construction are described below.

5.3.1 Domain

The spatial extent of the aquifer was taken from aerial surveys of the site. The western boundary of the aquifer was taken as the toe of the slope of the surrounding canyon walls. The eastern border of the site was taken as the eastern border of the San Miguel River. This assumption was based on the fact that there is a sandstone outcrop along the eastern edge of the river. The width of the alluvial aquifer becomes negligible in both the upstream and downstream locations and therefore the western and eastern boundaries effectively define the boundary of the aquifer.

Table 5.1 Input File For Flow Interruption Simulations

```
! Geochemical Conditions
Reaction Set 1              ! define geochemical reactions and solution compositions
  File
     phreeqa_no_ads.dat             ! thermodynamic data file to use

 Ignore          ! define species not considered in the solutions
   CO2(g) UO3(C) Gummite B_UO2(OH)2 Schoepite Rutherfordine

   Reaction
   SURFACE_SPECIES

  >SOH2 + UO2+2  = >SOH2UO2+ +  H+
          log_K   1.817
          name S_p
          rate_law
             General
             mass_action_kinetics
             kfor 2.0e-06
          end_rate_law

  >WOH2 + UO2+2  = >WOH2UO2+ +  H+
          log_K   2.570
          name W_p
          rate_law
             General
             mass_action_kinetics
             kfor 2.0e19
             rate_variable activity
          end_rate_law

  >ZOH2 + UO2+2  + H2O= >ZOH2UO2OH + 2H+
          log_K   -0.671
          name SS_n
          rate_law
             General
             mass_action_kinetics
             kfor 5.0e24
             rate_variable activity
          end_rate_law

  >SOH2 + UO2+2 + H2O= >SOH2UO2OH + 2H+
          log_K   -2.082
          name S_n
          rate_law
             General
```

Table 5.1 Input File For Flow Interruption Simulations (continued)

```
                mass_action_kinetics
                kfor 2.0e19
                rate_variable activity
            end_rate_law
        force_rate

    >WOH2 + UO2+2 +  H2O= >WOH2UO2OH + 2H+
            log_K   -5.318
            name W_n
            rate_law
                General
                !gibbs
                mass_action_kinetics
                kfor 2.0e19
                rate_variable activity
            end_rate_law
        End
    End

  !--DEFINE SOLUTION
  solution 1     ! average conditions at NAT-20
      H2O                 fixed      55
      Alkalinity          fixed      1.51E-03          2.0e-03  guess
      UO2+2               aqueous    1.0E-08      1.0e-24  guess
      H+                  pH         7.46
      >SOH2               total      0.248E-04
      >SOH2UO2+           fixed      0.19275E-04
      >SOH2UO2OH          fixed      0.16019E-05
  end_solution 1
  solution 2     !  composition of contaminated water
      H2O        fixed       55
      Alkalinity fixed       1.51E-03          2.0e-03  guess
      UO2+2      aqueous     1.0E-05       1.0e-24  guess
      H+         pH          7.46
  end_solution 2
  End of solutions
End of reactions

Calculation
    Transport
    reactions  1

    Ignore          ! define species not considered in the solutions
      CO2(g) UO3(C) Gummite  B_UO2(OH)2    Schoepite  Rutherfordine
```

Table 5.1 Input File For Flow Interruption Simulations (continued)

```
Domain
    6.4    xmax (cm)
    6.5     tmax (d)

Discretization
    60      ndx Pegrid Number     ! alt: 5 Pegrid Number
    .2      Courant Number        ! Cr = v*dt/dx
     4      PDE method

1D-Flow
    15.7248   velocity (m/year)
    6.10E-02  dispersivity
    1.0e-9    molecular diffusion

End_Calculation
Output
    Breakthrough
      Pore_volumes

      Species
        pH  H+ UO2+2 >SOH2 UO2(CO3)3-4 UO2+2(aqu)  HCO3-
        >SOH2UO2+ >SOH2UO2OH

    End

End output
Initial Conditions        ! Set the initial conditions on the grid
    1D  0.0   1.e19 1
End Initial Conditions
Timed Events

    Boundary conditions   ! event 1 Start pulse
        left 0 10  2
    Duration
        6.02  !13.69
    Boundary conditions  ! event 2  Resume Clean water
                left 0 10  1
    Duration
        1.90
    Velocity            ! event 3  Interupt flow
        1.0e-10
    Duration
        4.17
    Velocity            ! event 4 Resume flow
        15.7248
```

Table 5.1 Input File For Flow Interruption Simulations (continued)

Duration	
3.75	
Velocity	**! event 5 Interupt flow**
1.0e-10	
Duration	
4.17	
Velocity	**! event 6 Resume flow**
15.7248	
Duration	
500	
End Timed Events	

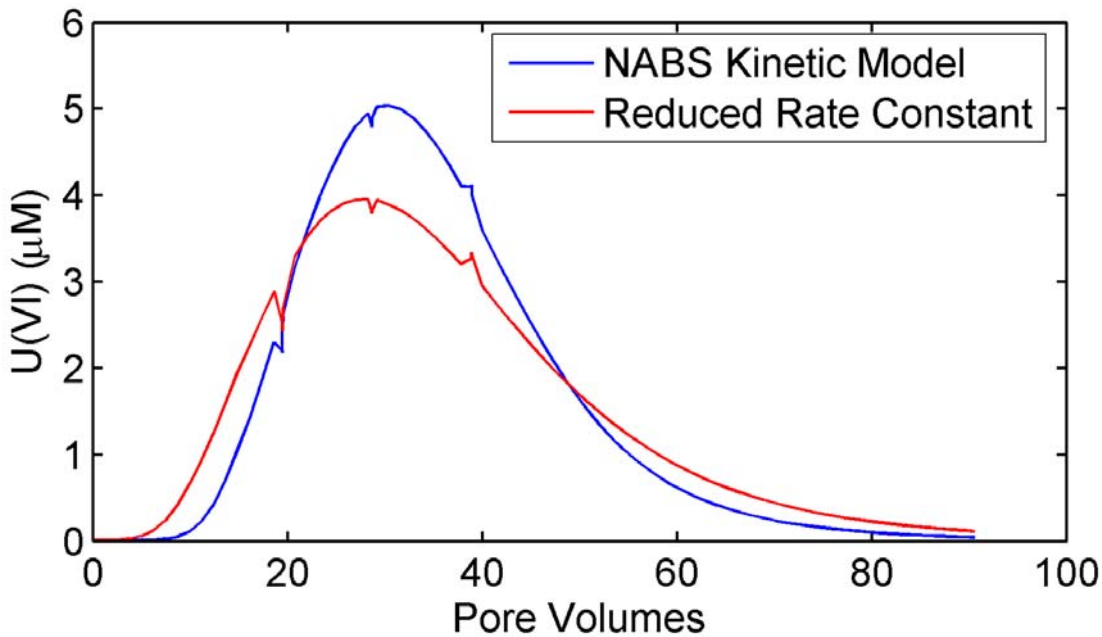

Figure 5.1. Simulated rate-controlled transport of U(VI) in laboratory columns packed with Naturita aquifer background sediments (NABS) using the flow interruption technique. Flow was interrupted for 4.17 hours after 19, 29 and 39 pore volumes. The two simulations used the same rate model but with rate constants that differed by a factor of 2.

The bottom of the aquifer was based on the elevation of the top of the fine-grained shale that underlies the alluvial aquifer. This elevation was taken from drilling logs obtained when ground water monitoring wells were installed in 1998 and 1999 by USGS, and in some cases in the 1980s by DOE (Davis and Curtis, 2003). Figure 5.2 illustrates the locations of where the wells were installed and contoured elevations of the bottom of the alluvial aquifer.

A uniform finite difference grid with nearly equal grid spacing was used. The grid consisted of 69 rows, each with a width of 25.12 feet (7.83m) and 263 columns with a width of 25.01 feet (7.80 m). The grid was rotated 30º counterclockwise to minimize inactive cells.

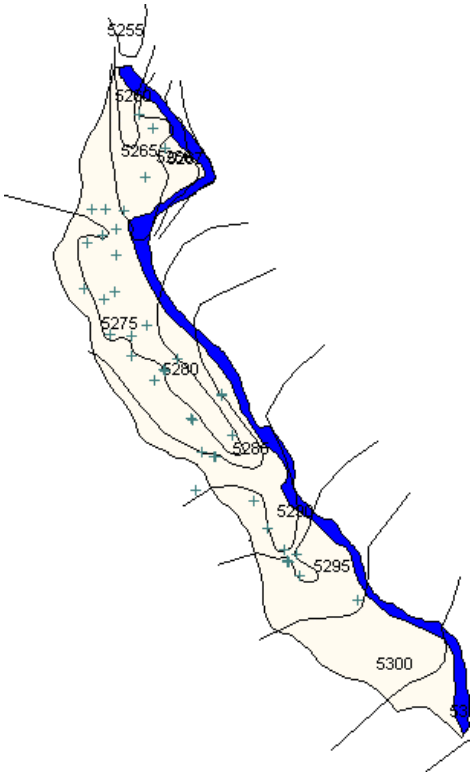

Figure 5.2. Location of groundwater wells and contoured elevations of the bottom of the alluvial aquifer.

5.3.2 Recharge

The simulations assumed a temporally and spatially uniform recharge rate equal to 1% of the average annual rainfall. The chemical composition of the recharge water was assumed to equal that of the average conditions of the upgradient wells where no contamination had been observed. However, below the former tailings pile and the former mill yard, the composition of the recharge was estimated during the calibration simulations (Davis and Curtis, 2003). The extent of the contamination was estimated from aerial photographs of the site taken in 1974, prior to when the tailings were removed from the site.

5.3.3 San Miguel River

The San Miguel River was simulated using the MODFLOW-2000 river package. The river was represented in the Argus graphical interface by approximately 1000 quadrilateral cells that were fitted to the shape of the river. The river elevations used in the simulations were based on river stage measurements taken during low flow conditions in the aquifer. The top of the river bed was assumed to be 1 foot below the water surface. The vertical conductivity of the river bed was assumed to equal 20 ft/d.

5.3.4 Simulation Results

Simulation results for U(VI) transport, as well as several other species have been presented previously (Davis and Curtis, 2003). Most of those simulations focused on the spatial distribution of U(VI), alkalinity, and pH after 62 years of transport. Little attention was given to the temporal behavior of any of the solutes. Figure 5.3 illustrates the temporal evolution of the simulated U(VI) plume. This figure illustrates the complex mixing that occurs between the San Miguel River and the alluvial aquifer, and that high concentrations of U(VI) exist near the bend on the western edge of the aquifer. The plume moves very slowly as shown by the simulation results for 40, 51 and 62 years.

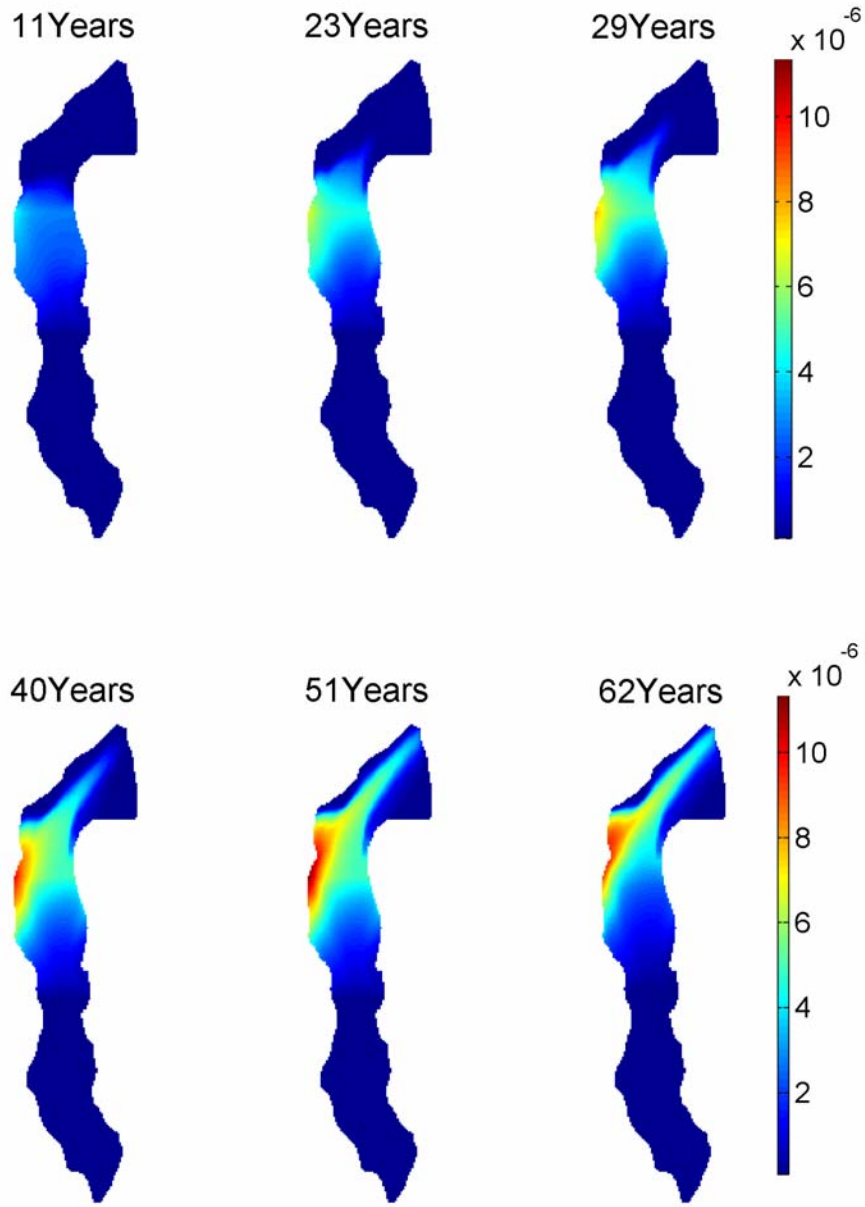

Figure 5.3 Predicted temporal evolution of U(VI) concentrations in the alluvial aquifer of the Naturita UMTRA site, Colorado.

5.4 Effect of Heterogeneity on Transport at the Naturita Field Site

Transport simulations were conducted to extend the reactive transport modeling discussed above to include the effects of spatially variable parameters. The specific surface area (A_{SP}) of the Naturita sediments is known to vary spatially in the aquifer, based on specific surface area measurements made on contaminated sediments (Kohler et al., 2004). Similarly, slug test results also demonstrated that hydraulic conductivity (K_H) is also variable at the site. Figure 5.4 shows that the A_{SP} measurements varied by approximately a factor of 4, whereas the slug test results varied by a

factor of nearly 30. Although the slug test results were biased upward relative to the K_H estimated from model calibration to chloride transport (Davis and Curtis, 2003), it was assumed that the variance from the slug test results was applicable to the calibrated K_H values. Using these results and assumptions, variograms were constructed for A_{SP} and K_H, and 10 realizations of the spatial distribution of A_{SP} and K_H were generated using sequential Gaussian simulation. These distributions are illustrated in Figures 5.5 and 5.6, respectively.

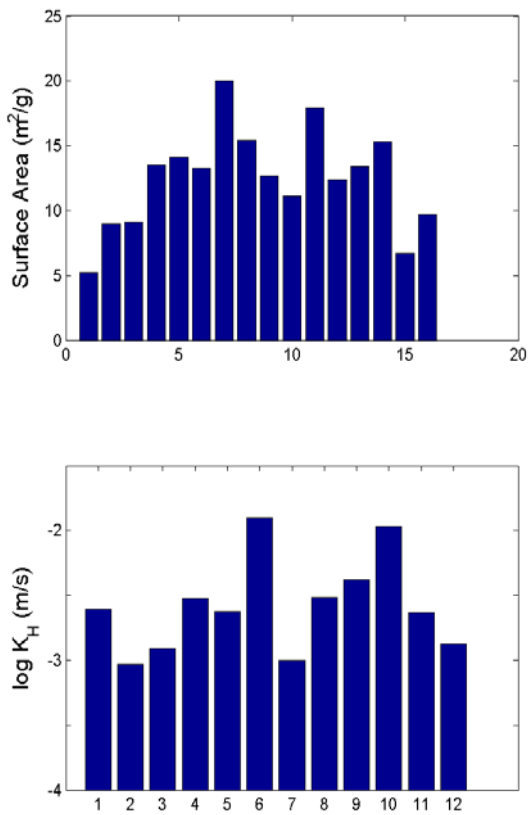

Figure 5.4. Summary of measured specific surface area and hydraulic conductivity measured at the Naturita field site.

Model simulations were conducted that considered: (1) spatially variable A_{SP} and constant K_H, (2) constant A_{SP} and spatially variable K_H, and (3) spatially variable A_{SP} and spatially variable K_H. For simulations with variable K_H, only the two-dimensional hydraulic conductivity input array for the MODFLOW BCF file was changed for each of the 10 simulations. When spatially variable A_{SP} was considered, the total weak, strong and very strong surface site concentrations were computed from the A_{SP} value for each model cell. These three site concentrations were input into RATEQ using separate two-dimensional arrays for each site concentration. The names of the files were entered into the BTN file as shown in Table 5.2.

The simulation results for the case of constant K_H and variable A_{SP} are shown in Figure 5.7. There is essentially no difference between any of the ten simulations, presumably because of averaging that occurs for the reacting water which encounters cells with higher and lower site concentrations. Simulation results for the variable K_H and constant specific surface area show a very strong effect of hydraulic conductivity on the simulated U(VI) concentration. The relatively large effect occurs because the measured K_H values varied by a factor of 30, whereas the ASP values varied by only a factor of 4. This causes the groundwater to have spatially variable velocity.

The simulations with variable K_H also had maximum concentrations that varied among the 10 realizations. In some cases, the concentrations were lower because more U(VI) was flushed into the river by a preferential flow path. Different concentrations can also result from differences in groundwater velocity. The velocity in each cell varied spatially, the recharge flux was the same in each cell. Therefore, recharge water that mixed with groundwater that had a low velocity would yield a higher U(VI) concentration, because there would be a smaller amount of groundwater available for dilution. Conversely recharge-derived U(VI) that mixed with a groundwater that had higher velocity would yield a smaller dissolved U(VI) concentration.

Table 5.2 Basic Transport File For Spatially Variable Surface Site Concentrations

Reactive Transport in the Naturita Alluvial Aquifer												
Initial concs determined from spatial input files - free format												
1	263	69	2	10	7	!NLAY,NROW,NCOL,NPER,NCOMP,MCOMP						
DAY	M	KG				!TUNIT,LUNIT,MUNIT						
T T T F T T F F F F						!TRNOP: ADV,DSP,SSM,RCT,GCG,RATEQ						
0 0						!LAYCON						
0	25.					!DELR						
0	25.					!DELC						
0	6080.					!HTOP						
0	6.					!DZ						
0	.20					!PRSITY-LAYER 1						
0	1					!ICBUND-LAYER 1						
170	const	H2O	fixed	55.		!H2O LAYER 1						
170	const	Calcite	total	1.0								
170	const	Alkalinity	fixed	4.87E-03								
170	const	Cl-	aqueous	0.008902								
170	const	Na+	aqueous	0.008902								
170	const	UO2+2	aqueous	6.05E-08								
170	const	H+	pH	7.1								
170	file	>WOHH2	total	WOH_1.dat								
170	file	>SOHH2	total	SOH_1.dat								
170	file	>SSOHH2	total	SSOH_1.dat								
999.99	0					!CINACT,THKMIN						
1	2	0	0	T		!OUTPUT CONTROL						
0						!NPRS						
1	1					!NOBS,NPROBS						
1	8	3				!KOBS,IOBS,JOBS						
T	1					!CHKMAS,NPRMAS						
20819	1	1.				!PERLEN,NSTP,TSMULT						
7.	40000	1.	0			!DT0,MXSTRN,TTSMULT,TTSMAX						
1826	1	1.				!PERLEN,NSTP,TSMULT						
7.	40000	1.	0			!DT0,MXSTRN,TTSMULT,TTSMAX						

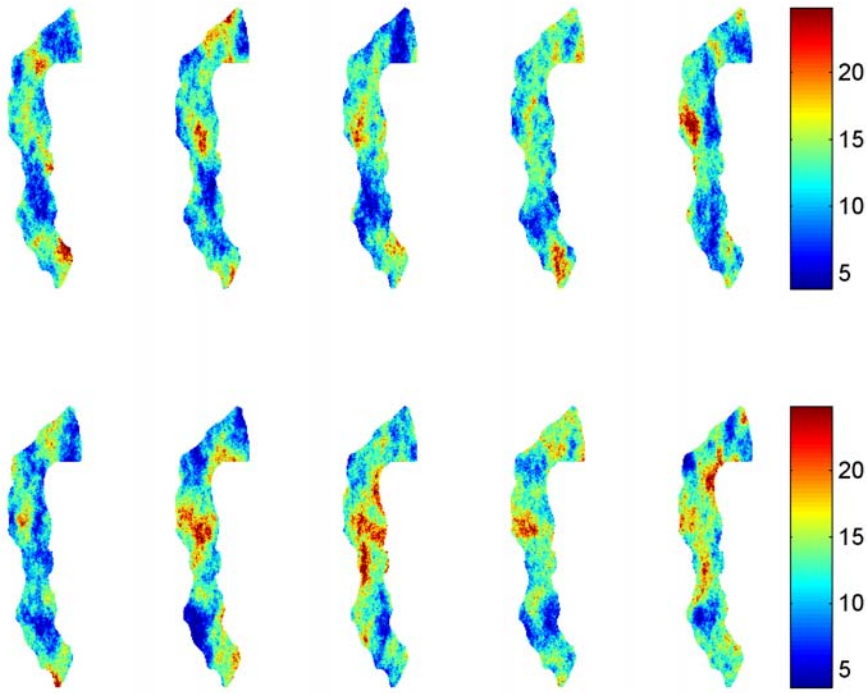

Figure 5.5. Ten realizations of the spatial distribution of specific surface area (m^2/g) generated by sequential Gaussian simulation.

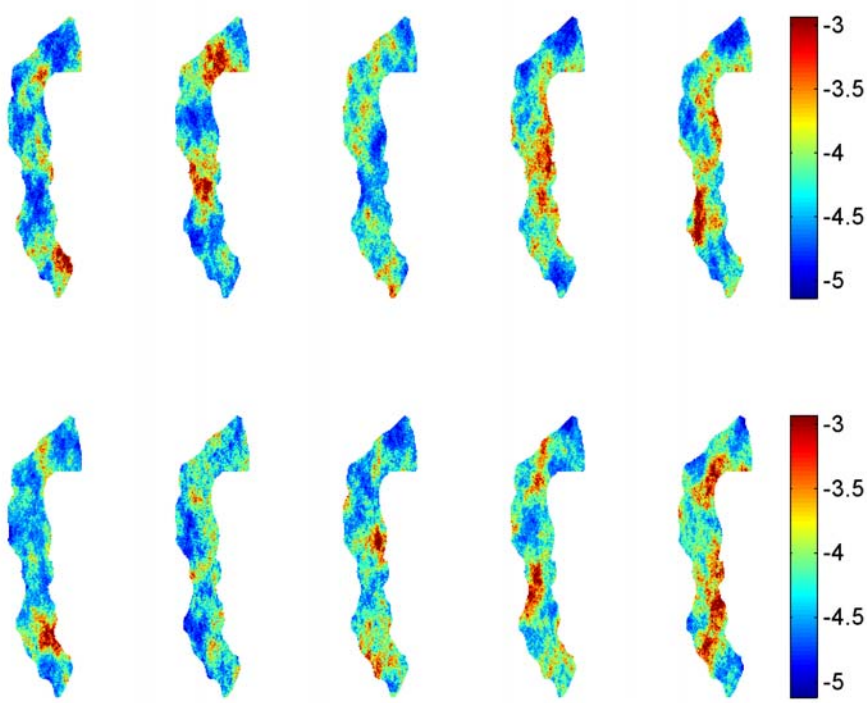

Figure 5.6. Ten realizations of the spatial distribution of log K_H (m/s) generated by sequential Gaussian simulation.

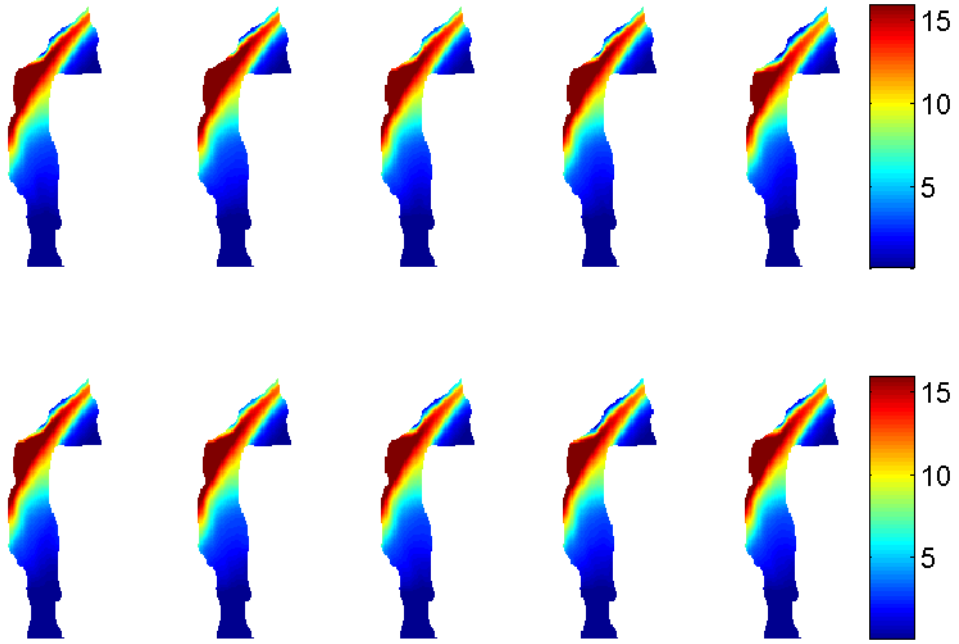

Figure 5.7. Ten simulations of U(VI) transport that used a fixed K_H and spatially variable A_{SP}. Plumes are shown after 62 years of transport.

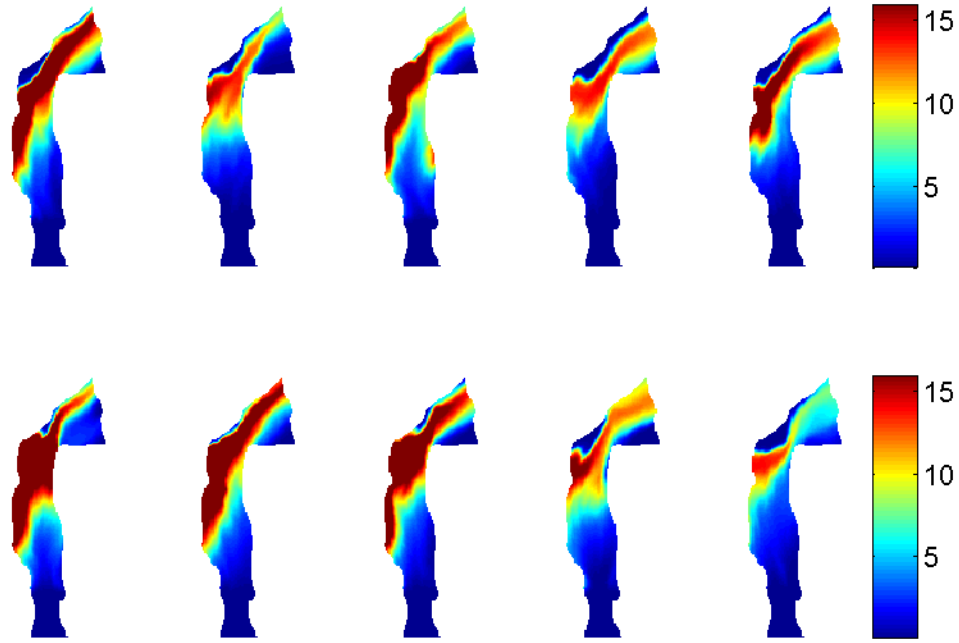

Figure 5.8. Ten simulations of U(VI) transport that used spatially variable K_H and a fixed A_{SP}. Plumes are shown after 62 years of transport.

6 EXAMPLE SIMULATIONS

6.1 Introduction

This section presents additional example simulations of reactive transport. The examples include transport with immobile zones, transport controlled with equilibrium-controlled redox reactions and simulations of biogeochemical transport. The parameter values (especially the rate parameter values) used in the simulations were selected for illustrative purposes only and new approaches are needed for determining reactions and parameter values for the purpose of reactive transport modeling.(Davis et al., 2004b).

6.2 Transport with immobile zones

Reactive transport in groundwater is often affected by the heterogeneous nature of the porous medium, which can cause the groundwater velocity to vary significantly in space. One simple approach to address this heterogeneity is to assume that this heterogeneity can be simulated by assuming that the velocity in some of the porous medium is zero. Transport of U(VI) was simulated for a one-dimensional porous medium where 25% of the porosity was assumed to be immobile. The simulations are loosely based on conditions observed at the Naturita UMTRA field site (Davis and Curtis, 2003). This simulations illustrate the effect of a transient pulse of low alkalinity water on U(VI) concentrations. The input file for this simulation is listed in Table 6.1 and the results are shown in Figure 6.1.

Table 6.1 Input File for Simulating Transport with Immobile Zones

```
REACTIONS
  Reaction Set 1            ! define geochemical reactions and solution compositions
  file
    PHREEQA_nat.dat
   ignore        ! define species not considered in the solutions
    Dolomite
   temperature
          15
  solution 1    ! average conditions at NAT-25
     H2O       fixed      55
     Mg+2      total      1.65e-03
     Calcite   total      1.0
     Alkalinity aqueous     9.0e-03       2.0e-03  guess
     Cl-       aqueous     3.44E-03              2.0e-03  guess
     Br-       aqueous     1.0E-05               2.0e-03  guess
     K+        aqueous     2.51e-04
     Na+       aqueous     1.99E-02              2.0e-03  guess
     UO2+2     aqueous     4.0E-06       1.0e-24  guess
     SO4-2     aqueous     9.03E-03
     H+        pH          7.06
     >WOH2     total       3.79E-02
     >SOH2     total       3.795E-05
     >ZOH2     total       3.795E-06
  end_solution 1
  solution 2    !  DOE 547
```

```
      H2O       fixed       55
      Mg+2      total       1.65e-03
      Calcite   total       1.0
      Alkalinity aqueous     3.0e-03       2.0e-03  guess
      Cl-       aqueous     3.44E-03              2.0e-03  guess
      Br-       aqueous     1.0E-05               2.0e-03  guess
      K+        aqueous     2.51e-04
      Na+       aqueous     1.99E-02              2.0e-03  guess
      UO2+2     aqueous     4.0E-06       1.0e-24  guess
      SO4-2     aqueous     9.03E-03
      H+        pH          7.06
   end_solution 2
   End of solutions
End of reactions
Calculation
   1D
   ignore          ! define species not considered in the solutions
       Dolomite
   Domain
       2.        xmax (meters)
       20        tmax (days)
   Discretization
       50        ndx
       0.6       Courant Number
   1D-Flow
       0.75      velocity (m/days)
       0.005     dispersivity !0.0030489159
       0.15      porosity
       0.05      kla 0.003052814
       0.1       immobile-theta
End Calculation
Output
     breakthru
       species
         pH    Alkalinity UO2+2(aqu)   UO2+2(ads)
End output
Initial Conditions        ! Set the initial conditions on the grid
       1D  0.0   1.e19 1
End Initial Conditions
Timed Events
   Boundary conditions
        left 0 10  2
   Duration
       2.5 !13.69
   Boundary conditions
            left 0 10  1
   Duration
   1000000
End Timed Events
```

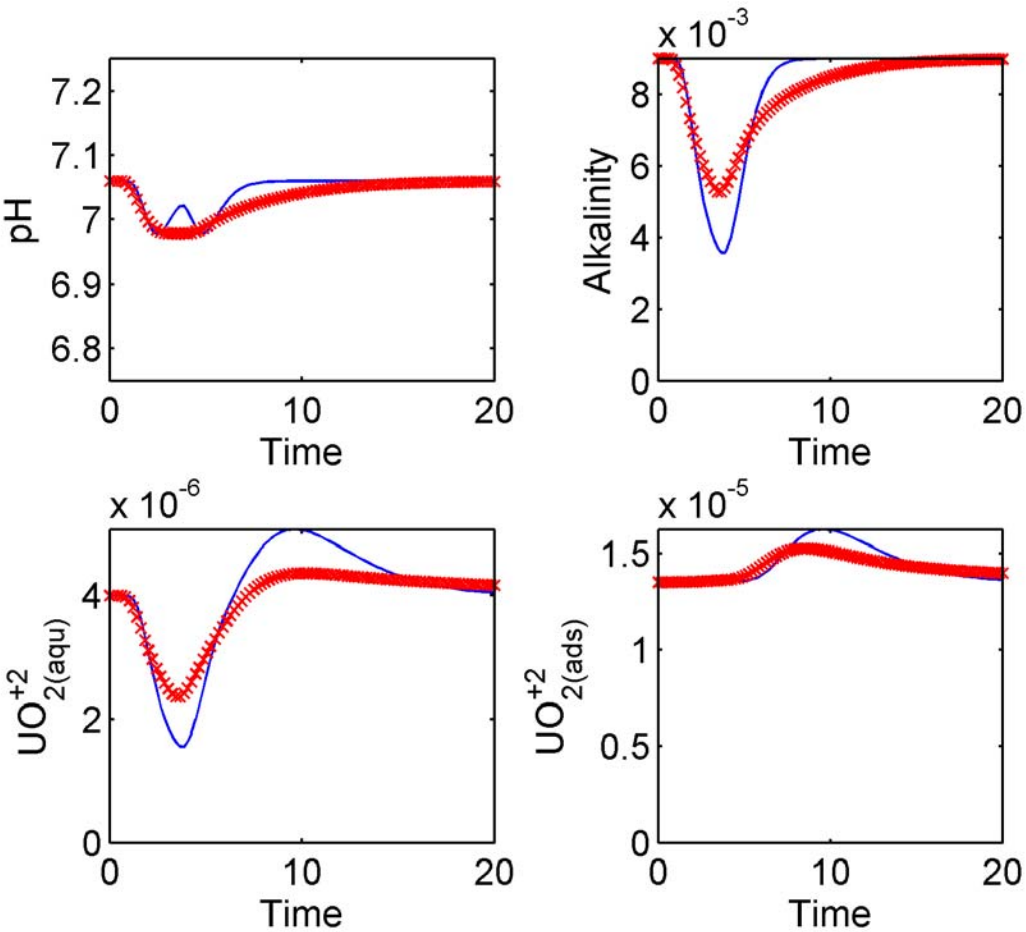

Figure 6.1. Comparison of U(VI) transport simulations assuming immobile zones (x) and no immobile porosity (—).

The results show that the pulse of low alkalinity water decreases the U(VI) concentration, even though the U(VI) in the boundary conditions was not changed. This was caused by an increase in adsorption, resulting from decreased aqueous complexation by carbonate. After the alkalinity peak elutes, the U(VI) held back by the increased adsorption is desorbed by native groundwater, which had the initial concentration of 4 μM. The desorption creates U(VI) concentrations that exceed that of the influent water. In the presence of a significant fraction of immobile porosity, the increase in dissolved U(VI) after 8 days is small, but in the absence of immobile porosity, the U(VI) concentrations are approximately 25 percent larger than the initial concentration.

6.3 Transport with oxidation-reduction reactions

Transport with redox reactions is often numerically difficult to solve, because concentrations of many species can vary significantly over very small spatial scales. This example presents a RATEQ simulation of the basic processes that lead to a uranium roll front deposit. In this scenario, oxidizing water enters a porous medium that contains reduced phases such as pyrite and uraninite. The oxidizing solution oxidizes U(IV) in uraninite to relatively mobile U(VI) species, which are transported downgradient. This process creates a front of uraninite dissolution. The U(VI) that is produced by uraninite oxidation migrates faster than the

mineral dissolution front. Therefore, the U(VI) encounters reduced phases, including pyrite, which reduces U(VI) back to U(IV), which forms uraninite. The input file for this simulation is shown in Table 6.2 and the simulated output is shown in Figure 6.2.

The simulations illustrate the numerical stability of RATEQ. In addition, the simulations also illustrate expected results, including the decrease in pH resulting from the pyrite oxidation, the increase in U(VI) concentration at the dissolution front, and the increase in uraninite at the roll front.

6.4 Simulations of biogeochemical transport

In many environments, microbial processes can have a significant effect on local geochemical conditions. These effects result in large part because of the changes in chemical properties that result when the valence state of an element changes. Conceptual models for simulating biogeochemical reactions vary widely and range from simple first order degradation kinetics to complex, multiple Monod formulations that include growth and decay of microorganisms (see section 4.3.1). With multiple electron acceptors, the number of parameters required for simulations using the Monod approach can be very large. An alternative is to use the partial equilibrium approach, which assumes that organic substrate is slowly converted to intermediates that react with the terminal electron acceptor via an equilibrium-controlled reaction.

This section presents simulations of the oxidation of an organic substrate by multiple terminal electron acceptors using the partial equilibrium approach. In the simulations, the organic substrate was represented by lactate (2-hydroxypropanoic acid) that slowly degrades, releasing H_2(g):

$$1/6\ \text{Lactate}^- + H_2O = 1/3H^+ + 1/2HCO_3^- + H_2$$

The H_2 then reacts with the terminal electron acceptor via an equilibrium-controlled reaction. This is a simple approach that honors the reaction stoichiometry and thermodynamics. In addition, the approach can be expanded to include multiple sources of H_2, intermediates other than H_2 such as acetate, and rate-controlled terminal electron accepting reactions.

Table 6.2. Input File for Uranium Roll Front Simulation

! Geochemical Conditions
Reaction Set 1 ! define geochemical reactions and solution compositions
file
phreeqa_nat6.dat
ignore ! define species not considered in the solutions
U4O9(C) UO2(am) U4O9(C) U3O8(C)
!--DEFINE SOLUTION
solution 1
H2O fixed 55
Calcite total 1.0
Pyrite total 0.0011
Uraninite total 0.0001
Goethite total 0.01
UO2+2 total 1.e-30
Alkalinity fixed 1.51E-03 2.0e-03 guess
H+ pH 7.46
>WOH2 total 2.26E-02 !2.026E-02
>SOH2 total 2.27E-05 !1.223E-04

```
      >ZOH2      total       2.27E-06 !1.223E-06
   end_solution 1

   solution 2     !  composition of contaminated water
      H2O        fixed       55
      Fe+2       aqueous     1.0e-40
      HS-        aqueous     1.0e-40
      Calcite    total       1.0
      Alkalinity fixed       1.51E-02              2.0e-03  guess
      H+         pH          7.46
      O2         aqueous     1.0e-03
   end_solution 2
   End of solutions
End of reactions
Calculation
   Transport
   reactions  1                  ! Solution 1 is used as the default
   ignore          ! define species not considered in the solutions
       UO3(C) Gummite    B_UO2(OH)2    Schoepite
              Rutherfordine  U4O9(C) UO2(am)   U4O9(C)     U3O8(C)
   Domain
       20  tmax PV
   Discretization
       60      ndx
End_Calculation
Output
     breakthru
       species
      pH  HCO3-  Fe+3 Pyrite O2  UO2+2(aqu) UO2+2(ads)  Uraninite
End output
Initial Conditions         ! Set the initial conditions on the grid
      1D  0.0   1.e19 1
End Initial Conditions
Timed Events
   ! event 1 Start pulse
      Boundary conditions
          left 0 10  2
      Duration
         20.02  !13.69

   ! event 2  Resume Clean water
      Boundary conditions
                       left 0 10  1
      Duration
         500
End Timed Events
```

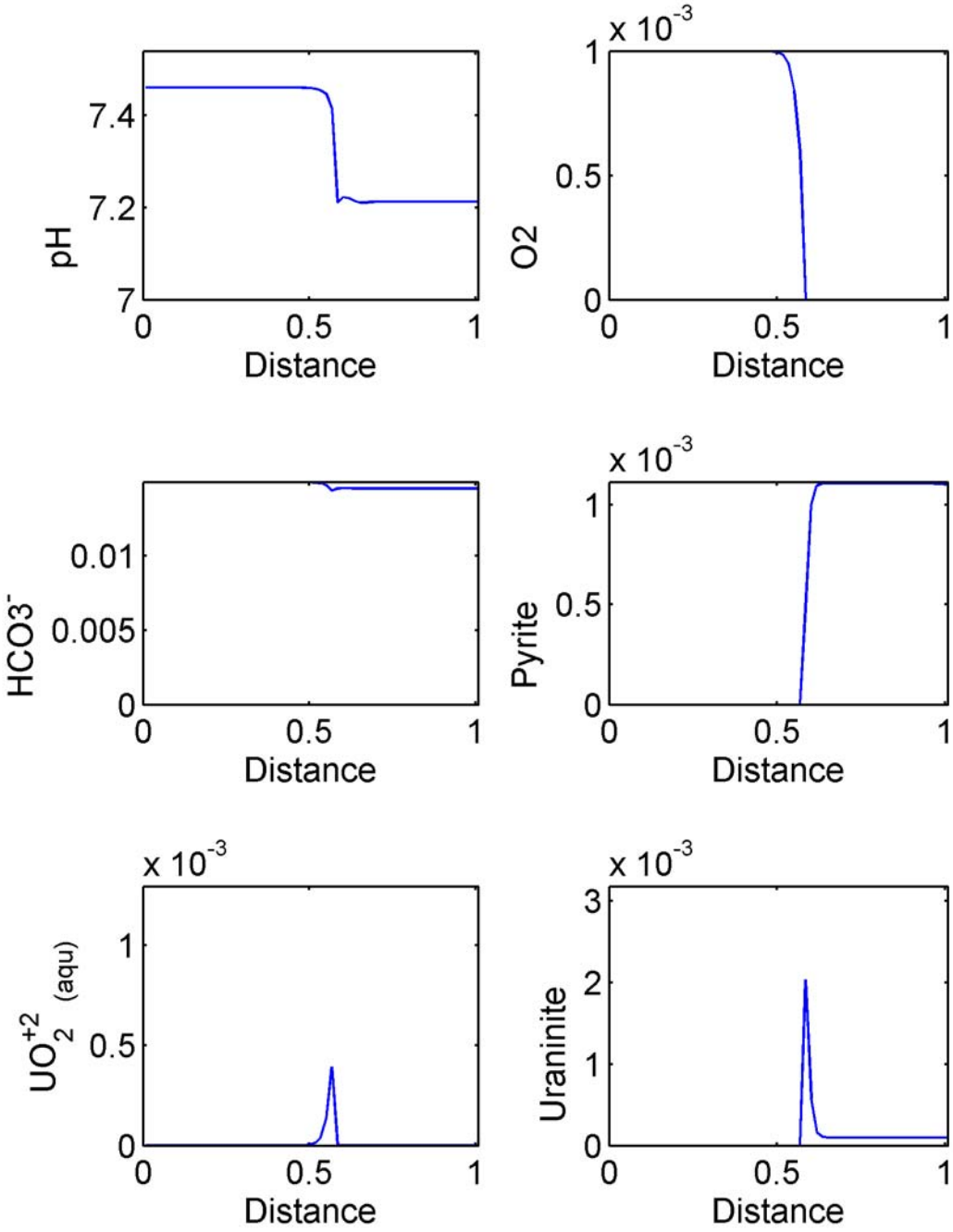

Figure 6.2. Simulated concentration profiles after 3 pore volumes of an oxidizing solution having entered a reducing zone containing pyrite and uraninite.

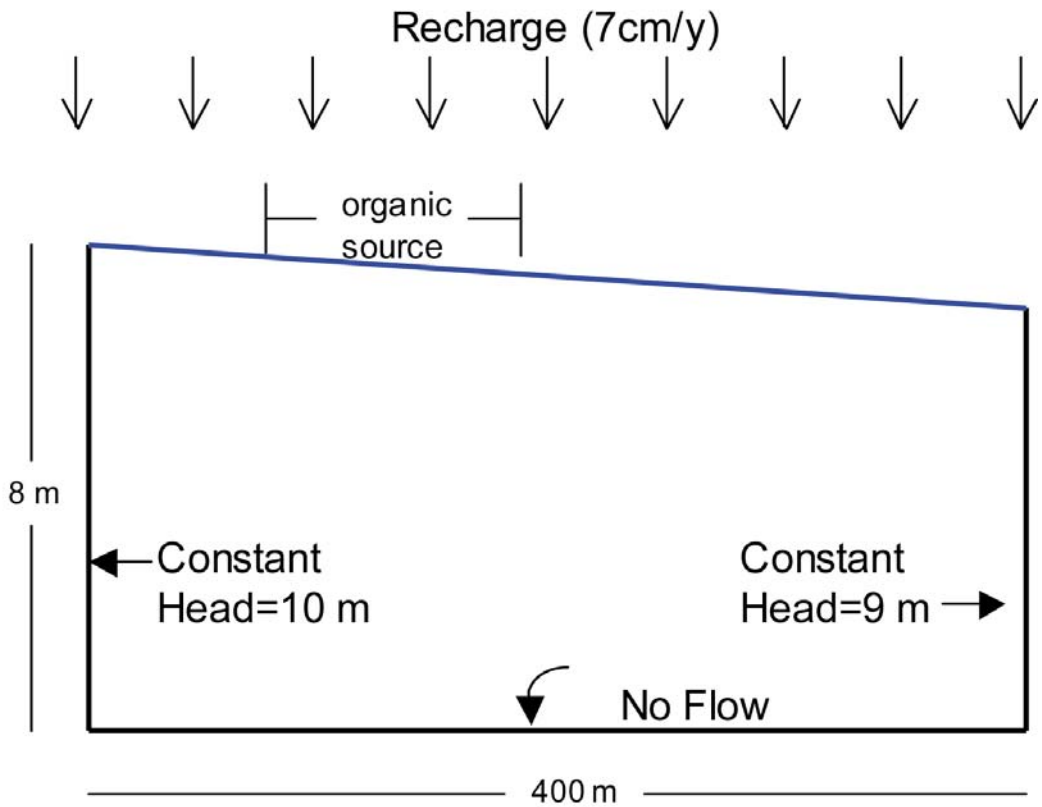

Figure 6.3. Two-dimensional cross section used for biogeochemical transport simulations.

The simulation examples were conducted for a two-dimensional domain illustrated in Figure 6.3. The system is driven by recharge that passes through an organic source, which transports lactate into an aquifer.

The electron acceptors in the simulation were 250 μM O_2, 1.5 mM FeOOH, 250 μM SO_4 and CO_2. The FeOOH was used to represent iron oxide coatings, and it was assumed to have an intermediate stability between that for freshly precipitated ferrihydrite and goethite. The input file is listed in Table 6.3.

Simulation results are shown after 10 years of transport in Figure 6.3. The results show that the electron acceptors O_2, FeOOH and SO_4 are significantly decreased below and downgradient of the waste source. For the mobile electron acceptors O_2 and SO_4, most of the decrease in concentration results because the contaminated water was assumed to have very small concentrations for each of these species. The reactions of O_2 and SO_4 were primarily confined to the boundaries of the plume. For the immobile FeOOH, the decrease in concentration results only from reaction. The FeOOH is completely exhausted immediately below the organic source, and a long area depleted in FeOOH extends downgradient. Immediately below the source area, a CH_4 plume develops at the end of the simulation, and some of the Fe^{+2} forms a precipitated FeS phase.

Table 6.3 Input File for Biogeochemical Transport Simulation

```
Reaction Set 1              ! define geochemical reactions and solution compositions
  file
    c:\rateq\data\phreeqa.dat
  ignore          ! define species not considered in the solutions
     e-

  temperature
     25 C                        ! degrees C

  Reaction
   Solution Species
     O2  + 2H2  = 2H2O
      log_K   83.11

     Fe+2 + .25O2 + 2.5H2O = FeOOH + 2H+
      rate_law
           general
              kfor 1.0e20        ! time units in days
              linear Fe+2
              linear O2
              linear OH-
              linear OH-
            end_rate_law

    H2O +   0.16667 Lactate- =  0.3333H+ + 0.50 HCO3- +   H2
           log_K    -8.33
           rate_law
             general
             kf 5.0e-04
             linear Lactate-
           end_rate_law
         force_rate

    0.25 SO4-2 + H2 + .25H+ = 0.25 HS- + H2O
         log_K  11.50

    .25 HCO3- +  H2 +.25H+ = .25 CH4 + .375 H2O
        log_K  10.08
    PHASES
     FeOOH
     FeOOH +    2 H+ +   0.500 H2 = Fe+2 +    2 H2O
         ! log_K   15.6   ! least stable lepidocrocite
         log_K   13.8   ! most stable lepidocrocite
         Rate_law
           General
           Kfor 1.0e02
           Mass_action_kinetics
           Linear FeOOH
```

```
        End_rate_law
        Force_eq

    FeS
      FeS + H+ = Fe+2 + HS-
        log_k  -4.648
        name Mack
        rate_law
        general
         mass_action_kinetics
         vmax 1.0e-3
        end_rate_law

  solution 1                          ! initial condition
    Alkalinity   fix      2.5e-03
    H+          pH       6.501
    Lactate-      fix      1.0e-05
    FeOOH        fix      1.5e-03
    SO4-2        total    1.0e-04
    H2O          fix     55.0100            ! conc (M)
    O2          fix      2.5e-04
    FeS     fix      0.0e-95
  end_solution 1
  solution 2                          ! boundary condition
    H2O          fix     55.0100            ! conc (M)
    H+          pH       6.501
    !CH4          fix      1.0e-50
    H2(g)        gas     -16.8
    Lactate-    fix      0.005
    Alkalinity   fix      2.5e-03
    Buf-         total   1.0e-2
    SO4-2        fix      1.0e-04
  end_solution 2
 End of solutions
End of reactions
Calculation
   MT3
   reactions  1
   ignore          ! define species not considered in the solutions
      Siderite  FeSppt Mackinawite
      CO2(g) O2(g)  H2(g)  H2S(g) CH4(g)  CO2(g) O2(g) H2(g) CH4(g)
      Melanterite  Hematite  Goethite  Fe(OH)3(a) Fe2O3 Hematite Goethite

End_Calculation
Output
   profile
       species
          O2 Lactate- pH HCO3- Fe+2 FeOOH  CH4 H2 SO4-2 HS- FeS
End output
```

Figure 6.5 shows the results from a similar simulation, except in this simulation the initial pH was 7.5 instead of 6.5. Comparison of Figures 6.4 and 6.5 shows that significantly less FeOOH is reduced at the higher pH. This decrease in the amount of FeOOH reduced occurs because the FeOOH reduction reaction is less favorable at higher pH values. As a consequence of the smaller extent of FeOOH consumption, less FeS forms and more CH_4 forms.

The final simulation is a slight modification of the previous case. Sulfate was removed from the system and was replaced by UO_2^{+2}. In addition, it was assumed that UO_2^{+2} was sorbed to the sediment, although only a 1-site adsorption model was used. Finally, it was assumed that excess calcite was present in the simulations. The simulation results are shown in Figure 6.6. The results are generally comparable to Figure 6.5 for O_2, FeOOH, pH, and CH_4.

Figure 6.6 also illustrates that the some of the U(VI) that was present in solution and adsorbed on the sediment was reduced to U(IV) and precipitated as uraninite. The extent of this reduction was strongly impacted by adsorption. When no adsorption was considered, very small amounts of uraninite were formed, because most of the dissolved U(VI) was displaced by advection, and there was minimal mixing and reaction between the reduced and oxidized water.

The results presented in this section as well as in Sections 4 and 5 demonstrate that RATEQ is a very useful tool for simulating complex geochemical systems. RATEQ is based on the widely used groundwater flow model MODFLOW-2000 and on the numerically stable TVD algorithm in MT3DMS. Thus, RATEQ should have applicability to many geochemical scenarios in the groundwater environment.

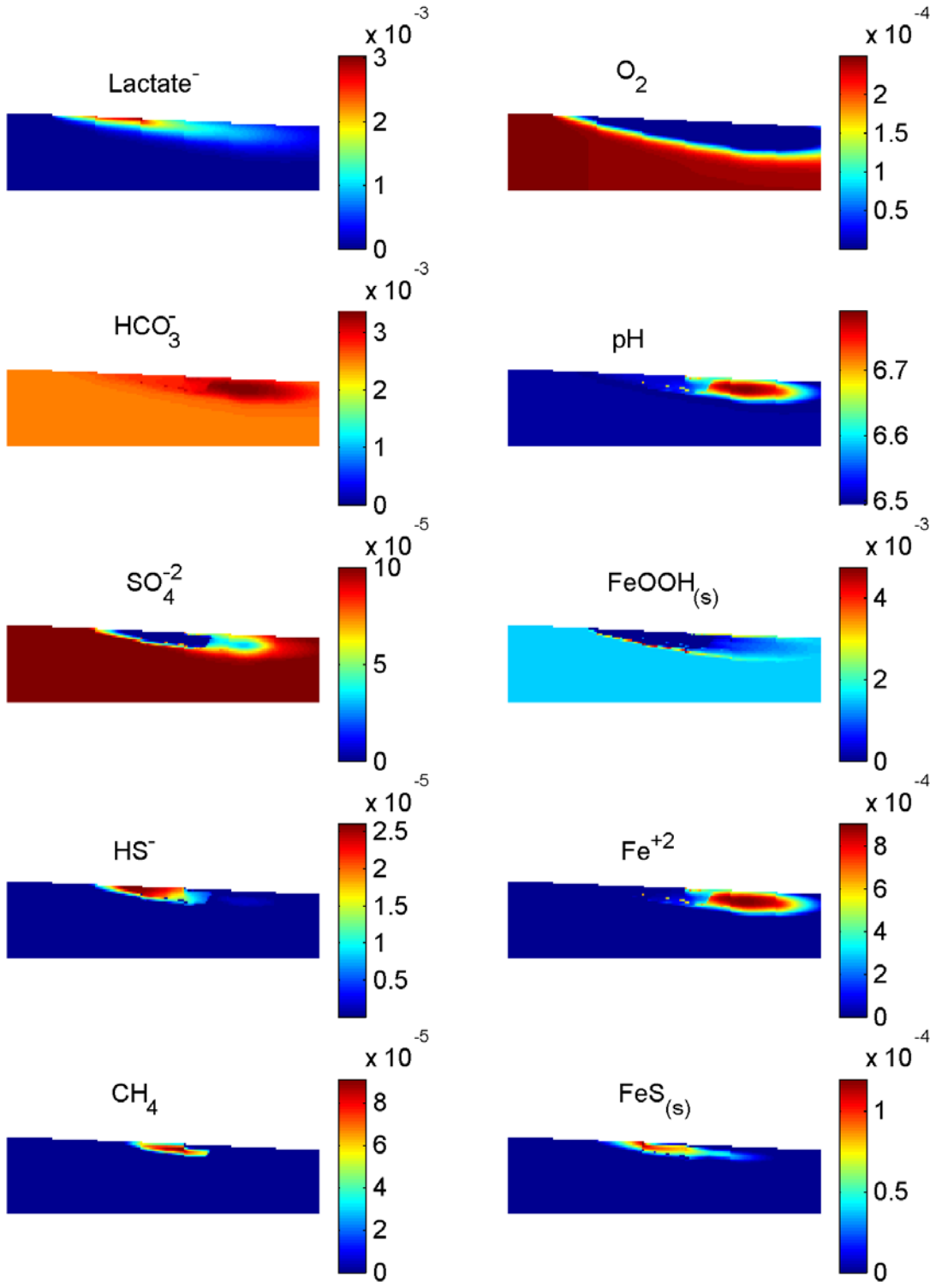

Figure 6.4. Two-dimensional biogeochemical simulation results for oxidation of lactate by multiple terminal electron acceptors at pH 6.5. The concentrations in each plot are given in units of M except pH.

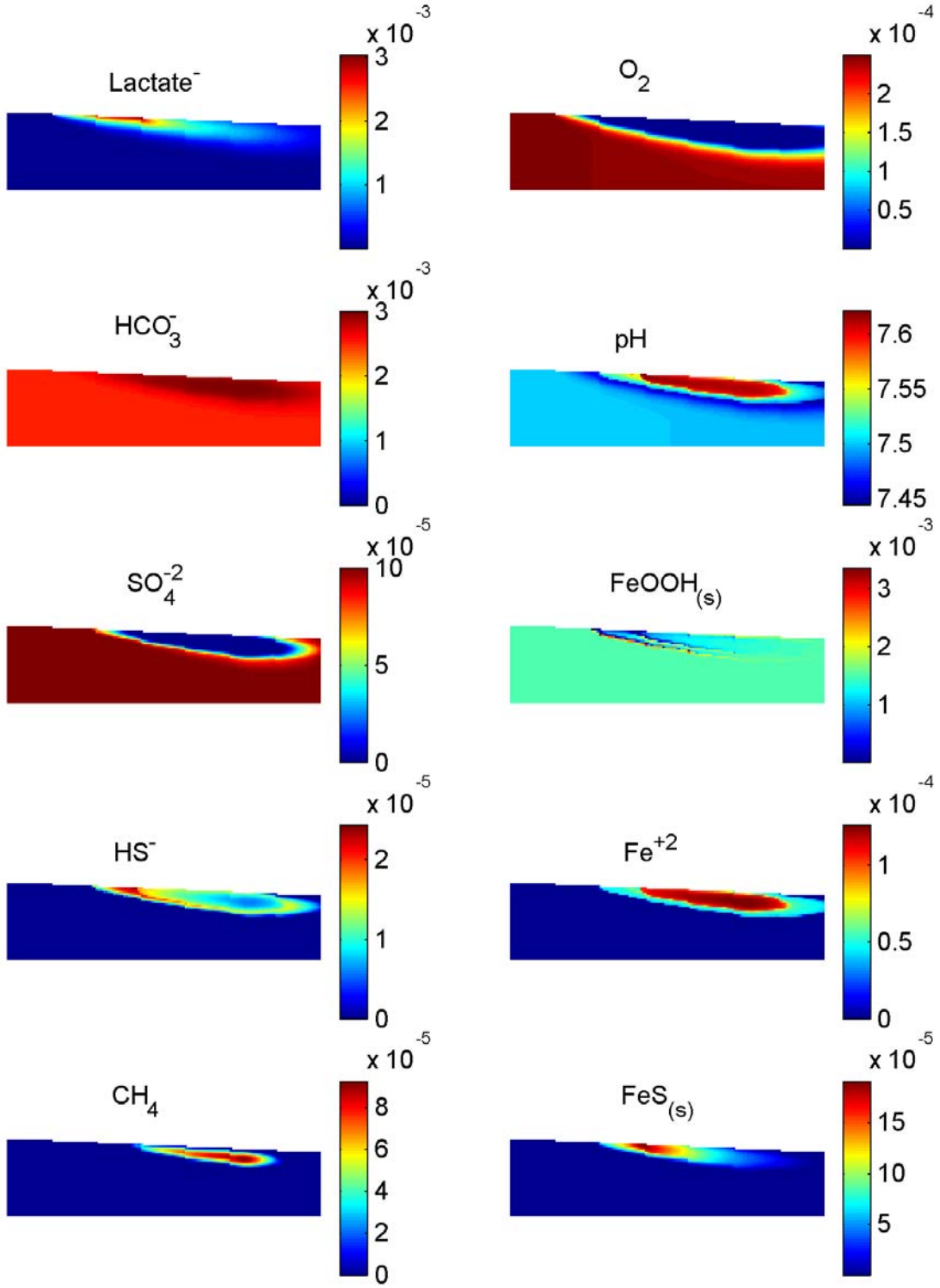

Figure 6.5. Two-dimensional biogeochemical simulation results for oxidation of lactate by multiple terminal electron acceptors at pH 7.5. The concentrations in each plot are given in units of M except pH.

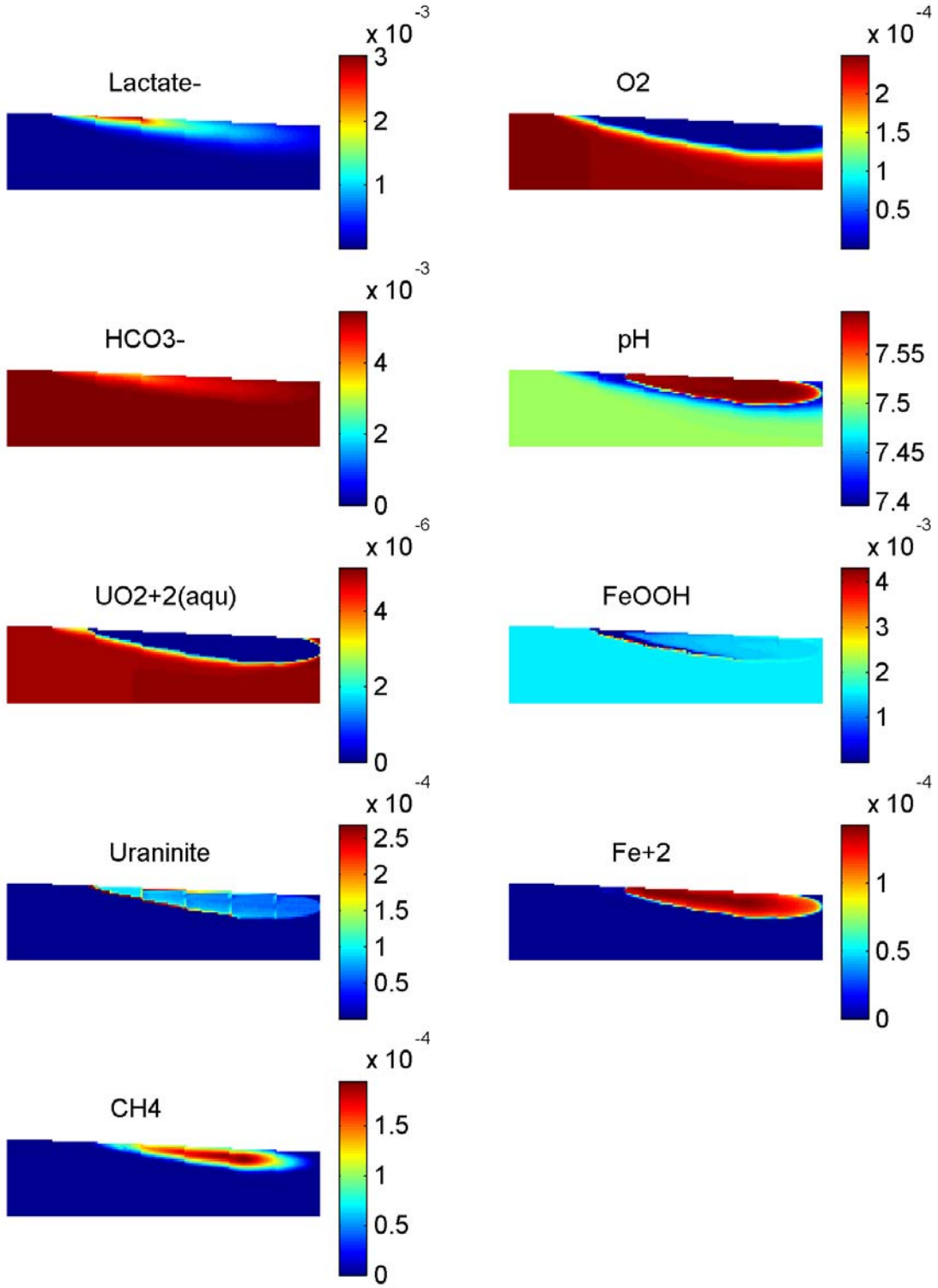

Figure 6.6. Two-dimensional biogeochemical simulation results for oxidation of lactate by multiple terminal electron acceptors, including U(VI), at pH 7.5. The concentrations in each plot are given in units of M except pH.

Appendix 1. Transformation of the Reactive Transport Equations

The reactive transport equations for all of the species in geochemical system can be represented as

$$\frac{\partial}{\partial t}\left(\theta_m \vec{C}_m + \theta_{im}\vec{C}_{im}\right) = L'\left(\vec{C}\right) + \nu_c^T \vec{R} \qquad (2\text{-}17)$$

where

$$L' = \left(\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_m^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(\theta v_i C_m^k\right) + q_s C_s^k\right)$$

as described in equation 2-8. This equation can also be written as

$$[I]\frac{\partial}{\partial t}\left(\theta_m \vec{C}_m + \theta_{im}\vec{C}_{im}\right) = \begin{bmatrix} I_m & 0 \\ 0 & 0 \end{bmatrix} L'\left(\vec{C}\right) + \nu_c^T \vec{R}$$

where,

I is the identity matrix of size N_{TOT},

I_m is the identity matrix of size N_M,

ν is matrix of stoichiometric coefficients of size N_{TOT} x N_R,

R is a vector of chemical reaction rates (MT^{-1}) of size N_R,

N_{TOT} is the total number of species,

N_M is the number of mobile species, and

N_R is the number of geochemical reactions.

In RATEQ, the equations are transformed by performing a gauss Jordan elimination of the matrix of stoichiometric coefficients, ν. Because the equation above is actually a set of equations, the same operations applied to ν must also be applied to $[I]$ and $\begin{bmatrix} I_m & 0 \\ 0 & 0 \end{bmatrix}$. The transformations are not unique and depend on the order of variables in the ν matrix. In RATEQ, the master species are used as basis species. This produces mass balance constraints for the master species. As a result of the linear transformation, the coefficients for the reaction rate R has the form $\begin{bmatrix} I_{Nr} \\ 0 \end{bmatrix}$ where Nr is the number of reactions and I is the identity matrix. This approach is quite general and applies to all types of reactions. In addition, it is not necessary to strictly write all reactions in terms of the master species, and redox reactions do not necessarily need to be written in terms of the electron

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