ORNL/TM-13668

ornl

OAK RIDGE
NATIONAL
LABORATORY

LOCKHEED MARTIN

HYDROBIOGEOCHEM: A Coupled Model of Hydrologic Transport and Mixed BiogeocheMical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media

G.-T. Yeh
K. M. Salvage
J. P. Gwo
J. M. Zachara
J. E. Szecsody

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL-27 (3-96)

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-13668

Center for Computational Sciences

HYDROBIOGEOCHEM: A Coupled Model of **HYDRO**logic Transport and Mixed **BIOGEOCHEM**ical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media

G.-T. Yeh[1], K. M. Salvage[1], J. P. Gwo, J. M. Zachara[2], and J. E. Szecsody[3]

---

[1]Department of Civil and Environmental Engineering, Pennsylvania State University
[2]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory
[3]Environmental and Health Sciences Division, Pacific Northwest National Laboratory

Center for Computational Sciences
Publication No. 0007

Date Published: July 1998

Prepared for the
U.S. Department of Energy
Office of Environmental Restoration and Waste Management
EX 20 10 30 2

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
Managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

CONTENTS

FIGURES

TABLES

Table | Page

ACRONYMS

CPU	Central Process Unit
FDM	Finite-Difference Method
FEM	Finite-Element Method
G-S	Gauss-Seidel iteration method
ICM	Integrated compartment method
IFDM	Integrated finite-difference method
L	Length
M	Mass
MOC	Method of Characteristics
SOR	Successive over-relaxation iteration method
SUR	Successive under-relaxation iteration method
T	time

ACKNOWLEDGMENTS

This work is funded by the Environmental Technology Partnership program of the US Department of Energy. This work is also partially supported by the ORNL Partnership in Computational Sciences (PICS) program, supported by the Department of Energy's Mathematical, Information, and Computational Sciences (MICS) Division of the Office of Computational and Technology Research. Implementation of the microbial kinetics and geochemical kinetics into this version of the HYDROGEOCHEM code was supported by The Department of Energy, Battelle Pacific Northwest Laboratory (Contract 41521224D). The present version reflects the many contributions made by a small army of colleagues. Dr. Hwai-Ping (Pearce) Cheng has provided the incorporation of multiple ion-exchange sites and multiple adsorbent components. Dr. Jing-Ru (Ruth) Cheng contributed also and performed significant debugging work on an early equilibrium version of the model.

ABSTRACT

The computer program HYDROBIOGEOCHEM is a coupled model of HYDROlogic transport and BIOGEOCHEMical kinetic and/or equilibrium reactions in saturated/unsaturated media. HYDROBIOGEOCHEM iteratively solves the two-dimensional transport equations and the ordinary differential and algebraic equations of mixed biogeochemical reactions. The transport equations are solved for all aqueous chemical components and kinetically controlled aqueous species.

HYDROBIOGEOCHEM is designed for generic application to reactive transport problems affected by both microbiological and geochemical reactions in subsurface media. Input to the program includes the geometry of the system, the spatial distribution of finite elements and nodes, the properties of the media, the potential chemical and microbial reactions, and the initial and boundary conditions. Output includes the spatial distribution of chemical and microbial concentrations as a function of time and space, and the chemical speciation at user-specified nodes.

1.0 INTRODUCTION

This document is the users' guide for the Coupled Model of **HYDRO**logic Transport and Mixed **BIOGEOCHEM**ical Reactions in Saturated-Unsaturated Media (HYDROBIOGEOCHEM). This code is a modification of HYDROGEOCHEM2.0 (Yeh and Salvage, 1995), a general purpose computer program written in FORTRAN 77 which is designed to solve coupled hydrologic transport and mixed kinetic and equilibrium geochemical reaction problems. The modification includes replacement of the KEMOD chemical reaction subroutines by a mixed microBIOlogical and chemical Kinetic and Equilibrium MODel (BIOKEMOD) to deal with species whose concentrations are affected by microbiological and/or geochemical reactions.

This document is intended to assist modelers in using this code for site-specific applications.

- Chapter 2.0 derives the governing equations and initial and boundary conditions solved by HYDROBIOGEOCHEM.
- Chapter 3.0 details the numerical method used in solving the equations for transport and for mixed biogeochemical kinetic and equilibrium reactions.
- Chapter 4.0 describes the program structure of HYDROBIOGEOCHEM. It is intended to assist users in modifying or extending the code to better meet their needs.
- Chapter 5.0 describes the program's storage and memory requirements and relates it via the parameter statements to the problem size (the finite-element grid size as well as the number of chemical and microbial species). The chapter also describes the input-output format and specifications of HYDROBIOGEOCHEM.
- Chapter 6.0 provides sample problems demonstrating use of the program.
- Appendix A contains a complete description of all the problem-specific input necessary for running a simulation.
- APPENDIX B contains example problem input and output files on floppy disk.
- APPENDIX C contains FORTRAN 77 Source Program on floppy disk.

The program must be run with a consistent set of units. Units of mass (M), length (L), and time (T) are indicated in the input description in Appendix A. The unit of length should be decimeter (dm). The unit of mass for any chemical species should be mole and for any other parameter should be kilogram (kg). The concentration unit of all individual species (aqueous, sorbed, and precipitated species) is mole/mass of phase (mol/kg); the corresponding unit for the sorption distribution coefficient is dm^3/kg (= ml/g). The ion-exchange capacity is in equivalents/mass of solid. The units of concentration for total concentrations of components is mole/unit total volume (mol/dm^3). Any units of time may be used as long as the same unit is used consistently throughout the input file.

HYDROBIOGEOCHEM is a flexible and comprehensive package. It is designed to:

- Treat heterogeneous and anisotropic media.
- Consider spatially and temporally distributed sources/sinks as well as point sources/sinks.
- Accept the prescribed initial conditions or obtain initial conditions by simulating the steady-state version of the system under consideration.
- Deal with prescribed transient concentrations distributed over a Dirichlet boundary.
- Handle time-dependent fluxes over variable boundaries.
- Include the off-diagonal dispersion coefficient tensor components in the governing equation for dealing with cases in which the coordinate system does not coincide with the principal directions of the dispersion coefficient tensor.
- Provide two options for treating the mass matrix (consistent and lumping).
- Give three options for estimating the nonlinear matrix (exact relaxation, under-relaxation, and over-relaxation).
- Include six options for solving the linearized matrix equations (direct solution with Gaussian elimination method, successive point iterations, and four preconditioned conjugate gradient methods).
- Include both quadrilateral and triangular elements to facilitate the discretization of the region.
- Include chemical processes of aqueous complexation, precipitation/dissolution, adsorption, ion-exchange, redox, and acid-base reactions.
- Handle multiple adsorption sites and multiple ion-exchange sites.
- Include colloid transport.
- Include microbial processes affecting chemical species concentrations as well as microbial growth and decay.

Limitations and Future Plans

There are some limitations in HYDROBIOGEOCHEM. Further development of the model to address these limitations may be warranted. These include:

- Inability to simulate co-precipitation (solid solution).
- The need to import hydrologic variables of flow velocity, moisture content, and pressure head generated by a subsurface flow model.
- The assumption of isothermal conditions.
- Applications limited to two-dimensional problems.
- Applications limited to single-fluid phase flows.

2.0 MATHEMATICAL FORMULATION

Hydrologic variables, including the Darcy's velocity, moisture content, and pressure head, are necessary in determining the transport of solutes through saturated-unsaturated subsurface systems. These hydrological variables can be specified by the user as described in the User's Guide (Data Set 16 in Appendix A) or a numerical model can be used to solve the saturated-unsaturated flow problem prior to simulation of solute transport with the HYDROBIOGEOCHEM code. A finite-element model has been constructed to achieve this purpose (Yeh, 1987). The relevant governing equations for saturated-unsaturated flow problems are briefly stated below.

2.1 Flow Equations

The derivation of the governing equations for flow through saturated-unsaturated media can be derived based on (Yeh and Ward, 1980; Yeh, 1987):

- Continuity of fluid.
- Continuity of solid.
- Motion of fluid (Darcy's law).
- Consolidation of the media.
- Compressibility of water.

Neglecting the compressibility of the media and water, we can write these equations as

$$\frac{\partial \rho_\ell \theta}{\partial t} = -\nabla \cdot (\rho_\ell \theta \mathbf{V}_{fs}) + \rho^* Q \ , \tag{2.1.1}$$

$$\theta \mathbf{V}_{fs} = -\mathbf{K} \cdot \left(\frac{\rho_0}{\rho_\ell} \nabla h + \nabla z \right) \ , \tag{2.1.2}$$

where

$$\mathbf{V}_f = \mathbf{V}_{fs} + \mathbf{V}_s \ , \tag{2.1.3}$$

$$\mathbf{V} = \theta (\mathbf{V}_f - \mathbf{V}_s) = \theta \, \mathbf{V}_{fs} \ . \tag{2.1.4}$$

where

θ = moisture content (L^3/L^3).

ρ_ℓ = density of the liquid phase (M of liquid/L^3 of liquid).

ρ_0 = reference density = density of pure water at STP (M of liquid/L^3 of liquid).

t = time (T).

$\mathbf{V}_{fs}$ = fluid velocity relative to the solid (L/T).

$\mathbf{V}_f$ = fluid velocity (L/T).

$\mathbf{V}_s$ = solid velocity (L/T).

$\mathbf{V}$ = Darcy's velocity (specific discharge) (L/T).

$\mathbf{K}$ = hydraulic conductivity tensor (L/T).

Q = source or sink representing the artificial injection or withdrawal of water, volume of water per volume of porous media per time $[(L^3/L^3)/T]$.

ρ^* = density of source/sink liquid, (M of liquid/L^3 of liquid)
= ρ_ℓ if sink or withdrawal (negative Q), or
= ρ_{in} if source or injection (positive Q).

h = pressure head (L).

z = potential head (L).

Equations **(2.1.1)** through **(2.1.4)** and the constitutive relationships among the pressure head, moisture content, and the hydraulic conductivity tensor, together with appropriate initial conditions and boundary conditions, can be used to compute the temporal-spatial distributions of the hydrological variables, including pressure head, total head, moisture content, and Darcy's velocity. Equations **(2.1.1)** through **(2.1.4)** are provided in this report because they are needed for deriving the advective form of the hydrological transport equations in the next section.

2.2 Hydrological Transport Equations

Two of the most frequently mentioned terms in chemical transport modeling are <u>components</u> and <u>species</u>. Definitions of these terms used in this document loosely follow those of Westall et al. (1976). Components are a set of linearly independent "basis" chemical entities through which every species can be uniquely represented as a linear combination. A component cannot be represented as a linear combination of components other than itself. For example, in a simple system containing water, carbon, and calcium, we can choose Ca^{2+}, CO_3^{2-}, and H^+ as the components, and all other species can be considered the products of these three chemical components: Ca^{2+} cannot be represented as a product of CO_3^{2-} and H^+, CO_3^{2-} cannot be represented as a combination of Ca^{2+} and H^+, and H^+ cannot be represented as a product of Ca^{2+} and CO_3^{2-}. In addition, we require that the global mass of a component be chemical reaction invariant (Rubin, 1983). A chemical species is the product of a chemical reaction involving the components as reactants (Westall et al., 1976). For example, in the above simple system the species HCO_3^- is the product of H^+ and CO_3^{2-}.

Let us consider a system of N chemical components and M_B microbial species. In HYDROBIOGEOCHEM, the N chemical components include N_a aqueous components (mobile components), N_s adsorbent components (immobile adsorbent sites), and NSITE immobile ion-exchange sites. The N_a aqueous components will react with each other to form M_x aqueous complexed species and M_p precipitated species. In addition, each aqueous component has a species that is not bound with other components. This "free" species is termed the aqueous component species. The total number of aqueous species, M_c, is the sum of N_a aqueous component species and M_x complexed species. The N_a aqueous components and N_s adsorbent components will react to form M_y adsorbed species for the case of sorption via surface complexation (adsorption). Each adsorbent component has a species that is not bound with other components. This "free" species is termed the adsorbent component species. In addition, M_z of N_a aqueous component species and M_x complexed species may compete with each other for the ion-exchange sites. The total number of sorbent species, M_s, is the sum of N_s adsorbent component species, M_y adsorbed species, and M_z ion-exchanged species. The total number of chemical species, M, is equal to the sum of M_c, M_s, and M_p. For the purpose of deriving the chemical transport equations, we assume that the aqueous component species and complexed species are subject to hydrological transport, whereas the precipitated species, adsorbent component species, adsorbed species, and ion-exchanged species are not subject to hydrological transport. Table 2.1 summarizes the relations among chemical components and species considered in HYDROBIOGEOCHEM.

Microorganisms can exist in both the aqueous and adsorbed phases. The M_B microbial species consist of M_b aqueous phase species and M_a adsorbed phase species. We assume that the aqueous microbial species are subject to hydrological transport, whereas the adsorbed microbial species are not subject to hydrological transport. A phase transfer reaction may be specified, allowing for the simulation of the attachment and detachment of microorganisms from the porous media. In HYDROBIOGEOCHEM, the term "microbial species" may refer to either an individual type of organism or a consortia of organisms. The parameters chosen to describe the microbiological reactions must be specified accordingly.

The general transport equation governing the temporal-spatial distribution of any chemical species in a multicomponent system can be derived on the basis of the principle of balance of mass. Let c_j be the concentration of the j-th aqueous component species. The governing equation for c_j can be obtained by applying this principle in integral form as follows:

$$\frac{D}{Dt}\int_{v}\theta\rho_{\ell}c_j\,dv = -\int_{\Gamma}\mathbf{n}\cdot(\theta\rho_{\ell}c_j)\mathbf{V}_{\mathbf{fs}}d\Gamma - \int_{\Gamma}\mathbf{n}\cdot\mathbf{J}_j\,d\Gamma + \int_{v}\theta\rho_{\ell}r_j{}^{c}\,dv - \int_{v}\theta\rho_{\ell}\imath_j^{c}\,dv + \int_{v}m_j{}^{c}\,dv \quad , \quad j\in N_a \quad , \tag{2.2.1}$$

where

v = material volume containing constant amount of media (L^3).

c_j = concentration of the j-th aqueous component species (M/M of liquid).

Γ = surface enclosing the material volume v (L^2).

$\mathbf{n}$ = outward unit vector normal to the surface Γ.

$\mathbf{J}_j$ = $\rho_\ell\,\theta\,c_j\,(\mathbf{V}_j - \mathbf{V}_f)$ is the surface flux of the j-th aqueous component species with respect to fluid velocity $\mathbf{V}_f$ [(M/T)/L^2].

r_j^c = production rate of the j-th aqueous component species per unit fluid mass due to all chemical and microbial reactions [(M/M of liquid)/T)].

Table 2.1 Chemical Components and Species Considered in HYDROBIOGEOCHEM

			Components										
			Aqueous						Adsorbed				Charge
Concentrations			1	2	...	j	...	N_a	1	2	... j	... N_s	ν
Aqueous Components	N_a	c_1	1	0	...	0	...	0	0	0	... 0	... 0	ν_1^a
		c_2	0	1	...	0	...	0	0	0	... 0	... 0	ν_2^a
		.											
		c_j	0	0	...	1	...	0	0	0	... 0	... 0	ν_j^a
		.											
		C_{N_a}	0	0	...	0	...	1	0	0	... 0	... 0	$\nu_{N_a}^a$
Absorbent Components	N_s	s_1	0	0	...	0	...	0	1	0	... 0	... 0	ν_2^s
		s_2	0	0	...	0	...	0	0	1	... 0	... 0	ν_1^s
		.											
		s_j	0	0	...	0	...	0	0	0	... 1	... 0	ν_j^s
		.											
		S_{N_s}	0	0	...	0	...	0	0	0	... 0	... 1	$\nu_{N_s}^s$
Complexed Species	M_x	x_1	a_{11}^x	a_{12}^x	...	a_{1j}^x	...	$a_{1N_a}^x$	0	0	... 0	... 0	ν_1^x
		x_2	a_{21}^x	a_{22}^x	...	a_{2j}^x	...	$a_{2N_a}^x$	0	0	... 0	... 0	ν_2^x
		.											
		x_i	a_{i1}^x	a_{i2}^x	...	a_{ij}^x	...	$a_{iN_a}^x$	0	0	... 0	... 0	ν_i^x
		.											
		x_{M_x}	$a_{M_x1}^x$	$a_{M_x2}^x$	...	$a_{M_xj}^x$	...	$a_{M_xN_a}^x$	0	0	... 0	... 0	$\nu_{M_x}^x$

			Components												
			Aqueous						Adsorbed						Charge
Concentrations			1	2	...	j	...	N_a	1	2	...	j	...	N_s	ν
Adsorbed Species		y_1	a_{11}^y	a_{12}^y	...	a_{1j}^y	...	$a_{1N_a}^y$	$a_{1(Na+1)}^y$	$a_{1(Na+2)}^y$	...	$a_{1(Na+j)}^y$	...	$a_{1(Na+Ns)}^y$	ν_1^y
		y_2	a_{21}^y	a_{22}^y	...	a_{2j}^y	...	$a_{2N_a}^y$	$a_{2(Na+1)}^y$	$a_{2(Na+2)}^y$	...	$a_{2(Na+j)}^y$	...	$a_{2(Na+Ns)}^y$	ν_2^y
		.													
	M_y	y_i	a_{i1}^y	a_{i2}^y	...	a_{ij}^y	...	$a_{iN_a}^y$	$a_{i(Na+1)}^y$	$a_{i(Na+2)}^y$	...	$a_{i(Na+j)}^y$	...	$a_{i(Na+Ns)}^y$	ν_i^y
		.													
		Y_{M_y}	$a_{M_y1}^y$	$a_{M_y2}^y$	...	$a_{M_yj}^y$	...	$a_{M_yN_a}^y$	$a_{M_y(Na+1)}^y$	$a_{M_y(Na+2)}^y$	...	$a_{M_y(Na+j)}^y$	...	$a_{M_y(Na+Ns)}^y$	$\nu_{M_y}^y$
Ion-Exchange Species		z_1	a_{11}^z	a_{12}^z	...	a_{1j}^z	...	$a_{1N_a}^z$	0	0	...	0	...	0	ν_1^z
		z_2	a_{21}^z	a_{22}^z	...	a_{2j}^z	...	$a_{2N_a}^z$	0	0	...	0	...	0	ν_2^z
		.													
	M_z	z_i	a_{i1}^z	a_{i2}^z	...	a_{ij}^z	...	$a_{iN_a}^z$	0	0	...	0	...	0	ν_i^z
		.													
		Z_{M_z}	$a_{M_z1}^z$	$a_{M_z2}^z$	...	$a_{M_zj}^z$	...	$a_{M_zN_a}^z$	0	0	...	0	...	0	$\nu_{M_z}^z$
Precipitated Species		p_1	a_{11}^p	a_{12}^p	...	a_{1j}^p	...	$a_{1N_a}^p$	0	0	...	0	...	0	ν_1^p
		p_2	a_{21}^p	a_{22}^p	...	a_{2j}^p	...	$a_{2N_a}^p$	0	0	...	0	...	0	ν_2^p
		.													
	M_p	p_i	a_{i1}^p	a_{i2}^p	...	a_{ij}^p	...	$a_{iN_a}^p$	0	0	...	0	...	0	ν_i^p
		.													
		P_{M_p}	$a_{M_p1}^p$	$a_{M_p2}^p$	...	$a_{M_pj}^p$	...	$a_{M_pN_a}^p$	0	0	...	0	...	0	$\nu_{M_p}^p$
Total Concentrations			T_1	T_2		T_j	...	T_{N_a}	W_1	W_2	...	W_j		W_{N_s}	

ι_j^c = rate of decay of the j-th aqueous component species [(M/M of liquid)/T].

m_j^c = external source/sink rate of the j-th aqueous component species per unit volume of media [(M/L^3)/T].

N_a = number of aqueous component species.

By the Reynolds transport theorem (Owczarek, 1964), Equation **(2.2.1)** can be written as

$$\int_v \frac{\partial \theta\rho_\ell c_j}{\partial t}\, dv + \int_\Gamma \mathbf{n}\cdot(\theta\rho_\ell c_j \mathbf{V}_f)\, d\Gamma + \int_\Gamma \mathbf{n}\cdot \mathbf{J}_j\, d\Gamma = \int_v \theta\rho_\ell r_j^c\, dv - \int_v \theta\rho_\ell \iota_j^c\, dv + \int_v m_j^c\, dv \;, \quad j \in N_a \tag{2.2.2}$$

Applying the Gaussian divergence theorem to Equation **(2.2.2)** and using the fact that v is arbitrary, one can obtain the following continuity equation for the j-th aqueous component species:

$$\frac{\partial \theta\rho_\ell c_j}{\partial t} + \nabla\cdot(\theta\rho_\ell c_j \mathbf{V}_f) + \nabla\cdot\mathbf{J}_j = \theta\rho_\ell(r_j^c - \iota_j^c) + m_j^c \;, \quad j \in N_a \;. \tag{2.2.3}$$

The surface flux $\mathbf{J}_j$ has been postulated to be proportional to the gradient of c_j as (Nguyen et al., 1982)

$$\mathbf{J}_j = -\rho_\ell\theta\mathbf{D}\cdot\nabla c_j \;, \quad j \in N_a \tag{2.2.4}$$

and

$$\theta\mathbf{D} = a_T|\mathbf{V}|\delta + (a_L - a_T)\,\mathbf{V}\mathbf{V}/|\mathbf{V}| + a_m\theta\tau\delta \;, \tag{2.2.5}$$

where

a_T = transverse diffusivity (L).
δ = Kronecker delta tensor.
$|\mathbf{V}|$ = magnitude of the Darcy velocity $\mathbf{V}$ (L/T).
a_L = longitudinal diffusivity (L).
a_m = molecular diffusion coefficient (L^2/T).
τ = tortuosity.
$\mathbf{D}$ = dispersion coefficient tensor, (L^2/T)

Substitution of Equations **(2.1.3)**, **(2.2.4)**, and **(2.2.5)** into Equation **(2.2.3)** and assuming vertical deformation only yields

$$\frac{\partial \rho_\ell \theta c_j}{\partial t} + \nabla \cdot (\rho_\ell \theta c_j \mathbf{V}_{\mathbf{fs}}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla c_j) = \rho_\ell \theta (r_j^c - \iota_j^c) - \rho_\ell \theta c_j \left(\alpha \frac{\partial p}{\partial t} \right) + m_j^c \qquad \textbf{(2.2.6)}$$

$$j \in N_a \quad .$$

where

α = compressibility of the media, (L T^2 /M).

p = pressure, (M/L T^2).

Equation **(2.2.6)** is simply the statement of mass balance over a differential volume. The first term represents the rate of mass accumulation, the second term represents the net rate of mass flux due to advection, the third term is the net mass flux due to dispersion and diffusion, the fourth term is the rate of mass production and reduction due to biogeochemical reactions and radioactive decay, the fifth term is the change in concentration due to compressibility of the media and the last term is for sources/sinks corresponding to artificial injection and/or withdrawal.

Since any aqueous complexed product species is subject to the same hydrological transport mechanism as the aqueous component species, its governing transport equation would be identical in form to Equation **(2.2.6)**. If we let x_i denote the concentration of the i-th aqueous complexed species, we have the following transport equation:

$$\frac{\partial \rho_\ell \theta x_i}{\partial t} + \nabla \cdot (\rho_\ell \theta x_i \mathbf{V}_{\mathbf{fs}}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla x_i) = \rho_\ell \theta (r_i^x - \iota_i^x) - \rho_\ell \theta x_i \left(\alpha \frac{\partial p}{\partial t} \right) + m_i^x \qquad \textbf{(2.2.7)}$$

$$i \in M_x \quad .$$

where

x_i = concentration of the i-th aqueous complexed species (M/M of liquid).

r_i^x = production rate of i-th complexed species per unit fluid mass due to all microbial and chemical reactions [(M/M of liquid)/T].

ι_i^x = rate of decay of the i-th complexed species per unit fluid mass [(M/M of liquid)/T].

m_i^x = external source/sink rate of the i-th complexed species per unit medium volume $[(M/L^3)/T]$.

Similarly, microorganisms which exist in the aqueous phase are subject to the same hydrological transport mechanism as the aqueous chemical species. The governing transport equation for aqueous microbial species is therefore identical in form to Equation **(2.2.6)**. Letting b_i denote the concentration of the i-th aqueous microbial species, we have the following transport equation:

$$\frac{\partial \rho_\ell \theta b_i}{\partial t} + \nabla \cdot (\rho_\ell \theta b_i \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla b_i) = \rho_\ell \theta (r_i^{\,b} - \iota_i^b) - \rho_\ell \theta b_i \left(\alpha \frac{\partial p}{\partial t} \right) + m_i^{\,b} \qquad \textbf{(2.2.8)}$$

$$i \in M_b \quad .$$

where

b_i = concentration of the j-th aqueous microbial species (M/M of liquid).

r_i^b = production rate of i-th aqueous microbial species per unit fluid mass due to all microbial reactions [(M/M of liquid)/T].

ι_i^b = rate of decay of the i-th microbial species per unit fluid mass [(M/M of liquid)/T].

m_i^b = external source/sink rate of the i-th microbial species per unit medium volume $[(M/L^3)/T]$.

Because it is assumed that adsorbent component species are not subject to hydrological transport, their transport equations (or more precisely the mass balance equations for these species) can be obtained by dropping the second and third terms on the left-hand side of Equation **(2.2.6)** and replacing $(\rho_\ell \theta c_j)$ with $(\rho_b s_j)$:

$$\frac{\partial \rho_b s_j}{\partial t} = \rho_b (r_j^{\,s} - \iota_j^s) - \left(\alpha \frac{\partial p}{\partial t} \right) \rho_b s_j + m_j^{\,s} \quad , \qquad j \in N_s \quad . \qquad \textbf{(2.2.9)}$$

where

ρ_b = bulk density of the porous medium, mass of solid per unit medium volume

(M of solid/L^3).

s_j = concentration of the j-th adsorbent component (M/M of solid).

r_j^s = production rate of the j-th adsorbent component species per unit solid mass due to all chemical and microbial reactions [(M/M of solid)/T].

m_j^s = external source/sink rate of the j-th adsorbent component species per unit medium volume [(M/L^3)/T].

ι_j^s = rate of decay of the j-th adsorbent component species per unit solid mass [(M/M of solid)/T].

Similarly, it is assumed that adsorbed chemical and microbial species, ion-exchanged species, and precipitated species are not subject to hydrological transport, so the mass balance equations for these species are identical in form to Equation **(2.2.9)**:

$$\frac{\partial \rho_b y_i}{\partial t} = \rho_b (r_i^y - \iota_i^y) - \left(\alpha \frac{\partial p}{\partial t} \right) \rho_b y_i + m_i^y \ , \qquad i \in M_y \ . \tag{2.2.10}$$

$$\frac{\partial \rho_b z_i}{\partial t} = \rho_b (r_i^z - \iota_i^z) - \left(\alpha \frac{\partial p}{\partial t} \right) \rho_b z_i + m_i^z \ , \qquad i \in M_z \ . \tag{2.2.11}$$

$$\frac{\partial \rho_b p_i}{\partial t} = \rho_b (r_i^p - \iota_i^p) - \left(\alpha \frac{\partial p}{\partial t} \right) \rho_b p_i + m_i^p \ , \qquad i \in M_p \ . \tag{2.2.12}$$

and

$$\frac{\partial \rho_b a_i}{\partial t} = \rho_b (r_i^a - \iota_i^a) - \left(\alpha \frac{\partial p}{\partial t} \right) \rho_b a_i + m_i^a \ , \qquad i \in M_a \ . \tag{2.2.13}$$

where

r_i^y = production rate of the i-th adsorbed species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

m_i^y = external source/sink rate of the i-th adsorbed species per unit medium volume [(M/L^3)/T].

ι_i^y = rate of decay of the i-th adsorbed species per unit mass of solid [(M/M of solid)/T].

r_i^z =production rate of the i-th ion-exchanged species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

m_i^z = external source/sink rate of the i-th ion-exchanged species per unit medium volume [(M/L^3)/T].

ι_i^z = rate of decay of the i-th ion-exchanged species per unit mass of solid [(M/M of solid)/T].

r_i^p = production rate of the i-th precipitated species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

m_i^p = external source/sink rate of the i-th precipitated species per unit medium volume [(M/L^3)/T].

ι_i^p = rate of decay of the i-th precipitated species per unit mass of solid [(M/M of solid)/T].

r_i^a = production rate of the i-th adsorbed microbial species per unit mass of solid due to all microbial reactions [(M/M of solid)/T].

m_i^a = external source/sink rate of the i-th adsorbed microbial species per unit medium volume [(M/L^3)/T].

ι_i^a = rate of decay of the i-th adsorbed microbial species per unit mass of solid [(M/M of solid)/T].

Equations **(2.2.6)** through **(2.2.13)** constitute eight sets of equations for eight sets of unknowns: c_j, x_i, b_i, s_j, y_i, z_i, p_i, and a_i. These equations form a closed system if the biogeochemical production rates r_j^c, r_i^x, r_i^b, r_j^s, r_i^y, r_i^z, r_i^p, and r_i^a are known functions of c_j, x_i, b_i, s_j, y_i, z_i, p_i, and a_i. The functional relationships can be postulated from the chemical and microbiological reactions.

Equations **(2.2.6)** through **(2.2.13)** can be further simplified regardless of whether the chemical reactions are in equilibrium or controlled by kinetics. The simplification is demonstrated in Section 2.2.1.

2.2.1 Transport of Aqueous Chemical Components

The chemical components are assumed to be in equilibrium with those chemical product species that are formed by relatively fast, reversible reactions. The chemical components can also be transformed into chemical product species by relatively slow or irreversible reactions. The first type of product species will be termed "equilibrium" product species and the second "kinetic" product species in this document. In HYDROBIOGEOCHEM, transport of the aqueous chemical components' free species and all equilibrium product species which contain that component are solved together. This total "equilibrium" concentration of each aqueous component is subjected to transport, and is allowed to re-equilibrate to determine the new concentrations of the equilibrium product species and free component species formed. Transport of the aqueous kinetic product species is solved separately. The reaction term couples changes in the total "equilibrium" concentration of the components with changes in the kinetic products species' concentrations.

Let a_{ij} denote the stoichiometric coefficient of the j-th chemical component in the i-th chemical product species. As identified previously, M_x, M_y, M_z, and M_p are the total number of aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Let K_x, K_y, K_z, and K_p denote the number of kinetic aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Then $(M_x - K_x)$, $(M_y - K_y)$, $(M_z - K_z)$, and $(M_p - K_p)$ are the number of equilibrium aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Multiplying Equation **(2.2.7)** by a_{ij} and summing over i from 1 to $(M_x - K_x)$, multiplying Equation **(2.2.10)** by a_{ij} and summing over i from 1 to $(M_y - K_y)$, multiplying Equation **(2.2.11)** by a_{ij} and summing over i from 1 to $(M_z - K_z)$, multiplying Equation **(2.2.12)** by a_{ij} and summing over i from 1 to $(M_p - K_p)$, and adding the results to Equation **(2.2.6)**, we obtain

$$\frac{\partial \rho_\ell \theta T'_j}{\partial t} + \nabla \cdot (\rho_\ell \theta C'_j \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla C'_j) = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell \theta T'_j \left(\alpha \frac{\partial p}{\partial t} \right) + M_j^c \qquad \textbf{(2.2.14)}$$

$$j \in N_a \quad .$$

in which

$$T'_j = \frac{T_j}{\rho_\ell \theta} \quad , \; j \in N_a \; , \tag{2.2.15}$$

$$T_j = \rho_\ell \theta \left(c_j + \sum_{i=1}^{(M_x - K_x)} a_{ij} x_i \right) + \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij} y_i + \sum_{i=1}^{(M_z - K_z)} a_{ij} z_i + \sum_{i=1}^{(M_p - K_p)} a_{ij} p_i \right) \; , \; j \in N_a \; , \tag{2.2.16}$$

$$C'_j = \frac{C_j}{\rho_\ell \theta} \quad , \; j \in N_a \; , \tag{2.2.17}$$

$$C_j = \rho_\ell \theta \left(c_j + \sum_{i=1}^{(M_x - K_x)} a_{ij} x_i \right) \; , \; j \in N_a \; , \tag{2.2.18}$$

$$\mathbb{R}_j^c = \rho_\ell \theta \left(r_j^{\,c} + \sum_{i=1}^{(M_x - K_x)} a_{ij} r_i^{\,x} \right) + \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^{\,y} + \sum_{i=1}^{(M_z - K_z)} a_{ij} r_i^{\,z} + \sum_{i=1}^{(M_p - K_p)} a_{ij} r_i^{\,P} \right) , \; j \in N_a , \tag{2.2.19}$$

$$\Lambda_j^c = \rho_\ell \theta \left(\iota_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ij} \iota_i^x \right) + \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij} \iota_i^y + \sum_{i=1}^{(M_z - K_z)} a_{ij} \iota_i^z + \sum_{i=1}^{(M_p - K_p)} a_{ij} \iota_i^P \right) , \; j \in N_a , \tag{2.2.20}$$

and

$$M_j^{\,c} = m_j^{\,c} + \sum_{i=1}^{(M_x - K_x)} a_{ij} m_i^{\,x} + \sum_{i=1}^{(M_y - K_y)} a_{ij} m_i^{\,y} + \sum_{i=1}^{(M_z - K_z)} a_{ij} m_i^{\,z} + \sum_{i=1}^{(M_p - K_p)} a_{ij} m_i^{\,P} \; , \; j \in N_a \; . \tag{2.2.21}$$

where

T_j = total equilibrium concentration of the j-th aqueous component, mass per unit medium volume (M/L^3).

T'_j = total equilibrium concentration of the j-th aqueous component, mass per mass of liquid (M/M of liquid).

C_j = total dissolved concentration of the j-th aqueous component (M/L^3).

C'_j = total dissolved concentration of the j-th aqueous component (M/M of liquid).

M_j^c = total rate of source/sink of the j-th aqueous component ($M/L^3/T$).

Λ_j^c = total decay rate of the j-th aqueous component ($M/L^3/T$).

$\mathbb{R}_j^c$ = total production/consumption of the j-th aqueous component due to all chemical and microbiological reactions ($M/L^3/T$).

Equation **(2.2.14)** is written in conservative form. It has been suggested that using the advective form is sometimes more appropriate, especially if the finite-element method is used to simulate the chemical transport equation (Huyakorn et al., 1985). More importantly, an advective form of transport equations allows one to use the mixed Lagrangian-Eulerian approach, which can better solve advection-dominant transport problems (Yeh et al., 1995). To derive an advective form of the transport equation, we expand the first and second terms of Equation **(2.2.14)** and use the definition of the Darcy velocity to obtain

$$\rho_\ell\theta\frac{\partial T'_j}{\partial t} + T'_j\frac{\partial \rho_\ell\theta}{\partial t} + \rho_\ell\mathbf{V}\,\nabla\cdot C'_j + C'_j\,\nabla\cdot(\rho_\ell\mathbf{V}) - \nabla\cdot(\rho_\ell\theta\mathbf{D}\cdot\nabla C'_j)$$
$$= \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell\theta T'_j\left(\alpha\frac{\partial p}{\partial t}\right) + M_j^c \qquad \textbf{(2.2.22)}$$
$$j \in N_a \quad .$$

Since it is preferable to use the total concentrations of the aqueous components as the primary dependent variables (Yeh and Tripathi, 1989), the terms involving the total dissolved concentration, C'_j will be expressed in terms of T'_j :

$$\rho_\ell\theta\frac{\partial T'_j}{\partial t} + T'_j\frac{\partial \rho_\ell\theta}{\partial t} + \rho_\ell\mathbf{V}\,\nabla\cdot\left(\frac{C'_j}{T'_j}T'_j\right) + \left(\frac{C'_j}{T'_j}T'_j\right)\nabla\cdot(\rho_\ell\mathbf{V})$$
$$- \nabla\cdot\left[\rho_\ell\theta\mathbf{D}\cdot\nabla\left(\frac{C'_j}{T'_j}T'_j\right)\right] = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell\theta T'_j\left(\alpha\frac{\partial p}{\partial t}\right) + M_j^c \qquad \textbf{(2.2.23)}$$
$$j \in N_a \quad .$$

This can be rearranged into a more convenient form for implementation in the numerical code by expanding the ∇ ({C/T} T) terms:

$$\rho_\ell\theta\frac{\partial T'_j}{\partial t} + T'_j\frac{\partial \rho_\ell\theta}{\partial t} + \rho_\ell\mathbf{V}\frac{C'_j}{T'_j}\,\nabla\cdot T'_j + \left(\rho_\ell\mathbf{V}\,\nabla\cdot\frac{C'_j}{T'_j}\right)T'_j + \left(\frac{C'_j}{T'_j}T'_j\right)\cdot\nabla\cdot(\rho_\ell\mathbf{V})$$
$$- \nabla\cdot\left[\rho_\ell\theta\,\mathbf{D}\,\frac{C'_j}{T'_j}\cdot\nabla T'_j\right] - \nabla\cdot\left[\left(\rho_\ell\theta\,\mathbf{D}\cdot\nabla\frac{C'_j}{T'_j}\right)T'_j\right] \qquad \textbf{(2.2.24)}$$
$$= \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell\theta T'_j\left(\alpha\frac{\partial p}{\partial t}\right) + M_j^c$$
$$j \in N_a \quad .$$

Separating the last term on the right hand side and combining similar terms:

$$\rho_\ell \theta \frac{\partial T'_j}{\partial t} + \left[\rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta\, \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right] \nabla \cdot T'_j - \nabla \cdot \left[\rho_\ell \theta\, \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right]$$

$$+ \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V}\, \nabla \cdot \frac{C'_j}{T'_j} + \frac{C'_j}{T'_j} \nabla \cdot (\rho_\ell \mathbf{V}) - \nabla \cdot \left(\rho_\ell \theta\, \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) + \rho_\ell \theta \left(\alpha \frac{\partial p}{\partial t} \right) \right] T'_j \qquad \textbf{(2.2.25)}$$

$$= \mathbb{R}^c_j - \Lambda^c_j + M^c_j$$

$$j \in N_a \quad .$$

Substituting the continuity equation for water flow, Equation **(2.1.1)**, Equation **(2.2.25)** can be expressed as:

$$\rho_\ell \theta \frac{\partial T'_j}{\partial t} + L(C'_j) + K\, T'_j + \rho^* Q \frac{C'_j}{T'_j} T'_j = \mathbb{R}^c_j + M^c_j \qquad \textbf{(2.2.26)}$$

$$j \in N_a \quad .$$

where $L(C'_j)$ and K are an advection-dispersion operator and first order rate term, respectively, given by

$$L(C'_j) = \left[\rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta\, \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right] \nabla \cdot T'_j - \nabla \cdot \left[\rho_\ell \theta\, \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right] \qquad \textbf{(2.2.27)}$$

and

$$K = \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C'_j}{T'_j} - \frac{C'_j}{T'_j} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) + \rho_\ell \theta \left(\alpha \frac{\partial p}{\partial t} \right) + \lambda^c_j \right] \qquad \textbf{(2.2.28)}$$

The decay term has been expressed as

$$\Lambda^c_j = \lambda^c_j\, T_j \quad , \quad j \in N_a \quad , \qquad \textbf{(2.2.29)}$$

where

λ^c_j = decay rate constant of the j-th aqueous component (1/T).

The source/sink term M_j^c can be defined by

$$M_j^{c} = \rho^{*} C_j^{*} Q \quad , \quad j \in N_a \tag{2.2.30}$$

where

C_j^{*} = concentration of the j-th aqueous component in the source/sink liquid, (M/M of liquid).
= $C_j^{\prime}$ if sink or withdrawal (negative Q), or
= C_{in}, input concentration , if source or injection (positive Q).

By the definition of C_j^{*}, the terms M_j^c and (ρ^{*} Q $C_j^{\prime}$) cancel each other for the case of sink (withdrawal). Thus, another advantage of using the advection form of the transport equation is that one does not need to include the sink in the equation.

Equation **(2.2.26)** can be simplified by separating the reaction term into the contributions from chemical and microbial reactions:

$$\mathbb{R}_j^{c} = R_j^{c(bio)} + R_j^{c(chem)} \quad , \text{ or}$$

$$\mathbb{R}_j^{c} = \rho_\ell \theta \left(r_j^{\,c}\,|^{bio} + \sum_{i=1}^{(M_x-K_x)} a_{ij} r_i^{\,x}\,|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} r_i^{\,y}\,|^{bio} + \sum_{i=1}^{(M_z-K_z)} a_{ij} r_i^{\,z}\,|^{bio} + \sum_{i=1}^{(M_p-K_p)} a_{ij} r_i^{\,p}\,|^{bio} \right) \tag{2.2.31}$$

$$+ \rho_\ell \theta \left(r_j^{\,c}\,|^{chem} + \sum_{i=1}^{(M_x-K_x)} a_{ij} r_i^{\,x}\,|^{chem} \right) + \rho_b \bigg(\sum_{i=1}^{(M_y-K_y)} a_{ij} r_i^{\,y}\,|^{chem} + \sum_{i=1}^{(M_z-K_z)} a_{ij} r_i^{\,z}\,|^{chem} + \sum_{i=1}^{(M_p-K_p)} a_{ij} r_i^{\,p}\,|^{che}$$

where

$R_j^{c\,(bio)}$ = production/consumption of the j-th aqueous component due to microbiological reactions (M/L^3/T).

$R_j^{c\,(chem)}$ = production/consumption of the j-th aqueous component due to chemical reactions (M/L^3/T).

and the superscripts " $|^{bio}$ " and " $|^{chem}$ " after the individual species reaction terms denotes "due to microbiological reactions" and "due to chemical reactions", respectively.

A chemical component must be chemical reaction invariant; the rate at which a component is consumed in chemical reactions is balanced by the rate at which chemical product species containing that component are produced. That is:

$$\rho_\ell \theta \left(r_j^c \Big|^{chem} + \sum_{i=1}^{M_x} a_{ij} r_i^x \Big|^{chem} \right) + \rho_b \left(\sum_{i=1}^{M_y} a_{ij} r_i^y \Big|^{chem} + \sum_{i=1}^{M_z} a_{ij} r_i^z \Big|^{chem} + \sum_{i=1}^{M_p} a_{ij} r_i^p \Big|^{chem} \right) = 0 \, , \qquad j \in N_a \tag{2.2.32}$$

Chemical component mass may not be conserved with respect to microbiological reactions. Separating the equilibrium and kinetic chemical product species and rearranging, Equation **(2.2.32)** becomes:

$$\begin{aligned} &\rho_\ell \theta \left(r_j^c \Big|^{chem} + \sum_{i=1}^{(M_x-K_x)} a_{ij} r_i^x \Big|^{chem} \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} r_i^y \Big|^{chem} + \sum_{i=1}^{(M_z-K_z)} a_{ij} r_i^z \Big|^{chem} + \sum_{i=1}^{(M_p-K_p)} a_{ij} r_i^p \Big|^{chem} \right) \\ &= - \rho_\ell \theta \sum_{i=1}^{K_x} a_{ij} r_i^x \Big|^{chem} - \rho_b \left(\sum_{i=1}^{K_y} a_{ij} r_i^y \Big|^{chem} + \sum_{i=1}^{K_z} a_{ij} r_i^z \Big|^{chem} + \sum_{i=1}^{K_p} a_{ij} r_i^p \Big|^{chem} \right) \end{aligned} \tag{2.2.33}$$

Equation **(2.2.26)** may therefore be rewritten as

$$\rho_\ell \theta \, \frac{\partial T'_j}{\partial t} + L(C'_j) + K \, T'_j + \rho^* Q \, \frac{C'_j}{T'_j} T'_j = R_j^c + M_j^c \qquad j \in N_a \ . \tag{2.2.34}$$

in which the reaction term is given by combining Equations **(2.2.19)**, **(2.2.31)**, and **(2.2.33)**:

$$\begin{aligned} R_j^c = &\ \rho_\ell \theta \left(r_j^c \Big|^{bio} + \sum_{i=1}^{(M_x-K_x)} a_{ij} r_i^x \Big|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} r_i^y \Big|^{bio} + \sum_{i=1}^{(M_z-K_z)} a_{ij} r_i^z \Big|^{bio} + \sum_{i=1}^{(M_p-K_p)} a_{ij} r_i^p \Big|^{bio} \right) \\ &- \rho_\ell \theta \sum_{i=1}^{(K_x)} a_{ij} r_i^x \Big|^{chem} - \rho_b \left(\sum_{i=1}^{(K_y)} a_{ij} r_i^y \Big|^{chem} + \sum_{i=1}^{(K_z)} a_{ij} r_i^z \Big|^{chem} + \sum_{i=1}^{(K_p)} a_{ij} r_i^p \Big|^{chem} \right) \end{aligned} \tag{2.2.35}$$

2.2.2 Mass Balance of Adsorbent Components

Similarly, we can derive the governing equations for the total equilibrium concentration of adsorbent components and the number of equivalents occupying the ion-exchange sites. Multiplying Equation **(2.2.10)** by a_{ij}, summing over i from 1 to M_y, and adding the results to Equation **(2.2.9)**, we obtain

$$\frac{\partial W_j}{\partial t} = R_j^s - \Lambda_j^s - \alpha \frac{\partial p}{\partial t} W_j + M_j^s \quad , \quad j \in N_s \quad , \tag{2.2.36}$$

in which

$$W_j = \rho_b \left(s_j + \sum_{i=1}^{M_y - K_y} a_{ij} y_i \right) \quad , \quad j \in N_s \quad , \tag{2.2.37}$$

$$M_j^s = m_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ij} m_i^y \quad , \quad j \in N_s \quad , \tag{2.2.38}$$

$$\Lambda_j^s = \rho_b \left(\iota_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ij} \iota_i^y \right) \quad , \quad j \in N_s \quad , \tag{2.2.39}$$

and

$$R_j^s = \rho_b \left(r_j^s \Big|^{bio} + \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^y \Big|^{bio} \right) - \rho_b \sum_{i=1}^{K_y} a_{ij} r_i^y \Big|^{chem} \quad , \quad j \in N_s \quad , \tag{2.2.40}$$

where

W_j = total equilibrium concentration of the j-th adsorbent component (M/L^3).

M_j^s = total rate of source/sink of the j-th adsorbent component ($M/L^3/T$).

Λ_j^s = total decay rate of the j-th adsorbent component ($M/L^3/T$).

$R_j^{s\,(bio)}$ = production/consumption of the j-th adsorbent component due to chemical and microbiological reactions ($M/L^3/T$).

The relationship that results from the requirement that adsorption be chemical reaction-invariant with respect to any adsorbent component has been used in deriving Equation **(2.2.36)**:

$$R_j^{s(chem)} = \rho_b \left(r_j^s \Big|^{chem} + \sum_{i=1}^{M_y} a_{ij} r_i^y \Big|^{chem} \right) = 0 \quad , \quad j \in N_s \quad , \tag{2.2.41}$$

where

$R_j^{s\,(chem)}$ = production/consumption of the j-th adsorbent component due to chemical reactions ($M/L^3/T$).

In addition, the source/sink term M_j^s is assumed to be zero:

$$M_j^s = 0 \quad , \quad j \in N_s \quad . \tag{2.2.42}$$

The decay term Λ_j^s can be defined as

$$\Lambda_j^s = \lambda_j^s W_j \quad , \quad j \in N_s \quad , \tag{2.2.43}$$

where

λ_j^s = decay rate constant of the j-th adsorbent component (1/T).

Equation **(2.2.36)** can therefore be restated as:

$$\frac{\partial W_j}{\partial t} = R_j^s - \left(\lambda_j^s + \alpha \frac{\partial p}{\partial t} \right) W_j \quad , \quad j \in N_s \tag{2.2.44}$$

2.2.3 Mass Balance of Ion-Exchange Sites

The governing equations for the ion-exchange sites are obtained similarly but with the exception that we have assumed that there are no free ion-exchange sites (i.e., the sites are completely occupied). Multiplying Equation **(2.2.11)** by ν_k and summing over k from (NOMZJ(i)+1) to (NOMZJ(i)+NOMZI(i)), we obtain

$$\frac{\partial N_{eqi}}{\partial t} = R_{eqi}^{(bio)} - \Lambda_{eqi} - \alpha \frac{\partial p}{\partial t} N_{eqi} + M_{eqi} \quad , \quad i \in NSITE \tag{2.2.45}$$

in which

$$N_{eqi} = \rho_b \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k \quad , \quad i \in NSITE \tag{2.2.46}$$

$$M_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k m_k^z \quad , \quad i \in NSITE \tag{2.2.47}$$

$$\Lambda_{eqi} = \rho_b \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k \iota_k^z \quad , \quad i \in NSITE \tag{2.2.48}$$

and

$$R_{eqi}^{(bio)} = \rho_b \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k r_k^z\big|^{bio} \quad , \quad i \in NSITE \tag{2.2.49}$$

where

ν_k = charge of the k-th ion exchanged species (equivalents/mol).

N_{eqi} = number of equivalents of the ion-exchange sites per liter of solution for the i-th site (equivalents/L^3).

M_{eqi} = total rate of source/sink of the ion-exchange site for the i-th site (equivalents/L^3/T).

Λ_{eqi} = total decay rate of the ion-exchange site for the i-th site (equivalents/L^3/T).

$R_{eqi}^{(bio)}$ = production/consumption of the ion-exchange site for the i-th site due to microbiological reactions (equivalents/L^3/T).

NSITE = number of ion-exchange sites.

NOMZI(i) = number of ion-exchanged species involved in the i-th ion-exchanged site.

NOMZJ(i) = number of ion-exchanged species involved in the first through (i-1)-th ion-exchanged site.

The following relationship that results from the requirement of invariability for the ion-exchange site in the absence of microbiological reactions and decay has been used in deriving Equation **(2.2.45)**:

$$R_{eqi}^{(chem)} = \rho_b \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k r_k^z\big|^{chem} = 0 \quad , \quad i \in NSITE \tag{2.2.50}$$

In addition, the source/sink term M_{eqi} is assumed to be zero; that is,

$$M_{eqi} = 0 \quad . \tag{2.2.51}$$

The decay term Λ_{eqi} can be defined as

$$\Lambda_{eqi} = \lambda_{eqi} N_{eqi} \quad , \tag{2.2.52}$$

where

λ_{eqi} = decay rate constant of the ion-exchange site (1/T).

Equation **(2.2.45)** can therefore be restated as

$$\frac{\partial N_{eqi}}{\partial t} = R_{eqi}^{(bio)} - \left(\lambda_{eqi} + \alpha \frac{\partial p}{\partial t} \right) N_{eqi} , \quad i \in NSITE \tag{2.2.53}$$

2.2.4 Summary of Governing Equations

The transport equations for the aqueous complexed species and the aqueous microbial species can also be expressed in advective form for numerical implementation. The derivation is analogous to that for the aqueous components, except that the dissolved and total concentrations for these species are always equal; ie. the term {C/T} always equals one and the gradient of {C/T} always equals zero in the definition of the advection-dispersion operator, L(!), and the first order term, K, defined by Equations **(2.2.27)** and **(2.2.28)**, respectively. Equations **(2.2.7)** and **(2.2.8)** are replaced by

$$\rho_\ell \theta \frac{\partial x_i}{\partial t} + L(x_i) + K\, x_i + \rho^* Q\, x_i = \rho_\ell \theta r_i^x + m_i^x \qquad i \in M_x . \tag{2.2.54}$$

$$\rho_\ell \theta \frac{\partial b_i}{\partial t} + L(b_i) + K\, b_i + \rho^* Q\, b_i = \rho_\ell \theta r_i^b + m_i^b \qquad i \in M_b . \tag{2.2.55}$$

Equations **(2.2.34)**, **(2.2.15)**, **(2.2.17)**, **(2.2.44)**, **(2.2.37)**, **(2.2.53)**, **(2.2.46)**, **(2.2.54)**, **(2.2.10)**, **(2.2.11)**, **(2.2.12)**, **(2.2.55)**, and **(2.2.13)** constitute ($3 \times N_a$, $2 \times N_s$, $2 \times$ NSITE, M_x, M_y, M_z, Mp, M_b, M_a) sets of equations defining ($3 \times N_a$, $2 \times N_s$, NSITE, M_x, M_y, M_z, Mp, M_b, M_a) sets of unknowns (T_j's, c_j's, C_j's, W_j's, s_j's, N_{eq}'s, x_i's, y_i's, z_i's, p_i's, b_i's, and a_i's). However, the formulation is not complete; the chemical and biological reaction rate terms in these equations (R_j^c, R_j^s, R_{eqi}, r_i^x, r_i^y, r_i^z, r_i^p, r_i^b, r_i^a) must be prescribed to complete the formulation. For coupled hydrological transport and biogeochemical reaction modeling in HYDROBIOGEOCHEM, a mixed chemical microbiological model is adopted to give the implicit functional relationships among T_j's, C_j's, c_j's, W_j's, N_{eq}'s, s_j's, x_i's, y_i's, z_i's, p_i's, b_i's, and a_i's as described in Sections 2.3 and 2.4.

2.2.5 Transport of Operational Electrons

Redox reactions are a class of chemical reactions involving a transfer of electrons. Hence, when redox reactions are present in a system, we must invoke the principle of conservation of electrons to ensure that all electrons donated by chemical species are accepted by another species. This is equivalent to the statement that oxidation numbers must be conserved in a chemical reaction.

In nonredox systems, the total concentrations of all components and the number of equivalents of the ion-exchange site must be known before one can calculate the concentrations of all species. In redox systems, the unknowns are not only the concentrations of all species but also include a redox parameter that describes the oxidation state of the system. To be consistent with the approach that uses concentrations or activities as unknowns, the "activity of electrons" designated by the symbol X_e is normally used as the redox parameter. Hence, in redox systems the total concentrations of all components, the number of equivalents of the ion-exchange site, and the total concentration of the "operational electrons" must be known before the concentrations of all species and the activity of electrons (or the pE value) can be computed (Walsh et al. 1984). Total concentrations of all components are determined by solving the transport equation, Equation **(2.2.34)**, for aqueous components and the mass balance equation, Equation **(2.2.44)**, for adsorbent components, respectively. The number of equivalents of the ion-exchange site is obtained by solving the mass balance equation, Equation **(2.2.53)**. A transport equation for operational electrons is needed to determine the total concentration of operational electrons. (Walsh et al. use the term "available electrons." We think the term "operational electrons" is more appropriate.)

Let

a^c_{je} = stoichiometric coefficient of the electron in the j-th aqueous component species;
a^x_{ie} = stoichiometric coefficient of the electron in the i-th complexed species;
a^s_{je} = stoichiometric coefficient of the electron in the j-th adsorbent component species;
a^y_{ie} = stoichiometric coefficient of the electron in the i-th adsorbed species;
a^z_{ie} = stoichiometric coefficient of the electron in the i-th ion-exchanged species;
a^p_{ie} = stoichiometric coefficient of the electron in the i-th precipitated species.

By multiplying Equation **(2.2.6)** by a^c_{je} and summing over j from 1 to N_a, multiplying Equation **(2.2.7)** by a^x_{ie} and summing over i from 1 to M_x, multiplying Equation **(2.2.9)** by a^s_{je} and summing over j from 1 to N_s, multiplying Equation **(2.2.10)** by a^y_{ie} and summing over i from 1 to M_y, multiplying Equation **(2.2.11)** by a^z_{ie} and summing over i from 1 to M_z, multiplying Equation **(2.2.12)** by a^p_{ie} and summing over i from 1 to M_p, adding the results, and invoking the principle of conservation of electrons, one obtains

$$\rho_\ell \theta \, \frac{\partial T'_e}{\partial t} + L(C'_e) + K\, T'_e + \rho^* Q\, C'_e = R_j^e + M_j^e \ . \tag{2.2.56}$$

which is identical in form to Equation **(2.2.34)** and describes the transport of operational electrons. However, the definitions of C_e, T_e, M_e, and Λ_e are slightly different from those of C_j, T_j, M_j^c, and Λ_j^c. The quantities C'_e, T'_e, C_e, T_e, M_e, and Λ_e are given by

$$T'_e = \frac{T_e}{\rho_\ell \theta} \tag{2.2.57}$$

$$T_e = \rho_\ell \theta \left(\sum_{j=1}^{N_a} a_{je}^c c_j + \sum_{i=1}^{(M_x-K_x)} a_{ie}^x x_i \right) + \rho_b \left(\sum_{i=1}^{(M_z-K_z)} a_{ie}^z z_i + \sum_{j=1}^{N_s} a_{je}^s s_j + \sum_{i=1}^{(M_y-K_y)} a_{ie}^y y_i + \sum_{i=1}^{(M_p-K_p)} a_{ie}^p p_i \right) \tag{2.2.58}$$

$$C'_e = \frac{C_e}{\rho_\ell \theta} \tag{2.2.59}$$

$$C_e = \rho_\ell \theta \left(\sum_{j=1}^{N_a} a_{je}^c c_j + \sum_{i=1}^{(M_x-K_x)} a_{ie}^x x_i \right) \ , \tag{2.2.60}$$

$$\begin{aligned} M_e = {} & \sum_{j=1}^{N_a} a_{je}^c \, m_j^c + \sum_{i=1}^{(M_x-K_x)} a_{ie}^x \, m_i^x + \sum_{i=1}^{(M_z-K_z)} a_{ie}^z \, m_i^z \\ & + \sum_{j=1}^{N_s} a_{je}^s \, m_j^s + \sum_{i=1}^{(M_y-K_y)} a_{ie}^y \, m_i^y + \sum_{i=1}^{(M_p-K_p)} a_{ie}^p \, m_i^p \ , \end{aligned} \tag{2.2.61}$$

$$\begin{aligned} \Lambda_e = {} & \rho_\ell \theta \left(\sum_{j=1}^{N_a} a_{je}^c \, \iota_j^c + \sum_{i=1}^{(M_x-K_x)} a_{ie}^x \, \iota_i^x \right) + \\ & \rho_b \left(\sum_{i=1}^{(M_z-K_z)} a_{ie}^z \, \iota_i^z + \sum_{j=1}^{N_s} a_{je}^s \, \iota_j^s + \sum_{i=1}^{(M_y-K_y)} a_{ie}^y \, \iota_i^y + \sum_{i=1}^{(M_p-K_p)} a_{ie}^p \, \iota_i^p \right) \ , \end{aligned} \tag{2.2.62}$$

and

$$R_e = \rho_\ell \theta \left(\sum_{j=1}^{N_a} a_{je}^{c} r_e^{c}\big|^{bio} + \sum_{i=1}^{(M_x-K_x)} a_{ie}^{x}\, r_i^{x}\big|^{bio} \right) +$$

$$\rho_b \left(\sum_{j=1}^{N_s} a_{je}^{s} r_e^{s}\big|^{bio} + \sum_{i=1}^{(M_y-K_y)} a_{ie}^{y}\, r_i^{y}\big|^{bio} + \sum_{i=1}^{(M_z-K_z)} a_{ie}^{z}\, r_i^{z}\big|^{bio} + \sum_{i=1}^{(M_p-K_p)} a_{ie}^{p}\, r_i^{p}\big|^{bio} \right) \qquad \textbf{(2.2.63)}$$

$$- \rho_\ell \theta \left(\sum_{i=1}^{K_x} a_{ie}^{x}\, r_i^{x}\big|^{chem} \right) - \rho_b \left(\sum_{i=1}^{K_y} a_{ie}^{y}\, r_i^{y}\big|^{chem} + \sum_{i=1}^{K_z} a_{ie}^{z}\, r_i^{z}\big|^{chem} + \sum_{i=1}^{K_p} a_{ie}^{p}\, r_i^{p}\big|^{chem} \right) \quad ,$$

where

C_e = concentration of operational electrons in aqueous phase (M/L^3) .
C'_e = concentration of operational electrons in aqueous phase (M/M).
T_e = total concentration of operational electrons (M/L^3) .
T'_e = total concentration of operational electrons (M/M).
M_e = external source/sink rate of the free electron species [(M/L^3)/T].
ι_e = rate of decay of the free electron species [(M/L^3)/T].
Λ_e = total rate of decay of the operational electron [(M/L^3)/T].
R_e = production/consumption of operational electrons due to chemical and microbiological reactions ($M/L^3/T$).

The above stoichiometric coefficients are given by

$$a_{je}^{c} = \sum_{k=1}^{N_e} h_{jk}^{c} \left(v_{mk} - v_{jk}^{c} \right) \quad , \quad j \in N_a \quad , \qquad \textbf{(2.2.64)}$$

$$a_{ie}^{x} = \sum_{k=1}^{N_e} h_{ik}^{x} \left(v_{mk} - v_{ik}^{x} \right) \quad , \quad i \in M_x \quad , \qquad \textbf{(2.2.65)}$$

$$a_{je}^{s} = \sum_{k=1}^{N_e} h_{jk}^{s} \left(v_{mk} - v_{jk}^{s} \right) \quad , \quad j \in N_s \quad , \qquad \textbf{(2.2.66)}$$

$$a_{ie}^{y} = \sum_{k=1}^{N_e} h_{ik}^{y} \left(v_{mk} - v_{ik}^{y} \right) \quad , \quad i \in M_y \quad , \qquad \textbf{(2.2.67)}$$

$$a_{ie}^{z} = \sum_{k=1}^{N_e} h_{ik}^{z} \left(v_{mk} - v_{ik}^{z} \right) 1 \quad , \quad i \in M_z \quad , \qquad \textbf{(2.2.68)}$$

and

$$a_{ie}^{p} = \sum_{k=1}^{N_e} h_{ik}^{p} \left(v_{mk} - v_{ik}^{p} \right) \quad , \quad i \in M_p \quad , \qquad \textbf{(2.2.69)}$$

where

h^c_{jk} = stoichiometric coefficient of the k-th chemical element in the j-th aqueous component species.

h^x_{ik} = stoichiometric coefficient of the k-th chemical element in the i-th complexed species.

h^s_{jk} = stoichiometric coefficient of the k-th chemical element in the j-th adsorbent component species.

h^y_{ik} = stoichiometric coefficient of the k-th chemical element in the i-th adsorbed species.

h^z_{ik} = stoichiometric coefficient of the k-th chemical element in the i-th ion-exchanged species.

h^p_{ik} = stoichiometric coefficient of the k-th chemical element in the i-th precipitated component species.

v^c_{jk} = valence of the k-th chemical element in the j-th aqueous component species.

v^x_{ik} = valence of the k-th chemical element in the i-th complexed species.

v^s_{jk} = valence of the k-th chemical element in the j-th adsorbent component species.

v^y_{ik} = valence of the k-th chemical element in the i-th adsorbed species.

v^z_{ik} = valence of the k-th chemical element in the i-th ion-exchanged species.

v^p_{ik} = valence of the k-th chemical element in the i-th precipitated species.

v_{mk} = valence of the k-th chemical element in its maximum oxidation state except for oxygen, in which $v_{mk} = -2$.

N_e = number of chemical elements considered in the system (Walsh et al. 1984).

If component species are chosen such that they contain only chemical elements in their maximum oxidation state, then the a^c_{je}'s and a^s_{je}'s are equal to zero, and Equations **(2.2.58)** through **(2.2.63)** have identical formulae to Equations **(2.2.15)** through **(2.2.21)**. Choosing such components is very useful for describing the computation of electron activity involving redox reactions because the operational electron can be considered computationally as an aqueous component. Nevertheless, even without such a choice the operational electron can still be considered an aqueous component, but with a possibility of having a negative total concentration of operational electrons.

2.2.6 Transport of Excess Protons

In a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the proton activity (or the pH value). The pH value may be simulated by using either the electroneutrality equation or proton condition. These two approaches are mathematically equivalent but not computationally equivalent. In coupling the hydrological transport and chemical reactions, it is preferable to use the proton-condition approach, in which the total concentration of the excess protons (H^+ - OH^-) must be known before activity of protons can be computed. Therefore, a transport equation for excess protons is needed to determine the total concentration of excess protons.

Applying the principle of conservation of mass to both oxygen and hydrogen yields two transport equations: one for hydrogen H and the other for oxygen O_2. Adding these two equations with appropriate multipliers produces a transport equation for hydroxide OH. Taking the difference of the transport equation for H and that for OH, one obtains (Miller 1983):

$$\rho_l \theta \frac{\partial T'_H}{\partial t} + L(C'_H) + K T'_H + \rho^* Q C'_H = R_j^H + M_j^H . \qquad \textbf{(2.2.70)}$$

which is identical in form to Equation **(2.2.34)** and which describes the transport of excess protons. The algebraic equations defining T_H, C_H, M_H, λ_H and R_H are identical in form to Equations **(2.2.14)** through **(2.2.19)**, with the subscript j replaced by the subscript H.

Because the simulation of pH and/or pe uses transport equations identical in form to Equation **(2.2.34)**, we can treat protons and/or electrons as aqueous components, and no special consideration to distinguish protons and/or electrons from other regular aqueous components is needed. The only thing we must keep in mind is that we use proton activity and electron activity rather than proton concentration and electron concentration as master variables in the geochemical reaction model.

2.2.7 Transport of Gas Component

In HYDROBIOGEOCHEM, one gas phase component may be specified. HYDROBIOGEOCHEM does not simulate the transport of gas within the porous media, but does allow the gas component to react to form aqueous product species, which are subject to transport. This capability was added specifically to provide the capability of simulating a system in which the partial pressure of $CO_{2\,(gas)}$ is specified and the resultant formation and transport of $H_2CO_3^*$, HCO_3^-, and CO_3^{2-} is simulated. This capability could be used to simulate any other gaseous species' interaction with the aqueous phase, as long as the transport of the gaseous species itself is not of significance to the problem.

2.3 Geochemical Reaction Equations

Chemical equilibrium can be dealt with in essentially two ways: the ion association theory (Bjerrum 1926; Fuoss 1935) and the mixed electrolyte theory (Reilly et al. 1971). Nearly all computerized models are based on the ion association theory (Nordstrom et al. 1979). Within this framework the species distribution can be formulated in two distinct but thermodynamically equivalent ways: the equilibrium-constant approach and the Gibbs free-energy approach. In the Gibbs free-energy approach, the species distributions are obtained by minimizing the total Gibbs free-energy function of a given set of species subject to the constraints of mass balance equations. In the equilibrium-constant approach, the set of nonlinear algebraic equations is obtained based on the law of mass action and the principle of mole balance (Morel and Morgan 1972). This set of nonlinear algebraic equations is then solved to yield the species distributions. In the latter approach, equilibrium constants are needed for the data base, whereas in the former approach, free energy values are needed. The equilibrium constant approach is chosen for handling of equilibrium geochemical reactions in HYDROBIOGEOCHEM. In the equilibrium-constant approach, the formation of an aqueous complexed species x_i, an adsorbed species y_i, an ion-exchanged species z_i, or a precipitated (solid) species p_i is described at equilibrium by the law of mass action.

Rate expressions based on collision theory are used to handle the kinetic geochemical reactions. Rate expressions based on Monod kinetics are used to describe biogeochemical reactions. The program has been developed in a modular fashion so that the user may readily incorporate rate expressions based on alternate theories to describe the kinetic reactions.

A general chemical reaction can be represented by

$$\sum_{j \in M} \nu'_{kj}\, \hat{g}_j <---> \sum_{j \in M} \nu''_{kj}\, \hat{g}_j \ , \quad k \in \text{NRXN} \tag{2.3.1}$$

where

M = $(N_a + N_s + M_x + M_y + M_z + M_p)$ is the total number of chemical species.

v_{kj}' = reactant stoichiometric coefficient of the j-th global species[1] in the k-th chemical reaction.

v_{kj}'' = product stoichiometric coefficient of the j-th global species in the k-th chemical reaction.

---

[1] "Global species" refers to all of the species, both components and products, in the simulation. The global species are numbered in the following order: N_a aqueous component species, N_s absorbent component species, M_x aqueous complexed species, M_y absorbed species, M_z ion-exchanged species, M_p precipitated species, M_b aqueous phase microbial specis, and M_a adsorbed phase microbial species.

$\hat{g}_j$ = chemical formula for the j-th species.

NRXN = number of reactions in the simulation.

We will divide chemical reactions into two groups: one group is comprised of equilibrium reactions and the other of kinetic reactions. Denoting NRXNE the number of equilibrium reactions and NRXNK the number of kinetic reactions, we have NRXN = NRXNE + NRXNK.

To quantitatively describe the chemical reactions, a rate law must be given for each reaction. For equilibrium reactions, the net reaction rate is zero resulting in the law of mass action. For kinetic chemical reactions, the reaction rate is assumed to be governed by collision theory in HYDROBIOGEOCHEM. However, to make this computer code general, any kinetic reaction may instead be described by an optional rate law prescribed by the user. Thus, three chemical reaction types are included in HYDROBIOGEOCHEM: (1) equilibrium reactions, (2) kinetic reactions whose rate laws are given by collision theory, and (3) kinetic reactions whose rate laws are prescribed by the users.

For an equilibrium reaction, the rate of the reaction is given by

$$\Omega_k = 0 = k_k^f \prod_{j \in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^b \prod_{j \in M} (\gamma_j g_j)^{\nu''_{kj}} \quad \text{if } KTYP(k) = 0 \tag{2.3.2}$$

where

Ω_k = reaction rate of the k-th reaction, (1/T).

g_j = concentration of the j-th global species, mass of chemical/mass of phase, (M/M). (i.e. mass/liquid mass or mass/solid mass).

γ_j = activity coefficient of the j-th global species, mass of phase/mass of chemical, (M/M).

k_k^f = forward rate constant for the k-th reaction, (1/T).

k_k^b = backward rate constant for the k-th reaction, (1/T).

KTYP(k) = reaction type of the k-th reaction,
= 0 if chemical equilibrium,
= 1 if chemical kinetic by collision theory,
= 2 if microbial by Monod kinetics,
= 3 if microbial phase transfer reaction,
= 4 if chemical kinetic using other rate law.

In HYDROBIOGEOCHEM, equilibrium species can appear in only one of the NRXNE equilibrium reactions and we associate this species with that equilibrium reaction. This restriction is made to facilitate the development of the mass action equations. For equilibrium reactions producing an aqueous complexed product species, Eq. **(2.3.2)** therefore simplifies to

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i x_i)^{v''_{ki}}, \quad \text{if KTYP(k)} = 0 \qquad (2.3.2a)$$

where K_k^{eq} = equilibrium constant for the k-th reaction

Similarly, for equilibrium reactions producing an adsorbed product species, Eq. **(2.3.2)** simplifies to

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in (N_a + N_s)} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i y_i)^{v''_{ki}}, \quad \text{if KTYP(k)} = 0 \qquad (2.3.2b)$$

And for equilibrium reactions producing a precipitated product species, Eq. **(2.3.2)** becomes

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i p_i)^{v''_{ki}}, \quad \text{if KTYP(k)} = 0 \qquad (2.3.2c)$$

In ion exchange reactions, free ions in solution are exchanged for ions of the same sign bound at the solid phase surface. Therefore each ion exchange reaction will involve an aqueous species and an ion exchanged species both as reactants and as products. Equilibrium controlled ion exchange species are subject to the constraint noted above that they participate in only one equilibrium reaction. Ion exchange reactions are discussed further in Section 2.3.1.

For a kinetic reaction with its rate law given by collision theory, the reaction rate is given by

$$\Omega_k = k_k^f \prod_{j \in M} (\gamma_j g_j)^{v'_{kj}} - k_k^b \prod_{j \in M} (\gamma_j g_j)^{v''_{kj}} \qquad \textbf{(2.3.3)}$$

$$\text{if KTYP(k)} = 1$$

For a kinetic reaction with its rate law prescribed the users, the reaction rate can be written as

$$\Omega_k = f_k(A_1, A_2, .., A_M; K_{k1}, K_{k2}, .., K_{kp}) \qquad \textbf{(2.3.4)}$$

$$\text{if} \quad \text{KTYP(k)} = 4$$

where f_k is the prescribed rate law for the k-th reaction written as a function of the activities of all M species and a number of parameters.

The contribution of the k-th reaction to the production/consumption rate of the i-th species is

$$r_i\big|_k^{chem} = \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i}\,\Omega_k \,, \qquad i \in M,\ k \in NRXNK \tag{2.3.5}$$

where

$r_i\big|_k^{chem}$ = the contribution of the k-th chemical reaction to the rate of production or consumption of the i-th chemical species, (mass/mass of phase)/time, ((M/M)/T).

The total production/consumption of the i-th species due to chemical reactions is the sum of the contributions from each of the reactions in which the species participates:

$$r_i\big|^{chem} = \sum_{k=1}^{NRXNK} r_i\big|_k^{chem} = \sum_{k=1}^{NRXNK} \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i}\,\Omega_k \,, \quad i \in M \tag{2.3.6}$$

where

$r_i\big|^{chem}$ = total production/consumption rate of the i-th chemical species due to chemical reactions, (mass/mass of phase)/time, ((M/M)/T)

Before concluding this section, we note that if the users specify the kinetic reaction rates, these rates cannot be arbitrary. They must satisfy the following constraints

$$\sum_{i=1}^{M} a_{ij} \sum_{k=1}^{NRXN} \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i}\,\Omega_k = 0 \,, \quad \text{for} \ \ j \in N \tag{2.3.7}$$

$$\sum_{i=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_i \sum_{k=1} \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i}\,\Omega_k = 0, \qquad \text{for} \ \ j \in NSITE \tag{2.3.8}$$

where a_{ij} = stoichiometry of the j-th component in the i-th species.

Eq. **(2.3.7)** results from the requirement that every component's mass must be conserved with respect to chemical reactions, i.e. that the rate at which a component is consumed must be balanced by the rate at which product species containing that component are produced. Similarly, Eq. **(2.3.8)** results from the fact that every ion-exchange site must be conserved with respect to ion-exchange reactions.

2.3.1 Ion Exchange

One class of surface-solution interaction reactions are ion-exchange reactions. Free ions in solution can be exchanged with an ion of the same sign bound at the solid-aqueous phase interface (Stumm and Morgan, 1981). Ion exchange sites possess a user specified ion exchange capacity and are assumed in HYDROBIOGEOCHEM to be fully occupied. Each ion-exchange reaction involves the removal of aqueous ions from solution (one of the N_a aqueous components or of the M_x aqueous complexed species) and the concurrent release of a previously existing ion-exchanged (immobile) species back into solution. In HYDROBIOGEOCHEM as many types of surfaces or ion-exchange sites as necessary to describe a scenario may be specified. For each site, it is necessary to specify one of the ion-exchanged species as a "reference species". All ion-exchange reactions at that site must then be written in terms of exchange of this reference species with the free ions in solution. The selectivity coefficient for all ion-exchange reactions at that site are therefore defined with respect to this reference species. The choice of this reference species is arbitrary; the user may choose the most prevalent ion bound initially to the surface material, or the most easily displaced ion that may participate in exchanges at that site, or any other ion which may participate in reactions at that site.

2.3.2 Adsorption

In the preceding sections, we model adsorption with a simple surface complexation approximation, i.e., the effect of electrostatic forces are not included. A simple surface complexation model can be treated numerically in the same manner as the aqueous complexation model. No special consideration in the numerical approach is needed.

The distribution of the j-th aqueous component between the aqueous and adsorbed phases can be described empirically using the “K_d partitioning concept”:

$$T_j = R_{dj} C_j \quad , \quad R_{dj} = 1 + \frac{\rho_b K_{dj}}{\theta} \quad , \quad j \in N_a \qquad \textbf{(2.3.9)}$$

and

$$S_j = \frac{\rho_b K_{dj}}{\theta} C_j \quad , \quad j \in N_a \quad , \qquad \textbf{(2.3.10)}$$

where

S_j = total sorbed concentration of the j-th aqueous component (M/L^3).
R_{dj} = retardation factor of the j-th component (dimensionless).
K_{dj} = distribution coefficient of the j-th aqueous component (L^3 liquid/M solid).

In HYDROBIOGEOCHEM, T_j, C_j, and S_j are determined once a solution has been reached for all individual species concentrations. K_{dj} and R_{dj} can then be determined from these values.

When the effect of electrostatic forces is to be included in modeling chemical adsorption, HYDROBIOGEOCHEM incorporates either the Constant Capacitance Model or the Triple Layer Model (Davis, et al., 1978; Stumm and Morgan, 1981). If the Constant Capacitance Model is used, one additional unknown (c_o) is needed for each adsorbent component. If the Triple Layer Model is employed, two additional unknowns (c_o and c_b) are introduced for each adsorbent component. These two additional unknowns are defined as

$$c_o = \exp\left(-\frac{e\psi_o}{kT} \right) \qquad \textbf{(2.3.11)}$$

and

$$c_b = \exp\left(-\frac{e\psi_b}{kT} \right) \qquad \textbf{(2.3.12)}$$

where k is the Boltzman constant, T is the absolute temperature, e is the electronic charge, ψ_o is the electric potential at the surface, and ψ_b is the electric potential at the beta layer.

In the case of the Constant Capacitance Model, the additional unknown c_o defined by Eq. **(2.3.11)** can be obtained by setting up one additional equation. This additional equation is obtained by assuming that the total charge calculated by summing over the charges on the 'o' plane is equal to the total charge calculated by electro-static theory as

$$BC\psi_o = \sum_{i=1}^{M_y} a_{io}^{y} y_i \qquad \textbf{(2.3.13)}$$

where C is the capacitance of the region, B is a conversion factor from charge per unit area to moles per mass of solid, and a^y_{io} is the stoichiometric coefficient of c_o in the i-th adsorbed species y_i. For the evaluation of Jacobian, one needs to compute $\frac{\partial \psi_o}{\partial c_o}$, which can be easily computed from Eq. **(2.3.11)** as follows:

$$\frac{\partial \psi_o}{\partial c_o} = -\frac{kT}{e} c_o \qquad (2.3.13)$$

In the case of the Triple Layer Model, the two additional unknowns c_o and c_b can be obtained by assuming that the total charge calculated by summing over the charges of all surface species is equal to the total charge calculated by electro-static theory as given by

$$BC_1(\psi_o - \psi_b) - B\sigma_o = 0 \tag{2.3.15}$$

$$B\sigma_o = \sum_{i=1}^{M_y} a_{io}^y y_i \tag{2.3.16}$$

and

$$C_1(\psi_b - \psi_o)B + C_2(\psi_b - \psi_d)B - B\sigma_b = 0 \tag{2.3.17}$$

$$B\sigma_b = \sum_{i=1}^{M_y} a_{ib}^y y_i \tag{2.3.18}$$

where C_1 is the capacitance of the region between the "o" plane and "b" plane, B is a conversion factor from charge per unit area to moles per unit solid mass, σ_o is the charge density in moles per unit area on the "o" plane, a^y_{io} is the stoichiometric coefficient of c_o in the i-th adsorbed species y_i, C_2 is the capacitance of the region between the "b" plane and "d" plane, σ_b is the charge density in moles per unit area on the "b" plane, and a^y_{ib} is the stoichiometric coefficient of c_b in the i-th adsorbed species y_i.

Electroneutrality requires that the following relationship must be satisfied

$$\sigma_o + \sigma_b + \sigma_d = 0 \tag{2.3.19}$$

and the Gouy-Chapman diffuse layer theory yields

$$\sigma_d = -(8\epsilon\epsilon_o RIT)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \tag{2.3.20}$$

where σ_d is the charge density in moles per unit area in the diffusive layer "d", R is the universal gas constant, I is ionic strength, ϵ is the relative dielectric constant, ϵ_o is the permitivity of the free space, and z is valence of the ion. It should be noted that Eq. **(2.3.20)** is valid only for the cases of symmetrical monovalent electrolyte. The charge potential relationship gives

$$C_2(\psi_d - \psi_b) = \sigma_d \tag{2.3.21}$$

Combining Eqs. **(2.3.20)** and **(2.3.21)**, we relate the unknowns ψ_d to ψ_b implicitly as follows

$$C_2(\psi_d - \psi_b) = -(8\epsilon\epsilon_o RIT)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \qquad \textbf{(2.3.22)}$$

To solve Eqs. **(2.3.15)** and **(2.3.17)** with Newton-Raphson method, we need to evaluate σ_o, σ_b, ψ_o, ψ_b, and ψ_d, and their partial derivatives with respect to c_o and c_b -- $\frac{\partial\sigma_o}{\partial c_o}$, $\frac{\partial\sigma_o}{\partial c_b}$, $\frac{\partial\sigma_b}{\partial c_o}$, $\frac{\partial\sigma_b}{\partial c_b}$, $\frac{\partial\psi_o}{\partial c_o}$, $\frac{\partial\psi_o}{\partial c_b}$, $\frac{\partial\psi_b}{\partial c_o}$, $\frac{\partial\psi_b}{\partial c_b}$, $\frac{\partial\psi_d}{\partial c_o}$, $\frac{\partial\psi_d}{\partial c_b}$. The evaluation of $B\sigma_o$ and $B\sigma_b$, and $B\frac{\partial\sigma_o}{\partial c_o}$, $B\frac{\partial\sigma_o}{\partial c_b}$, $B\frac{\partial\sigma_b}{\partial c_o}$, and $B\frac{\partial\sigma_b}{\partial c_b}$ can be performed similarly to the evaluation for other aqueous components. The evaluation of ψ_o, ψ_b, and ψ_d, and $\frac{\partial\psi_o}{\partial c_o}$, $\frac{\partial\psi_o}{\partial c_b}$, $\frac{\partial\psi_b}{\partial c_o}$, $\frac{\partial\psi_b}{\partial c_b}$, $\frac{\partial\psi_d}{\partial c_o}$, and $\frac{\partial\psi_d}{\partial c_b}$ requires a little further elaboration. Knowing c_o and c_b from previous iteration, we compute ψ_o and ψ_b from inverting Eqs. **(2.3.11)** and **(2.3.12)** as

$$\psi_o = -\frac{kT}{e}\ln(c_o) \qquad \textbf{(2.3.23)}$$

and

$$\psi_b = -\frac{kT}{e}\ln(c_b) \qquad \textbf{(2.3.24)}$$

respectively. Having computed σ_o and σ_b from Eqs. **(2.3.16)** and **(2.3.18)**, respectively, we compute σ_d from Eq. **(2.3.19)** and then invert Eq. **(2.3.20)** to obtain ψ_d as

$$\psi_d = \frac{2kT}{ze}\sinh^{-1}\left[-\frac{\frac{\sigma_d}{B}}{(8\epsilon\epsilon RIT)^{\frac{1}{2}}}\right] \qquad \textbf{(2.3.25)}$$

Differentiating Eq. (2.3.10) with respect to c_o and c_b, respectively, we obtain

$$\frac{\partial \psi_o}{\partial c_o} = \left(-\frac{kT}{e}\frac{1}{c_o} \right) \qquad \textbf{(2.3.26)}$$

and

$$\frac{\partial \psi_o}{\partial c_b} = 0 \qquad \textbf{(2.3.27)}$$

Similarly, taking the derivative of Eq. **(2.3.12)** with respect to c_o and c_b, respectively, we obtain

$$\frac{\partial \psi_b}{\partial c_o} = 0 \qquad \textbf{(2.3.28)}$$

and

$$\frac{\partial \psi_b}{\partial c_b} = \left(-\frac{kT}{e}\frac{1}{c_b} \right) \qquad \textbf{(2.3.29)}$$

Finally, taking the differentiation of Eq. **(2.3.22)** with respect to c_o and c_b, respectively, and substituting Eqs. **(2.3.28)** and **(2.3.29)** into the resulting equation, we obtain

$$\frac{\partial \psi_d}{\partial c_o} = 0 \qquad \textbf{(2.3.30)}$$

and

$$\frac{\partial \psi_d}{\partial c_b} = \left(-\frac{kT}{e}\frac{1}{c_b} \right) \frac{1}{1 + \frac{e}{2kT}\left(8\epsilon\epsilon_o RIT\right)^{\frac{1}{2}} \cosh\left(\frac{ze\psi_d}{2kT} \right) \frac{1}{C_2}} \qquad \textbf{(2.3.31)}$$

2.3.3 Precipitation-Dissolution

According to convention (Stumm and Morgan, 1981), the activities of pure solid species are assumed to be constant and equal to one. (HYDROBIOGEOCHEM does not handle "solid solutions" which are characterized by activities equal to their mole fractions). The absence of the precipitated species activities from the chemical action expressions characterizes the chemical reaction of precipitation-dissolution and distinguishes it from other heterogeneous classes of chemical reactions such as adsorption and ion exchange, and from homogeneous reactions such as soluble complexation. This implies that models developed specifically for dealing with complexation and sorption are not necessarily capable of handling precipitation-dissolution.

In HYDROBIOGEOCHEM, a check is made on the solubility of the potentially precipitated species and whether conditions permit the precipitated species to exist. A check is made that a phase rule violation does not occur if an equilibrium precipitated species is allowed to form. These checks and a detail of the treatment of precipitation in the numerical solution routines in HYDROBIOGEOCHEM are discussed further in Section 3.3.4.

2.3.4 Activity Coefficients and Thermodynamic Equilibrium Constants

Since the activity coefficients of all aqueous chemical species are functions of the ionic strength of the system, the ionic strength must be known before one can compute the activity coefficients. The ionic strength, I, is given by the following formula:

$$I = \frac{1}{2}\sum_{i=1}^{M_{aq}} a_i v_i^2 \quad , \qquad \textbf{(2.3.32)}$$

where

$v_i =$ charge of the i-th aqueous species.

$a_i =$ the molality of the i-th aqueous species.

$M_{aq} =$ the number of aqueous chemical species = the number of aqueous component species plus the number of aqueous complexed species.

Many semi-empirical formulae, usually based on the Debye-Huckel theory of ion clustering, have been proposed to calculate activity coefficients of aqueous species. All these semi-empirical formulae have the same generalized form (Kincaid et al., 1984):

$$\text{Log}(\gamma_i) = -Av_i^2\left(\frac{\sqrt{I}}{1+a_iB\sqrt{I}} + B'I\right) + b_iI + B_iI^2 \quad , \qquad \textbf{(2.3.33)}$$

where A, B, and B′ are constants, depending only on the dielectric constant, the density of water, and the temperature of the solution, and a_i, b_i, and B_i are species-dependent, adjustable parameters. For example, to obtain the Davies Formula (1962), one simply sets b_i and B_i equal to 0; for the Debye-Huckel Formula, one sets B′, b_i, and B_i equal to 0; and for the extended Debye-Huckel Formula used in WATEQ (Truesdell and Jones, 1974), one sets B′ and B_i equal to zero.

In HYDROBIOGEOCHEM, the Davies Formula is used to determine aqueous activity coefficients, with $A = 0.5$, $a_iB = 1$, $B' = -0.3$, $b_i = 0$ and $B_i = 0$. The activity coefficients of all adsorbed species are assumed to be 1. The activity coefficients of the ion-exchanged species are assumed to be the inverse of the total molal concentration at the exchange site. By convention, the activity of precipitated species is unity; in HYDROBIOGEOCHEM, the activity coefficients of precipitated species are set to 1 for convenience. In other words, the following equations are used to compute the activity coefficients for all species

$$
\begin{gathered}
\gamma_j^c \text{ or } \gamma_i^x = \text{given by Eq. (2.3.32)}, \quad j \in N_a \text{ or } i \in M_x \\
\gamma_j^s \text{ or } \gamma_i^y = 1.0, \quad j \in N_s \text{ or } i \in M_y \\
\gamma_i^z = \frac{1}{\sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} z_k}, \quad i \in NOMZI(j), \quad j \in NSITE \qquad \textbf{(2.3.34)} \\
\gamma_i^p \, p_i = 1.0, \quad i \in M_p
\end{gathered}
$$

where

γ_j^c = activity coefficient of the j-th aqueous component species,

γ_i^x = activity coefficient of the i-th aqueous complexed species,

γ_j^s = activity coefficient of the j-th adsorbent component species,

γ_i^y = activity coefficient of the i-th adsorbed species,

γ_i^z = activity coefficient of the i-th ion-exchanged species,

γ_i^p = activity coefficient of the i-th precipitated species.

The thermodynamic equilibrium constants or chemical kinetic forward and backward rate constants are normally given for conditions of 25°C and 1 atm. Under conditions other than this, the thermodynamic equilibrium constants must be corrected for temperature and pressure (Truesdell and Jones, 1974). This correction is not done within the HYDROBIOGEOCHEM code; it must be done by the user prior to running a simulation.

2.4 Microbiological Reaction Equations

Microbiological reactions can be defined using the same general form as Eq. **(2.3.1)** for chemical reactions, but one of the species involved is a microbial species:

$$
\sum_{j=1}^{M+M_B} \nu'_{kj} \, \hat{g}_j \;<\!\!---\!\!>\; \sum_{j=1}^{M+M_B} \nu''_{kj} \, \hat{g}_j \;, \quad k \in NBRXNK \qquad \textbf{(2.4.1)}
$$

Typically, reactant species will include a substrate, an electron acceptor, and other necessary nutrients. Product species will include the byproducts of the biodegradation reaction and new biomass. Using modified Monod kinetics to describe the rate of the k-th microbiological reaction,

$$\Omega_k = \Gamma_k \left[\frac{S_k}{K_{S-k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right] \quad \text{if KRTYP(k)} = 2 \tag{2.4.2}$$

where

Ω_k = rate of the k-th reaction per unit biomass activity, (1/T).

Γ_k = growth rate constant for the k-th microbial reaction per unit biomass activity, (1/T).

S_k = concentration of the substrate in the k-th microbial reaction, mass/mass of phase (M/M).

A_k = concentration of the electron acceptor in the k-th microbial reaction, mass/mass of phase (M/M).

N_k = concentration of the nutrient in the k-th microbial reaction, mass/mass of phase (M/M).

K_{S-k} = half saturation constant for the substrate in the k-th microbial reaction, mass/mass of phase (M/M).

K_{A-k} = half saturation constant for the electron acceptor in the k-th microbial reaction, mass/mass of phase (M/M).

K_{N-k} = half saturation constant for the nutrient in the k-th microbial reaction, mass/mass of phase (M/M).

NBRXNK = number of kinetic microbiological reactions.

In HYDROBIOGEOCHEM, the substrate, electron acceptor, and nutrients may be any chemical species in any phase (i.e., $(S_k, A_k, N_k) \in (N_a + N_s + M_x + M_y + M_z + M_p)$).

A metabolic lag coefficient (Kono, 1968; Wood et al., 1994) is used to allow for an acclimation period, if any, of microorganisms to new substrates:

$$\mathcal{L}_k = 0 \qquad \text{if } t \le \tau_{L-k} ,$$

$$= \frac{\tau_k - \tau_{L-k}}{\tau_{E-k} - \tau_{L-k}} \qquad \text{if } \tau_{L-k} < t \le \tau_{E-k} , \qquad \textbf{(2.4.3)}$$

$$= 1 \qquad \text{if } t > \tau_{E-k}$$

where

$\mathcal{L}_k$ = lag coefficient for the k-th reaction.

τ_k = time microorganisms in the k-th reaction have been exposed to the substrate, (T).

τ_{L-k} = lag time for the k-th reaction, (T).

τ_{E-k} = time for microorganisms in the k-th reaction to reach exponential growth, (T).

Incorporating this lag coefficient, Eq. **(2.4.2)** becomes:

$$\Omega_k = \Gamma_k \left[\frac{S_k}{K_{S-k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right]\mathcal{L}_k \qquad \textbf{(2.4.4)}$$

$$\text{if KRTYP(k)} = 2$$

Microbial processes can be hindered by the presence of toxicants or excess amounts of certain substances. Inhibition may occur by different mechanisms (Bailey and Olis, 1986) and as a result affect the magnitude of the growth rate for the reaction and/or the the half velocity coefficient for the substrate, as summarized in Table 2.2.

Table 2.2 Effect of Inhibition on Microbiological Reactions.

Competitive Inhibition	$\Gamma_{k\,(\text{apparent})} = \Gamma_{k\,(\text{no inhibitor})}$	$K_{S\,(\text{apparent})} > K_{S\,(\text{no inhibitor})}$
Noncompetitive Inhibition	$\Gamma_{k\,(\text{apparent})} < \Gamma_{k\,(\text{no inhibitor})}$	$K_{S\,(\text{apparent})} = K_{S\,(\text{no inhibitor})}$
Uncompetitive Inhibition	$\Gamma_{k\,(\text{apparent})} < \Gamma_{k\,(\text{no inhibitor})}$	$K_{S\,(\text{apparent})} < K_{S\,(\text{no inhibitor})}$
Mixed Inhibition	$\Gamma_{k\,(\text{apparent})} < \Gamma_{k\,(\text{no inhibitor})}$	$K_{S\,(\text{apparent})} > K_{S\,(\text{no inhibitor})}$

Two inhibition coefficients are used to incorporate the effects of inhibition in HYDROBIOGEOCHEM:

$$I_{1k} = \left(1 + \frac{[I]}{K_{I1}}\right)^{p} \quad , \quad I_{2k} = \left(1 + \frac{[I]}{K_{I2}}\right)^{q} \tag{2.4.5}$$

where

I_{1k} = inhibition factor for the growth rate for the k-th reaction.

I_{2k} = inhibition factor for the half saturation constant for the substrate in the k-th reaction.

$[I]$ = concentration of the inhibitory substance, (M/M).

K_{I1} = inhibition coefficient for the growth rate for the k-th reaction, (M/M).

K_{I2} = inhibition coefficient for the half saturation constant for the substrate in the k-th reaction, (M/M).

p = fitting parameter, generally 0 (no inhibition), 1, or -1 (inhibition).

q = fitting parameter, generally 0 (no inhibition), 1, or -1 (inhibition).

The inhibitory substance may be any of the chemical or microbial species. Incorporating these inhibition factors into Eq. **(2.4.4)**, the rate of the k-th reaction becomes:

$$\Omega_k = (\Gamma_k\ I_{1k}) \left[\frac{S_k}{(K_{S\text{-}k}\ I_{2k})+S_k}\right] \left[\frac{A_k}{K_{A\text{-}k}+A_k}\right] \left[\frac{N_k}{K_{N\text{-}k}+N_k}\right] \mathcal{L}_k \qquad \text{if KRTYP(k)} = 2 \tag{2.4.6}$$

The production/consumption rate of the j-th chemical species due to the k-th microbial biodegradation reaction is:

$$r_j\Big|_k^{\text{biodeg}} = \frac{(\nu''_{kj} - \nu'_{kj})}{\gamma_j}\ \Omega_k\ (\gamma_{Bk}\ B_k)\ , \quad j \in M \tag{2.4.7}$$

where

$r_j\Big|_k^{\text{biodeg}}$ = the contribution of the k-th microbial biodegradation reaction to the rate of production or consumption of the j-th chemical species, (mass/mass of phase)/time, ((M/M)/T).

B_k = concentration of the k-th microbial species, either aqueous (b_k) or adsorbed (a_k), mass/mass of phase (M/M).

γ_{Bk} = activity coefficient for the microbial species B_k, (M/M).

The activity coefficients for microbial species are assumed to be unity. The total production/consumption rate of the j-th chemical species due to microbial degradation reactions is the sum of the contributions from all of the reactions in which the j-th species participates:

$$r_j|^{biodeg} = \sum_{k=1}^{NBRXNK} r_j|_k^{biodeg} = \sum_{k=1}^{NBRXNK} \frac{(\nu''_{kj} - \nu'_{kj})}{\gamma_j} \Omega_k \ (\gamma_{Bk} B_k) , \quad j \in M \qquad \textbf{(2.4.8)}$$

The production rate of biomass due to the k-th microbial reaction is given by:

$$r_i^{Bg}|_k = \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \Omega_k \ (\gamma_{Bk} B_k) , \quad i \in M_B \qquad \textbf{(2.4.9)}$$

where

$r_i^{Bg}|_k$ = growth rate of the i-th microbial species, either aqueous (b_k) or adsorbed (a_k), due to the k-th microbial reaction, (mass/mass of phase)/time, ((M/M)/T).

The total growth of each microbial species is the sum of the contributions from each biodegradation reaction in which the microbial species participates:

$$r_i^{Bg} = \sum_{k=1}^{NBRXNK} r_i^{Bg}|_k = \sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \Omega_k \ (\gamma_{Bk} B_k), \quad i \in M_B \qquad \textbf{(2.4.10)}$$

where

r_i^{Bg} = total growth rate of the i-th microbial species, either aqueous or adsorbed, (mass/mass of phase)/time, ((M/M)/T).

The commonly used Monod kinetic parameters are incorporated in the above equations using the following relationships:

$$\mu_{max\text{-}k} = (\nu''_{ki} - \nu'_{ki})\ \Gamma_k \ , \quad i \in M_B \tag{2.4.11}$$

$$Y_{j\text{-}k} = \frac{(\nu''_{ki} - \nu'_{ki})}{(\nu''_{kj} - \nu'_{kj})} \ , \quad i \in M_B, \ j \in M \tag{2.4.12}$$

where

$\mu_{max\text{-}k}$ = maximum specific growth rate for the k-th microbial reaction, (1/T).

$Y_{j\text{-}k}$ = growth yield coefficient for the j-th species in the k-th microbial reaction, mass of microorganisms produced/mass of the j-th chemical species utilized, (M/M).

The user provides values for $\mu_{max\text{-}k}$ and the reaction stoichiometry. HYDROBIOGEOCHEM determines the value for Γ_k accordingly. It should be noted that the above formulation allows for a unique growth yield coefficient for each chemical species participating in the reaction.

2.4.1 Microbial Death/Decay and Endogenous Respiration

The rate of microbial death/decay is assumed to be proportional to the concentration of biomass present:

$$r_i^{Bd} = K_i^d\ B_i \ , \quad i \in M_B \tag{2.4.13}$$

where

r_i^{Bd} = death/decay rate of the i-th microbial species, either aqueous or adsorbed, (mass/mass of phase)/time, ((M/M)/T).

K_i^d = rate constant for death/decay of the i-th microbial species (1/T).

Cellular maintenance and cellular decay processes can utilize chemical species, most commonly oxygen as an electron acceptor. Endogenous respiration's effect on electron acceptor concentration has been observed to follow Monod type kinetics (Kappeler and Gujer, 1992). Although it is likely that only oxygen or another electron acceptor will be consumed in endogenous maintenance, HYDROBIOGEOCHEM allows the flexibility of specifying any chemical species' consumption through this process:

$$r_j|^{bioresp} = \sum_{i=1}^{M_B} \alpha_{ij} K_i^d B_i \left[\frac{g_j}{\kappa_{ij} + g_j} \right], \quad j \in M \qquad \mathbf{(2.4.14)}$$

where

$r_j^{bioresp}$ = rate of consumption of j-th chemical species due to cellular maintenance/decay processes.

α_{ij} = stoichiometric coefficient for use of the j-th chemical species due to maintenance/decay of the i-th microbial species.

κ_{ij} = half saturation constant for the j-th chemical species in the maintenance/decay processes of the i-th microbial species.

Incorporating consumption of chemical species due to microbial decay, the total rate of production/consumption of chemical species due to microbiological reactions combines Eqs. **(2.4.8)** and **(2.4.14)** and becomes:

$$r_j|^{bio} = r_j|^{biodeg} - r_j|^{bioresp} , \quad j \in M \qquad \mathbf{(2.4.15)}$$

2.4.2 Adsorption of Microbial Species

In HYDROBIOGEOCHEM, microorganisms may be either aqueous phase or adsorbed phase species, and may be transferred from one phase to the other. Transfer of microbial species between phases is handled by a simple kinetic transfer reaction:

$$\nu'_{ki} b_i \leftrightarrow \nu''_{kj} a_j , \quad i \in M_b , \quad j \in M_a , \qquad \mathbf{(2.4.16)}$$
$$KRTYP(k) = 3$$

The reaction rate is described using forward and backward rate constants, as for kinetic chemical reactions, but microbial species activities are used instead of chemical species activities:

$$\Omega_k = k_k^f (\gamma_i b_i)^{\nu'_{ki}} - k_k^b (\gamma_j a_j)^{\nu''_{kj}} , \; i \in M_b , \; j \in M_a \qquad \mathbf{(2.4.17)}$$
$$\text{if } KTYP(k) = 3$$

where

Ω_k = reaction rate of the k-th reaction, (1/T).

k_k^f = forward rate constant for the k-th reaction, (1/T).

k_k^b = backward rate constant for the k-th reaction, (1/T).

So the rate of change of the i-th microbial species between phases is:

$$r_i^{xfr} = \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \, \Omega_k \quad , \quad i \in M_B \tag{2.4.18}$$

2.5 Treatment of Colloids

Colloids are water borne particles with diameters less than approximately 10 μm (Stumm and Morgan 1981). The surface of colloids can act as sites for adsorption of chemical species. Any chemical species adsorbed to the colloid will be transported with the colloid as it moves through the porous media. In HYDROBIOGEOCHEM's handling of hydrologic transport, colloids are treated as aqueous components which are subject to advective-dispersive transport per Equation **(2.2.34)**. In the model's handling of biogeochemical reactions, colloids are treated as adsorbent components which may provide sites for adsorption of aqueous chemical species. Adsorption to the colloid may be equilibrium or kinetic and may be simulated using the surface complexation, Constant Capacitance, or Triple Layer Models. The colloids themselves are considered stable particles; HYDROBIOGEOCHEM does not address aggregation of colloids or colloid stability.

2.6 Initial and Boundary Conditions

To complete the description of the hydrological transport and mass balance Equations **(2.2.34)**, **(2.2.44)**, **(2.2.53)**, **(2.2.54)**, **(2.2.55)** and **(2.2.10)** through **(2.2.13)**, initial and boundary conditions must be specified in accordance with dynamic and physical considerations. It will be assumed initially that the total equilibrium concentrations for all components and all kinetically controlled chemical and microbiological species and the number of equivalents of the ion-exchange site are known throughout the region of interest; that is,

$$T_j = T_{jo} \quad \text{at } t = 0 \quad , \quad j \in N_a \quad , \tag{2.6.1}$$

$$W_j = W_{jo} \quad \text{at } t = 0 \quad , \quad j \in N_s \quad , \tag{2.6.2}$$

$$N_{eqi} = N_{eqio} \quad \text{at } t = 0 \quad , \quad i \in \text{NSITE} \tag{2.6.3}$$

$$x_j = x_{jo} \quad \text{at } t = 0 \quad , \quad j \in K_x \quad , \tag{2.6.4}$$

$$y_j = y_{jo} \quad \text{at } t = 0 \quad , \quad j \in K_y \quad , \tag{2.6.5}$$

$$z_j = z_{jo} \quad \text{at } t = 0 \quad , \quad j \in K_z \quad , \tag{2.6.6}$$

$$p_j = p_{jo} \quad \text{at } t = 0 \quad , \quad j \in K_p \quad , \tag{2.6.7}$$

$$b_j = b_{jo} \quad \text{at } t = 0 \quad , \quad j \in M_b \quad , \tag{2.6.8}$$

and

$$a_j = a_{jo} \quad \text{at } t = 0 \quad , \quad j \in M_a \quad , \tag{2.6.9}$$

where

T_{jo} = initial total equilibrium concentration of the j-th aqueous component (M/L^3).
W_{jo} = initial total equilibrium concentration of the j-th adsorbent component (M/L^3).
N_{eqio} = initial number of equivalents of the i-th ion-exchange site (equivalents/L^3).
x_{jo} = initial concentration of the j-th kinetically controlled aqueous complexed species, (M/M of liquid).
y_{jo} = initial concentration of the j-th kinetically controlled adsorbed species (M/M of solid).
z_{jo} = initial concentration of the j-th kinetically controlled ion-exchanged species (M/M of solid).
p_{jo} = initial concentration of the j-th kinetically controlled precipitated species (M/M of solid).
b_{jo} = initial concentration of the j-th aqueous phase microbial species (M/M of liquid).
a_{jo} = initial concentration of the j-th adsorbed phase microbial species (M/M of solid).

Equilibrium product species concentrations are obtained from mass action equations involving the components, and hence do not have to be independently specified. Initial concentrations for aqueous components may be obtained from field measurements or by solving the steady-state version of Equation **(2.2.34)** with time-invariant boundary conditions.

The specification of boundary conditions is the most difficult and intricate task in multicomponent transport modeling. From the dynamic point of view, a boundary segment may be classified as either flow-through or impervious. From a physical point of view, it is a soil-air interface, a soil-soil interface, or a soil-water interface. From the mathematical point of view, it may be treated as a Dirichlet boundary, for which the total concentration is prescribed; a Neumann boundary, for which the flux due to the gradient of total concentration is known; or a Cauchy boundary, for which the total flux is given. An even more difficult mathematical boundary is the variable condition, in which the boundary conditions are not known a priori but are themselves part of the solution. In other words, on the mathematically variable boundary, either Neumann or Cauchy conditions may prevail and change with time. Which condition prevails at a particular time can be determined only in the cyclic processes of solving the governing equations (Freeze 1972a, 1972b; Yeh and Ward 1980, 1981).

Whatever point of view is chosen, all boundary conditions eventually must be transformed into mathematical equations for quantitative simulations. Thus, we can specify the boundary conditions from the mathematical point of view in concert with dynamic and physical considerations. Boundary conditions must be specified for all entities that are subject to hydrologic transport, that is all aqueous chemical components (Eq. **(2.2.34)**), all kinetically controlled aqueous product species (Eq. **(2.2.54)**), and all aqueous phase microbial species (Eq. **(2.2.55)**). (Equilibrium aqueous complexed species concentrations are obtained from mass action equations involving the aqueous components, and hence do not have to be independently specified). The boundary conditions imposed on any segment of the boundary can be either Dirichlet, Neumann, Cauchy, or variable for T_j with $j = 1, 2, \ldots, N_a$, for x_j with $j = 1, 2, \ldots, K_x$, and for b_j with $j = 1, 2, \ldots, M_b$ independently of each other. Thus, for any T_j, x_j, or b_j, the global boundary may be split into four parts: B_D, B_N, B_C, and B_V, denoting Dirichlet, Neumann, Cauchy, and variable boundaries, respectively. The conditions imposed on the first three types of boundaries are given as

$$T_j = T_{jD} \quad \text{on} \quad B_D \ , \ j \in N_a \ , \tag{2.6.10}$$

$$x_j = x_{jD} \quad \text{on} \quad B_D \ , \ j \in K_x \ , \tag{2.6.11}$$

$$b_j = b_{jD} \quad \text{on} \quad B_D \ , \ j \in M_b \ , \tag{2.6.12}$$

$$-\mathbf{n} \cdot [\rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jN} \quad \text{on} \quad B_N \ , \ j \in N_a \ , \tag{2.6.13}$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla x_j) = q_{jN} \quad \text{on} \quad B_N \ , \ j \in K_x \ , \tag{2.6.14}$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla b_j) = q_{jN} \quad \text{on} \quad B_N \ , \ j \in M_b \ , \tag{2.6.15}$$

$$\mathbf{n} \cdot [\rho_\ell \mathbf{V}(C_j/\rho_\ell \theta) - \rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jC} \quad \text{on} \quad B_C \ , \ j \in N_a \ , \tag{2.6.16}$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} x_j - \rho_\ell \theta \mathbf{D} \cdot \nabla x_j) = q_{jC} \quad \text{on} \quad B_C \ , \ j \in K_x \ , \tag{2.6.17}$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} b_j - \rho_\ell \theta \mathbf{D} \cdot \nabla b_j) = q_{jC} \quad \text{on} \quad B_C \ , \ j \in M_b \ , \tag{2.6.18}$$

where

T_{jD} = prescribed Dirichlet total equilibrium concentration for aqueous component j (M/L^3).
x_{jD} = prescribed Dirichlet total concentration for kinetic aqueous complexed species j (M/M of liquid).
b_{jD} = prescribed Dirichlet total concentration for aqueous microbial species j (M/M of liquid).
q_{jN} = normal Neumann flux ($M/L^2/T$).
q_{jC} = normal Cauchy flux ($M/L^2/T$).
$\mathbf{n}$ = an outward unit vector normal to the boundary.

The conditions imposed on the variable-type boundary, which is normally the soil-air interface or soil-water interface, are either the Neumann with zero gradient flux or the Cauchy with given total flux. The former is specified when the water flow is directed out of the region from the far away boundary, whereas the latter is specified when the water flow is directed into the region. This type of variable condition would normally occur at flow-through boundaries. Written mathematically, the variable boundary condition is given by

$$-\mathbf{n}\cdot[\rho_\ell\theta\mathbf{D}\cdot\nabla(C_j/\rho_\ell\theta)] = q_{jV} \quad \text{if } V\cdot n > 0 \quad \text{on} \quad B_V \;,\; j\in N_a \tag{2.6.19}$$

$$-\mathbf{n}\cdot(\rho_\ell\theta\mathbf{D}\cdot\nabla x_j) = q_{jV} \quad \text{if } V\cdot n > 0 \quad \text{on} \quad B_V \;,\; j\in K_x \tag{2.6.20}$$

$$-\mathbf{n}\cdot(\rho_\ell\theta\mathbf{D}\cdot\nabla b_j) = q_{jV} \quad \text{if } V\cdot n > 0 \quad \text{on} \quad B_V \;,\; j\in M_b \tag{2.6.21}$$

and

$$\mathbf{n}\cdot[\rho_\ell\mathbf{V}(C_j/\rho_\ell\theta) - \rho_\ell\theta\mathbf{D}\cdot\nabla(C_j/\rho_\ell\theta)] = q_{jV} \quad \text{if} \quad V\cdot n < 0 \quad \text{on} \quad B_V \;,\; j\in N_a \;. \tag{2.6.22}$$

$$\mathbf{n}\cdot(\rho_\ell\mathbf{V}x_j - \rho_\ell\theta\mathbf{D}\cdot\nabla x_j) = q_{jV} \quad \text{if} \quad V\cdot n < 0 \quad \text{on} \quad B_V \;,\; j\in K_x \;. \tag{2.6.23}$$

$$\mathbf{n}\cdot(\rho_\ell\mathbf{V}b_j - \rho_\ell\theta\mathbf{D}\cdot\nabla b_j) = q_{jV} \quad \text{if} \quad V\cdot n < 0 \quad \text{on} \quad B_V \;,\; j\in M_b \;. \tag{2.6.24}$$

HYDROBIOGEOCHEM allows specification of Dirichlet and variable type boundary conditions to handle the range of physical boundaries needed for subsurface transport problems.

3.0 NUMERICAL IMPLEMENTATION

3.1 Solution of Coupled Transport and Biogeochemical Reaction Problems

Section 2.0 presents a system of equations describing coupled hydrological transport and biogeochemical reactions for the unknowns: T_j's, c_j's, C_j's, W_j's, s_j's, N_{eqi}'s, x_i's, y_i's, z_i's, p_i's, b_i's, and a_i's. Analytical solution to the system in general is beyond the capability of present-day applied mathematics. Numerical methods are the only tools that can be used to achieve a solution. Because the number of equations in the system is large, in the order of hundreds for most practical applications, the system is divided into two subsystems: hydrologic transport and biogeochemical reactions.

The species which are affected directly by hydrologic transport are solved for in the hydrologic transport subsystem[1]. The governing equations for hydrologic transport are Equations (2.2.34), (2.2.54), and (2.2.55) which are used to determine the T_j's, K_x kinetic x_i's, and b_i's, respectively, and are modified here for numerical implementation:

For mobile chemical components:

$$\rho_\ell \theta \frac{\partial T'_j}{\partial t} = - L(T'_j) - K\, T'_j + R_j^c + M_j^c - \rho^* Q\, C'_j \qquad j \in N_a \quad . \tag{3.1.1}$$

where

$$T'_j = \frac{T_j}{\rho_\ell \theta} \quad , \; j \in N_a \; , \tag{3.1.2}$$

$$C'_j = \frac{C_j}{\rho_\ell \theta} \quad , \; j \in N_a \; , \tag{3.1.3}$$

$$L(T'_j) = \left[\rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta\, \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right] \nabla \cdot T'_j - \nabla \cdot \left[\rho_\ell \theta\, \mathbf{D}\, \frac{C'_j}{T'_j} \cdot \nabla T'_j \right] \qquad j \in N_a \quad . \tag{3.1.4}$$

---

[1] Colloids are subject to hydrologic transport and are therefore included as mobile component species in the hydrologic subsystem of equations. Colloids are considered adsorbent components in the biogeochemical subsystem.

$$K = \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C_j'}{T_j'} - \frac{C_j'}{T_j'} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C_j'}{T_j'} \right) + \rho_\ell \theta \left(\alpha \frac{\partial p}{\partial t} \right) + \lambda_j^c \right] \tag{3.1.5}$$

$$j \in N_a \ .$$

$$\begin{aligned} R_j^{\ c} = {} & \rho_\ell \theta \left(r_j^{\ c}\big|^{bio} + \sum_{i=1}^{(M_x - K_x)} a_{ij} \ r_i^{\ x}\big|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij} \ r_i^{\ y}\big|^{bio} + \sum_{i=1}^{(M_z - K_z)} a_{ij} \ r_i^{\ z}\big|^{bio} + \sum_{i=1}^{(M_p - K_p)} a_{ij} \ r_i^{\ p}\big|^{bio} \right) \\ & - \rho_\ell \theta \left(\sum_{i=1}^{K_x} a_{ij} \ r_i^{\ x}\big|^{chem} \right) - \rho_b \left(\sum_{i=1}^{K_y} a_{ij} \ r_i^{\ y}\big|^{chem} + \sum_{i=1}^{K_z} a_{ij} \ r_i^{\ z}\big|^{chem} + \sum_{i=1}^{K_p} a_{ij} \ r_i^{\ p}\big|^{chem} \right) \end{aligned} \tag{3.1.6}$$

$$j \in N_a \ .$$

and where

T'_j = total equilibrium concentration of the j-th aqueous component, mass per mass of liquid (M/M of liquid).

C'_j = total dissolved concentration of the j-th aqueous component (M/M of liquid).

This equation is solved subject to either Dirichlet or variable boundary conditions:

$$T_j = T_{jD} \quad \text{on} \quad B_D \ , \ j \in N_a \ , \tag{3.1.7}$$

or

$$\mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) \cdot T'_j - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right) = \mathbf{n} \cdot \rho_\ell \mathbf{V} C'_j \tag{3.1.8}$$

$$\text{if } V \cdot n > 0 \quad \text{on} \quad B_V \ , \ j \in N_a \ ,$$

$$\mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) \cdot T'_j - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right) = q_{jV} \tag{3.1.9}$$

$$\text{if } V \cdot n < 0 \quad \text{on} \quad B_V \ , \ j \in N_a$$

For the kinetic aqueous complexed chemical species:

$$\rho_\ell \theta \frac{\partial x_i}{\partial t} = - L(x_i) - K \, x_i + \rho_\ell \theta \, r_i^{\ x} + m_i^{\ x} - \rho^* Q \, x_i \quad , \ i \in K_x \ . \tag{3.1.10}$$

where

$$L(x_i) = \rho_\ell \mathbf{V} \cdot \nabla x_i - \nabla \cdot \left[\rho_\ell \theta \mathbf{D} \cdot \nabla x_i \right] \quad , \ i \in K_x \ . \tag{3.1.11}$$

$$K = \left[\rho_\ell \theta \left(\alpha \frac{\partial p}{\partial t} \right) + \iota_i^x \right] \quad , \ i \in K_x \ . \tag{3.1.12}$$

and

$$\begin{aligned} r_i^{\ x} &= \sum_{k=1}^{NRXNK} r_i^{\ x}\Big|_k^{chem} + \sum_{k=1}^{NBRXNK} r_i^{\ x}\Big|_k^{biodeg} - r_i^{bioresp} \\ &= \sum_{k=1}^{NRXNK} \frac{\nu''_{ki} - \nu'_{ki}}{\gamma_i} \left(k_k^{\ f} \prod_{j \in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^{\ b} \prod_{j \in M} (\gamma_j g_j)^{\nu''_{kj}} \right) + \\ & \sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathscr{L}_k(\gamma_{Bk} B_k) \\ & - \sum_{j=1}^{M_B} \alpha_{ji} K_j^{\ d} B_j \left[\frac{x_i}{K_{ji} + x_i} \right] \\ & i \in K_x \end{aligned} \tag{3.1.13}$$

This equation is solved subject to either Dirichlet or variable boundary conditions:

$$x_i = x_{iD} \quad \text{on} \quad B_D \ , \ i \in K_x \ , \tag{3.1.14}$$

or

$$\begin{gathered} \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} x_i \right) - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla x_i \right) = \mathbf{n} \cdot \rho_\ell \mathbf{V} x_i \\ \text{if } V \cdot n > 0 \ \text{ on } \ B_V \ , \ i \in K_x \ , \end{gathered} \tag{3.1.15}$$

$$\begin{gathered} \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} x_i \right) - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla x_i \right) = q_{iV} \\ \text{if } \ V \cdot n < 0 \ \text{ on } \ B_V \ , \ i \in K_x \end{gathered} \tag{3.1.16}$$

For the aqueous microbial species:

$$\begin{gathered} \rho_\ell \theta \frac{\partial b_i}{\partial t} + L(b_i) + K\, b_i = \rho_\ell \theta\, r_i^{\ b} + m_i^{\ b} - \rho^* Q\, b_i \\ i \in M_b \ . \end{gathered} \tag{3.1.17}$$

where

$$L(b_i) = \rho_\ell \mathbf{V} \cdot \nabla b_i - \nabla \cdot \left[\rho_\ell \theta \mathbf{D} \cdot \nabla b_i \right] \quad , \quad i \in M_b \ . \tag{3.1.18}$$

$$K = \left[\rho_\ell \theta \left(\alpha \frac{\partial p}{\partial t} \right) + \iota_i^b \right] \quad , \quad i \in M_b \ . \tag{3.1.19}$$

and

$$\begin{aligned} r_i^{\ b} &= r_i^{\ bg} - r_i^{\ bd} + r_i^{\ xfr} = \\ &\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k (\gamma_{Bk} B_k) \\ &- K_i^{\ d} \, b_i + \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \left(k_k^{\ f} (\gamma_i \, b_i)^{\nu'_{ki}} - k_k^{\ b} (\gamma_j \, a_j)^{\nu''_{kj}} \right) \ , \\ &i \in M_b \ , \ j \in M_a \end{aligned} \tag{3.1.20}$$

This equation is solved subject to either Dirichlet or variable boundary conditions:

$$b_i = b_{iD} \quad \text{on} \quad B_D \ , \ i \in M_b \ , \tag{3.1.21}$$

or

$$\begin{aligned} &\mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \, b_i \right) - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla b_i \right) = \mathbf{n} \cdot \rho_\ell \mathbf{V} b_i \\ &\text{if } V \cdot n > 0 \quad \text{on} \quad B_V \ , \ i \in M_b \ , \end{aligned} \tag{3.1.22}$$

$$\begin{aligned} &\mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \, b_i \right) - \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla b_i \right) = q_{iV} \\ &\text{if } \ V \cdot n < 0 \quad \text{on} \quad B_V \ , \ i \in M_b \end{aligned} \tag{3.1.23}$$

The remaining unknowns are solved for in the biogeochemical subsystem. The governing biogeochemical equations are the mass balance, mole balance, and equivalents balance equations, mass action equations for the equilibrium chemical species and reaction rate expressions for the kinetic chemical and microbial species. These biogeochemical system equations are regrouped as:

Mobile, aqueous chemical component species are represented by a mass balance equation, Equation **(3.1.24)**, in which the latest value of T_j is provided from transport. The equation is used to solve for the free species concentration, c_j. The new value of T_j including the effect of reactions is recalculated using Equation **(3.1.25)** once the new values of all individual species concentrations are known.

Mass balance for the aqueous component species concentrations -

$$\frac{\partial T_j}{\partial t} = R_j^c \quad , \qquad j \in N_a \tag{3.1.24}$$

where

$$T_j = \rho_\ell \theta \left(c_j + \sum_{i=1}^{(M_x-K_x)} a_{ij} x_i \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} y_i + \sum_{i=1}^{(M_z-K_z)} a_{ij} z_i + \sum_{i=1}^{(M_p-K_p)} a_{ij} p_i \right) \, , \quad j \in N_a \tag{3.1.25}$$

and

$$\begin{aligned} R_j^c = {} & \rho_\ell \theta \left(r_j^c \big|^{bio} + \sum_{i=1}^{(M_x-K_x)} a_{ij} r_i^x \big|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} r_i^y \big|^{bio} + \sum_{i=1}^{(M_z-K_z)} a_{ij} r_i^z \big|^{bio} + \sum_{i=1}^{(M_p-K_p)} a_{ij} r_i^p \big|^{bio} \right) . \\ & - \rho_\ell \theta \sum_{i=1}^{(K_x)} a_{ij} r_i^x \big|^{chem} - \rho_b \left(\sum_{i=1}^{(K_y)} a_{ij} r_i^y \big|^{chem} + \sum_{i=1}^{(K_z)} a_{ij} r_i^z \big|^{chem} + \sum_{i=1}^{(K_p)} a_{ij} r_i^p \big|^{chem} \right) \end{aligned} \tag{3.1.26}$$

Similarly, mobile, adsorbent chemical components (colloids) are represented by a mass balance equation, Equation **(3.1.27)**, in which the latest value of W_j is provided from transport, and the equation is used to solve for the free species concentration, s_j. The new value of Wj including the effect of reactions is recalculated using Equation **(3.1.28)** once the new values of all individual species concentrations are known. Immobile, adsorbent chemical components are represented by a mass balance equation, Equation **(3.1.27)**, in which the latest value of W_j is provided from the prior time step, since its value will not be affected by hydrological transport.

Mass balance for the adsorbent component species concentrations -

$$\frac{\partial W_j}{\partial t} = R_j^s \quad , \qquad j \in N_s \ , \tag{3.1.27}$$

where

$$W_j = \rho_b \left(s_j + \sum_{i=1}^{(M_y-K_y)} a_{ij} y_i \right) \quad , \ j \in N_s \ , \tag{3.1.28}$$

and

$$R_j^s = \rho_b \left(r_j^s \big|^{bio} + \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^y \big|^{bio} \right) - \rho_b \sum_{i=1}^{K_y} a_{ij} r_i^y \big|^{chem} \quad , \quad j \in N_s \ . \qquad \textbf{(3.1.29)}$$

Each chemical product species is represented by one equation: either the mass action equation for an equilibrium species (Eq. (2.3.2)) or the sum of the rate expressions for all of the kinetic reactions in which the species participates (Eq. (2.3.6) for chemical reactions, Eq. (2.4.8) for microbial reactions, and Eq. (2.4.14) for microbial endogenous respiration).

Mass action equation for equilibrium aqueous complexed species -

$$x_i = \left[\frac{K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{\nu'_{kj}}}{(\gamma_i)^{\nu''_{ki}}} \right]^{\frac{1}{\nu''_{ki}}} , \qquad \textbf{(3.1.30)}$$

$$i \in (M_x - K_x), \quad k \in NRXNE$$

Mass balance equation for kinetic aqueous complexed species with the combined effects of chemical reactions, microbial reactions, and microbial endogenous respiration -

$$\frac{\partial x_i}{\partial t} = r_i^x - \iota_i^x - \left(\alpha \frac{\partial p}{\partial t} \right) x_i - \frac{1}{\rho_\ell \theta} \frac{\partial \rho_\ell \theta}{\partial t} x_i \quad , \qquad i \in K_x \ . \qquad \textbf{(3.1.31)}$$

where

$$r_i^x = \sum_{k=1}^{NRXNK} r_i^x\Big|_k^{chem} + \sum_{k=1}^{NBRXNK} r_i^x\Big|_k^{biodeg} - r_i^{bioresp}$$

$$= \sum_{k=1}^{NRXNK} \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i} \left(k_k^f \prod_{j\in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^b \prod_{j\in M} (\gamma_j g_j)^{\nu''_{kj}} \right) +$$

$$\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki}-\nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k})+S_k}\right] \left[\frac{A_k}{K_{A-k}+A_k}\right] \left[\frac{N_k}{K_{N-k}+N_k}\right] \mathcal{L}_k(\gamma_{Bk} B_k) \qquad \textbf{(3.1.32)}$$

$$- \sum_{j=1}^{M_B} \alpha_{ji}\, K_j^d\, B_j \left[\frac{x_i}{K_{ji} + x_i}\right]$$

$$i \in K_x$$

Mass action equation for equilibrium adsorbed species -

$$y_i = \left[\frac{K_k^{eq} \prod_{j\in(N_a+N_s)} (\gamma_j g_j)^{\nu'_{kj}}}{(\gamma_i)^{\nu''_{ki}}}\right]^{\frac{1}{\nu''_{ki}}} , \qquad \textbf{(3.1.33)}$$

$$i \in (M_y - K_y), \quad k \in NRXNE$$

Mass balance equation for kinetic adsorbed species with the combined effects of chemical reactions, microbial reactions, and microbial endogenous respiration -

$$\frac{\partial y_i}{\partial t} = r_i^y - \iota_i^y - \left(\alpha \frac{\partial p}{\partial t}\right) y_i - \frac{1}{\rho_b}\frac{\partial \rho_b}{\partial t} y_i , \qquad i \in K_y . \qquad \textbf{(3.1.34)}$$

where

$$
\begin{aligned}
r_i^y &= \sum_{k=1}^{NRXNK} r_i^y\Big|_k^{chem} + \sum_{k=1}^{NBRXNK} r_i^y\Big|_k^{biodeg} - r_i^{bioresp} \\
&= \sum_{k=1}^{NRXNK} \frac{\nu''_{ki}-\nu'_{ki}}{\gamma_i} \left(k_k^f \prod_{j\in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^b \prod_{j\in M} (\gamma_j g_j)^{\nu''_{kj}} \right) + \\
&\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki}-\nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k})+S_k} \right] \left[\frac{A_k}{K_{A-k}+A_k} \right] \left[\frac{N_k}{K_{N-k}+N_k} \right] \mathcal{L}_k(\gamma_{Bk} B_k) \qquad \textbf{(3.1.35)} \\
&- \sum_{j=1}^{M_B} \alpha_{ji} K_j^d B_j \left[\frac{y_i}{\kappa_{ji} + y_i} \right]
\end{aligned}
$$

$$i \in K_y$$

Each ion-exchange site is represented by an equivalents balance equation, Equation **(3.1.36)**.

Equivalents balance for the ion exchange site constraint equations -

$$\frac{\partial N_{eqi}}{\partial t} = R_{eqi}^{(bio)} - \left(\lambda_{eqi} + \alpha \frac{\partial p}{\partial t} \right) N_{eqi} \quad , \quad i \in \text{NSITE} \qquad \textbf{(3.1.36)}$$

where

$$R_{eqi}^{(bio)} = \rho_b \sum_{k=\text{NOMZJ(i)}+1}^{\text{NOMZJ(i)+NOMZI(i)}} \nu_k r_k^z \big|^{bio} \quad , \quad i \in \text{NSITE} \qquad \textbf{(3.1.37)}$$

and

$$N_{eqi} = \rho_b \sum_{k=\text{NOMZJ(i)}+1}^{\text{NOMZJ(i)+NOMZI(i)}} \nu_k z_k \quad , \quad i \in \text{NSITE} \qquad \textbf{(3.1.38)}$$

Equation **(3.1.36)** is solved for the NSITE "reference" ion-exchange species instead of a mass action or mass balance equation.

For equilibrium ion-exchanged species -

$$0 = K_k^{eq} \prod_{j \in (N_a+M_x+M_z)} (\gamma_j g_j)^{\nu'_{kj}} - \prod_{j \in (N_a+M_x+M_z)} (\gamma_j g_j)^{\nu''_{kj}} \qquad \textbf{(3.1.39)}$$

$$k \in \text{NRXNE}$$

where one of the species produced in the k-th reaction is an equilibrium controlled ion-exchanged species (and is not the "reference" ion-exchanged species).

Mass balance equation for kinetic ion-exchanged species with the combined effects of chemical reactions, microbial reactions, and microbial endogenous respiration -

$$\frac{\partial z_i}{\partial t} = r_i^z - \iota_i^z - \left(\alpha \frac{\partial p}{\partial t} \right) z_i - \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} z_i \quad , \quad i \in K_z \ . \qquad \textbf{(3.1.40)}$$

where

$$
\begin{aligned}
r_i^{\,z} &= \sum_{k=1}^{NRXNK} r_i^{\,z}\Big|_k^{chem} + \sum_{k=1}^{NBRXNK} r_i^{\,z}\Big|_k^{biodeg} - r_i^{bioresp} \\
&= \sum_{k=1}^{NRXNK} \frac{\nu''_{ki} - \nu'_{ki}}{\gamma_i} \left(k_k^{\,f} \prod_{j \in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^{\,b} \prod_{j \in M} (\gamma_j g_j)^{\nu''_{kj}} \right) + \\
&\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k (\gamma_{Bk} B_k) \\
&- \sum_{j=1}^{M_B} \alpha_{ji}\, K_j^{\,d}\, B_j \left[\frac{z_i}{\kappa_{ji} + z_i} \right] \\
&i \in K_z
\end{aligned}
\qquad \textbf{(3.1.41)}
$$

For equilibrium precipitated species -

$$
1 = K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{\nu'_{kj}} \quad , \quad i \in (M_p - K_p), \quad k \in NRXNE \qquad \textbf{(3.1.42)}
$$

where K_p = number of kinetically controlled precipitated species.

Mass balance equation for kinetic precipitated species with the combined effects of chemical reactions, microbial reactions, and microbial endogenous respiration -

$$
\frac{\partial p_i}{\partial t} = r_i^{\,p} - \iota_i^p - \left(\alpha \frac{\partial p}{\partial t} \right) p_i - \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} p_i \quad , \qquad i \in M_p \quad . \qquad \textbf{(3.1.43)}
$$

where

$$
r_i^{\,p} = \sum_{k=1}^{NRXNK} r_i^{\,p}\Big|_k^{chem} + \sum_{k=1}^{NBRXNK} r_i^{\,p}\Big|_k^{biodeg} - r_i^{bioresp}
$$

$$
= \sum_{k=1}^{NRXNK} \frac{\nu''_{ki} - \nu'_{ki}}{\gamma_i} \left(k_k^{\,f} \prod_{j \in M} (\gamma_j g_j)^{\nu'_{kj}} - k_k^{\,b} \prod_{j \in M} (\gamma_j g_j)^{\nu''_{kj}} \right) +
$$

$$
\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k \ I_{1k}) \left[\frac{S_k}{(K_{S-k} \ I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{G}_k(\gamma_{Bk} B_k) \qquad \textbf{(3.1.44)}
$$

$$
- \sum_{j=1}^{M_B} \alpha_{ji} \ K_j^{\,d} \ B_j \left[\frac{p_i}{\kappa_{ji} + p_i} \right]
$$

$$
i \in K_p
$$

Each microbiological species is represented by the sum of the rate expressions for microbial growth, Eq. (2.4.10), microbial death/decay, Eq. (2.4.13), and the transfer between phases, Eq. (2.4.18).

Mass balance equation for the aqueous phase microbial species with the change in concentration due to microbial growth, microbial death/decay, and transfer to the adsorbed phase -

$$
\frac{\partial b_i}{\partial t} = r_i^{\,b} - \iota_i^{\,b} - \left(\alpha \frac{\partial p}{\partial t} \right) b_i - \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} b_i \ , \qquad i \in M_b \ . \qquad \textbf{(3.1.45)}
$$

where

$$
r_i^{\,b} = r_i^{\,bg} - r_i^{\,bd} + r_i^{\,xfr} =
$$

$$
\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{G}_k(\gamma_{Bk} B_k)
$$

$$
- K_i^{\,d} \ b_i + \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \left(k_k^{\,f} \ (\gamma_i \ b_i)^{\nu'_{ki}} - k_k^{\,b} \ (\gamma_j \ a_j)^{\nu''_{kj}} \right) \ , \qquad \textbf{(3.1.46)}
$$

$$
i \in M_b \ , \ j \in M_a
$$

Mass balance equation for adsorbed phase microbial species with the change in concentration due to microbial growth, microbial death/decay, and transfer to the aqueous phase -

$$\frac{\partial a_i}{\partial t} = r_i^{\,a} - \iota_i^{\,a} - \left(\alpha \frac{\partial p}{\partial t} \right) a_i - \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} a_i \quad , \qquad i \in M_a \quad . \tag{3.1.47}$$

where

$$r_i^{\,a} = r_i^{\,ag} - r_i^{\,ad} + r_i^{\,xfr} =$$

$$\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathscr{L}_k(\gamma_{Bk} B_k)$$

$$- K_i^{\,d}\, a_i + \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} \left(k_k^{\,f} (\gamma_j\, b_j)^{\nu'_{kj}} - k_k^{\,b} (\gamma_i\, a_i)^{\nu''_{ki}} \right) \quad , \tag{3.1.48}$$

$$i \in M_a \quad , \quad j \in M_b$$

Secondary equations describe the distribution of the aqueous chemical components between the dissolved, sorbed, and precipitated phases:

$$C_j = \rho_\ell \theta \left(c_j + \sum_{i=1}^{(M_x - K_x)} a_{ij}\, x_i \right) \quad , \quad j \in N_a \tag{3.1.49}$$

$$S_j = \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij}\, y_i + \sum_{i=1}^{(M_z - K_z)} a_{ij}\, z_i \right) \quad , \quad j \in N_a \tag{3.1.50}$$

$$P_j = \rho_b \sum_{i=1}^{(M_p - K_p)} a_{ij}\, p_i \quad , \quad j \in N_a \tag{3.1.51}$$

where

C_j = total dissolved concentration of the j-th aqueous component, mass of chemical per per unit medium volume (M/L^3).

S_j = total sorbed concentration of the j-th aqueous component, mass of chemical per per unit medium volume (M/L^3).

P_j = total precipitated concentration of the j-th aqueous component, mass of chemical per per unit medium volume (M/L^3).

Table 3.1 summarizes the species which are included in each subsystem of equations and the order in which they are stored in the program. An array is used to map species from one subsystem to the other.

Two alternate approaches for solving coupled hydrologic transport and biogeochemical reaction problems are included in HYDROBIOGEOCHEM: a fully implicit approach and an operator splitting approach. For both approaches, the non-mobile species concentrations are solved for only in the geochemical reaction subsystem of equations. The two approaches differ in their coupling of transport and reaction subsystems of equations for the mobile species. The fully implicit approach solves the two subsystems of equations sequentially and iteratively; the operator splitting approach solves them sequentially but does not iterate between them during a given time step.

For the operator splitting approach, the concentrations of mobile species are solved for in both subsystems of equations. There is no iteration between the transport and biogeochemical subsystems of equations for a given time step with this approach. The mobile species are first subjected to transport, without considering the reaction term, to yield an intermediate value of their concentrations. These transported concentrations are then subjected to the biogeochemical reactions, yielding final values of the concentrations for the current time step. Neglecting sources/sinks, decay, and compressibility and using a simplified notation for simplicity of presentation, the transport equation **(3.1.1)** solved using this approach is:

$$\frac{\partial T}{\partial t} = L(T) + R \qquad \textbf{(3.1.52)}$$

where L() is an advective-dispersive transport operator and R is a biogeochemical reaction operator. In the operator splitting approach, this equation is solved in two steps:

$$\frac{T^{(n+1/2)} - T^{(n)}}{\Delta t} = L(T^{(n+1/2)}) \qquad \textbf{(3.1.53)}$$

$$\frac{T^{(n+1)} - T^{(n+1/2)}}{\Delta t} = R^{(n+1)} \qquad \textbf{(3.1.54)}$$

where the superscripts (n), (n+1/2), and (n+1) denote the values at the prior time, at an intermediate point in the current computation, and at the new time, respectively. The same approach is taken in solving for the kinetic aqueous species concentrations (x's) and the aqueous microbial species concentrations (b's).

For all simulations regardless of the solution approach chosen, the first step is to initialize the system to equilibrium based on the input initial conditions by first fixing the concentration of the kinetic species at their specified initial concentrations and then solving Equations **(3.1.24)** through **(3.1.47)** for all other species concentrations. The total dissolved concentrations for the components, C_j's, are then calculated using Equation **(3.1.49)**.

Table 3.1 Species in the Two Subsystems of HYDROBIOGEOCHEM

Hydrologic Transport Subsystem Species		
Mobile Aqueous Components	N_{HA}	TH_1 . . . TH_{NHA}
Mobile Adsorbent Components (Colloids)	N_{HS}	WH_1 . . WH_{NHS}
Kinetic Complexed Species	K_x	x_1 . . x_{Kx}
Aqueous Microbial Species	M_b	b_1 . . b_{Mb}

Biogeochemical Reaction Subsystem Species		
Aqueous Components	N_A	T_1 . . T_{NA}
Adsorbent Components	N_S	W_1 . . . W_{NS}
Complexed Species	M_x	x_1 . . . x_{Mx}
Adsorbed Species	M_y	y_1 . . y_{My}
Ion Exchanged Species	M_z	z_1 . . z_{My}
Precipitated Species	M_p	p_1 p_2 . . p_{My}
Aqueous Microbial Species	M_b	b_1 . . b_{Mb}
Adsorbed Microbial Species	M_a	a_1 . . a_{Mb}

The solution procedure for every time step using operator splitting is outlined below:

1. Set the value of the reaction terms in the transport equations **(3.1.1)**, **(3.1.10)**, and **(3.1.17)** to zero.

2. Solve the transport subsystem of equations (**(3.1.1)**, **(3.1.10)**, and **(3.1.17)**) for mobile components $T_j^{(n+1/2)}$'s, K_x kinetic complexed species' $x_j^{(n+1/2)}$'s, and aqueous microbial species' $b_i^{(n+1/2)}$'s.

3. With these intermediate values of $T_j^{(n+1/2)}$'s, K_x $x_j^{(n+1/2)}$'s, and $b_i^{(n+1/2)}$'s, and prior values of $W_j^{(n)}$'s, $N_{eqi}^{(n)}$'s, K_y $y_j^{(n)}$'s, K_z $z_j^{(n)}$'s, K_p $p_j^{(n)}$'s, and $a_i^{(n)}$'s, solve Equations **(3.1.24)** through **(3.1.47)** for new values of all species concentrations.

4. Compute new values for $T_j^{(n+1)}$'s, $W_j^{(n+1)}$'s, $N_{eqi}^{(n+1)}$'s and $C_j^{(n+1)}$'s using Equations **(3.1.25)**, **(3.1.28)**, **(3.1.38)**, and **(3.1.49)** respectively.

5. Proceed to the next time step computation, repeating steps 1 though 4 for each time step.

In the fully implicit approach, the concentration of the aqueous components, kinetic aqueous complexed species, and aqueous microbial species are solved for in the hydrologic transport subsystem using the concentrations of all species from the previous iteration to evaluate the reaction term; they are not solved again in the second subsystem. The concentrations of these mobile species determined in the hydrological transport subsystem are passed into the biogeochemical subsystem for use in the mass balance and other equations as needed. The concentration of all remaining species are solved for in the biogeochemical reaction subsystem. Neglecting sources/sinks, decay, and compressibility and using a simplified notation for simplicity of presentation, the transport equation solved using this approach is :

$$\frac{T_j^{(k+1)}-T_j^{(k)}}{\Delta t} = L_j(T_j^{(k)}) + R_j(c^{(k)},s^{(k+1)},x^{(k)},y^{(k+1)},z^{(k+1)},p^{(k+1)},b^{(k)},a^{(k+1)}) \quad , j \in N_a \qquad \mathbf{(3.1.55)}$$

where L() is an advective-dispersive transport operator and R is a biogeochemical reaction operator. The superscript (k) denotes the value at the prior iteration and (k+1) denotes the value at the current iteration.

The solution procedure for the fully implicit approach for every time step is outlined below:

1. Based on the initial values or prior iterates of the T_j's, W_j's, N_{eqi}'s, and K_x x_i's and b_i's, solve the biogeochemical reaction Equations **(3.1.24)** through **(3.1.47)** for c_j's, s_j's, $(M_x - K_x)$ equilibrium x_i's, y_i's, z_i's, p_i's, and a_i's.

2. Compute new values for $C_j^{(k+1)}$'s using Equation **(3.1.49)**.

3. Estimate the value of the reaction terms for Equations **(3.1.1)**, **(3.1.10)**, and **(3.1.17)** based on working values for all species concentrations.

4. Solve the hydrologic transport Equations **(3.1.1)**, **(3.1.10)**, and **(3.1.17)** for mobile components T_j's, K_x kinetic complexed species' x_j's, and aqueous microbial species' b_i's.

5. Check convergence of T_j's, K_x x_j's, and b_i's using relative change from the prior iteration against the specified error tolerance.

6. If the solution is not convergent, update the iterates of the total concentration of all components and the concentration of all kinetic species, and repeat Steps 1 through 5. If a convergent solution is obtained, proceed to the next time-step computation.

The solution of the transport equations for aqueous chemical components, kinetic chemical species, and microbiological species are not independent of each other because they are coupled through the reaction terms. They must be solved either simultaneously or iteratively. The simultaneous solution of the partial differential equations governing the transport and the solution of the biogeochemical reaction equations for realistically complex systems constitutes the major effort in terms of computational time and computer storage.

A large number of numerical approximations can be used to reduce the partial differential equations governing the hydrologic transport to a system of algebraic equations. The most common numerical methods used to approximate Equation 2 are finite-difference methods (FDMs) and finite-element methods (FEMs) (Forsythe and Wasow 1960; Huebner 1975; Lapidus and Pinder 1982). Many other numerical techniques, such as the integrated finite-difference method (IFDM) (Narasimhan and Witherspoon 1977), the integrated compartment method (ICM) (Yeh and Luxmoore 1983), or the method of characteristics (MOC) (Konikow and Bredehoeft 1978), have been employed to deal with special cases of the hydrologic transport equations. Only the FDMs and the FEMs can be applied to the most generalized form of the transport equations.

The advantages of FEMs are their inherent ability to make complex boundaries discrete, to make flux-type boundary conditions easy to deal with, and to allow the flexibility to include cross-derivative terms. Disadvantages of FEMs include the central processing unit (CPU) time required to obtain element matrices and the inflexibility of using iteration methods to solve the resulting matrix equation. The FDM offers great economy because it allows simple interpolation for the derivatives and provides flexibility of solving the resulting matrix equation with various iteration methods. However, it suffers from the following aspects: the regular rectangular grid system has to be used, the flux-type boundary conditions have to be extrapolated, and the cross-derivative terms cannot be consistently approximated.

The most severe limitations of the IFDM are its inability to treat anisotropic media and its use of the Jacobian iteration method, in which the rate of convergency is extremely slow; however, it offers even more flexibility than the FEMs in making the complex boundaries discrete, and the physical representation of the method is clearly understood. The ICM, while retaining the advantage of the IFDM, can deal with anisotropic media by defining new variables but at the expense of having to solve a large number of simultaneous field equations (Yeh and Luxmoore 1983). In addition, ICM provides options of using the direct elimination method and iteration methods with the Gauss-Seidel (G-S) or successive over-relaxation (SOR) schemes to solve the matrix equation (Yeh and Luxmoore 1983). The MOC is best used to solve advection-dominant transport problems. The main limitations of the MOC lay in the fact that computer codes based on the method are problem specific and are very difficult to modify for generic applications.

In light of these discussions, FEMs are the preferred numerical methods for addressing reactive hydrologic transport problems. In addition, there has been significant progress in using iterative methods to solve finite-element equations (Yeh 1985, 1986), and influence coefficient methods have been proposed to analytically and economically compute the element matrices (Huyakorn et al. 1985).

3.2 Solution of Transport Equations

Because the hybrid Lagrangian-Eulerian FEM is used to solve the transport equations, Equation **(3.1.1)** is rearranged in the implicit Lagrangian form. Disregarding the decay and compressibility terms and dropping the subscript to simplify the notation, we obtain

For mobile chemical components:

$$\rho_\ell \theta \, \frac{DT'}{Dt} - \nabla \cdot \left[\rho_\ell \theta \, \mathbf{D} \, \frac{C'}{T'} \cdot \nabla T' \right] + K \, T' + \rho^* Q \, \frac{C'}{T'} T' = R^c + M^c \qquad \textbf{(3.2.1)}$$

where the Lagrangian tracking velocity is

$$V_L = \frac{1}{\rho_\ell \theta} \left[\rho_\ell \mathbf{V} \frac{C_j'}{T_j'} - \rho_\ell \theta \, \mathbf{D} \cdot \nabla \frac{C_j'}{T_j'} \right] \qquad \textbf{(3.2.2)}$$

and

$$K = \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C'}{T'} - \frac{C'}{T'} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) \right] \qquad \textbf{(3.2.3)}$$

and

$$
\begin{aligned}
R_j^c = \rho_\ell \theta \left(r_j^c \big|^{bio} + \sum_{i=1}^{(M_x - K_x)} a_{ij}\ r_i^x \big|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y - K_y)} a_{ij}\ r_i^y \big|^{bio} + \sum_{i=1}^{(M_z - K_z)} a_{ij}\ r_i^z \big|^{bio} + \sum_{i=1}^{(M_p - K_p)} a_{ij}\ r_i^p \big|^{bio} \right) \\
- \rho_\ell \theta \left(\sum_{i=1}^{K_x} a_{ij}\ r_i^x \big|^{chem} \right) - \rho_b \left(\sum_{i=1}^{K_y} a_{ij}\ r_i^y \big|^{chem} + \sum_{i=1}^{K_z} a_{ij}\ r_i^z \big|^{chem} + \sum_{i=1}^{K_p} a_{ij}\ r_i^p \big|^{chem} \right)
\end{aligned}
\qquad \textbf{(3.2.4)}
$$

Similarly, expressing Equation **(3.1.10)** for the kinetic aqueous complexed chemical species in Lagrangian form:

$$
\rho_\ell \theta \frac{Dx}{Dt} - \nabla \cdot \left[\rho_\ell \theta\ \mathbf{D} \cdot \nabla x \right] + K\ x + \rho^* Q\ x = \rho_\ell \theta\ r^x + m^x \qquad \textbf{(3.2.5)}
$$

where the Lagrangian velocity is

$$
V_L = \frac{1}{\rho_\ell \theta} \left[\rho_\ell\ \mathbf{V} \right] \qquad \textbf{(3.2.6)}
$$

and

$$
K = 0 \qquad \textbf{(3.2.7)}
$$

and

$$
r^x = \sum_{k=1}^{NRXNK} r^x \big|_k^{chem} + \sum_{k=1}^{NBRXNK} r^x \big|_k^{biodeg} - r^{bioresp} \qquad \textbf{(3.2.8)}
$$

Similarly, expressing Equation **(3.1.17)** for the aqueous microbial species in Lagrangian form:

$$
\rho_\ell \theta \frac{Db}{Dt} - \nabla \cdot \left[\rho_\ell \theta\ \mathbf{D} \cdot \nabla b \right] + K\ b + \rho^* Q\ b = \rho_\ell \theta\ r^b + m^b \qquad \textbf{(3.2.9)}
$$

where K and the Lagrangian velocity are given by Equations **(3.2.6)** and **(3.2.7)**, respectively, and

$$
r^b = r^{bg} - r^{bd} + r^{xfr} \qquad \textbf{(3.2.10)}
$$

The kinetic aqueous complexed species and the aqueous microbial species by definition exist only in the aqueous phase. The ratio of their concentration in the aqueous phase to their total concentration is therefore unity. Equations **(3.2.5)** and **(3.2.9)** are therefore identical in form to Eq. **(3.2.1)**, with C/T = 1, ∇ (C/T) = 0, and the reaction terms defined appropriately for these cases. The remainder of this section will discuss the solution of the transport equations in terms of Eq. **(3.2.1)**; the discussion is applicable to the solution of Equations **(3.2.5)** and **(3.2.9)** as well.

3.2.1 Spatial Discretization of Transport Equations

Equation **(3.2.1)** is integrated in the spatial dimensions by the weighted residual method in conjunction with finite elements. Because the formulation and use of the FEM has been well documented, the theoretical basis will not be presented here. Only the numerical procedures are summarized in the following discussion. The region of interest is subdivided into an assemblage of smaller domains called elements, which are interconnected by nodes either on the vertices or the boundaries of the elements. Following the procedure of the finite-element weighted-residual method, the approximate formulation of the distribution of the total analytical concentration T in Equation **(3.2.1)** is obtained. Thus, let the variable T be approximated by

$$T' = \sum_{j=1}^{n} T_j' N_j \qquad \textbf{(3.2.11)}$$

where

N_j = the basis function of the spatial coordinate for j-th node.
T_j' = the value of T' at node j.
n = number of finite-element nodes in the region.

Upon substituting Equation **(3.2.11)** into Equation **(3.2.1)** and applying the Galerkin FEM, we obtain the following matrix equation:

$$[A]\left\{\frac{DT'}{D\tau}\right\} + \left([D] + [C] + [Q] \right)\{T'\} = \{R\} + \{S\} + \{B\} \qquad \textbf{(3.2.12)}$$

where

$\left\{\frac{DT'}{D\tau}\right\}$ = column vector containing the values of $\frac{DT'}{D\tau}$.

$\{T'\}$ = column vector containing the value of T' at all nodes.

$[A]$ = mass matrix.

$[D]$ = stiff matrix resulting from dispersion.

$[C]$ = matrix resulting from the first order rate constant term.

$[Q]$ = matrix resulting from the source term.

$\{R\}$ = load vector from the biogeochemical reactions.

$\{S\}$ = load vector from the external source.

{B} = load vector from the boundary source.

The matrices [A], [D], [C], and [Q] are given by

$$A_{ij} = \sum_{e \in M_e} \int_{R_e} N_\alpha^e \, (\rho_\ell \theta) \, N_\beta^e \, dR \ , \tag{3.2.13}$$

$$D_{ij} = \sum_{e \in M_e} \int_{R_e} \left(\nabla N_\alpha^e\right) \cdot \rho_\ell \theta \mathbf{D} \, \frac{C'}{T'} \cdot \left(\nabla N_\beta^e\right) dR \tag{3.2.14}$$

$$C_{ij} = \sum_{e \in M_e} \int_{R_e} N_\alpha^e \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C'}{T'} - \frac{C'}{T'} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) \right] N_\beta^e \, dR \tag{3.2.15}$$

and

$$Q_{ij} = \sum_{e \in M_e} \int_{R_e} N_\alpha^e \, Q \rho^* \, \frac{C'}{T'} \, N_\beta^e \, dR \tag{3.2.16}$$

where

R_e = region of element e.
M_e = set of elements that have a local side α-β coinciding with the global side i-j.
N_α^e = α-th local base function of element e.

Similarly, the load vectors {R}, {S}, and {B} are given by

$$R_i = \sum_{e \in M_e} \int_{R_e} N_\alpha^e R^e \, dR \tag{3.2.17}$$

$$S_i = \sum_{e \in M_e} \int_{R_e} N_\alpha^e Q C_{in} \, dR \tag{3.2.18}$$

and

$$B_i = \sum_{e \in N_{se}} \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \frac{C'}{T'} \cdot \nabla T' \right) dB \ , \tag{3.2.19}$$

where

B_e = the length of boundary segment e.
N_{se} = set of boundary segments having a local node α coinciding with global node i.

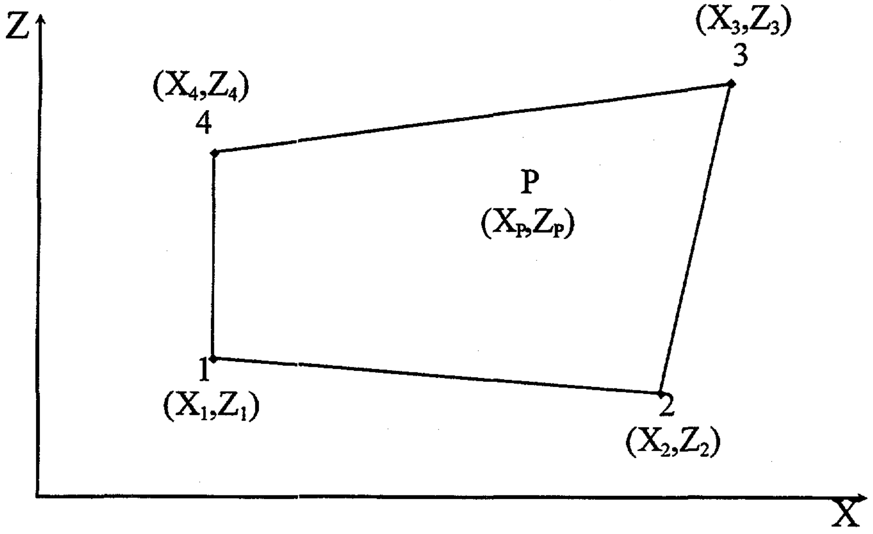
The reduction of the partial differential equation, Equation **(3.2.1)**, to the set of ordinary differential equations, Equation **(3.2.12)**, simplifies to the evaluation of integrals on the right-hand side of Equations **(3.2.13)** through **(3.2.19)** for every element or boundary segment. The major task that remains is the specification of base functions and the performance of numerical integration to yield the element matrices. This will be carried out for both the quadrilateral and triangular elements because both types of elements are employed in this computer program.

3.2.2 Base and Weighting Functions

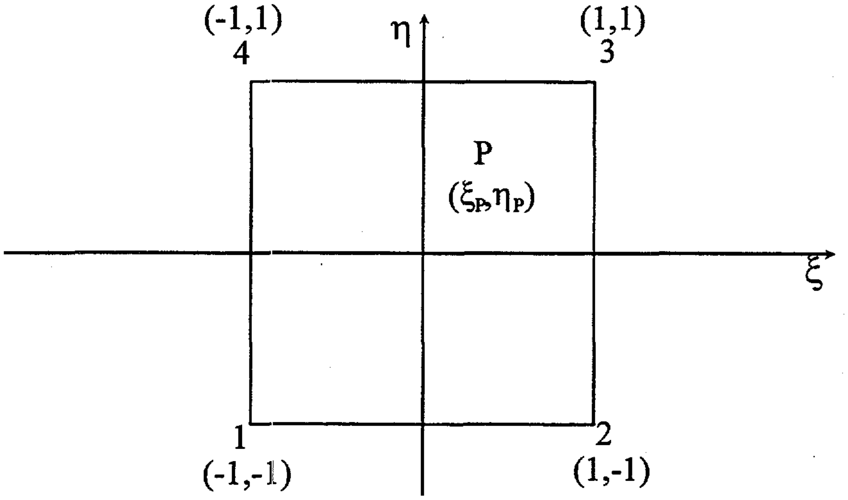
For a quadrilateral element having four corner nodes, a bilinear polynomial base function for the α-th node may be written in terms of local normalized coordinates as

$$N_\alpha^e = \frac{1}{4}(1 + \xi_\alpha \xi)(1 + \eta_\alpha \eta) \quad \text{and} \quad \alpha = 1, 2, 3, 4 \quad , \tag{3.2.20}$$

where ξ_α and η_α are the local coordinates of the corner nodes, which are numbered 1 to 4 and which progress around the element in a counterclockwise direction as shown in Figure 3.1.



Global Coordinates



Local Coordinates

Fig. 3.1 Global Versus Local Coordinates for a Typical Quadrilateral Element

The transformation from local coordinate (ξ_α,η_α) to the global coordinate (x,z) is achieved by

$$x = \sum_{\alpha=1}^{4} x_\alpha N_\alpha^e(\xi,\eta) \quad \text{and} \quad z = \sum_{\alpha=1}^{4} z_\alpha N_\alpha^e(\xi,\eta) \quad . \tag{3.2.21}$$

For a linear triangular element e (Figure 3.2), the base functions are given by

$$N_1^e = L_1 \quad , \quad N_2^e = L_2 \quad , \quad N_3^e = L_3 \quad , \tag{3.2.22}$$

where

N_α^e (α = 1, 2, or 3) = the base function of node α in terms of local coordinate (L_1,L_2,L_3) (Figure 3.2).

The local coordinates are also called area coordinates for a reason to be explained later. The global coordinates (x,z) and the area coordinates (L_1,L_2,L_3) are related by

$$L_1 = \frac{1}{2A}\left(a_1 + b_1x + c_1z\right) \quad ,$$

$$L_2 = \frac{1}{2A}\left(a_2 + b_2x + c_2z\right) \quad , \tag{3.2.23}$$

and

$$L_3 = \frac{1}{2A}\left(a_3 + b_3x + c_3z\right) \quad ,$$

where

$$a_1 = x_2z_3 - x_3z_2 \quad , \quad b_1 = z_2 - z_3 \quad , \quad c_1 = x_3 - x_2$$

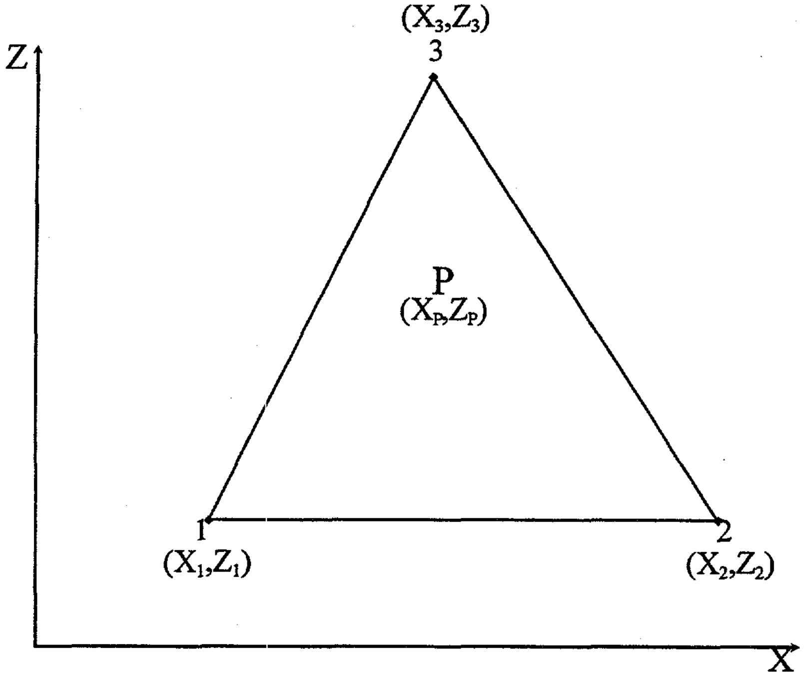
$$a_2 = x_3z_1 - x_1z_3 \quad , \quad b_2 = z_3 - z_1 \quad , \quad c_2 = x_1 - x_3 \tag{3.2.24}$$

$$a_3 = x_1z_2 - x_2z_1 \; , \quad b_3 = z_1 - z_2 \quad , \quad \text{and} \quad c_3 = x_2 - x_1 \quad ,$$

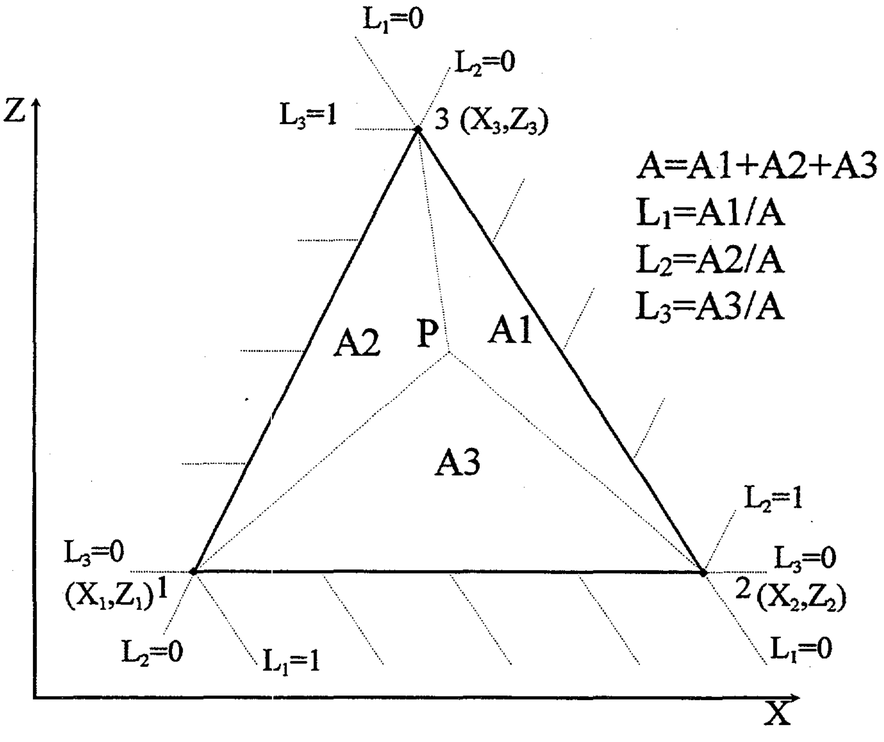
and A is the area of the triangle. It is seen from Equations **(3.2.23)** and **(3.2.24)** that

$$L_1 + L_2 + L_3 = 1 \quad . \tag{3.2.25}$$

Thus, it is clear that only two of the area coordinates can be independent, just as in the original coordinate system, where there are only two independent coordinates, x and z. Furthermore, a little algebraic manipulation will reveal that the coordinates L_1, L_2, and L_3 are in fact the ratios of the areas A_1, A_2, and A_3, respectively, to the triangular area A (Figure 3.2). This is why they are called area coordinates.



Global Coordinates



Natural Coordinates

Fig. 3.2 Global Coordinates vs. Local Coordinates for a Typical Triangular Element

3.2.3 Evaluation of Element Matrices

To complete the reduction of the partial differential equation [Equation **(3.2.1)**] to the ordinary differential equation [Equation **(3.2.12)**], one has to evaluate the integrals on the right-hand sides of Equations **(3.2.13)** through **(3.2.19)** for every element to yield the element mass matrix [A^e], dispersion matrix [D^e], first order rate matrix [C^e], fluid source matrix [Q^e], element reaction vector {R^e} and source vector {S^e} as

$$A^e_{\alpha\beta} = \int_{R_e} N^e_\alpha (\rho_\ell \theta) N^e_\beta \, dR \quad , \tag{3.2.26}$$

$$D^e_{\alpha\beta} = \int_{R_e} \left(\nabla N^e_\alpha\right) \cdot \rho_\ell \theta \mathbf{D} \, \frac{C'}{T'} \cdot \left(\nabla N^e_\beta\right) dR \tag{3.2.27}$$

$$C^e_{\alpha\beta} = \int_{R_e} N^e_\alpha \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C'}{T'} - \frac{C'}{T'} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) \right] N^e_\beta \, dR \tag{3.2.28}$$

$$Q^e_{\alpha\beta} = \int_{R_e} N^e_\alpha \, Q\rho^* \, \frac{C'}{T'} \, N^e_\beta \, dR \tag{3.2.29}$$

$$R^e_\alpha = \int_{R_e} N^e_\alpha R^c \, dR \tag{3.2.30}$$

and

$$S^e_\alpha = \int_{R_e} N^e_\alpha Q C_{in} \, dR \tag{3.2.31}$$

where the superscript or subscript e denotes the element, α, $\beta = 1, 2, 3$, or 4 for bilinear quadrilateral elements, and α, $\beta = 1, 2$, or 3 for linear triangular elements.

Equations **(3.2.26)** through **(3.2.31)** are computed by either Gaussian (Conte 1965) or nodal quadrature as specified by the user . With the element matrices [A^e], [D^e], [C^e], and [Q^e] and the element column vectors {R^e} and {S^e} computed, the global matrices [A], [D], [C], and [Q] and the global column vectors {R} and {S} are then assembled element by element.

3.2.4 Mass Lumping Option

Referring to the element mass matrix [A^e], first order rate matrix [C^e], and source matrix [Q^e], one may note that these are the unit matrices if the finite-difference formulation is adopted in the spatial discretization. Hence, by proper scaling these matrices can be reduced to the finite-difference equivalent by lumping (Clough 1971). In many cases, the lumped matrices result in a better solution.

Furthermore, with these lumped element matrices, the problem can be reduced to a beaker system when advection and dispersion-diffusion terms are not involved in the transport equation. Under such circumstances, they are preferred to the nonlumped mass, fluid source, and growth matrices. Therefore, an option is provided for the lumping of these matrices. A systematic and mathematically acceptable procedure for such lumping has been well established (Zienkiewicz 1977). For example, the fluid source matrix can be lumped according to the following:

$$Q^e_{\alpha\alpha} = \sum_{\beta=1}^{4} \int_{R_e} N^e_\alpha \, Q\rho^* \, \frac{C'}{T'} \, N^e_\beta \, dR \qquad \textbf{(3.2.32)}$$

$$\text{and } Q^e_{\alpha\beta} = 0 \quad \text{if} \quad \beta \neq \alpha \ .$$

3.2.5 Time Integration

An important advantage of the finite-element approximation is the inherent ability to handle complex boundaries and obtain the normal derivatives therein. In the time dimension, such advantages are not evident. Thus, FDMs are typically used in the approximation of the time derivative. Using a time weighting factor, w, we obtain from Equation **(3.2.12)** the following matrix equation:

$$[G]\{T\}_{t+\Delta t} = [H]\{T^*\} + \{R\} + \{S\} + \{B\} \ , \qquad \textbf{(3.2.33)}$$

where

$\{T\}_{t+\Delta t}$	=	column vector representing the value of $\{T\}$ at time $(t+\Delta t)$.
$\{T^*\}$	=	the Lagrangian concentration.
Δt	=	time-step size.

The matrices [G] and [H] are given as

$$[G] = \frac{[A]}{\Delta\tau} + w([D] + [C] + [Q]) \ ,$$

$$[H] = \frac{[A]}{\Delta\tau} - (1-w)([D] + [C] + [Q]) \qquad \textbf{(3.2.34)}$$

When w = 0, the time integration is explicit. When w = 0.5, it is the Crank-Nicolson central difference. For the implicit (or backward) difference, w = 1.0.

The Lagrangian concentration $\{T^*\}$ is computed by the backward method of characteristics as follows:

$$x_i^* = x_i - \int_t^{t+\Delta\tau} V_L d\tau$$

$$T_i^* = \sum_j T_j'(t) N_j(x_i^*) \qquad \textbf{(3.2.35)}$$

where

x_i^* = the Lagrangian point = the location at time t of a fictitious particle which would arrive at the node x_i at time t+Δt.

$T_j'(t)$ = the value of concentration at node j at time t.

$N_j(x_i^*)$ = the interpolation function associated with node j evaluated at the Lagrangian point x_i^*.

and V_L is the Lagrangian tracking velocity given by Equation **(3.2.2)** and repeated here:

$$V_L = \frac{1}{\rho_\ell \theta}\left[\rho_\ell \mathbf{V}\frac{C'}{T'} - \rho_\ell \theta\ \mathbf{D} \cdot \nabla \frac{C'}{T'}\right] \qquad \textbf{(3.2.36)}$$

If x_i^* is located within the region of interest, we define Δτ in Equation **(3.2.35)** as

$$\Delta\tau = \Delta t \ . \qquad \textbf{(3.2.37)}$$

If x_i^* is located outside the region of interest, we must find a $\Delta\tau(x_i^*)$ such that

$$x_i^* = x_i - \int_{t+\Delta t-\Delta\tau(x_i^*)}^{t+\Delta t} V_L dt \qquad \textbf{(3.2.38)}$$

will locate x^*_i on the boundary. Thus, Δτ is less than or equal to Δt.

3.2.6 Conventional Finite Element Method

HYDROBIOGEOCHEM allows the user to choose the conventional finite element method rather than the hybrid Lagrangian-Eulerian method for solution of the matrix equations if desired. In this case, the matrix equation **(3.2.33)** is instead:

$$[G]\{T'\}_{t+\Delta t} = [H]\{T'\}_t + \{R\} + \{S\} + \{B\} \ , \qquad \textbf{(3.2.39)}$$

where

$\{T'\}_t$ = column vector representing the value of $\{T'\}$ at time t.

The matrices [G] and [H] are given as

$$[G] = \frac{[A]}{\Delta t} + w([D] + [C] + [Q]) + wv[V] \quad ,$$

$$[H] = \frac{[A]}{\Delta t} - (1-w)([D] + [C] + [Q]) - (1-wv)[V] \tag{3.2.40}$$

where

wv = time weighting factor for the velocity term
[V] = matrix resulting from the velocity term, given by

$$V_{ij} = \sum_{e \in M_e} \int_{R_e} N_\alpha^e \frac{1}{\rho_\ell \theta} \left[\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \, \mathbf{D} \cdot \nabla \frac{C'}{T'} \right] \cdot \left(\nabla N_\beta^e \right) dR \tag{3.2.41}$$

This global velocity matrix [V] is assembled element by element from the velocity matrix for each element $[\, V_{\alpha\beta}^{e} \,]$:

$$V_{\alpha\beta}^e = \int_{R_e} N_\alpha^e \frac{1}{\rho_\ell \theta} \left[\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \, \mathbf{D} \cdot \nabla \frac{C'}{T'} \right] \cdot \left(\nabla N_\beta^e \right) dR \tag{3.2.42}$$

3.2.7 Boundary Conditions

To incorporate the boundary conditions, we have to evaluate the right-hand side of Equation **(3.2.19)** for every boundary segment B_e to yield the load vector $\{B^e\}$:

$$B_\alpha^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \theta \mathbf{D} \frac{C'}{T'} \cdot \nabla T' \right) dB \quad , \tag{3.2.43}$$

Variable boundary conditions are imposed on the flow-through boundary segments, where the flow direction is not known a priori. When the flow is directed out of the region, the Neumann boundary condition given by Equation **(3.1.8)** is implemented. Combining Equation **(3.2.43)** and **(3.1.8)** yields the following for a Neumann boundary segment:

$$B_\alpha^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) \cdot T' \, dB - \int_{B_e} N_\alpha^e \, \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} T' dB \quad , \qquad \alpha = 1, 2 \quad . \qquad \textbf{(3.2.44)}$$

This represents the normal fluxes through the two nodal points of the segment B_e on the variable boundary when $\mathbf{V} \cdot \mathbf{n} > 0$.

The total analytical concentration on the boundary segment B_e can be approximated by

$$T' = \sum_{\beta=1}^{2} T_\beta' N_\beta^e \quad . \qquad \textbf{(3.2.45)}$$

Using Equation **(3.2.45)**, the boundary-element column vector $\{B_n^e\}$ for a Neumann segment can be expressed as:

$$\{B_n^e\} = \left(\left[V1_n^e \right] + \left[V2_n^e \right] \right) \{T'\} \quad , \qquad \textbf{(3.2.46)}$$

where the Neuman boundary matrices are given by

$$V1_{n\alpha\beta}^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) N_\beta^e \, dB \quad ,$$

$$V2_{n\alpha\beta}^e = - \int_{B_e} N_\alpha^e \, \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} N_\beta^e dB \quad , \qquad \textbf{(3.2.47)}$$

$$\alpha = 1, 2 \quad \text{and} \quad \beta = 1, 2 \quad .$$

When flow on the variable boundary is directed into the region, the Cauchy boundary condition given by Equation **(3.1.9)** is implemented. Combining Equation **(3.2.43)** and **(3.1.9)** yields the following for a Cauchy boundary segment:

$$B_\alpha^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) \cdot T' \, dB - \int_{B_e} N_\alpha^e \, q_v \, dB \quad , \qquad \alpha = 1, 2 \qquad \textbf{(3.2.48)}$$

Using Equation **(3.2.45)**, we obtain the boundary-element column vector $\{B_c^e\}$ for a Cauchy segment:

$$\{B_c^e\} = \left[V_c^e \right] \{T\} + \{q_c\} \quad , \qquad \textbf{(3.2.49)}$$

in which the Cauchy boundary flux vector $\{q_c^e\}$ and the Cauchy boundary matrix $[V_c^e]$ are given by

$$q_{c\alpha}^{e} = -\int_{B_e} N_\alpha^e \mathbf{n}\cdot \mathbf{V} C_{in} dB \quad , \quad \alpha = 1, 2$$

$$\text{and } V_{c\alpha\beta}^{e} = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C^\prime}{T^\prime} - \rho_\ell \theta \mathbf{D}\cdot\nabla \frac{C^\prime}{T^\prime}\right) N_\beta^e \, dB \quad , \qquad \textbf{(3.2.50)}$$

$$\alpha = 1, 2 \quad \text{and} \quad \beta = 1, 2$$

where

C_{in} = the total dissolved concentration in the incoming fluid.

Note that $V^e_{c\alpha\beta}$ in Eq. **(3.2.50)** and $V1^e_{n\alpha\beta}$ in Eq. **(3.2.47)** have the same form.

Since the flow direction is not known a priori on the variable boundary, Equations **(3.2.46)** and **(3.2.49)** can be combined across all variable boundary segments into a general expression for the global boundary column vector {B}:

$$\{B\} = \{q\} + ([V1] + [V2])\{T\} \quad , \qquad \textbf{(3.2.51)}$$

in which

$$\{q\} = \sum_{e\in N_{ve}} \{q_v^e\} = \sum_{e\in N_{ce}} \{q_v^e\}$$

$$[V1] = \sum_{e\in N_{ve}} \left[V1_v^e\right] = \sum_{e\in N_{ce}} \left[V_c^e\right] + \sum_{e\in N_{ne}} \left[V1_n^e\right] \qquad \textbf{(3.2.52)}$$

$$[V2] = \sum_{e\in N_{ve}} \left[V2_v^e\right] = \sum_{e\in N_{ne}} \left[V2_n^e\right]$$

where

N_{ve} = the number of variable-boundary segments (= $N_{ce} + N_{ne}$),
N_{ce} = the number of Cauchy boundary segments on the variable boundary,
N_{ne} = the number of Neuman boundary segments on the variable boundary,

and

$$
\begin{aligned}
q^{e}_{v\alpha} &= -\int_{B_e} N^{e}_{\alpha}(\mathbf{n}\cdot \mathrm{V})C_{in}\,dB \quad , \quad \alpha = 1,\, 2 \\
V1^{e}_{v\alpha\beta} &= \int_{B_e} N^{e}_{\alpha}\mathbf{n}\cdot\left(\rho_\ell \mathbf{V}\,\frac{C'}{T'} - \rho_\ell\theta\mathbf{D}\cdot\nabla\frac{C'}{T'}\right)N^{e}_{\beta}\,dB \quad , \\
V2^{e}_{v\alpha\beta} &= -\int_{B_e} N^{e}_{\alpha}\,\mathbf{n}\cdot\rho_\ell\mathbf{V}\frac{C'}{T'}N^{e}_{\beta}dB \quad , \\
&\alpha = 1,\, 2 \quad \text{and} \quad \beta = 1,\, 2 \quad .
\end{aligned}
\tag{3.2.53}
$$

When the flow is directed out of the region, $\{q^{e}_{v}\}$ is set equal to 0. When the flow is directed into the region, $[V2^{e}{}_{v\alpha\beta}]$ is set equal to 0.

Substituting Equation **(3.2.51)** into Equation **(3.2.33)**, we obtain

$$
[U]\{T'\}_{t+\Delta t} = [W]\{T^{*}\} + \{R\} + \{S\} + \{q\} \tag{3.2.54}
$$

where [U] and [W] are given by the following equations:

$$
\begin{aligned}
[U] &= [G] - w([V1] + [V2]) = \frac{[A]}{\Delta\tau} + w([D] + [C] + [Q] - [V1] - [V2]) \; , \\
[W] &= [H] + (1-w)([V1] + [V2]) = \frac{[A]}{\Delta\tau} - (1-w)([D] + [C] + [Q] - [V1] - [V2])
\end{aligned}
\tag{3.2.55}
$$

At nodes where Dirichlet boundary conditions are applied, an identity equation is generated for each node and included in the matrices of Equation **(3.2.54)**. The detailed method of applying this type of boundary condition can be found elsewhere (Wang and Connor 1975).

Equation **(3.2.54)**, after modified for the Dirichlet boundary condition, is solved sequentially and iteratively with the the biogeochemical reaction problem specified by Equations **(3.1.24)** through **(3.1.51)** to yield $\{T'\}$, $\{W\}$, $\{N_{eq}\}$, $\{c\}$, $\{s\}$, $\{x\}$, $\{y\}$, $\{z\}$, $\{p\}$, $\{b\}$, and $\{a\}$ for all species, and $\{C\}$, $\{S\}$, and $\{P)$ for all chemical components.

Boundary conditions need to be implemented in the computation of the Lagrangian concentrations $\{T^{*}\}$. If flow on the variable boundary is directed out from the region of interest (i.e. a Neumann boundary condition), the boundary condition need not be implemented. On the Neumann boundary, backtracking would locate x^{*}_{i} in the interior of the domain; hence, the Lagrangian concentration at the i-th Neumann boundary node is simply computed via interpolation. If the flow is directed into the region (i.e. a Cauchy boundary condition), then the Lagrangian concentration on the i-th variable boundary node T^*_{vi} is computed by

$$T^*_{vi} = \frac{\int_{B_v} N_i \mathbf{n} \cdot \mathbf{V} C_{in} dB}{\int_{B_v} N_i \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} T' dB} \tag{3.2.56}$$

where

C_{in} = the concentration in the fluid entering through the variable boundary.

On the Dirichlet boundary nodes, the Lagrangian concentration is simply set to the specified value.

3.2.8 Solution of the Matrix Equations

Although both the matrices [U] and [W] are not functions of the unknown {T}, Equation **(3.2.54)** still represents a system of nonlinear algebraic equations because of the reaction terms, {R}. The solution of this system requires some type of iterative procedure. The approach taken here is to make an initial estimate of the unknown {T}. We compute the value of the reaction terms using the biogeochemical subsystem of equations and the working values for the concentrations of the species involved in these reactions. Substituting the reaction term vectors into Equation **(3.2.54)**, we linearize the matrix equation, which is then solved by the method of linear algebra to obtain the new solution {T}. The new estimate is obtained by the weighted average of the new solution and the previous estimate,

$$\{T^{k+1}\} = \omega\{T\} + (1 - \omega)\{T^k\} \ , \tag{3.2.57}$$

where

$\{T^{(k+1)}\}$ = the new estimate.
$\{T^k\}$ = the previous estimate.
$\{T\}$ = the new solution.
ω = the iteration relaxation parameter.

The procedure is repeated until the new solution {T} is reached within a prescribed tolerance of error. When the iteration parameter is greater than or equal to 0 but is less than 1, the iteration is termed under-relaxation. If $\omega = 1$, the method is exact-relaxation. For the cases in which ω is greater than 1 but less than or equal to 2, the iteration is termed over-relaxation.

The individual terms in the reaction load vector {R} may be positive, negative, or zero depending upon the progress over the current time step of the reactions in which the chemical or microbial species associated with that equation participates. An adaptive explicit-implicit scheme is incorporated to handle the reaction load vector to help achieve convergent solutions for the case when the reaction term is negative. Incorporating this scheme into Equation **(3.2.54)**:

$$[U]\{T\}_{t+\Delta t} = [W]\{T^{*}\} + \{R\} + \{S\} + \{q\} \quad , \quad \{R\} \geq 0 \tag{3.2.58}$$

$$[U]\{T\}_{t+\Delta t} - \frac{[R]}{\{T^{k}\}}\{T\}_{t+\Delta t} = [W]\{T^{*}\} + \{S\} + \{q\} \quad , \quad \{R\} < 0 \tag{3.2.59}$$

where [R], the matrix resulting from the reaction term used on the left hand side of Equation **(3.2.59)** is given by

$$R_{ij} = \sum_{e \in M_e} \int_{R_e} N_\alpha^e \frac{R^c}{T^{/}} N_\beta^e \, dR \tag{3.2.60}$$

The handling of the reaction term as explicit or implicit can vary for each of the matrix equations at one time step and can vary from one time step to the next for a given species' equation.

Six options are employed to solve the linearized matrix equation: the direct elimination method, the pointwise iteration method and four preconditioned conjugate gradient methods. When the direct elimination method is used to solve the matrix equation, a single iteration loop is employed to iterate the nonlinearity. However, when the pointwise iterations are used, a double loop is required: the inner loop to solve the linearized equation and the outer loop to iterate the nonlinearity. Three options can be employed when the pointwise iteration method is used to solve the linearized matrix equation: the successive under-relaxation (SUR), Gauss-Seidel (G-S), and successive over-relaxation (SOR) iteration methods. These methods are unified by a relaxation parameter, ω. When ω is less than 1 but greater than or equal to 0, the method is termed SUR iteration. When ω equals 1, the method is termed G-S iteration. If ω is greater than 1 but less than or equal to 2, the method is termed SOR iteration.

3.3 Solution of Geochemical Reaction Equations

The total concentration of the aqueous components (T_j's), the concentration of the kinetic aqueous complexed species (K_x x_i's), and the concentration of aqueous microbial species (b_i's) are obtained from the hydrologic transport subsystem of the program and the adsorbent components' W_j's, ion exchange sites' N_{eqi}'s, and other kinetic species' concentrations are given by the values at the prior time step. With these values, the remaining governing equations involve 7 sets of unknowns in 7 sets of algebraic equations after the kinetic rate equations are discretized by implicit time difference: N_a c_k's, N_s s_k's, $(M_x - K_x)$ x_i's, M_y y_i's, M_z z_i's, M_p p_i's, and M_a a_i's. The Newton-Raphson iterative technique is used in HYDROBIOGEOCHEM to solve these sets of equations.

For computational efficiency in the Newton-Raphson method, the number of simultaneous equations are kept to a minimum. Simplifications can be made to reduce the number of simultaneous equations to be solved. When dealing with equilibrium reactions for both complexed and adsorbed species it is seen in equations **(3.1.30)** and **(3.1.33)** that the complexed species (x_i's) and the adsorbed species (y_i's) concentration values are functions of the aqueous and adsorbed component species. Thus the equilibrium complexed species (x_i) and the adsorbed species (y_i) can be eliminated from the solution matrix by substituting for each using these functional relations to the component species. This allows the program to solve the equilibrium equations for the complexed and adsorbed species outside of the matrix solver after the other species concentrations have been obtained, thereby reducing the number of simultaneous equation.

Substitution of Equations **(3.1.30)** and **(3.1.33)** into Equation **(3.1.25)** yields the following mole balance equation for mobile aqueous components:

$$T_j = \rho_\ell \theta \left(c_j + \sum_{i=1}^{(M_x-K_x)} a_{ij} \left[\frac{K_\kappa^{eq} \prod\limits_{r \in N_a} (\gamma_r g_r)^{\nu'_{\kappa r}}}{(\gamma_i)^{\nu''_{\kappa i}}} \right]^{\frac{1}{\nu''_{\kappa i}}} \right) +$$

$$\rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{ij} \left[\frac{K_\kappa^{eq} \prod\limits_{r \in (N_a+N_s)} (\gamma_r g_r)^{\nu'_{\kappa r}}}{(\gamma_i)^{\nu''_{\kappa i}}} \right]^{\frac{1}{\nu''_{\kappa i}}} + \sum_{i=1}^{(M_z-K_z)} a_{ij} z_i + \sum_{i=1}^{(M_p-K_p)} a_{ij} p_i \right) , \qquad \textbf{(3.3.1)}$$

$$j \in N_a$$

where $\kappa \in NRXNE$ is the equilibrium reaction in which the equilibrium complexed or adsorbed species is formed.

Substitution of Equations **(3.1.33)** into Equation **(3.1.28)** yields the following mole balance equation for adsorbent components:

$$W_j = \rho_b \left(s_j + \sum_{i=1}^{(M_y-K_y)} a_{ij} \left[\frac{K_\kappa^{eq} \prod\limits_{r \in (N_a+N_s)} (\gamma_r g_r)^{\nu'_{\kappa r}}}{(\gamma_i)^{\nu''_{\kappa i}}} \right]^{\frac{1}{\nu''_{\kappa i}}} \right) , \quad j \in N_s \qquad \textbf{(3.3.2)}$$

3.3.1 Solution of the Nonlinear Algebraic Equations

The sets of equations for the biogeochemical subsystem can be solved by methods of nonlinear algebra. The Newton-Raphson iterative technique has been described in detail elsewhere (Westall et al. 1976) and is summarized as follows. Consider a system of algebraic equations of the form

$$y(x) = 0 \quad . \tag{3.3.3}$$

Taylor expansion of Equation **(3.3.3)** about the previous iterate yields

$$y^n + \frac{dy}{dx}\left(x^{n+1} - x^n\right) = 0 \ , \tag{3.3.4}$$

where

y^n = value of $y(x)$ evaluated at x^n.
x^n = value of x from the previous iteration.
x^{n+1} = value of x at the new iteration.

Written in matrix notation, Equation **(3.3.4)** becomes

$$\mathbf{Z}^n\left(\mathbf{X}^n - \mathbf{X}^{n+1}\right) = \mathbf{Y}^n \quad , \tag{3.3.5}$$

where

Y = residues.
Z = Jacobian of **Y** with respect to **X**.
superscript **n** = value at the previous iteration.
superscript **n+1** = value at the new iteration.

Thus, the solution of Equation **(3.3.3)** involves the following steps:

1. Given the function y(x) and the value of x^n, compute the residue Y_n.
2. Compute the Jacobian $\mathbf{Z}^n$.
3. Find the values $\Delta\mathbf{X}$ (where $\Delta\mathbf{X}$ denotes $\mathbf{X}^n$-$\mathbf{X}^{n+1}$) by Equation (3.3.4).
4. Compute the new iterate by

$$\mathbf{X}^{n+1} = \mathbf{X}^n - \Delta\mathbf{X} \quad . \tag{3.3.6}$$

The above steps are repeated until a convergent solution is obtained. The application of the Newton-Raphson method to the geochemical reaction model is straightforward. The residues are computed from Equations **(3.1.24)** through **(3.1.47)** (or their reduced sets). The Jacobian is computed by taking the partial differential of Equations **(3.1.24)** through **(3.1.47)** (or their reduced sets) with respect to the species concentrations (or the reduced set of species concentrations).

For the Newton-Raphson method, it is advantageous to keep the number of simultaneous equations at a minimum. As noted above, Equations **(3.1.30)** and **(3.1.33)** for the equilibrium complexed and adsorbed species are not independent from the other equations and can be solved outside of the matrix solver. Therefore, the remaining governing equations for the biogeochemical reactions are solved simultaneously for the c_j's, s_j's, K_y kinetic y_i's, z_i's, p_i's, and a_i's during one iteration. After they are obtained, the $(M_x - K_x)$ equlibrium x_i's and $(M_y - K_y)$ equlibrium y_i's are computed from Equations **(3.1.30)** and **(3.1.33)**. The major tasks are thus the evaluation of the residuals and Jacobians for

Equations **(3.1.24)** through **(3.1.47)**.

3.3.2 Evaluation of the Residuals

The first set of residuals that is computed are those based on the component governing equations. The computation is relatively simple, where one just substitutes the iterates of all species concentrations into the equations below.

Residuals for the aqueous component species concentrations:

$$
\begin{aligned}
GR_i = R_m &= \frac{\partial T_m}{\partial t} - R_m^c * IOPTRS + \left(\lambda_m^c + \alpha \frac{\partial p}{\partial t} \right) T_m , \quad m \in N_a , \quad i=m \\
&= \frac{T_m^{(n+1)} - T_m^{(n)}}{\Delta t} - R_m^c * IOPTRS + \left(\lambda_m^c + \alpha \frac{\partial p}{\partial t} \right) T_m
\end{aligned}
\qquad \textbf{(3.3.7)}
$$

where

$$
T_m = \rho_\ell \theta \left(c_m + \sum_{i=1}^{(M_x-K_x)} a_{im} x_i \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{im} y_i + \sum_{i=1}^{(M_z-K_z)} a_{im} z_i + \sum_{i=1}^{(M_p-K_p)} a_{im} p_i \right) \qquad \textbf{(3.3.8)}
$$

and

$$
\begin{aligned}
R_m^c = {} & \rho_\ell \theta \left(r_m^c \big|^{bio} + \sum_{i=1}^{(M_x-K_x)} a_{im} r_i^x \big|^{bio} \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{im} r_i^y \big|^{bio} + \sum_{i=1}^{(M_z-K_z)} a_{im} r_i^z \big|^{bio} + \sum_{i=1}^{(M_p-K_p)} a_{im} r_i^p \big|^{bio} \right) \\
& - \rho_\ell \theta \sum_{i=1}^{K_x} a_{im} r_i^x \big|^{chem} - \rho_b \left(\sum_{i=1}^{K_y} a_{im} r_i^y \big|^{chem} + \sum_{i=1}^{K_z} a_{im} r_i^z \big|^{chem} + \sum_{i=1}^{K_p} a_{im} r_i^p \big|^{chem} \right)
\end{aligned}
\qquad \textbf{(3.3.9)}
$$

and where GR_i is the residual of the equation for the i-th species under consideration. IOPTRSis an indicator for the solution scheme selected. IOPTRS=1 if the operator splitting scheme is used and =0 if the fully implicit scheme is used.

For a steady state simulation, $\partial T_m / \partial t = 0$, or $T_m^{(n+1)} = T_m$, and the residual is simply:

$$
\begin{aligned}
GR_i = R_m &= T_m^{(n+1)} - T_m^{(n)} \\
&= \rho_\ell \theta \left(c_m + \sum_{i=1}^{(M_x-K_x)} a_{im} x_i \right) + \rho_b \left(\sum_{i=1}^{(M_y-K_y)} a_{im} y_i + \sum_{i=1}^{(M_z-K_z)} a_{im} z_i + \sum_{i=1}^{(M_p-K_p)} a_{im} p_i \right) - T_m^{(n)}
\end{aligned}
\qquad \textbf{(3.3.10)}
$$

Residuals for the adsorbent component species concentrations:

If species m is an adsorbent component, $W_m^{(n+1)}$ is not known and $W_m^{(n)}$ is provided from the prior iteration. The new individual species concentrations are solved for using:

$$GR_i = R_m = \frac{\partial W_m}{\partial t} - R_m^s + \left(\lambda_m^s + \alpha \frac{\partial p}{\partial t} \right) W_m \quad , \quad m \in N_s \quad , \quad i = m + N_a$$

$$= \frac{W_m^{(n+1)} - W_m^{(n)}}{\Delta t} - R_m^s + \left(\lambda_m^s + \alpha \frac{\partial p}{\partial t} \right) W_m \qquad \textbf{(3.3.11)}$$

where

$$R_m^s = \rho_b \left(r_m^s \Big|^{bio} + \sum_{k=1}^{(M_y-K_y)} a_{km} r_k^y \Big|^{bio} \right) - \rho_b \sum_{k=1}^{K_y} a_{km} r_k^y \Big|^{chem} \qquad \textbf{(3.3.12)}$$

and

$$W_m = \rho_b \left(s_m + \sum_{k=1}^{(M_y-K_y)} a_{km} y_k \right) \qquad \textbf{(3.3.13)}$$

The new values of $W_m^{(n+1)}$ are calculated after the new values for the s_j's and y_i's are determined. For a steady state simulation, $\partial W_m / \partial t = 0$, or $W_m^{(n+1)} = W_m$, and the residual is simply:

$$GR_i = R_m = W_m^{(n+1)} - W_m^{(n)} = \rho_b \left(s_m + \sum_{k=1}^{(M_y-K_y)} a_{km} y_k \right) - W_m^{(n)} \qquad \textbf{(3.3.14)}$$

Since the equilibrium aqueous complexed and adsorbed species' concentrations are not computed in the matrix solver, their residuals do not need to be calculated.

For the fully implicit approach, the concentrations of the kinetic aqueous complexed species are determined in the hydrologic transport subsystem of equations before the biogeochemical subsystem is entered. The residuals for these species within the biogeochemical subsystem are therefore zero.

$$GR_i = R_m = \frac{\partial x_m}{\partial t} = 0 \quad \text{if IOPTRS=0.} \qquad m \in K_x \; , \quad i = m + N \qquad \textbf{(3.3.15)}$$

where N = the total number of components, both aqueous and adsorbent, $(N_a + N_s)$.

If the operator splitting scheme is used, the concentrations of the kinetic aqueous complexed species are adjusted in both the hydrologic transport and biogeochemical subsystem of equations. With this approach, the residuals for the kinetic aqueous complexed species are[2]

$$GR_i = R_m = \frac{\partial x_m}{\partial t} - r_m^x + \lambda_m^x x_m + \alpha \frac{\partial p}{\partial t} x_m + \frac{1}{\rho_\ell \theta} \frac{\partial \rho_\ell \theta}{\partial t} y_m \qquad \text{if IOPTRS=1.} \tag{3.3.16}$$

$$m \in K_x \,, \quad i = m + N$$

For kinetic adsorption[3]:

$$GR_i = R_m = \frac{\partial y_m}{\partial t} - r_m^y + \lambda_m^y y_m + \alpha \frac{\partial p}{\partial t} y_m + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} y_m \tag{3.3.17}$$

$$m \in K_y \,, \quad i = m + N + K_x$$

Ion exchange site constraint equation used for the "reference" ion-exchange species:

$$GR_i = R_m = \frac{\partial N_{eqj}}{\partial t} - R_{eqj}^{(bio)} + \left(\lambda_{eqj} + \alpha \frac{\partial p}{\partial t} \right) N_{eqj} \;, \tag{3.3.18}$$

$$j \in \text{NSITE} \quad m = \text{Reference species for Site } j, \quad i = m + N + K_x + K_y$$

where

$$N_{eqj} = \rho_b \sum_{k=\text{NOMZJ(j)}+1}^{\text{NOMZJ(j)}+\text{NOMZI(j)}} \nu_k z_k \tag{3.3.19}$$

and

---

[2] The change in moisture content term, $\left(\frac{1}{\rho_\ell \theta} \frac{\partial \rho_\ell \theta}{\partial t} g_m \right)$, is evaluated explicitly using the concentration values for species m at the old iteration if the change is negative and implicitly using the concentration values at the new iteration if the change is positive. This is also the case for the aqueous phase microbial species equations.

[3] The change in bulk density term, $\left(\frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} g_m \right)$, is evaluated explicitly using the concentration values for species m at the old iteration if the change is negative and implicitly using the concentration values at the new iteration if the change is positive. This is also the case for the ion exchanged, precipitated, and adsorbed microbial species equations.

$$R_{eqj}^{(bio)} = \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k r_k^z |^{bio} \qquad \textbf{(3.3.20)}$$

Note that for a steady state simulation, $\partial N_{eqj} / \partial t = 0$, and the residual is expressed as:

$$GR_i = R_m = N_{eqj}^{(n+1)} - N_{eqj}^{(n)} = \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k z_k - N_{eqj}^{(n)} \ , \qquad \textbf{(3.3.21)}$$

$$j \in NSITE \quad m = \text{Reference species for Site } j, \quad i = m + N + K_x + K_y$$

For equilibrium ion-exchange:

$$GR_i = R_m = 0 + \prod_{j \in (N_a + M_x + M_z)} (\gamma_j g_j)^{\nu''_{kj}} - K_k^{eq} \prod_{j \in (N_a + M_x + M_z)} (\gamma_j g_j)^{\nu'_{kj}}$$

$$k \in NRXNE \qquad \textbf{(3.3.22)}$$

$$m \in (M_z - K_z) \ , \quad m \neq \text{Reference ion exchange species} \ ,$$

$$i = m + N + K_x + K_y$$

For kinetic ion-exchange:

$$GR_i = R_m = \frac{\partial z_m}{\partial t} - r_m^z + \lambda_m^z z_m + \alpha \frac{\partial p}{\partial t} z_m + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} z_m$$

$$m \in K_z \ , \ m \neq \text{Reference ion exchange species} \ , \qquad \textbf{(3.3.23)}$$

$$i = m + N + K_x + K_y$$

For equilibrium precipitation:

$$GR_i = R_m = 1 - K_k^{eq} \prod_{j \in M} (\gamma_j g_j)^{\nu'_{kj}} \quad , \quad k \in NRXNE \qquad \textbf{(3.3.24)}$$

$$m \in (M_p - K_p) \ , \quad i = m + N + K_x + K_y + M_z$$

For kinetic precipitation:

$$GR_i = R_m = \frac{\partial p_m}{\partial t} - r_m^p + \lambda_m^p p_m + \alpha \frac{\partial p}{\partial t} p_m + \frac{1}{\rho_b}\frac{\partial \rho_b}{\partial t} p_m \qquad (3.3.25)$$

$$m \in K_p\ , \quad i = m + N + K_x + K_y + M_z$$

For the fully implicit approach, the concentrations of the aqueous phase microbial species are determined in the hydrologic transport subsystem of equations before the biogeochemical subsystem is entered. The residuals for these species within the biogeochemical subsystem are therefore zero.

$$GR_i = R_m = \frac{\partial b_m}{\partial t} = 0 \ \text{ if IOPTRS=0.} \quad m \in M_b\ , \ i = m+N+K_x+K_y+M_z+M_p \qquad (3.3.26)$$

If the operator splitting scheme is used, the concentrations of the aqueous phase microbial species are adjusted in both the hydrologic transport and biogeochemical subsystem of equations. With this approach, the residuals for these species are

$$GR_i = R_m = \frac{\partial b_m}{\partial t} - r_m^b + K_m^d b_m + b_m\, \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta}\frac{\partial \rho_\ell \theta}{\partial t} a_m \ \text{ if IOPTRS=1} \qquad (3.3.27)$$

$$m \in M_b\ , \quad i = m + N + K_x + K_y + M_z + M_p$$

For adsorbed phase microbial species:

$$GR_i = R_m = \frac{\partial a_m}{\partial t} - r_m^a + K_m^d a_m + a_m\, \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b}\frac{\partial \rho_b}{\partial t} a_m \qquad (3.3.28)$$

$$m \in M_a\ , \quad i = m + N + K_x + K_y + M_z + M_p + M_b$$

3.3.3 Evaluation of Jacobians

3.3.3.1 Rows for N_a Species

The first set of Jacobians are those involved with the component species. In the following, GJ_{ij} is the entry in the i-th row, j-th column of the Jacobian array. For a transient simulation, the Jacobians for the rows corresponding to the aqueous components, $m = 1, 2, ..., N_a$, $i = m$, are:

$$
\begin{aligned}
GJ_{ij} = \frac{\partial R_m}{\partial c_n} = {} & \frac{1}{\Delta t}\,\rho_\ell \theta \delta_{mn} + \frac{1}{\Delta t}\,\rho_\ell \theta \sum_{l=1}^{(M_x-K_x)} a_{lm}\left(\frac{\partial x_l}{\partial c_n}\right) + \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial c_n}\right) \\
& + \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\left(\frac{\partial z_l}{\partial c_n}\right) + \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\left(\frac{\partial p_l}{\partial c_n}\right) \\
& - \mathrm{IOPTRS} * \left\{\rho_\ell \theta \left(\frac{\partial r_m^c|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_x-K_x)} a_{lm} \frac{\partial r_l^x|^{bio}}{\partial c_n} \right)\right\} \\
& - \mathrm{IOPTRS} * \left\{\rho_b \left(\sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_z-K_z)} a_{lm} \frac{\partial r_l^z|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_p-K_p)} a_{lm} \frac{\partial r_l^p|^{bio}}{\partial c_n} \right)\right\} + \\
& \mathrm{IOPTRS} * \left\{\rho_\ell \theta \sum_{l=1}^{K_x} a_{lm} \frac{\partial r_l^x|^{chem}}{\partial c_n} + \rho_b \left(\sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^y|^{chem}}{\partial c_n} + \sum_{l=1}^{K_z} a_{lm} \frac{\partial r_l^z|^{chem}}{\partial c_n} + \sum_{l=1}^{K_p} a_{lm} \frac{\partial r_l^p|^{chem}}{\partial c_n} \right)\right\}
\end{aligned}
\tag{3.3.29}
$$

$$
\begin{aligned}
= {} & \frac{1}{\Delta t}\,\rho_\ell \theta \delta_{mn} + \frac{1}{\Delta t}\,\rho_\ell \theta \sum_{l=1}^{(M_x-K_x)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\,\frac{x_l}{c_n}\right] + \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\,\frac{y_l}{c_n}\right] \\
& - \mathrm{IOPTRS} * \left\{\rho_\ell \theta \left(\frac{\partial r_m^c|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_x-K_x)} a_{lm} \frac{\partial r_l^x|^{bio}}{\partial c_n} \right)\right\} \\
& - \mathrm{IOPTRS} * \left\{\rho_b \left(\sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_z-K_z)} a_{lm} \frac{\partial r_l^z|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_p-K_p)} a_{lm} \frac{\partial r_l^p|^{bio}}{\partial c_n} \right)\right\} + \\
& \mathrm{IOPTRS} * \left\{\rho_\ell \theta \sum_{l=1}^{K_x} a_{lm} \frac{\partial r_l^x|^{chem}}{\partial c_n} + \rho_b \left(\sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^y|^{chem}}{\partial c_n} + \sum_{l=1}^{K_z} a_{lm} \frac{\partial r_l^z|^{chem}}{\partial c_n} + \sum_{l=1}^{K_p} a_{lm} \frac{\partial r_l^p|^{chem}}{\partial c_n} \right)\right\},
\end{aligned}
$$

$$k \in \mathrm{NRXNE}$$

$$n \in N_a,\ j = n$$

where $k \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial s_n}\right)$$

$$-\ \mathrm{IOPTRS}*\rho_b\left(\sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{\,y}|^{\text{bio}}}{\partial s_n} - \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{\,y}|^{\text{chem}}}{\partial s_n}\right)$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\,\frac{y_l}{s_n}\right] - \mathrm{IOPTRS}*\rho_b\left(\sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{\,y}|^{\text{bio}}}{\partial s_n} - \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{\,y}|^{\text{chem}}}{\partial s_n}\right), \tag{3.3.30}$$

$$k \in \mathrm{NRXNE}$$

$$n \in N_a,\ j = n$$

where $k \in \mathrm{NRXNE}$ is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\ \mathrm{IOPTRS}*\rho_\ell\theta\left(-\sum_{l=1}^{K_x} a_{lm}\frac{\partial r_l^{\,x}|^{\text{chem}}}{\partial x_n}\right),\quad n \in K_x,\ \ j = n+N \tag{3.3.31}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\ \mathrm{IOPTRS}*\rho_b\left(-\sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{\,y}|^{\text{chem}}}{\partial y_n}\right),\quad n \in K_y,\ \ j = n+N+K_x \tag{3.3.32}$$

$$J_{ij} = \frac{\partial R_m}{\partial z_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\left(\frac{\partial z_l}{\partial z_n}\right) - \mathrm{IOPTRS}*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^{\,z}|^{\text{bio}}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^{\,z}|^{\text{chem}}}{\partial z_n}\right)$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\delta_{ln} - \mathrm{IOPTRS}*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^{\,z}|^{\text{bio}}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^{\,z}|^{\text{chem}}}{\partial z_n}\right) \tag{3.3.33}$$

$$= \frac{1}{\Delta t}\,\rho_b a_{nm} - \mathrm{IOPTRS}*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^{\,z}|^{\text{bio}}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^{\,z}|^{\text{chem}}}{\partial z_n}\right),$$

$$n \in (M_z-K_z)\ \ ,\ j = n + N + K_x + K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\ \mathrm{IOPTRS}*\rho_b\left(-\sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^{\,z}|^{\text{chem}}}{\partial z_n}\right),\quad n \in K_z\ \ ,\ j = n+N+K_x+K_y \tag{3.3.34}$$

$$J_{ij} = \frac{\partial R_m}{\partial p_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\left(\frac{\partial p_l}{\partial p_n}\right) - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l{}^{p}|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l{}^{p}|^{chem}}{\partial p_n}\right),$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\delta_{ln} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l{}^{p}|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l{}^{p}|^{chem}}{\partial p_n}\right) \qquad \textbf{(3.3.35)}$$

$$= \frac{1}{\Delta t}\,\rho_b a_{nm} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l{}^{p}|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l{}^{p}|^{chem}}{\partial p_n}\right),$$

$$n \in (M_p-K_p)\ ,\ j = n + N + K_x + K_y + M_z$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = -\,IOPTRS*\rho_b\left(-\sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l{}^{p}|^{chem}}{\partial p_n}\right),\quad n \in K_p\ ,\ j = n+N+K_x+K_y+M_z \qquad \textbf{(3.3.36)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\,IOPTRS*\left\{\rho_\ell\theta\left(\frac{\partial r_m{}^{c}|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_x-K_x)} a_{lm}\frac{\partial r_l{}^{x}|^{bio}}{\partial g_n}\right)\right\}$$

$$-IOPTRS*\left\{\rho_b\left(\sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l{}^{y}|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l{}^{z}|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l{}^{p}|^{bio}}{\partial g_n}\right)\right\}, \qquad \textbf{(3.3.37)}$$

$$n \in M_b+M_a\ ,\ j = n + N + K_x + K_y + M_z + M_p$$

The partial derivatives of the reaction terms are evaluated as follows for any chemical species f:

$$\frac{\partial r_f|^{chem}}{\partial g_n} = \sum_{k=1}^{NRXNK} \frac{\partial r_f|_k^{chem}}{\partial g_n} = \sum_{k=1}^{NRXNK} \frac{\partial}{\partial g_n}\left[\left(\frac{\nu''_{kf}-\nu'_{kf}}{\gamma_f}\right)\left(k_k^{f}\prod_{\ell\in M}(\gamma_\ell g_\ell)^{\nu'_{k\ell}} - k_k^{b}\prod_{\ell\in M}(\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right)\right] \qquad \textbf{(3.3.38)}$$

and

$$\frac{\partial r_f|^{bio}}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial (r_f|_k^{biodeg})}{\partial g_n} - \frac{\partial (r_f^{bioresp})}{\partial g_n}$$

$$= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n}\left[\left(\frac{v''_{kf}-v'_{kf}}{\gamma_f}\right)(\Gamma_k I_{1k})\left[\frac{S_k}{(K_{S-k} I_{2k})+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right]\mathcal{G}_k(\gamma_{Bk}B_k)\right] \qquad \textbf{(3.3.39)}$$

$$- \sum_{k=1}^{M_B} \frac{\partial}{\partial g_n}\left[\alpha_{kf}\, K_k^d\, B_k \left(\frac{g_f}{\kappa_{kf} + g_f}\right)\right]$$

The derivative with respect to g_n is taken term by term for each reactant and product in each kinetic chemical and microbiological reaction and their contributions to the Jacobian matrix for row m are summed. For a given species "f" and a given reaction "k", the evaluation of the derivatives will depend only on a column "n", and not on the row "m" being considered. The evaluation of these derivatives with respect to g_n is therefore applicable for all rows and is presented in sections 3.3.3.9 through 3.3.3.11.

For a steady state simulation, the Jacobians for the rows corresponding to the aqueous components, $m = 1, 2, ..., N_a$, $i = m$, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \rho_\ell \theta \delta_{mn} + \rho_\ell \theta \sum_{l=1}^{(M_x-K_x)} a_{lm}\left(\frac{\partial x_l}{\partial c_n}\right) + \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial c_n}\right)$$

$$+ \rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\left(\frac{\partial z_l}{\partial c_n}\right) + \rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\left(\frac{\partial p_l}{\partial c_n}\right)$$

$$\textbf{(3.3.40)}$$

$$= \rho_\ell \theta \delta_{mn} + \rho_\ell \theta \sum_{l=1}^{(M_x-K_x)} a_{lm}\left[\frac{v'_{kn}}{v''_{kl}}\frac{x_l}{c_n}\right] + \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{v'_{kn}}{v''_{kl}}\frac{y_l}{c_n}\right]$$

$$k \in NRXNE$$

$$n \in N_a,\ j = n$$

where $k \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial s_n}\right) = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{y_l}{s_n}\right] \tag{3.3.41}$$

$$k \in NRXNE$$

$$n \in N_a,\ j = n$$

where k ϵ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0\ ,\quad n \in (K_x + K_y)\ ,\ \ j = n + N \tag{3.3.42}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\left(\frac{\partial z_l}{\partial z_n}\right) = \rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\delta_{ln} = \rho_b a_{nm}\ , \tag{3.3.43}$$

$$n \in (M_z-K_z)\ \ ,\ j = n + N + K_x + K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = 0\ ,\quad n \in K_z\ \ ,\ j = n + N + K_x + K_y \tag{3.3.44}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = \rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\left(\frac{\partial p_l}{\partial p_n}\right) = \rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\delta_{ln} = \rho_b a_{nm}\ , \tag{3.3.45}$$

$$n \in (M_p-K_p)\ \ ,\ j = n + N + K_x + K_y + M_z$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0\ ,\quad n \in K_p\ \ ,\ j = n + N + K_x + K_y + M_z \tag{3.3.46}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0\ ,\quad n \in M_b + M_a\ \ ,\ j = n + N + K_x + K_y + M_z + M_p \tag{3.3.47}$$

3.3.3.2 Rows for N_s Species

For a transient simulation, the Jacobians for the rows corresponding to the adsorbent component species, $m = 1, 2, \ldots, N_s$, $i = m + N_a$ are:

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial c_n}\right) - \rho_b\left(\frac{\partial r_m^s\big|^{\text{bio}}}{\partial c_n} + \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^y\big|^{\text{bio}}}{\partial c_n}\right) + \rho_b \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^y\big|^{\text{chem}}}{\partial c_n}$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\,\frac{y_l}{c_n}\right] - \rho_b\frac{\partial r_m^s\big|^{\text{bio}}}{\partial c_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^y\big|^{\text{bio}}}{\partial c_n} + \rho_b \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^y\big|^{\text{chem}}}{\partial c_n}\,, \qquad \textbf{(3.3.48)}$$

$$k \in NRXNE$$

$$n \in N_a,\ j = n$$

where $k \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \frac{1}{\Delta t}\,\rho_b\,\delta_{mn} + \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\,\frac{y_l}{s_n}\right] - \rho_b\frac{\partial r_m^s\big|^{\text{bio}}}{\partial s_n}$$

$$- \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^y\big|^{\text{bio}}}{\partial s_n} + \rho_b \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^y\big|^{\text{chem}}}{\partial s_n}\,, \qquad \textbf{(3.3.49)}$$

$$k \in NRXNE$$

$$n \in N_s,\ j = n + N_a$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\rho_b\frac{\partial r_m^s\big|^{\text{bio}}}{\partial x_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^y\big|^{\text{bio}}}{\partial x_n} + \rho_b \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^y\big|^{\text{chem}}}{\partial x_n}\,, \qquad \textbf{(3.3.50)}$$

$$n \in K_x,\ j = n + N$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\rho_b\frac{\partial r_m^s\big|^{\text{bio}}}{\partial y_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^y\big|^{\text{bio}}}{\partial y_n} + \rho_b \sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^y\big|^{\text{chem}}}{\partial y_n}\,, \qquad \textbf{(3.3.51)}$$

$$n \in K_y,\ j = n + N + K_x$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\rho_b \frac{\partial r_m^s\big|^{bio}}{\partial g_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{bio}}{\partial g_n} + \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{chem}}{\partial g_n} , \qquad \textbf{(3.3.52)}$$

$$n \in M_z+M_p \ , \quad j=n+N+K_x+K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\rho_b \frac{\partial r_m^s\big|^{bio}}{\partial g_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{bio}}{\partial g_n} , \qquad \textbf{(3.3.53)}$$

$$n \in M_b+M_a \ , \quad j=n+N+K_x+K_y+M_z+M_p$$

The evaluation of the partial derivatives of the reaction rate terms is presented in sections 3.3.3.9 through 3.3.3.11.

For a steady state simulation, the Jacobians for the rows corresponding to the adsorbent component species, $m = 1, 2, \ldots, N_s$, $i = m + N_a$ are:

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \left(\frac{\partial y_l}{\partial c_n} \right) = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \left[\frac{v'_{kn}}{v''_{kl}} \frac{y_l}{c_n} \right] \qquad \textbf{(3.3.54)}$$

$$k \in NRXNE$$

$$n \in N_a, \ j=n$$

where $k \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \rho_b \delta_{mn} + \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \left[\frac{v'_{kn}}{v''_{kl}} \frac{y_l}{s_n} \right] , \qquad \textbf{(3.3.55)}$$

$$k \in NRXNE$$

$$n \in N_s, \ j=n+N_a$$

$$GJ_{ij} = 0 \ , \quad n \in (K_x+K_y+M_z+M_p+M_b+M_a) \ , \ j=n+N \qquad \textbf{(3.3.56)}$$

3.3.3.3 Rows for K_x Species

The next set of Jacobians is for the rows corresponding to the K_x kinetic complexed species. If the fully implicit approach is used (IOPTRS = 0), the Jacobians for rows the $m = 1, 2, ..., K_x$, $i = m + N$ and $N = N_a + N_s$ are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in N \, , \, j = n \tag{3.3.57}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = \delta_{mn} \, , \qquad n \in K_x \, , \, j = n + N \tag{3.3.58}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in K_y + M_z + M_p + M_b + M_a \, , \, j = n + N + K_x \tag{3.3.59}$$

If the operator splitting approach is used (IOPTRS =1), the Jacobians for the rows $m = 1, 2, ..., K_x$, $i = m + N$ and $N = N_a + N_s$ are[4]:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^x}{\partial g_n} \quad , \qquad n \in N_a + N_s \, , \, j = n \tag{3.3.60}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = - \frac{\partial r_m^x}{\partial x_n} + \left(\frac{1}{\Delta t} + \lambda_m^x + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta} \frac{\Delta \rho_\ell \theta}{\Delta t} \right) \delta_{mn} \, , \qquad n \in K_x \, , \, j = n + N \tag{3.3.61}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^y}{\partial g_n} \quad , \qquad n \in K_y + M_z + M_p + M_b + M_a \, , \, j = n + N + K_x \tag{3.3.62}$$

The evaluation of the reaction terms is detailed in sections 3.3.3.9 through 3.3.3.11.

---

[4] The change in moisture content term is included in Eq. **(3.3.61)** if $\partial \rho_\ell \theta / \partial t$ is positive, since the term is evaluated in the residual using the working concentration for this case. If $\partial \rho_\ell \theta / \partial t$ is negative, this term is included explicitly in the residual and therefore does not appear in Eq. **(3.3.61)**. See Section 3.3.2.

3.3.3.4 Rows for K_y Species

The next set of Jacobians, for the kinetic adsorbed species, is similar in form to that for the kinetic aqueous complexed species. The Jacobians for the rows corresponding to the K_y kinetic adsorbed species[5], $m = 1, 2, ..., K_y$, $i = m + N + K_x$, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial r_m^y}{\partial g_n} , \quad n \in N_a + N_s + K_x , \ j = n \tag{3.3.63}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r_m^y}{\partial y_n} + \left(\frac{1}{\Delta t} + \lambda_m^y + \alpha\frac{\partial p}{\partial t} + \frac{1}{\rho_b}\frac{\Delta\rho_b}{\Delta t}\right)\delta_{mn} , \quad n \in K_y , \ j = n + N + K_x \tag{3.3.64}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial r_m^y}{\partial g_n} , \quad n \in M_z + M_p + M_b + M_a , \ j = n + N + K_x + K_y \tag{3.3.65}$$

The evaluation of the reaction terms is detailed in sections 3.3.3.9 through 3.3.3.11.

3.3.3.5 Rows for M_z Species

The Jacobians for rows corresponding to the ion-exchanged species are $m = 1, 2, ..., M_z$, $i = m + N + K_x + K_y$, depend on whether the species m is (1) a "reference" ion exchange species for one of the ion exchange sites, (2) an equilibrium controlled ion exchanged species, or (3) a kinetic controlled ion exchanged species. The Jacobians for each of these three cases follow:

If species m is the "reference" species for an ion exchange site, the residual for this species for a transient simulation is given by Eq. **(3.3.18)** and the Jacobian for this row is evaluated as follows:

---

[5] The change in bulk density term is included in Eq. **(3.3.64)** if $\partial\rho_b/\partial t$ is positive, since the term is evaluated in the residual using the working concentration for this case. If $\partial\rho_b/\partial t$ is negative, this term is included explicitly in the residual and therefore does not appear in Eq. **(3.3.64)**. See Section 3.3.2.

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial R_{eqj}^{(bio)}}{\partial g_n} = - \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^z|^{bio}}{\partial g_n} \quad , \tag{3.3.66}$$

$$n \in N_a+N_s+K_x+K_y \ , \ j=n$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \frac{\rho_b \nu_n}{\Delta t} - \frac{\partial R_{eqj}^{(bio)}}{\partial z_n} = \frac{\rho_b \nu_n}{\Delta t} - \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^z|^{bio}}{\partial z_n} \quad , \tag{3.3.67}$$

$$z_n \in NOMZI(\iota) \quad ,$$

$$n \in M_z \ , \ j=n+N+K_x+K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = - \frac{\partial R_{eqj}^{(bio)}}{\partial z_n} = - \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^z|^{bio}}{\partial z_n} \quad , \tag{3.3.68}$$

$$z_n \notin NOMZI(\iota) \quad ,$$

$$n \in M_z \ , \ j=n+N+K_x+K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial R_{eqj}^{(bio)}}{\partial g_n} = - \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^z|^{bio}}{\partial g_n} \quad , \tag{3.3.69}$$

$$n \in M_p+M_b+M_a \ , \ j=n+N+K_x+K_y+M_z$$

For a steady state simulation, the residual for the "reference" species is given by Eq. **(3.3.21)** and the Jacobian for this row is evaluated as follows:

$$GJ_{ij} = 0 \quad , \quad n \in N_a+N_s+K_x+K_y \ , \ j=n \tag{3.3.70}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \rho_b \nu_n \quad , \quad z_n \in NOMZI(\iota) \quad , \quad n \in M_z \ , \ j=n+N+K_x+K_y \tag{3.3.71}$$

$$GJ_{ij} = 0 \quad , \quad z_n \notin NOMZI(\iota) \quad , \quad n \in M_z \ , \ j=n+N+K_x+K_y \tag{3.3.72}$$

$$GJ_{ij} = 0 \quad , \quad n \in M_p+M_b+M_a \ , \ j=n+N+K_x+K_y+M_z \tag{3.3.73}$$

If species m is an equilibrium controlled ion exchanged species and is not the “reference” species for an ion exchange site, the residual for this species is given by Eq. **(3.3.22)** and the Jacobian for this row is evaluated as follows:

For columns $n \in N_a$, $j = n$, the contribution to the Jacobian is:

From reactant $r \in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = -K_k^{eq}\left(\frac{\nu'_{kn}}{c_n}\right)\left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu'_{k\ell}}\right) \qquad \text{if } r = n \tag{3.3.74}$$

From product $p \in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = \left(\frac{\nu''_{kn}}{c_n}\right)\left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right) \qquad \text{if } p = n \tag{3.3.75}$$

From reactant $r \in (M_x - K_x)$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = -K_k^{eq}\left(\frac{\nu'_{kr}}{c_n}\right)\left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}}\right)\left(\prod_{\ell \in N_a+M_x+M_z} (\gamma_\ell g_\ell)^{\nu'_{k\ell}}\right) \tag{3.3.76}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species r.

From product $p \in (M_x - K_x)$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = \left(\frac{\nu''_{kp}}{c_n}\right)\left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa p}}\right)\left(\prod_{\ell \in N_a+M_x+M_z} (\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right) \tag{3.3.77}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species p.

For any other reactant species r or product species p, the contribution to the Jacobian in columns n $\in N_a$ is zero.

For columns $n \in N_s, K_x, K_y, j = n + N_a$, the Jacobian entry is zero:

$$\frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in N_s + K_x + K_y \quad , \quad j = n + N_a \tag{3.3.78}$$

For columns $n \in M_z$, $j = n + N + K_x + K_y$, the contribution to the Jacobian is:

For reactant $r \in M_z$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial z_n} = - K_k^{eq} \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \nu'_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } r = n \tag{3.3.79}$$

$$= K_k^{eq} \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \nu'_{kr} \, \gamma_r \qquad \text{if } r \neq n \text{ , but } n \in \text{NOMZI}(\iota) \tag{3.3.80}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } r \neq n \text{ , } \quad n \notin \text{NOMZI}(\iota) \tag{3.3.81}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

For product $p \in M_z$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial z_n} = \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \nu''_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } p = n \tag{3.3.82}$$

$$= - \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \nu''_{kp} \, \gamma_p \qquad \text{if } p \neq n \text{ , but } n \in \text{NOMZI}(\iota) \tag{3.3.83}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } p \neq n \text{ , } \quad n \notin \text{NOMZI}(\iota) \tag{3.3.84}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

For any other reactant or product species, the contribution to the Jacobian for columns $n \in M_z$ is zero.

For columns $n \in M_p + M_b + M_a, j = n + N + K_x + K_y + M_z$, the contribution to the Jacobian is zero.

$$\frac{\partial R_m}{\partial g_n} = 0 \tag{3.3.85}$$

If species m is a kinetic controlled ion exchanged species and is not a "reference" species, the residual for this row is given by Eq. **(3.3.23)** and the Jacobian for this row is evaluated as follows:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^z}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x + K_y \ , \ j = n \qquad \textbf{(3.3.86)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = - \frac{\partial r_m^z}{\partial z_n} + \left(\frac{1}{\Delta t} + \lambda_m^z + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b}\frac{\Delta \rho_b}{\Delta t}\right) \delta_{mn} \ ,$$
$$n \in M_z \ , \ j = n + N + K_x + K_y \qquad \textbf{(3.3.87)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^z}{\partial g_n} \quad , \qquad n \in M_p + M_b + M_a \ , \ j = n + N + K_x + K_y + M_z \qquad \textbf{(3.3.88)}$$

As was done for the other kinetic species rows, the partial derivatives of the reaction terms are evaluated by taking the partial derivatives term by term for each species participating in each chemical and microbiological reaction. The equations in Section 3.3.3.9 through 3.3.3.11 can be used to evaluate these terms. However, because sorbent component species, adsorbed species or precipitated species do not participate in chemical reactions involving ion exchange, the contribution to the Jacobian from chemical reactions for these columns will be zeroes for the kinetic ion exchanged species rows.

3.3.3.6 Rows for M_p Species

For the rows corresponding to the precipitated species, $m = 1, ..., M_p$, $i = m + N + K_x + K_y + M_z$, the Jacobians will depend on whether the species is equilibrium or kinetic controlled. For the equilibrium case, the residual equation is **(3.3.24)** and the Jacobians for row m are:

For columns $n \in N_a$, $j = n$:

From reactant $r \in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{v'_{kn}}{c_n} \right) \left(\prod_{\ell M} (\gamma_\ell g_\ell)^{v'_{k\ell}} \right) \ , \qquad \text{for } r = n \qquad \textbf{(3.3.89)}$$

From reactant r $\in (M_x - K_x)$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{\nu'_{kr}}{c_n} \right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}} \right) \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \tag{3.3.90}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species r.

For other columns, contribution to the Jacobian is zero:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in N_s + K_x + K_y + M_z + M_p + M_b + M_a \ , \ j = n + N_a \tag{3.3.91}$$

For the kinetic precipitated species, the residual equation is **(3.3.25)** and the Jacobians for row m are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^p}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x + K_y + M_z \ , \ j = n \tag{3.3.92}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = - \frac{\partial r_m^p}{\partial p_n} + \left(\frac{1}{\Delta t} + \lambda_m^z + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn} \ , \qquad n \in M_p \ , \ j = n + N + K_x + K_y + M_z \tag{3.3.93}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^p}{\partial g_n} \quad , \quad n \in M_b + M_a \ , \ j = n + N + K_x + K_y + M_z + M_p \tag{3.3.94}$$

As was done for the other kinetic chemical species rows, the partial derivatives of the production/consumption rate terms are evaluated by taking the partial derivatives term by term for each species participating in each chemical and microbiological reaction. The equations in Section 3.3.3.9 through 3.3.3.11 can be used to evaluate these terms. However, because sorbent component species, adsorbed species or ion exchanged species do not participate in chemical reactions involving precipitation, the contribution to the Jacobian from chemical reactions for these columns will be zeroes for the kinetic precipitated species rows.

3.3.3.7 Rows for M_b Species

If the fully implicit scheme is used (IOPTRS = 0), the Jacobians for the rows corresponding to the aqueous phase microbial species, $m = 1, \ldots, M_b$, $i = m + N + K_x + K_y + M_z + M_p$, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \quad n \in N_a + N_s + K_x + K_y + M_z + M_p \ , \ j = n \tag{3.3.95}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = \delta_{mn} \ , \quad n \in M_b \ , \ j = n + N + K_x + K_y + M_z + M_p \tag{3.3.96}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = 0 \ , \ n \in M_a , \ j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.97}$$

If the operator splitting approach is used (IOPTRS = 0), the Jacobians for the rows corresponding to the aqueous phase microbial species, $m = 1, \ldots, M_b$, $i = m + N + K_x + K_y + M_z + M_p$, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial r_m^{bg}}{\partial g_n} \quad , \quad n \in N_a + N_s + K_x + K_y + M_z + M_p \ , \ j = n \tag{3.3.98}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^{bg}}{\partial b_n} - \frac{\partial r_m^{xfr}}{\partial b_n} + \left(\frac{1}{\Delta t} + K_m^d + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta} \frac{\Delta \rho_\ell \theta}{\Delta t}\right) \delta_{mn} \ ,$$
$$n \in M_b , \ j = n + N + K_x + K_y + M_z + M_p \tag{3.3.99}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial (r_m^{xfr})}{\partial a_n} \ , \ n \in M_a \ , \ j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.100}$$

The partial derivatives of the microbial growth rate terms are evaluated as follows:

$$\frac{\partial (r_m^{bg})}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial (r_m^{bg}|_k)}{\partial g_n}$$
$$= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n}\left[\frac{(\nu''_{km} - \nu'_{km})}{\gamma_m} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right] \mathcal{L}_k(\gamma_{Bk} B_k)\right] \tag{3.3.101}$$

The derivative with respect to g_n is taken term by term for each species in each microbiological reaction and their contributions to the Jacobian for row m are summed. For a given row m, the evaluation of these derivatives is analogous to that outlined for the Jacobians for the kinetic chemical species rows. The equations in Section 3.3.3.10 can be used to evaluate the microbiological growth contributions in the Jacobian for the microbial species.

The partial derivatives of the microbial phase transfer terms are evaluated as follows:

$$\begin{aligned}\frac{\partial(r_m^{xfr})}{\partial g_n} &= \sum_{k=1}^{NBRXNK} \frac{\partial(r_m^{xfr}|_k)}{\partial g_n} \\ &= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n}\left[\frac{(v''_{km} - v'_{km})}{\gamma_m}\left(k_k^f\,(\gamma_m\, b_m)^{v'_{km}} - k_k^b\,(\gamma_j\, a_j)^{v''_{kj}}\right)\right] \quad , \; j \in M_a\end{aligned} \tag{3.3.102}$$

For columns $n \in N_a + N_s + K_x + K_y + M_z + M_p$, $j = n$, the contribution to the Jacobian from the microbial phase transfer reactions is zero.

For columns $n \in M_b$, $j = n + N_a + N_s + K_x + K_y + M_z + M_p$, the contribution to the Jacobian from the microbial phase transfer reactions is:

$$\frac{\partial(r_m^{xfr}|_k)}{\partial b_n} = \frac{(v''_{km} - v'_{km})}{\gamma_m}\; k_k^f\; v'_{km}\; (\gamma_m\, b_m)^{v'_{km}-1}\; \delta_{mn} \tag{3.3.103}$$

For columns $n \in M_a$, $j = n + N_a + N_s + K_x + K_y + M_z + M_p + M_b$, the contribution to the Jacobian from the microbial phase transfer reactions is:

$$\frac{\partial(r_m^{xfr}|_k)}{\partial a_n} = -\frac{(v''_{km} - v'_{km})}{\gamma_m}\; k_k^b\; v''_{kj}\; (\gamma_j\, a_j)^{v''_{kj}-1}\; \delta_{jn} \tag{3.3.104}$$

3.3.3.8 Rows for M_a Species

For the rows corresponding to the adsorbed phase microbial species, $m = 1, ..., M_a$, $i = m + N + K_x + K_y + M_z + M_p + M_b$, the residual equation is **(3.3.28)** and the Jacobians for row m are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial r_m^{bg}}{\partial g_n} \quad , \qquad n \in N_a{+}N_s{+}K_x{+}K_y{+}M_z{+}M_p \; , \; j = n \tag{3.3.105}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial (r_m^{xfr})}{\partial b_n} \, , \; n \in M_b \, , \; j = n + N + K_x + K_y + M_z + M_p \tag{3.3.106}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_m^{bg}}{\partial a_n} - \frac{\partial r_m^{xfr}}{\partial a_n} + \left(\frac{1}{\Delta t} + K_m^d + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b}\frac{\Delta \rho_b}{\Delta t}\right) \delta_{mn} \, ,$$
$$n \in M_a, \; j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.107}$$

The partial derivatives of the microbial growth rate and phase transfer terms are evaluated as for the aqueous phase microbial species rows, the derivative with respect to g_n is taken term by term for each species and their contributions to the Jacobian for row m are summed.

3.3.3.9 Contribution from chemical reactions

The contribution to the Jacobian from each term in the k-th chemical reaction (k $\in$ NRXNK) is as follows:

$$\frac{\partial r_f|_k^{chem}}{\partial g_n} = \frac{\partial}{\partial g_n}\left[\left(\frac{\nu''_{kf} - \nu'_{kf}}{\gamma_f}\right)\left(k_k^f \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} - k_k^b \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right)\right] \tag{3.3.108}$$

For columns $n \in N_a + N_s$, $j = n$, the contribution to the Jacobian from the k-th chemical reaction is:

From reactant $r \in N_a$ or N_s:

$$\frac{\partial (r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^f \left(\frac{\nu'_{kn}}{g_n}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \text{if } r = n \tag{3.3.109}$$

From product $p \in N_a$ or N_s:

$$\frac{\partial (r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kn}}{g_n}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \qquad \text{if } p = n \tag{3.3.110}$$

From reactant r ∈ (M_x-K_x) or (M_y-K_y), i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^f \left(\frac{\nu'_{kr}}{g_n}\right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \tag{3.3.111}$$

where κ ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species r.

From product p ∈ (M_x-K_x) or (M_y-K_y):

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kp}}{g_n}\right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa p}}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \tag{3.3.112}$$

where κ ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species p.

For any other reactant species r or product species p, the contribution to the Jacobian in columns n ∈ $N_a + N_s$ is zero.

For columns n ∈ $K_x + K_y$, j = n + N, the contribution to the Jacobian from the k-th chemical reaction is:

For reactant r ∈ $K_x + K_y$, i.e. kinetic complexed or adsorbed species:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^f \left(\frac{\nu'_{kn}}{g_n}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \text{if } r = n \tag{3.3.113}$$

From product p ∈ $K_x + K_y$:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kn}}{g_n}\right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \qquad \text{if } p = n \tag{3.3.114}$$

For any other reactant or product species, the contribution to the Jacobian in columns n ∈ K_x+K_y is zero.

For columns $n \in M_z$, $j = n + N + K_x + K_y$, the contribution to the Jacobian from the k-th chemical reaction is:

For reactant $r \in M_z$:

$$\frac{\partial(r_m|_k^{chem})}{\partial z_n} =$$

$$= \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^f \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}}\right) \nu'_{kn} \left(\frac{1}{z_n} - \gamma_n\right) \qquad \text{if } r = n \tag{3.3.115}$$

$$= -\left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^f \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}}\right) \nu'_{kr}\, \gamma_r \qquad \text{if } r \neq n \text{ , } n \in NOMZI(\iota) \tag{3.3.116}$$

where $\iota \in NSITE$ is the ion exchange site of reaction k

$$= 0 \qquad \text{if } r \neq n \text{ , } \quad n \notin NOMZI(\iota) \tag{3.3.117}$$

where $\iota \in NSITE$ is the ion exchange site of reaction k

For product $p \in M_z$:

$$\frac{\partial(r_m|_k^{chem})}{\partial z_n} =$$

$$= -\left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^b \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right) \nu''_{kn} \left(\frac{1}{z_n} - \gamma_n\right) \qquad \text{if } p = n \tag{3.3.118}$$

$$= \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m}\right) k_k^b \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}}\right) \nu''_{kp} \gamma_p \qquad \text{if } p \neq n \text{, but } n \in NOMZI(\iota) \tag{3.3.119}$$

where $\iota \in NSITE$ is the ion exchange site of reaction k

$$= 0 \qquad \text{if } p \neq n \text{ , } \quad n \notin NOMZI(\iota) \tag{3.3.120}$$

where $\iota \in NSITE$ is the ion exchange site of reaction k

For any other reactant or product species, the contribution to the Jacobian for columns $n \in M_z$ is zero.

For columns $n \in M_p$, $M_b + M_a$, $j = n + N + K_x + K_y + M_z$, the contribution to the Jacobian from the k-th chemical reaction is zero:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = 0 \qquad \textbf{(3.3.121)}$$

3.3.3.10 Contribution from microbiological degradation

The contribution to the Jacobian from each term in the k-th microbial biodegradation reaction ($k \in$ NBRXNK) is:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{\partial}{\partial g_n}\left[\left(\frac{v''_{kf}-v'_{kf}}{\gamma_f}\right)(\Gamma_k I_{1k})\left[\frac{S_k}{(K_{S\text{-}k} I_{2k})+S_k}\right]\left[\frac{A_k}{K_{A\text{-}k}+A_k}\right]\left[\frac{N_k}{K_{N\text{-}k}+N_k}\right]\mathcal{L}_k(\gamma_{Bk}B_k)\right] \qquad \textbf{(3.3.122)}$$

For columns $n \in N_a + N_s$, $j = n$, the contribution to the Jacobian from the k-th microbial reaction is:

If substrate $S_k \in N_a$ or N_s and $S_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{K_{S\text{-}k} I_{2k}}{(K_{S\text{-}k} I_{2k}+S_k)^2}\right]\left[\frac{A_k}{K_{A\text{-}k}+A_k}\right]\left[\frac{N_k}{K_{N\text{-}k}+N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.123)}$$

$$\text{if } S_k = n$$

If electron acceptor $A_k \in N_a$ or N_s and $A_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S\text{-}k} I_{2k}+S_k}\right]\left[\frac{K_{A\text{-}k}}{(K_{A\text{-}k}+A_k)^2}\right]\left[\frac{N_k}{K_{N\text{-}k}+N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.124)}$$

$$\text{if } A_k = n$$

If nutrient $N_k \in N_a$ or N_s and $N_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\, \Gamma_k\, \mathscr{L}_k\, I_{1k} [\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}] [\frac{A_k}{K_{A\text{-}k} + A_k}] \left[\frac{K_{N\text{-}k}}{(K_{N\text{-}k} + N_k)^2}\right] (\gamma_k B_k)\ , \qquad \text{if } N_k = n \tag{3.3.125}$$

If inhibitor $I \in N_a$ or N_s, and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$, $I \neq B_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\, \Gamma_k\, \mathscr{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} [\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}] [\frac{A_k}{K_{A\text{-}k} + A_k}] [\frac{N_k}{K_{N\text{-}k} + N_k}] (\gamma_k B_k) \; -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\, \Gamma_k\, \mathscr{L}_k\, I_{1k} \frac{S_k q K_s \left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \frac{I}{K_{I2}}\right)^{q} + S_k\right]^2} [\frac{A_k}{K_{A\text{-}k} + A_k}] [\frac{N_k}{K_{N\text{-}k} + N_k}] (\gamma_k B_k) \qquad \text{if } I = n \tag{3.3.126}$$

If inhibitor $I \in N_a$ or N_s, and $I = S_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\, \Gamma_k\, \mathscr{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} [\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}] [\frac{A_k}{K_{A\text{-}k} + A_k}] [\frac{N_k}{K_{N\text{-}k} + N_k}] (\gamma_k B_k) \; -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\, \Gamma_k\, \mathscr{L}_k\, I_{1k} \frac{K_s\left(1 + \frac{I}{K_{I2}}\right)^{q} - \frac{S_k q K_s}{K_{I2}}\left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{\left[K_s\left(1 + \frac{I}{K_{I2}}\right)^{q} + S_k\right]^2} [\frac{A_k}{K_{A\text{-}k} + A_k}] [\frac{N_k}{K_{N\text{-}k} + N_k}] (\gamma_k \qquad \text{if } I = S_k = n \tag{3.3.127}$$

If inhibitor $I \in N_a$ or N_s, and $I = A_k$:

$$\frac{\partial(r_f|_k^{\text{biodeg}})}{\partial g_n} =$$

$$\begin{aligned}
&\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\ - \\
&\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \\
&\quad + \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{K_A}{(K_{A-k}+A_k)^2}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \\
&\qquad \text{if } I = A_k = n
\end{aligned} \tag{3.3.128}$$

If inhibitor $I \in N_a$ or N_s, and $I = N_k$:

$$\frac{\partial(r_f|_k^{\text{biodeg}})}{\partial g_n} =$$

$$\begin{aligned}
&\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\ - \\
&\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \\
&\quad + \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{K_N}{(K_{N-k}+N_k)^2}\right](\gamma_k B_k) \\
&\qquad \text{if } I = N_k = n
\end{aligned} \tag{3.3.129}$$

If substrate $S_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $S_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{K_{S-k}I_{2k}\left(\frac{S_k}{\nu''_{\kappa S_k}}\;\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{S-k}I_{2k}+S_k)^2}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\quad,\quad \text{if } \nu'_{\kappa n}\neq 0 \tag{3.3.130}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species S_k.

If electron acceptor $A_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $A_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{K_{A-k}\left(\frac{A_k}{\nu''_{\kappa A_k}}\right)\left(\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{A-k}+A_k)^2}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\quad,\quad \text{if } \nu'_{\kappa n}\neq 0 \tag{3.3.131}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species A_k.

If nutrient $N_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $N_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{K_{N-k}\left(\frac{N_k}{\nu''_{\kappa N_k}}\right)\left(\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{N-k}+N_k)^2}\right](\gamma_k B_k)\quad,\quad \text{if } \nu'_{\kappa n}\neq 0 \tag{3.3.132}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species N_k.

If inhibitor I $\in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species and I $\neq S_k$, I $\neq A_k$, I $\neq N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)[\frac{S_k}{K_{S\text{-}k}I_{2k}+S_k}][\frac{A_k}{K_{A\text{-}k}+A_k}][\frac{N_k}{K_{N\text{-}k}+N_k}](\gamma_k B_k$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1+\frac{I}{K_{I2}}\right)^{q-1}\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)}{K_{I2}\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\,[\frac{A_k}{K_{A\text{-}k}+A_k}][\frac{N_k}{K_{N\text{-}k}+N_k}](\gamma_k B_k) \qquad \textbf{(3.3.133)}$$

$$\text{if } \nu'_{\kappa n}\neq 0$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species I.

If inhibitant I = substrate $S_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)[\frac{S_k}{K_{S\text{-}k}I_{2k}+S_k}][\frac{A_k}{K_{A\text{-}k}+A_k}][\frac{N_k}{K_{N\text{-}k}+N_k}](\gamma_k$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}-\frac{K_S qI}{K_{I2}}\left(1+\frac{I}{K_{I2}}\right)^{q-1}\right]\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)}{\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}[\frac{A_k}{K_{A\text{-}k}+A_k}][\frac{N_k}{K_{N\text{-}k}+N} \qquad \textbf{(3.3.134)}$$

$$\text{if } \nu'_{\kappa n}\neq 0$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species I = S_k.

If inhibitant I = electron acceptor $A_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}} \right)^{p-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n} \right) [\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_S \left(1 + \frac{I}{K_{I2}} \right)^{q-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n} \right)}{K_{I2} \left[K_s \left(1 + \frac{I}{K_{I2}} \right)^q + S_k \right]^2} [\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k) + \quad \textbf{(3.3.135)}$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k}[\frac{S_k}{K_{S-k} I_{2k} + S_k}] \left[\frac{K_{A-k} \left(\frac{A_k}{\nu''_{\kappa A_k}} \right) \left(\frac{\nu'_{\kappa n}}{g_n} \right)}{(K_{A-k} + A_k)^2} \right] [\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k) \quad , \text{ if } \nu'_{\kappa n}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species $I = A_k$.

If inhibitant I = nutrient $N_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}} \right)^{p-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n} \right) [\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_S \left(1 + \frac{I}{K_{I2}} \right)^{q-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n} \right)}{K_{I2} \left[K_s \left(1 + \frac{I}{K_{I2}} \right)^q + S_k \right]^2} [\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k) + \quad \textbf{(3.3.136)}$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k}[\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}] \left[\frac{K_{N-k} \left(\frac{N_k}{\nu''_{\kappa N_k}} \right) \left(\frac{\nu'_{\kappa n}}{g_n} \right)}{(K_{N-k} + N_k)^2} \right] (\gamma_k B_k) \quad , \text{ if } \nu'_{\kappa n}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species $I = N_k$.

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian for columns $n \in N_a$ or N_s is zero.

For columns $n \in K_x + K_y + M_z + M_p$, $j = n + N$, the contribution to the Jacobian from the k-th microbial degradation reaction is:

If substrate $S_k \in K_x + K_y + M_z + M_p$ and $S_k \neq I$:

$$\frac{\partial\left(r_f\big|_k^{\text{biodeg}}\right)}{\partial g_n} =$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\, \Gamma_k\, \mathcal{L}_k\, I_{1k} \left[\frac{K_{S\text{-}k} I_{2k}}{(K_{S\text{-}k} I_{2k} + S_k)^2}\right] \left[\frac{A_k}{K_{A\text{-}k} + A_k}\right] \left[\frac{N_k}{K_{N\text{-}k} + N_k}\right] (\gamma_k B_k) \ , \qquad \textbf{(3.3.137)}$$

$$\text{if } S_k = n$$

If electron acceptor $A_k \in K_x + K_y + M_z + M_p$ and $A_k \neq I$:

$$\frac{\partial\left(r_f\big|_k^{\text{biodeg}}\right)}{\partial g_n} =$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\, \Gamma_k\, \mathcal{L}_k\, I_{1k} \left[\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}\right] \left[\frac{K_{A\text{-}k}}{(K_{A\text{-}k} + A_k)^2}\right] \left[\frac{N_k}{K_{N\text{-}k} + N_k}\right] (\gamma_k B_k) \ , \qquad \textbf{(3.3.138)}$$

$$\text{if } A_k = n$$

If nutrient $N_k \in K_x + K_y + M_z + M_p$ and $N_k \neq I$:

$$\frac{\partial\left(r_f\big|_k^{\text{biodeg}}\right)}{\partial g_n} =$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\, \Gamma_k\, \mathcal{L}_k\, I_{1k} \left[\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A\text{-}k} + A_k}\right] \left[\frac{K_{N\text{-}k}}{(K_{N\text{-}k} + N_k)^2}\right] (\gamma_k B_k) \ , \qquad \textbf{(3.3.139)}$$

$$\text{if } N_k = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$:

$$\frac{\partial(r_f|_k^{\text{biodeg}})}{\partial g_n} =$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathscr{L}_k\,\frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A\text{-}k} + A_k}\right]\left[\frac{N_k}{K_{N\text{-}k} + N_k}\right](\gamma_k B_k)\ -$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathscr{L}_k\,I_{1k}\,\frac{S_k q K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A\text{-}k} + A_k}\right]\left[\frac{N_k}{K_{N\text{-}k} + N_k}\right](\gamma_k B_k) \tag{3.3.140}$$

$$\text{if } I = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = S_k$:

$$\frac{\partial(r_f|_k^{\text{biodeg}})}{\partial g_n} =$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathscr{L}_k\,\frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S\text{-}k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A\text{-}k} + A_k}\right]\left[\frac{N_k}{K_{N\text{-}k} + N_k}\right](\gamma_k B_k)\ -$$

$$\frac{(v''_{kf} - v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathscr{L}_k\,I_{1k}\,\frac{K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q} - \dfrac{S_k q K_s}{K_{I2}}\left(1 + \dfrac{I}{K_{I2}}\right)^{q-1}}{\left[K_s\left(1 + \dfrac{I}{K_{I2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A\text{-}k} + A_k}\right]\left[\frac{N_k}{K_{N\text{-}k} + N_k}\right](\gamma_k \tag{3.3.141}$$

$$\text{if } I = S_k = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = A_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\begin{aligned}
&\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\ -\\
&\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1+\dfrac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1+\dfrac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\\
&+\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{K_A}{(K_{A-k}+A_k)^2}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\\
&\text{if } I = A_k = n
\end{aligned} \tag{3.3.142}$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\begin{aligned}
&\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\ -\\
&\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1+\dfrac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1+\dfrac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)\\
&+\frac{(v''_{kf}-v'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{K_N}{(K_{N-k}+N_k)^2}\right](\gamma_k B_k)\\
&\text{if } I = N_k = n
\end{aligned} \tag{3.3.143}$$

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian for columns $n \in K_x + K_y + M_z + M_p$ is zero.

For columns $n \in M_b + M_a$, $j = n + N + K_x + K_y + M_z + M_p$, the contribution to the Jacobian from the k-th microbial degradation reaction is:

If $B_k \neq I$:

$$\frac{\partial (r_f|_k^{\text{biodeg}})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right] \delta_{mn} \qquad \textbf{(3.3.144)}$$

If $B_k = I$:

$$\frac{\partial (r_f|_k^{\text{biodeg}})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s \left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2} \left[K_s \left(1 + \frac{I}{K_{i2}}\right)^{q} + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B_k) \qquad \textbf{(3.3.145)}$$

$$+ \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right] \delta_{mn}$$

if $I = n$

3.3.3.11 Contribution from microbial respiration

The contribution to the Jacobian from endogenous respiration of the k-th microbial species ($k \in M_B$) is:

$$\frac{\partial r_f^{\text{bioresp}}|_k}{\partial g_n} = \frac{\partial}{\partial g_n}\left[\alpha_{kf} K_k^d B_k \left(\frac{g_f}{\kappa_{kf} + g_f}\right)\right] \qquad \textbf{(3.3.146)}$$

If the species $f \in (N_a + N_s + K_x + K_y + M_z + M_p)$, it will contribute to its own column and to the column corresponding to microbial species k. For this case, the contribution to column n in the Jacobian from maintenance/respiration of the k-th microbial species is:

$$\frac{\partial (r_f^{\text{bioresp}})}{\partial g_n} = \alpha_{kf} K_k^d B_k \left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2}\right] \delta_{fn} \quad , \quad n \in (N_a + N_s + K_x + K_y + M_z + M_p) \qquad \textbf{(3.3.147)}$$

and

$$\frac{\partial(r_f^{\text{bioresp}})}{\partial g_n} = \alpha_{kf} K_k^d \left[\frac{g_f}{\kappa_{jf} + g_f} \right] \delta_{kn} \quad , \quad n \in M_b + M_a \tag{3.3.148}$$

If the species $f \in (M_x - K_x)$ or $(M_y - K_y)$, it will contribute to the columns for the components is contains and to the column corresponding to microbial species k. For this case, the contribution to column n in the Jacobian from maintenance/respiration of the k-th microbial species is:

$$\frac{\partial(r_f^{\text{bioresp}})}{\partial g_n} = \alpha_{kf} K_k^d B_k \left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2} \right] \frac{\partial g_f}{\partial g_n} = \alpha_{kf} K_k^d B_k \left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2} \right] \left[\frac{\nu'_{\kappa n}}{\nu''_{\kappa f}} \frac{g_f}{g_n} \right] , \tag{3.3.149}$$

$$f \in (M_x - K_x) \text{ or } (M_y - K_y) \quad , \quad n \in (N_a + N_s)$$

where $\kappa \in$ NRXNE is the equlibrium reaction defining the formation of equilibrium species f, and

$$\frac{\partial(r_f^{\text{bioresp}})}{\partial g_n} = \alpha_{kf} K_k^d \left[\frac{g_f}{\kappa_{jf} + g_f} \right] \delta_{kn} \quad , \quad n \in M_b + M_a \tag{3.3.150}$$

3.3.4 Treatment of Precipitation/Dissolution

Precipitation/dissolution can be considered with two different approaches. The first one is to consider the concentrations of all precipitated species as independent unknowns in addition to the component species concentrations. This approach has been used in several geochemical equilibrium models such as EQ3/EQ6 (Wolery 1979), PHREEQE (Parkhurst et al. 1980), and some multispecies transport models such as THCC (Carnahan 1986). The second approach is to substitute the mass action equation for each precipitated species into the other equations to eliminate M_p c_k's out of N_a c_k's and M_p p_i's from the set of governing equations. The detail of this type of substitution and the subsequent reduction of the number of equations can be found on pages 56 through 63 in the MINEQL manual (Westall et al. 1976). For every precipitated species eliminated, the number of simultaneous equations can be reduced by two: one mass action equation describing that species and any one mole balance equation containing that species (Westall et al. 1976). However, by using the first approach, one is able to treat mixed chemical equilibrium and chemical kinetics so that precipitation/dissolution kinetics can be simulated. This version of the code uses the first approach to treat precipitation-dissolution reactions.

3.3.5 Treatment of a System Involving Oxidation-Reduction Reactions

Oxidation-reduction reactions are treated by defining electron activity as a component species and considering operational electrons as aqueous components. For multivalent elements, a species in one of the higher oxidation states of an element is chosen as the component species to represent that element. Reduction to a lower oxidation state is described by a half-cell reaction, which is analogous to complexation. The total concentration of "operational" electrons is obtained by summing over all added chemicals that contain lower oxidation state elements. The mole balance equation for operational electrons is different from those for other aqueous components in that the first term on the right-hand side is set to zero and c_e in all other terms is interpreted as the activity of the electrons rather than the concentration of free electrons.

Mathematically, operational electrons can be treated just as other aqueous components. Numerically, however, this component requires special attention. Because the electron activity can span over at least 40 orders of magnitude, an ill-conditioned matrix often results when this equation is solved simultaneously with other mole balance equations with the Newton-Raphson method. To circumvent this difficulty, a split scheme is used in this version of the code. In this split scheme, the mole balance equation for operational electrons is solved with a modified bisection method (Forsythe et al. 1977), while all other mole balance equations are solved simultaneously with the Newton-Raphson method. This split scheme is particularly effective for reducing conditions when the solution fails to converge without the split scheme.

3.3.6 Treatment of a System Involving Acid-Base Reactions

Acid-base reactions are treated by defining hydrogen activity as a component species. The "excess" hydrogen is subject to transport as are other aqueous components. The mole balance equation for the excess hydrogen is different from those for other aqueous components. The first term on the right-hand side of Equation (3.3.1) is written as c_H/γ_H where γ_H is the activity coefficient of the free hydrogen ion. In all other terms, C_k is replaced by c_H and is interpreted as the activity of hydrogen rather than the concentration of free hydrogen. If an (OH) appears in any species, the stoichiometric coefficient of the hydrogen in that species is set to -1. If n (OH)s appear in any species, the stoichiometric coefficient of hydrogen in that species is set to -n.

4.0 THE HYDROBIOGEOCHEM PROGRAM STRUCTURE

4.1 The General Solution Strategy of HYDROBIOGEOCHEM

HYDROBIOGEOCHEM is designed to solve a system of equations describing hydrologic transport and biogeochemical reactions in a reactive multicomponent system. The transport equations are derived from the continuity of mass and the law of flux. The biogeochemical equations are material balances coupled with the mass action and kinetic rate equations. The transport equations, along with initial and boundary conditions, and the equations for the biogeochemical reactions govern the migration and chemical transformation of multicomponent species in saturated-unsaturated media. The major transport processes are advection, dispersion/diffusion, and source/sinks. The major chemical processes are aqueous complexation, adsorption, ion-exchange, precipitation/dissolution, redox, and acid-base reactions. The major microbiological processes are biodegradation and microbial respiration.

Two basic types of equations are necessary for modeling the transport of reactive multicomponent species in the subsurface environment. Transport is described by a set of partial or ordinary differential equations. The biochemical reactions are described by a set of nonlinear algebraic equations. The governing transport equations along with the initial conditions are given by Equations (3.1.1) through (3.1.23). The chemical reaction equations are Equations (3.1.24) through (3.1.48). The steps to solve the governing equations are as follows:

1. Equilibrate the system.
2. Estimate the reaction terms in Equations (3.1.1), (3.1.10), and (3.1.17).
3. Solve Equations (3.1.1) through (3.1.23) to obtain estimate of mobile species concentrations, T_j's, kinetic x_i's, and b_i's.
4. Solve Equations (3.1.24) through (3.1.48) for all other species concentrations.
5. Revise estimate of the reaction terms in Equations (3.1.1), (3.1.10), and (3.1.17).
6. Solve Equations (3.1.1) through (3.1.23) to obtain new estimate of T_j's, kinetic x_i's, and b_i's.
7. Compare the newly obtained values with the prior estimates from Step 3.
8. If the difference is within the error tolerance, proceed to the next time step. If the difference is greater than the tolerance, repeat Steps 2 through 7 until the system converges.

4.2 Description of HYDROBIOGEOCHEM Subroutines

HYDROBIOGEOCHEM consists of a short MAIN routine, 125 subroutines, and a function. The MAIN module is used to specify the sizes of all arrays, read data file names, and open data files. The control and coordination activities are performed by subroutine GM2D. The linkage between the hydrologic transport model and biogeochemical reaction model is performed by the subroutine OCSPIT. The subroutines called by GM2D can be classified into four major categories:

- 31 subroutines are used to perform hydrologic transport.
- 25 subroutines and the function are used to compute the Lagrangian concentrations.
- 55 subroutines are used to simulate chemical equilibrium and kinetics.
- 13 subroutines are to perform utility functions.

Figure 4.1 shows the structure of the program. The subroutines are described below.

Subroutine GM2D: Subroutine GM2D controls the entire sequence of operations, a function generally performed by the MAIN program. It is preferable, however, to keep a short MAIN module and utilize variable storage allocation. This makes it possible to deal with a site-specific problem without making changes in array dimensions throughout all subroutines.

Subroutine GM2D will calculate

- The steady-state solution (KSS = 0 and NTI = 0 in Data Set 2 of Appendix A).
- A transient solution using the steady-state solution as the initial conditions (KSS = 0, NTI > 0).
- A transient solution using user-supplied initial conditions (KSS = 1, NTI > 0).

Subroutine GM2D calls:

- Subroutine DATAHT to read and print input data required for hydrologic transport calculations.
- Subroutine CONECT to arrange node connections in ascending order, to locate the diagonal entry for each row and to compute the number of entries in each row.
- Subroutine READR to read the liquid density field.

- Subroutine DATACS to read and print input data required for biogeochemical calculations.

- Subroutine AFABTA to compute the upstream weighting factor.

- Subroutine NODVAL to compute values of the moisture content, bulk density, initial cation exchange capacity, capacitances, and surface area of adsorbent sites at nodes.

- Subroutine VELDC to calculate the average darcy velocity at each node over the current time step and the dispersion coefficient for each element.

- Subroutine EFCTVK to compute the velocity of the fluid with respect to the solid, and the components of the tracking velocity and the constant K which are independent of species concentration.

- Subroutine SSBV to compute source/sink and boundary values.

- Subroutine OCSPIT to obtain individual chemical and microbial species distributions and total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components at all nodes.

- Subroutine TWDVK to compute the concentration dependent velocity and concentration dependent first order rate constant.

- Subroutine ADVWRK to prepare working arrays for Lagrangian integration.

- Subroutine LGRNSTP to perform the Lagrangian Step.

- Subroutine ELRNSTP to perform the Eulerian Step for the hydrologic transport calculations.

- Subroutine SFLOW to compute the net rate of chemical flow through open boundaries.

- Subroutine CALKD to compute equivalent K_d values.

- Subroutine PRINTT to print the results.

- Subroutine PRITER to print the intermediate results between hydrologic transport and biogeochemical iterations.

- Subroutine STORE to store the results for plotting.

Subroutines for Utility Functions:

Subroutine DATAHT: is called by GM2D to read the system geometry and hydrologic transport input data from Data Sets 2 through 15 as described in Appendix A. It also prints all the input information to a tabular output file. DATAHT calls subroutine SURF to identify the boundary segments and boundary nodes, and subroutines READR and READN to automatically generate real and integer numbers, respectively, and subroutine LNDGEN to generate the relationships between node number and equation number when pointwise iteration solution strategies are used.

- **Subroutine SURF**: is called by DATAHT to identify the boundary sides, sequence the boundary nodes, calculate the boundary side length, and compute the directional cosine of the surface sides. The mapping from boundary nodes to global nodes is stored in NPBB(I), where NPBB(I) is the global node number of the I-th boundary node. The element number associated with the boundary sides is stored in MBES. The length and directional cosines for each side are stored in DLB and DCOSXB and DCOSZB, respectively. The local and global nodal numbers of two nodes of each side are stored in ISB. SURF calls Subroutine SLBDY to calculate the shortest element side connected to each boundary node, SLSCAL. The information contained in NPBB, MBES, ISB, DLB, DCOSXB, DCOSZB, and SLSCAL along with the number of boundary nodes and the number of boundary sides, are returned to subroutine DATAHT for use by other subroutines.

- **Subroutine READR**: is called by DATAHT to generate real numbers for Data Sets 7 and 11 described in Appendix A. Automatic generation of regularly patterned data is built into this subroutine. READR is also called by GM2D to generate real numbers for Data Set 16.

- **Subroutine READN**: is called by DATAHT to generate integers for Data Sets 9, 13, 14, and 15 described in Appendix A.

- **Subroutine LNDGEN**: is called by DATAHT to preprocess the pointer arrays needed to assemble the global matrix in compressed form when pointwise solution methods are used. These pointer arrays are generated based on the element connectivity IE(M,J), which is the global node number of the J-th node of element M. Pointer array LRN(J,N) is the global node number of the J-th node connected to the global node N. Pointer array LRL(K,N) is the global element number of the K-th element connected to the global node N, and array NLRL(N) contains the number of elements connected to global node N.

Subroutine CONECT: is called by GM2D to arrange nodal connections in ascending order, to locate the diagonal entry for each row, and to compute the number of entries in each row.

Subroutine DATACS: is called by GM2D to read the biogeochemical system input data from Data

Sets 17 through 28 as described in Appendix A and prints all input information.

Subroutine SFLOW: is called by GM2D to compute mass fluxes through all open boundary nodes.

Subroutine CALKD: is called by GM2D to calculate the equivalent partition coefficient K_d for all components.

Subroutine PRINTT: is called by GM2D to print the transport variables. These include the total analytical concentrations, total dissolved concentrations, total sorbed concentrations, total precipitated concentrations of all components, and the negative logarithm of concentration for all component species, and the concentration of all kinetic chemical product species or microbial species.

Subroutine PRITER: is called by GM2D to print the intermediate total analytical concentrations of all components between hydrologic transport and geochemical reaction iterations.

Subroutine STORE: is called by subroutine GM2D to store the transport variables on Logical Unit 12 in binary form. This data is intended for plotting and other post processing use and includes region geometry and transport variables.

Subroutines for Lagrangian Concentration Calculations:

Subroutine ADVWRK: is called by GM2D to prepare all the working arrays to be used in particle tracking in LGRNSTP. This subroutine is called only when the transient simulation is required.

Subroutine LGRNSTP: is called by GM2D to implement the Lagrangian step to obtain the Lagrangian value of the total analytical concentrations for the component/species being subjected to trasnport. This subroutine calls ADVBC to implement the upstream and downstream boundary conditions and GNTRAK to perform the backward particle tracking and interpolation.

Subroutine ADVBC: is called by LGRNSTP to implement the variable and Dirichlet boundary conditions upstream and downstream of the particle track. For a Dirichlet boundary, the Lagrangian concentration is specified. For variable boundaries, the fictitious particle associated with the boundary node must come from the interior nodes if the flow is directed out of the region or from the incoming fluid if the flow is directed into the region. Hence for the downstream (or outflow) variable boundary nodes, the Lagrangian concentration for the boundary node is computed in subroutine GNTRAK when particle tracking within the interior is performed and the implementation for such a boundary segment is bypassed. For upstream (or inflow) variable boundary nodes, the incoming fluid concentration is specified if the flow is directed into the region. The Lagrangian concentration is then calculated according to Eq. (3.2.55), repeated here:

$$T_{vi}^{*} = \frac{\int_{B_v} N_i \mathbf{n} \cdot \mathbf{V} C_{in} dB}{\int_{B_v} N_i \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} T' dB} \tag{4.2.1}$$

This subroutine calls

- **Subroutine Q2ADVB** to implement the variable boundary condition for a given boundary side, applying mass lumping. It evaluates the following integrations for a boundary segment:

$$RIQ(i) = \int_{B_v} N_i \mathbf{n} \cdot \mathbf{V} C_{in} dB \tag{4.2.2}$$

$$RLQ(i) = \int_{B_v} N_i \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} T' dB \tag{4.2.3}$$

where

RIQ(i) = the rate of chemical passing through node i.
RLQ(i) = the rate of liquid passing through node i.

Subroutine GNTRAK: is called by LGRNSTP to perform the backward particle tracking and interpolation. It is designed to get the Lagrangian concentrations of all the particles sitting on the global nodes at the current time step. In the subroutine, each particle is tracked one element by one element until either the tracking time is completely consumed or the particle encounters a specified boundary side. This subroutine calls:

- **Subroutine REPLAS:** to set values of x, y, vx, and vy at point P.
- **Subroutine ELENOD:** to determine the shape (triangular or quadrilateral) for a specified element.
- **Subroutine WRKARY:** to prepare working arrays for particle tracking in an element or subelement.
- **Subroutine ELETRK:** to track a particle using the “in-element” approach. This subroutine is described in further detail below.
- **Subroutine FIXCHK:** to process particle tracking after the particle encounters a boundary. This subroutine calls:

    - **Subroutine ALGBDY** to achieve particle tracking along an unspecified boundary. Tracking is executed one boundary side by one boundary side based on the nodal velocity component along the side being considered. The tracking will not be stopped until either the tracking time is completely consumed or the particle encounters a specified boundary side. ALGBDY calls ELENOD to determine an element's shape.

- **Subroutine CKCOIN:** to examine whether a given node corresponds with node N1 or N2.

- **Subroutine CKCNEL:** to determine the elements that are connected to the element side with nodes N1 and N2 as its ends.

- **Subroutine INTRP:** to compute the Lagrangian concentration by interpolation. This subroutine calls:

    - **Subroutine BASE1** to determine the shape function values associated with a specified point based on the given two-dimensional global coordinates. BASE1 calls **Subroutine XSI2D** to compute the local coordinate of an element based on the given original global coordinates.

Subroutine ELETRK: is called by LGRNSTP to track a particle using the "in-element" approach. In order to increase the accuracy of particle tracking, regular refinement is used to divide the element into as many subelements as the user specifies, and the tracking is executed one subelement by one subelement. Tracking is not stopped until either the tracking time is completely consumed or the particle encounters a side of the element. This subroutine calls subroutines REPLAS, CKCNEL, WRKARY, and CKCOIN described above and :

- **Subroutine VALBDL:** to determine the velocity at a point by interpolation.

- **Subroutine MMLOC:** to locate the starting point for the "in-element" particle tracking in a specified element. MMLOC calls REPLAS to set values at point P and calls **Subroutine ONLINE** to assure that point (XP,YP) is on the line segment with nodes J1 and J2 as its end nodes.

- **Subroutine TRACK2:** to determine (1) if the particle will pass through the working subelement and (2) where the ending point is if the particle passes through the working element. This subroutine is employed when the starting point is not on any of the working subelement nodes. For accuracy, the average velocity of both the source point and the target point is first considered in locating the target point. However, if this average velocity approach is not able to deal with very complex velocity fields, the single velocity of the source point is used to determine the location of the target point. This subroutine calls:

  - **Subroutine LOCQ2D** to determine the location and velocity at the target point, q, as well as the available time for further tracking when the target side is specified. This subroutine calls **Subroutine CHNGSGN** to change the sign of velocity arrays and **Subroutine SURE2D** to locate the target point for a tracking path when the single velocity approach is employed.

- **Subroutine IBWCHK:** to determine the two global nodes whose associated element side is where the target point rests at the end of the "in-element" particle tracking in a specified element.

- **Subroutine TRACK1:** to determine (1) if the particle will pass through the working subelement and (2) where the ending point is if the particle passes through the working element. This subroutine is employed when the starting point is one of the working subelement nodes. As in Subroutine TRACK2, the average velocity of both the source point and the target point is considered first for accuracy in locating the target point. If this average velocity approach is not able to deal with very complex velocity fields, the single velocity of the source point is used to determine the location of the target point. This subroutine calls Subroutine LOCQ2D.

Subroutines for Hydrologic Transport Calculations:

Subroutine AFABTA: is called by GM2D to compute the optimum weighting factors for all sides of an element. The results are stored in array WETAB(J,M), where M = 1, 2, ..., NEL and J = 1, 2, 3, 4 for quadrilateral elements and J = 1, 2, 3 for triangular elements.

Subroutine NODVAL: is called by GM2D to convert the values of the cation ion exchange capacities and the surface area and capacitance of adsorbing sites, the moisture content, and the bulk density of the materials associated with each element into values at the nodal points. It examines the size and properties associated with each element connected to each node and determines a weighted average value for these properties at each node.

Subroutine VELDC: is called by GM2D to calculate the average darcy velocity (specific discharge) at each node over the current time step and the dispersion coefficient for each element.

$$\text{AKDC(3,4,M)} = \rho_\ell \theta \mathbf{D} \tag{4.2.4}$$

Subroutine EFCTVK: is called by GM2D to compute the velocity of the fluid with respect to the solid (pore water velocity) and the components of the tracking velocity and the first order rate constant K which are independent of species concentration at each node:

$$\text{EFCTV(NP,2)} = \rho_\ell \mathbf{V} \tag{4.2.5}$$

$$\mathrm{EFCTK(NP)} = -\frac{\partial \rho_{\ell}\theta}{\partial t} \qquad \mathbf{(4.2.6)}$$

Subroutine SSBV: is called by GM2D to compute the source/sink and boundary values for the species subject to transport. SSBV linearly interpolates the input source/sink and boundary condition profiles to values at the current time. SSBV calls **Subroutine INTERP** to perform the interpolation.

Subroutine TWDVK: is called by GM2D to compute the values at each node for the concentration dependent velocity and concentration dependent first order rate constant for each species subject to transport:

$$\begin{aligned} \mathrm{VTRK(NP,2)} &= \mathrm{EFCTV(NP,2)}\,\frac{C'}{T'} - \mathbf{AKDC}\cdot\nabla\frac{C'}{T'} \\ &= \left[\rho_{\ell}\mathbf{V}\frac{C'}{T'} - \rho_{\ell}\theta\,\mathbf{D}\cdot\nabla\frac{C'}{T'}\right] \end{aligned} \qquad \mathbf{(4.2.7)}$$

$$\begin{aligned} \mathrm{RATK(NP)} &= \mathrm{EFCTK(NP)}\frac{C'}{T'} + \mathrm{EFCTV(NP,2)}\cdot\nabla\frac{C'}{T'} - \nabla\cdot\left[\mathbf{AKDC}\cdot\nabla\frac{C'}{T'}\right] - \mathrm{EFCTK(NP)} \\ &= \left[\frac{\partial\rho_{\ell}\theta}{\partial t} + \rho_{\ell}\mathbf{V}\nabla\cdot\frac{C_j'}{T_j'} - \frac{C_j'}{T_j'}\frac{\partial\rho_{\ell}\theta}{\partial t} - \nabla\cdot\left(\rho_{\ell}\theta\mathbf{D}\cdot\nabla\frac{C_j'}{T_j'}\right)\right] \end{aligned} \qquad \mathbf{(4.2.8)}$$

This subroutine calls

- **Subroutine GRADFN**: to calculate the gradient of (C/T). GRADF is a general subroutine to calculate the gradient of any specified function using the finite element method. GRADFN calls **Subroutine Q4D** to calculate the element matrix for quadrilateral elements and **Subroutine Q3D** to calculate the element matrix for triangular elements. Q4D calls **Subroutine SHAPE** to evaluate the base and weighting functions and derivatives of the base functions at a Gaussian point.

- **Subroutine DDOTGFN**: to calculate $\rho_{\ell}\ \theta\ \mathbf{D} \cdot \nabla$ (C/T). DDOTGFN is a general subroutine to calculate $\rho_{\ell}\ \theta\ \mathbf{D}$ • the gradient of any specified function using the finite element method. DDOTGFN calls Q4D and Q3D.

- **Subroutine DIVVEC**: to calculate $\nabla \cdot \{\rho_{\ell}\ \theta\ \mathbf{D} \cdot \nabla (C/T)\}$. DIVVEC is a general subroutine to calculate the divergence of any specified vector function using the finite element method. DDOTGF calls **Subroutine Q4DIV** to to calculate the element matrix for quadrilateral elements and **Subroutine Q3DIV** to to calculate the element matrix for triangular elements.

Subroutine ELRNSTP: is called by GM2D to implement the Eulerian step of the hydrologic transport calculations. This subroutine calls ASEMBL to compose the matrix equations, BC to implement the boundary conditions, and SOLVE, PISS, PPCG, ILUCG, MICPCG, or SSORCG to solve the matrix equations.

Subroutine ASEMBL: is called by subroutine ELRNSTP to compose the matrix equations. It sums over all element matrices to form the compressed global matrix CMTRX and the global load vector RLD. This subroutine calls:

- **Subroutines Q4 and Q3**: to compute the element matrices for quadrilateral and triangular elements, respectively, given by

$$A_{\alpha\beta}^{e} = \int_{R_e} N_{\alpha}^{e}(\rho_{\ell}\theta)N_{\beta}^{e}\,dR \quad , \tag{4.2.9}$$

$$D_{\alpha\beta}^{e} = \int_{R_e} \left(\nabla N_{\alpha}^{e}\right)\cdot \rho_{\ell}\theta\mathbf{D}\,\frac{C'}{T'}\cdot\left(\nabla N_{\beta}^{e}\right) dR \tag{4.2.10}$$

$$C_{\alpha\beta}^{e} = \int_{R_e} N_{\alpha}^{e}\left[\frac{\partial\rho_{\ell}\theta}{\partial t} + \rho_{\ell}\mathbf{V}\nabla\cdot\frac{C'}{T'} - \frac{C'}{T'}\frac{\partial\rho_{\ell}\theta}{\partial t} - \nabla\cdot\left(\rho_{\ell}\theta\mathbf{D}\cdot\nabla\frac{C'}{T'}\right)\right]N_{\beta}^{e}\,dR \tag{4.2.11}$$

$$Q_{\alpha\beta}^{e} = \int_{R_e} N_{\alpha}^{e}\,Q\rho^{*}\,\frac{C'}{T'}\,N_{\beta}^{e}\,dR \tag{4.2.12}$$

Subroutines Q4 and Q3 also calculate the element load vectors given by

$$R_{\alpha}^{e} = \int_{R_e} N_{\alpha}^{e}R^{c}\,dR \tag{4.2.13}$$

and

$$S_{\alpha}^{e} = \int_{R_e} N_{\alpha}^{e}QC_{in}\,dR \tag{4.2.14}$$

Subroutine Q4 calls subroutine SHAPE to evaluate the base and weighting functions and derivatives of the base functions at a Gaussian point.

Subroutine BC: is called by subroutine ELRNSTP to incorporate the Dirichlet and variable-boundary conditions into the the compressed global matrix CMTRX and the global load vector RLD. For a Dirichlet boundary condition, an identity algebraic equation is generated for each Dirichlet nodal point. Any other equation having this nodal variable is modified accordingly to simplify computations. Subroutine BC implements the variable-boundary conditions by calling subroutine Q2VB:

- **Subroutine Q2VB**: is called by subroutine BC to compute the contributions of a variable-boundary segment to the global matrix equation. It computes a two-by-two matrix, QB, and a load vector, QR, for each variable-boundary segment as follows:

$$QB(I,J) = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) dB \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) < 0 \quad , \tag{4.2.15}$$

$$QB(I,J) = \int_{B_e} N_\alpha^e \left[\mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) - \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} \right] dB \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) \geq 0 \quad , \tag{4.2.16}$$

$$QR(I) = - \int_{B_e} N_\alpha^e (\mathbf{n} \cdot \mathbf{V}) C_{in} dB \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) < 0 \quad , \tag{4.2.17}$$

and

$$QR(I) = 0 \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) \geq 0 \quad . \tag{4.2.18}$$

Subroutine SOLVE: is called by subroutine ELRNSTP to solve a matrix equation of the type

$$[C]\{x\} = \{y\} \quad , \tag{4.2.19}$$

where

[C] = coefficient matrix.
{x} = unknown vector to be determined.
{y} = known load vector.

The subroutine returns the solution {y} and stores it in {y}. SOLVE uses a standard-banded, Gaussian direct elimination procedure.

Subroutine PISS: is called by subroutine ELRNSTP to solve the linearized matrix equation with point iteration solution strategies when specified by the user.

Subroutine PPCG: is called by subroutine ELRNSTP to solve the linearized matrix equation with the preconditioned conjugate gradient method using the polynomial as a preconditioner. PPCG calls to **Subroutine POLYP** to invert the preconditioner.

Subroutine ILUCG: is called by subroutine ELRNSTP to solve the linearized matrix equation with the preconditioned conjugate gradient method using the incomplete Cholesky decomposition as a preconditioner. It calls to **Subroutine LLTINV** to invert the preconditioner.

Subroutine MICPCG: is called by subroutine ELRNSTP to solve the linearized matrix equation with the preconditioned conjugate gradient method using the modified incomplete Cholesky decomposition as a preconditioner. It calls to **Subroutine MICP** to invert the preconditioner.

Subroutine SSORCG: is called by subroutine ELRNSTP to solve the linearized matrix equation with the preconditioned conjugate gradient method using the symmetric successive over-relaxation as a preconditioner. It calls to **Subroutine SSORP** to invert the preconditioner.

Subroutines for Biogeochemical Subsystem Calculations:

Subroutine OCSPIT: is called by subroutine GM2D. It calculates the individual chemical and microbial species concentrations and the total dissolved, total sorbed, and total precipitated concentrations of all components by calling the subroutine KEMOD. It then calculates the rate of change of all species subject to transport based on the new concentrations determined by KEMOD by calling subroutine RATECB. Finally, it calls to LPOUT to print chemical species distributions.

Subroutine KEMOD: The subroutine KEMOD is called by the subroutine OCSPIT and will perform either the steady-state computation alone (KSS = 0 and NTI = 0), or a transient state computation using the steady-state solution as the initial conditions (KSS = 0, NTI > 0), or a transient computation using user-supplied initial conditions (KSS = 1, NTI > 0). It initializes the concentrations of all product species given the estimate of component concentrations from subroutine OCSPIT. KEMOD then calls to subroutine KINEQL to solve a set of mixed ordinary differential and algebraic equations governing mole balance, and kinetic and equilibrium reactions. It calls to subroutine TOTDSP to compute total dissolved, total sorbed, and total precipitated concentrations of all components after concentrations of all species have been found.

Subroutine KINEQL: This subroutine solves the system of mixed ordinary differential and nonlinear algebraic equations specified by Eqs. (3.1.13) through (3.1.25). The solution is determined with the Newton-Raphson iteration method. For each iteration, subroutine KINEQL calls:

- Subroutine DGELG to decompose the Jacobian matrix with full pivoting and for back substitution to obtain the differences between new iteration and previous iterations of all unknowns. New iterates are obtained by adding these differences to the old iterations.

Subroutine ACOEF: This subroutine is called by subroutine KINEQL to compute ionic strength and activity coefficients of all species.

Subroutine MODPRK: This subroutine is called by subroutine KINEQL to calculate the modified equilibrium formation constants for all precipitated species.

Subroutine MODBFK: This subroutine is called by subroutine KINEQL to calculate the modified equilibrium constants for all equilibrium reactions and the modified forward and backward rate constants for all chemical kinetic reactions.

Subroutine RESIDU: This subroutine is called to evaluate residuals of discretized ordinary differential and nonlinear algebraic equations governing biogeochemical kinetics and equilibrium. It calls:

- **Subroutine RAQC**: to evaluate residuals for equations governing the mole balance for aqueous components.
- **Subroutine RADC**: to evaluate residuals for equations governing the mole balance for adsorbent components, except for the contribution from reactions.
- **Subroutine RKXY**: to evaluate residuals for the kinetic complexed and adsorbed species, except for the contribution from reactions.
- **Subroutine RIES**: to evaluate residuals for ion-exchanged species, except for the contribution from reactions.
- **Subroutine RPRC:** to evaluate residuals for the kinetic precipitated species, except for the contribution from reactions.
- **Subroutine RMBA:** to evaluate residuals for the microbial species, except for the contribution from reactions.
- **Subroutine RRXNS:** to evaluate the contribution to all residual equations from reactions. This subroutine calls:
    - **Subroutine RATEL1:** to evaluate the contribution from equilibrium reactions (KRTYP = 0). This subroutine calls **Subroutine PRODBF** to perform some of the repetitive calculations.
    - **Subroutine RATEL2:** to evaluate the contribution from chemical kinetic reactions (KRTYP = 1). This subroutine calls **Subroutine PRODBF** to perform some of the repetitive calculations.
    - **Subroutine RATEL3:** to evaluate the contribution from Monod kinetic microbial reactions (KRTYP = 2). This subroutine calls **Subroutine BIOLAGK** to determine the lag coefficient for a reaction, **Subroutine BIOINH** to determine the inhibition coefficients for a reaction, and **Subroutine BIORATE** to determine the rate of a reaction.
    - **Subroutine RATEL4:** to evaluate the contribution from microbial phase transfer reactions (KRTYP = 3).

Subroutine JACOBI: This subroutine is called to evaluate the Jacobians of discretized ordinary differential and nonlinear algebraic equations governing biogeochemical kinetics and equilibrium. It calls:

- **Subroutine JAQC**: to evaluate Jacobians for equations governing the mole balance for aqueous components.
- **Subroutine JADC**: to evaluate Jacobians for equations governing the mole balance for adsorbent components, except for the contribution from reactions.
- **Subroutine JKXY**: to evaluate Jacobians for the kinetic complexed and adsorbed species, except for the contribution from reactions.
- **Subroutine JIES**: to evaluate Jacobians for ion-exchanged species, except for the contribution from reactions.
- **Subroutine JPRC:** to evaluate Jacobians for the kinetic precipitated species, except for the contribution from reactions.
- **Subroutine JMBA:** to evaluate Jacobians for the microbial species, except for the contribution from reactions.
- **Subroutine JRXNS:** to evaluate the contribution to all Jacobians from reactions. This subroutine calls:
    - **Subroutine JRATE1:** to evaluate the contribution from equilibrium reactions (KRTYP = 0). This subroutine calls **Subroutine PRODBF** to calculate constants for a given reaction that do not depend on the row and column in the Jacobian. It also calls **Subroutines JERZ and JERP** to evaluate the Jacobian for equilibrium ion-exchanged and precipitated species, respectively. JERZ and JERP call **Subroutine JEQXY** to evaluate the case when an equilibrium aqueous complexed species is involved in the reaction.
    - **Subroutine JRATE2:** to evaluate the contribution from chemical kinetic reactions (KRTYP = 1). This subroutine calls **Subroutine PRODBF** to calculate constants for a given reaction that do not depend on the row and column in the Jacobian. It also calls **Subroutine JKRC** to perform some of the repetitive calculations.
    - **Subroutine JRATE3:** to evaluate the contribution from Monod kinetic microbial reactions (KRTYP = 2). This subroutine calls **Subroutine BIORATE** to determine the rate of a reaction, and **Subroutine JBIO** to calculate constants for a given reaction that do not depend on the row in the Jacobian. It then calls **Subroutine JCOL** to calculate the Jacobian for a given row from a given reaction for each column. JCOL calls **Subroutine**

JKRB to perform some of the repetitive calculations.

- **Subroutine JRATE4:** to evaluate the contribution from microbial phase transfer reactions (KRTYP = 3).

Subroutine DGELG: This subroutine is called by subroutine KINEQL to solve the Jacobian matrix equation using Gaussian elimination with full pivoting.

Subroutine DECOMP: This subroutine is called by subroutine KINEQL to solve the Jacobian matrix equation with partial pivoting if specified by the user.

Subroutine SOLVP: This subroutine is called by subroutine KINEQL to solve the Jacobian matrix equation with partial pivoting if specified by the user.

Subroutine INDEXX: This subroutine is called by subroutine KINEQL to index the saturation value among all potential species that are subject to precipitation/dissolution reactions.

Subroutine NPPT: This subroutine is used to determine the number of species allowed to precipitate without violating the phase rule.

Subroutine DISOLV: This subroutine is called by KINEQL to dissolve an assumed precipitated species that has shown negative concentrations during two successive iterations.

Subroutine GUESS: This subroutine is called by KINEQL to make a better starting guess for species concentrations based on a directional search to minimize the expected residuals. It calls **Subroutine RESGUES**, which is similar to RESIDU.

Subroutine TOTDSP: This subroutine is called by subroutines KINEQL and KEMOD to evaluate the log of component free species concentrations and total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components.

Subroutine LPOUT: This subroutine is called by the subroutines KINEQL and OCSPIT to line print chemical species distribution at desired nodes at desired time intervals. The output includes concentrations, modified equilibrium constants, and stoichiometric coefficients of all species.

Subroutine RATECB: This subroutine is called by the subroutine OCSPIT to evaluate the rate of change due to all reactions for the species subject to transport. It calls **Subroutine RCHEM** to evaluate the contribution from chemical reactions, **Subroutine RBIOL** to evaluate the contribution from microbial degradation reactions, **Subroutine RBIOXF** to evaluate the contribution from microbial phase transfer reactions, and **Subroutine RBIOER** to evaluate the contribution from microbial endogenous respiration.

5.0 ADAPTATION OF HYDROBIOGEOCHEM TO SITE SPECIFIC APPLICATIONS

The following describes the maximum control integers that must be defined by the user for each site-specific application and the data files that should be prepared.

5.1 Specification of Maximum Control Integers

For each site-specific application, 44 maximum control integers must be assigned by the user with the PARAMETER statements in the MAIN program to specify the size of the problem. The definitions of these parameters are given below.

5.1.1 Maximum Control Integers for the Spatial Domain

MAXNPK = maximum number of nodes.
MAXELK = maximum number of elements.
MXBNPK = maximum number of boundary nodal points.
MXBESK = maximum number of boundary-element surfaces.
MAXBWK = maximum bandwidth size.
MXJBDK = maximum number of nodes connecting to any node.
MXKBDK = maximum number of elements connecting to any node.

5.1.2 Maximum Control Integers for the Time Domain

MXNTIK = maximum number of time steps.
MXDTCK = maximum number of times to reset time step to a small number.

5.1.3 Maximum Control Integers for Source/Sinks

MXSELK = maximum number of distributed source/sink elements.
MXSPRK = maximum number of distributed source/sink profiles (source value vs. time).
MXSDPK = maximum number of data points on each element source/sink profile.
MXWNPK = maximum number of well nodal points.
MXWPRK = maximum number of well source/sink profiles.
MXWDPK = maximum number of data points on each well source/sink profile.

5.1.4 Maximum Control Integers for Variable Boundary Conditions

MXVNPK = maximum number of variable nodal points.
MXVESK = maximum number of variable element surfaces.
MXVPRK = maximum number of variable boundary condition (rainfall) profiles.
MXVDPK = maximum number of data points on each variable boundary condition profile.

5.1.5 Maximum Control Integers for Dirichlet Boundary Conditions

MXDNPK = maximum number of Dirichlet nodal points.
MXDPRK = maximum number of Dirichlet total head profiles.
MXDDPK = maximum number of data points on each Dirichlet profile.

5.1.6 Maximum Control Integers for Material Properties

MXMATK = maximum number of material types.
MXMPMK = maximum number of material properties per material (= 4 for this code version).

5.1.7 Maximum Control Integers for Transport Components

MAXHAK = maximum number of mobile hydro-components
MAXHSK = maximum number of immobile hydro-components
MAXKXK = maximum number of kinetic aqueous complexed chemical species
MAXKYK = maximum number of kinetic adsorbed chemical species
MAXKZK = maximum number of kinetic ion-exchanged chemical species
MAXKPK = maximum number of kinetic precipitated chemical species
MAXBK = maximum number of microbial species (aqueous + adsorbed)

HYDROBIOGEOCHEM calculates:

MAXHK = maximum number of hydrologic transport system components. (=MAXHAK+MAXHSK)
MAXTK = maximum number of mobile hydro-components, kinetic aqueous complexed species, and microbial species. (= MAXHAK+MAXKXK+MAXBK)
MAXT2K = MAXTK + 2
MXHKK = maximum number of hydro compoments and all kinetic species. (=MAXHK+MAXKXK+MAXKYK+MAXKZK+MAXKPK+MAXBK)

5.1.8 Maximum Control Integers for Biogeochemical Reactions

MAXNK = maximum number of chemical components.
MAXMZK = maximum number of ion-exchanging species.
MAXMPK = maximum number of species allowed for precipitation-dissolution.
MAXPDK = maximum number of chemical product species.
MXNIXK = maximum number of ion-exchange sites.
MXNSBK = maximum number of adsorbing sites.
MXRXNK = maximum number of all reactions.
MXRTSK = maximum number of reactant species in any reaction.
MXPDSK = maximum number of product species in any reaction.

HYDROBIOGEOCHEM calculates:

MAXEQK = maximum number of equations to be solved in biochemical reaction subsystem. (= MAXNK+MAXKXK+MAXKYK+MAXMZK + MAXMPK+MAXBK).
MXPDBK = maximum number of chemical product species and microbial species. (=MAXPDK + MAXBK)
MAXMK = maximum number of all species (= MAXNK + MAXPDK+MAXBK)

5.1.9 Maximum Control Integers for Subelement Particle Tracking

MXNPWK = maximum number of nodal points in any element for tracking.
MXELWK = maximum number of subelements in any element for tracking.
NXWK = maximum number of subelements in the x-direction in any element for tracking.
NYWK = maximum number of subelements in the y-direction in any element for tracking.

5.2 Specification of Maximum Control Integers with PARAMETER Statements

Let us assume that a region of interest is discretized into 15 by 89 nodes and 14 by 88 rectangular elements, i.e., 89 nodes along the longitudinal, or x-direction, and 15 nodes along the vertical, or z-direction. Because we have a total of 15 x 89 = 1,335 nodes, the maximum number of nodes is MAXNPK = 1335. The total number of elements is 14 x 88 = 1,232, i.e., MAXELK = 1232. For this simple discretization problem, the maximum number of nodes connected to any of the 1,335 nodes in the region of interest is nine (The nine nodes connecting to any node include the left node, the right node, the lower node, the upper node, the lower-left node, the lower-right node, the upper left node, the upper right node, and the node itself.) for a quadrilateral element (i.e., MXJBDK = 9), and the maximum number of elements connecting to any node is four (i.e, MXKBDK = 4). There will be 14 boundary element sides each on the right and left sides and 88 boundary element sides each on the top and bottom sides of the region, for a total of 204 boundary element sides (i.e., MXBESK = 204). By similar computations, the number of boundary nodes is 204 (i.e., MXBNPK = 204). The bandwidth is equal to 33 (i.e., MAXBWK = 33). (The bandwidth is equal to 2*MAXDIF + 1 where MAXDIF is the maximum difference of the four element indices for any element. For this simple discretization, we number the nodes from 1 to 15 in the first column, 16 to 30 in the second column, etc. For element 1, the four indices are 1, 16, 17, and 2; hence MAXDIF is 17 - 1 = 16. All other elements will have the same MAXDIF. Thus the bandwidth is 2*32 + 1 = 33.)

In this version of the code, there are four material properties per material, so MXMPMK = 4. If we assume that the whole region of interest is composed of three different kinds of materials, then we have MXMATK = 3. Assuming we will complete a 500-time-step simulation and change the time-step size 20 times during our simulation, then we have MXNTIK = 500 and MXDTCK = 20.

Assume that we are dealing with 12 transport components, all mobile (i.e., MAXHAK = 12, MAXHSK = 0). Let us further assume that we will deal with 12 chemical components, (i.e., MAXNK = 12). Among these 12 components, there will be 78 chemical reactions that result in a maximum of 78 chemical product species, 10 of which may be involved ion-exchange, 8 of which are potentially precipitated species. In addition, there are two microbial species which degrade some of the chemical species per two biodegradation reactions. Thus, we have MAXPDK = 78, MAXMZK = 10, MAXMPK = 8, and MAXBK = 2. There are a total of 80 reactions (78 chemical and 2 microbiological), with a maximum of four reactants and three product species in a single reaction, so MXRXNK = 80, MXRTSK = 4, MXPDSK = 3. Two of the aqueous complexed product species will be formed by kinetic reactions, but all other product species are defined by equilibrium reactions, so we have MAXKXK = 2, MAXKYK = 0, MAXKZK = 0, MAXKPK = 0. If we have three types of ion-exchange sites and four types of adsorption sites (e.g., four colloids), then we have MXNIXK=3 and MXNSBK=4.

Assume there are a maximum of 11 elements with distributed sources/sinks (i.e., MXSELK = 11) and a maximum of 10 nodes that can be considered well (point) sources/sinks (i.e., MXWNPK = 10). Also assume there are three different distributed source/sink profiles (i.e., MXSPRK = 3) and five point source/sink profiles (i.e., MXWPRK = 5). Let us further assume four data points are needed to describe the distributed source/sink profiles as functions of time, and eight data points are required to described the point source/sink profiles (i.e., MXSDPK = 4 and MXWDPK = 8).

To specify maximum control integers for boundary conditions, let us assume that the total analytical concentrations on the left side of the domain and the left half of the top side are known. The right half of the top side, bottom side, and right side are specified as variable boundaries. On the left side there are 15 nodes, and on the left half of the top side there are 44 nodes. Thus, we have a total of 59 Dirichlet nodes, so MXDNPK = 59. Let us assume that the middle nine nodes on the left side have one specified total analytical concentration, the bottom three nodes on the left side have a different specified concentration, and the other 47 nodes have yet another specified total analytical concentration, so MXDPRK = 3. We further assume that these analytical concentrations can be described as a function of time using eight data points, so MXDDPK = 8. There are 147 nodes and 146 element sides on the right half of the top side, bottom side, and right side: MXVNPK = 147 and MXVESK = 146. We also assume there are three different incoming fluid concentrations (i.e., MXDPRK = 3) going into the region through the top, bottom, and right sides, respectively, and each of these three concentrations is a function of time that can be described by two data points. With these descriptions, we have MXVPRK = 3 and MXVDPK = 2.

Finally, to accurately perform particle tracking, let us assume that for each element we need to divide it into 3 by 3 subelements. Thus, we have MXNPWK=16, MXELWK=9, NXWK=3, NYWK=3.

From the above discussion, the following PARAMETER statements can be used to specify the maximum control integers in the MAIN program for the problem at hand. Most compilers will not accept zero as an array dimension, so any maximum control integers that are zero have been specified as =1 instead:

```
PARAMETER (MAXELK=1232,MAXNPK=1335,MXBESK=204,MXBNPK=204)
PARAMETER (MAXBWK=33,MXJBDK=9,MXKBDK=4,MXNTIK=500,MXDTCK=20)

PARAMETER (MXSELK=11,MXSPRK=3,MXSDPK=4)
```

```
PARAMETER (MXWNPK=10,MXWPRK=5,MXWDPK=8)

PARAMETER (MXDNPK=59,MXDPRK=3,MXDDPK=8)
PARAMETER (MXVESK=146,MXVNPK=147,MXVPRK=3,MXVDPK=2)

PARAMETER (MXMATK=3,MXMPMK=4)

PARAMETER (MAXHAK=12,MAXHSK=1)
PARAMETER (MAXKXK=2, MAXKYK=1, MAXKZK=1, MAXKPK=1, MAXBK=2)
PARAMETER (MAXHK=MAXHAK+MAXHSK)
PARAMETER (MAXTK= MAXHAK+MAXKXK+MAXBK, MAXT2K=MAXTK+2)
PARAMETER (MXHKK=MAXHK+MAXKXK+MAXKYK+MAXKZK+MAXKPK+MAXBK)

PARAMETER (MAXNK=12,MAXMZK=10,MAXMPK=8,MAXPDK=78)
PARAMETER (MXNIXK=3,MXNSBK=4)
PARAMETER (MAXEQK=MAXNK+MAXKXK+MAXKYK+MAXMZK+MAXMPK+MAXBK).
PARAMETER (MXPDBK=MAXPDK+MAXBK, MAXMK=MAXNK+MAXPDK+MAXBK)

PARAMETER (MXRXNK=80, MXRTSK=4, MXPDSK=3)

PARAMETER (MXNPWK=16, MXELWK=9, NXWK=3, NYWK=3)
```

If we use the point iteration method to solve the matrix equation instead of the direct band matrix solver, we should set the maximum bandwidth, MAXBWK, equal to the maximum number of nodes connected to any node, MXJBDK. (The solution method is specified in Data Set 2 by input parameter IPNTS. See Appendix A).

5.3 Input and Output Devices

Five logical units are needed to execute HYDROGEOCHEM. Logical Units 15 and 16 are used for data input and line printer output, respectively. Logical Unit 11 is used to read flow variables produced by HYDROFLOW (a simplified version of FEMWATER) if KVI ≥ 0. Logical Unit 12 must be specified to store the simulation results in binary form, which can be used for plotting purposes, or for initial conditions for a subsequent simulation. Logical Unit 13 is used to read initial conditions if the restart option is used. If the restart option is active, the file associated with Logical Unit 13 for the current job should be the same file associated with Logical Unit 12 of the previous job.

6.0 SAMPLE PROBLEMS

Sample problems are presented in this section to demonstrate the application of HYDROBIOGEOCHEM to a variety of problems. Each example includes a description of the physical and biogeochemical aspects of the problem. The input data sets for each example are presented in tabular form in the text. Comments follow some data lines where format allows, and are not required. The input and output data files for each problem can be obtained on floppy disk by contacting the authors as noted in Appendix B.

Examples 1 through 4 were originally presented in the User's Manual for the model LEHGC, Version 1.1 (Yeh et al., 1995); their problem descriptions are taken directly from that document. Examples 1 and 2 are tests of advection and diffusion, respectively. Example 3 is a test of fracture flow with matrix diffusion. Example 4 tests hydrologic transport coupled with simple adsorption. The input data files are modified to meet the new data requirements for HYDROBIOGEOCHEM. The results of these examples as computed by HYDROBIOGEOCHEM are in agreement with those of LEHGC, and with the analytical solution (for Example 1 and 4), other numerical solution (for Example 2), and experimental data (for Example 2 and 3) presented originally in the LEHGC manual (Yeh et al., 1995).

Examples 5 through 8 are new problems which involve reactive contaminant transport. Example 5 couples biodegradation with 1D transport, and examines the impact of differing conditions for biomass mobility on the level of degradation attained. Example 6 is a benchmark reactive transport problem developed by Valocchi and Tebes (1997). It couples biodegradation, adsorption/desorption, and aqueous speciation reactions with 1D transport. The impact of buffered versus variable pH and of kinetic versus fast adsorption/desorption conditions on transport and transformation are examined. Example 7 is a benchmark reactive transport problem developed by Lichtner (1997) simulating mining of a copper ore using an acidic injection solution to leach the ore from the deposit. This problem involves 2D transport under variable pH and redox conditions and with moving, kinetic precipitation/dissolution fronts. Example 8 involves the injection of a microorganism into a contaminated region of an aquifer to achieve remediation of the area. This problem involves biodegradation by both adsorbed and aqueous microorganisms, equilibrium and kinetic geochemistry including pH dependent adsorption and desorption, coupled with 2D transport.

6.1 Problem 1: Test Problem for Advection

An analytical solution described by Martinez and Bixler (1983) was used to benchmark the use of HYDROBIOGEOCHEM in problems involving advection. The solution to the problem defined by

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} = D\frac{\partial^2 C}{\partial z^2} \tag{6.1.1}$$

subject to the boundary and initial conditions

$$\begin{aligned} C(z,0) &= 0 \\ C(0,t) &= 1, \quad t > 0 \\ C(l,t) &= 0, \quad l \Rightarrow \infty \end{aligned} \tag{6.1.2}$$

is given as

$$C(z,t) = 0.5 * \left[\operatorname{erfc}\left(\frac{z-vt}{2\sqrt{Dt}}\right) + \exp\left(\frac{vz}{D}\right)\operatorname{erfc}\left(\frac{z+vt}{2\sqrt{Dt}}\right)\right] \tag{6.1.3}$$

In the application presented here, $v = V/\theta$ and $D = [a_L V]/\theta$, where V is the Darcy velocity, θ the moisture content, and a_L the longitudinal dispersivity.

In this example, a steady flow field is established by applying a constant flux, V, of 1.0 cm/dy to the top of a one-dimensional column 100 cm in depth. The moisture content, θ, is 0.18; a dispersivity, a_L, of 5 cm is assumed. At time t = 0, a conservative tracer (Nickel) at a concentration of 1×10^{-7} gm/ml is introduced into the flux applied at the top boundary. The problem was run with a Dirichlet boundary condition (i.e., the top boundary nodes are fixed at a concentration of 1×10^{-7} gm/ml), as defined by the analytical solution. The bottom boundary is defined as variable, and because the flow is directed out of the bottom boundary, the concentration at the bottom nodes will be computed as part of the solution. Note that this representation at a finite boundary is not the same as the infinite boundary suggested by the analytical solution. The computational grid is composed of 58 equally spaced elements, except for the bottom element which is 0.24 cm larger. The vertical axis is the z-axis; in this coordinate system, flow from top to bottom has a negative velocity (V = -1.0 cm/day in Data Set 16). The simulation time was carried out to 30 days (121 time steps of 0.25 days).

The input data sets are prepared according to Appendix A and are given in Table 6.1. The LEHGC code simulates total concentrations in units of M/L^3 of liquid (eg. mol/liter). In HYDROBIOGEOCHEM, however, total concentrations have units of M/L^3 total media (i.e. are different from those of LEHGC by a factor of θ, the volumetric moisture content). Moisture content in this problem has a constant and uniform value of 0.18. Accounting for this factor of θ, the results computed by HYDROBIOGEOCHEM are in agreement with those of LEHGC, and with the analytical solution.

Table 6.1 Input Data Sets for Problem 1

```
    1 Advection Benchmark: (Units in cm-gm-day)
 0 0 0 10 1
C ******* DATA SET 2: BASIC INTEGER PARAMETERS
 118 58 1  0 121   1 4 -1 1 0   1 0 10 1 150   0 1 0 1 22   1 0 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.25D0 0.0D0 0.25D0 30.0D0 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
44000000000000000000400000000000000000004000000000000000000000000000000000000000
40000000000000000000400000000000000000004
11000000000000000000100000000000000000001000000000000000000000000000000000000000
10000000000000000000100000000000000000001
1.0D6
C ******* DATA SET 5: CHEMICAL PRINTOUT
 7
 1 19 39 59 79 99 117
C ******* DATA SET 6: MATERIAL PROPERTIES
 5.0D0  0.0D0 0.0D0 1.5D0
C ******* DATA SET 7: NODAL POINT COORDINATES
    1    58    2      0.0D0   0.0D0     0.0D0         DEFINE X FOR ODD NODES
    2    58    2      1.0D0   0.0D0     0.0D0         DEFINE X FOR EVEN NODES
    0     0    0      0.0        0.0    0.0           END OF X-COORD
    1     1    2      0.0D0   1.96D0    0.0D0         DEFINE Z FOR ALL NODES
    2     1    2      0.0D0   1.96D0    0.0D0         OF VARYING ELEMENT SIZES
    5    56    2      3.68D0  1.72D0    0.0D0
    6    56    2      3.68D0  1.72D0    0.0D0
    0     0    0      0.0D0     0.0D0     0.0D0       END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1   58
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 1  0 0 0 0 0 0 0  NOHA HS NOKX KY KZ KP NOMB MA
Nickel
 1 0
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 117 1  1.0D-20 0.0D0 0.0D0           Essentially zero concentration
  0  0 0  0.0      0.0   0.0             END OF I.C. FIRST CHEMICAL
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
  0 0 0  0 0 0  2 1 2  2 1 1 2
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
     0.0D0  0.00D0  1.0D6 0.00D0          BOTTOM BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                   END OF B.C. FIRST CHEMICAL
    1    1    1    1    1
    0    0    0    0    0                           END NVNP
    1    0    1    1    2    0    0    0    0
    0    0    0    0    0    0    0    0    0      END OF NVES
C ******* DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
     0.0D0  1.0D-7  1.0D6 1.0D-7          TOP BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                   END OF B.C. FIRST CHEMICAL
    1    1    1  117    1
    0    0    0    0    0                           END NDNP
```

Table 6.1 Input Data Sets for Problem 1 (continued)

```
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   1 117 1  0.0D0   -1.0D0  0.0D0 0.0D0
   0   0 0  0.0      0.0    0.0   0.0        END OF VELOCITY
   1  57 1  0.18D0   0.0D0
   0  0  0  0.0      0.0                     END OF THETA
   1 117 1  1.0D0    0.0D0 0.0D0
   0  0  0  0.0      0.0   0.0               END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 1 0 0 0 0 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0 0 0 0
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.0 1.0
 -20.0 20.0 0.0 20.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0  50 50 1.0D-6  2.0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Nickel
 1 0
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Nickel
0 0 0
C ******* DATA SET 28: REACTIONS
0
                    End of Job
```

6.2 Problem 2: Test Problem for Diffusion

To validate transport by diffusion, HYDROBIOGEOCHEM was benchmarked against LEHGC Version 1.1 and against a well-established finite element code for nonlinear heat conduction, COYOTE (Gartling, 1982). The problem solved is based on an experiment involving the diffusion of a conservative tracer (tritium) through a 1.43 cm wafer of dolomite (Dyhuizen and Casey, 1989). The wafer was placed between two reservoirs, or cells, each with a volume of 381.1 cm^3. The cell, wafer and background solution were allowed to approach chemical and thermal equilibrium before adding the tritium tracer to the bottom cell. The cells were periodically rotated so that a nearly uniform solution concentration was produced in the cells. Tritium activity in the top cell was then measured as a function of time.

The experiment was modeled as a one-dimensional column. The material properties used were those inferred by the analysis of the experimental results of Dykhuizen and Casey. The thickness and diameter of the wafer were 1.43 and 6.1 cm, respectively. Given the cell volume and wafer diameter, a corresponding cell height was computed (13.1 cm) for each cell. Although the model geometry does not correspond exactly to the experimental design, the wafer surface area in contact with the solution (which is mixed), and the ratio of volumes (wafer to cell) are maintained. The computational mesh is made up of 54 elements (110 nodes) with the largest vertical spacing of 1.0 cm in the cell regions away from the wafer, decreasing to 0.0715 cm adjacent to and within the wafer. The wafer perimeter is impermeable.

Concentrations were normalized to the initial concentration in the bottom cell (C_0). In the original LEHGC problem formulation, the initial normalized concentration (C/C_0) in the bottom cell was 1.0 and in the wafer and top cell, 1.0 x 10^{-11}(essentially zero). The simulation was run allowing the bottom-cell concentration to vary as time progresses and the tracer source is depleted. The cell mixing (by rotation in the experiment) was simulated by assigning a very large diffusion coefficient in the cells. The top and bottom boundaries are defined as variable boundaries which, with no flow in or out of the boundaries, indicates that the concentration at these nodes is to be determined as part of the solution procedure. The wafer moisture content and effective diffusion coefficient are 0.045 and 6.89 x 10^{-7} cm^2/s, respectively.

The LEHGC code requires initial conditions have units of M/L^3 of liquid (i.e. mol/liter). In HYDROBIOGEOCHEM, however, initial conditions must have units of M/L^3 total media. Thus the initial conditions specified in the LEHGC problem formulation have to be adjusted by the volumetric moisture content, θ, to produce consistent results in HYDROBIOGEOCHEM. For the nodes within the bottom cell, the moisture content, θ, equals 1, and the LEHGC concentration is 1.0, so the initial condition for HYDROBIOGEOCHEM is also 1.0. For the cells in the interior of the wafer, the moisture content equals 0.045 and the LEHGC concentration is 1.0 x 10^{-11}, so the initial condition for HYDROBIOGEOCHEM is 0.045 x 10^{-11}. The nodes at the transitions between reservoirs and the wafer have a moisture content in the element on the reservoir side of the node 1.0 and a moisture content in the element on the wafer side of the node of 0.045. The elements adjacent to and within the wafer all have a uniform size. Thus, the moisture content used to compute the initial condition for these transition nodes is (1.0 + 0.045)/2 or 0.5225. The initial concentrations at these nodes are 0.5225 x 10^{-11}. Finally, for the top cell, the moisture content equals 1, the LEHGC concentration is 1.0 x 10^{-11}, so the corresponding HYDROBIOGEOCHEM initial condition is also 1.0 x 10^{-11}.

The simulation was carried out to 1200 hours (100 time steps of 4.32 x 10^4 sec each). The input data sets are prepared according to Appendix A and are given in Table 6.2. Note that the units in this problem are consistently cm-gm-sec. The results computed by HYDROBIOGEOCHEM are in agreement with those of LEHGC, and with those of COYOTE, as presented in the LEHGC Version 1.1 User Manual.

Table 6.2 Input Data Sets for Problem 2

```
    2 Caseys Diffusion Experiment: (Units in cm-gm-sec) **T=ORIG*THETA***
 1 0 0 10 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 110 54 2 20 100   1 4 -1 1 0   1 0 10 1 150   0 1 0 1 22   1 0 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 4.32D4 0.0D0 4.32D4 4.32D6 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
44000000040000000004000000000400000000040000000004000000000400000000040000000004
00000000040000000004
10100010010010001001001000100100100010010010001001001000100100100010010010001001
00100010010010001001
1.0D38
C ******* DATA SET 5: CHEMICAL PRINTOUT
 7
 1 25 35 55 75 85 109
C ******* DATA SET 6: MATERIAL PROPERTIES
 0.0D0  0.0D0 3.00D-3 1.0D0
 0.0D0  0.0D0 6.89D-7 2.7D0
C ******* DATA SET 7: NODAL POINT COORDINATES
    1   54    2      0.0D0   0.0D0     0.0D0          DEFINE X FOR ODD NODES
    2   54    2      6.1D0   0.0D0     0.0D0          DEFINE X FOR EVEN NODES
    0    0    0      0.0       0.0       0.0          END OF X-COORD
    1   12    2      0.0D0   1.0D0     0.0D0          DEFINE Z FOR ALL NODES
    2   12    2      0.0D0   1.0D0     0.0D0          OF VARYING ELEMENT SIZES
   27    1    2     12.5D0   0.3D0     0.0D0
   28    1    2     12.5D0   0.3D0     0.0D0
   31   24    2     12.957D0 0.0715D0  0.0D0
   32   24    2     12.957D0 0.0715D0  0.0D0
   81    1    2     14.83D0  0.3D0     0.0D0
   82    1    2     14.83D0  0.3D0     0.0D0
   85   12    2     15.63D0  1.0D0     0.0D0
   86   12    2     15.63D0  1.0D0     0.0D0
    0    0    0      0.0D0   0.0D0     0.0D0          END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1   54             IE
C ******* DATA SET 9: MATERIAL TYPE CORRECTION
   18 19  1   2  0   MAKE WAFER MATERIAL TYPE 2
    0  0  0   0  0   END OF MATERIAL CORRECTION
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 1 0 0 0 0 0 0 0
Tritium
 1    0
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 33 1  1.0D0       0.0D0 0.0D0          Bottom cell
 35  1 1  0.5225D-11  0.0D0 0.0D0          Transition nodes: Bottom cell/Wafer
 37 37 1  0.045D-11   0.0D0 0.0D0          Wafer
 75  1 1  0.5225D-11  0.0D0 0.0D0          Transition nodes: Wafer/Top cell
 77 33 1  1.0D-11     0.0D0 0.0D0          Top cell
  0  0 0  0.0         0.0   0.0            END OF I.C. FIRST CHEMICAL
```

Table 6.2 Input Data Sets for Problem 2 (continued)

```
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
  0 0 0  0 0 0  0 0 0  4 2 2 2
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
     0.0D0   0.00D00    1.0D38   0.00D00
     0.0D0   0.00D00    1.0D38   0.00D00
    1    1    1    1    1
    0    0    0    0    0                 END OF B.C. FIRST CHEMICAL
    1    1    1    1    1
    3    1    1  109    1
    0    0    0    0    0                         END NVNP
    1    1    1    1    2    1   53    2    2
    0    0    0    0    0    0    0    0    0     END OF NVES
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   1 109 1  0.0   0.0  0.0  0.0
   0  0  0  0.0   0.0  0.0  0.0        END OF VELOCITY
   1 16  1  1.0   0.0  0.0
  18 19  1  0.045 0.0  0.0
  38 16  1  1.0   0.0  0.0
   0  0  0  0.0   0.0  0.0             END OF TH
   1 109 1  1.0   0.0  0.0  0.0
   0   0 0  0.0   0.0  0.0  0.0        END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 1 0 0 0 0 0 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0 0 0 0
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.0 1.0
 -20.0 20.0 0.0 20.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0 50 50 1.0D-6 2.0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Tritium
 1 0
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Tritium                 0
  0 0 0
C ******* DATA SET 28: REACTIONS
0
                         END OF JOB
```

6.3 Problem 3: Test Problem for Fracture Flow and Matrix Diffusion

This problem simulates the effect of matrix diffusion on solute transport through fractured media and is based on a model tested by Grisak and Pickens (1980). The model was based on a longitudinal cross-section of a 0.76 meter high column with a 120 μm wide fracture in the center, running the length of the column. Due to symmetry, one-half of the cross-section can be used; the resulting domain is 7.6 dm high by 0.325 dm wide with a 6×10^{-4} dm wide fracture on the left hand side. The fracture is simulated by assigning specific elements to the fracture. The fracture elements are then assigned a moisture content, θ, of 1.0 and a bulk density, ρ_b, of 1.0×10^{-20} kg/dm^3 (to avoid a "divide-by-zero" error if a bulk density of zero is used). The matrix elements have a moisture content and bulk density of 0.35 and 1.7 kg/dm^3, respectively. The diffusion coefficient D, is 3.6×10^{-4} dm^2/hr in the fracture cells and 3.6×10^{-5} dm^2/hr in the matrix cells. Longitudinal dispersivity, a_L, for all elements is set to 7.6 dm while lateral dispersivity, a_T, is set to 0.0 dm for all elements.

The grid is made up of 21 rows by 17 columns of rectangular elements, with the three left-hand columns of elements representing the fracture and the remaining elements representing the matrix. The fracture element widths (x-direction) are 1.2×10^{-4} dm in the first column and 2.4×10^{-4} dm in the second and third columns. The matrix element widths gradually increased from being equal to the fracture element width, 2.4×10^{-4} dm, at the fracture side to 0.1 dm at the opposite side. The heights (z-direction) of rows of elements gradually increase from 6×10^{-4} dm to 0.2 dm, from the top to the bottom.

The upper boundary of the model has a constant concentration, Dirichlet boundary. The specified concentration along this boundary in the original LEHGC problem formulation was 1.0 mol/liter. For HYDROBIOGEOCHEM, this is adjusted by volumetric moisture content, θ, for units of mol/dm^3 of total media. In the fracture $\theta = 1.0$, in the matrix $\theta = 0.35$, and at the fracture/matrix interface nodes $\theta = 0.675$, since the elements to either side of this interface have equal size and therefore equal contribution to moisture content at these nodes. The specified initial and boundary concentrations along the upper boundary are therefore 1.0, 0.675, and 0.35 mol/dm^3 media for the fracture nodes, interface node, and matrix nodes, respectively.

The other three boundaries are treated as Cauchy boundaries with zero total flux. In the LEHGC problem formulation, this was implemented using the variable boundary condition with a zero total flux specified for the inflow condition. In HYDROBIOGEOCHEM, this boundary specification introduced a problem in the simulation. Diffusion creates a very small component of velocity from outside of the left edge of the domain (i.e. the centerline of the fracture), giving an incoming concentration of 0.0 rather than 1.0 from points on this edge of the domain. This is not consistent with the physical system being simulated. The HYDROBIOGEOCHEM input is revised to simply leave these three boundaries as unspecified, creating the Cauchy condition with zero total flux.

Vertical velocity values at each node in the fracture are calculated assuming a parabolic velocity profile and an average fracture velocity of -0.313 dm/hr (downward). This results in velocities of -0.469 dm/hr, -0.45 dm/hr and -0.3 dm/hr in the first, second and third columns respectively. Since the fourth column of nodes represents the boundary between the matrix and fracture, these nodes have velocities equal to those in the matrix. The vertical Darcy velocity in the matrix is derived by first solving equation (6.3.1), which describes fracture flow velocity, to obtain the hydraulic gradient.

$$V_f = \frac{\rho \; g \; (2b)^2 \; \frac{dh}{dx}}{12 \; \mu} \qquad \textbf{(6.3.1)}$$

where: dh/dx is the hydraulic gradient (L/L), ρ is density of the fluid (M/L^3), g is gravitational acceleration (L/T^2), 2b is the width of the fracture (L), μ is dynamic viscosity of the fluid (M/LT), and V_f is the average velocity of the fluid in the fracture (L/T).

Equation (6.3.2) is then used to solve for the vertical Darcy velocity in the matrix using the calculated value for the hydraulic gradient.

$$V_m = -K \frac{dh}{dx} \qquad \textbf{(6.3.2)}$$

where: K is the hydraulic conductivity (L/T), and V_m is the Darcy velocity of the fluid in the matrix (L/T). The value of the hydraulic conductivity, 2.16×10^{-6} dm/hr (6×10^{-9} cm/s), is obtained from Grisak et al. (1980) whose column study was the basis for Grisak and Pickens' model.

A time step of 0.24 hours was used; a total of six days (144 hours) are simulated using 600 time steps. The input data sets are prepared according to Appendix A and are given in Table 6.3. The results computed by HYDROBIOGEOCHEM are in agreement with those of LEHGC, and with those of Grisak and Pickens, as presented in the LEHGC Version 1.1 User Manual.

Table 6.3 Input Data Sets for Problem 3

```
 3   FRACTURE FLOW & MATRIX DIFFUSION: (Units in dm-kg-hr) *** removed var bc
0  0  0 0  1
C ******* DATA SET 2: BASIC INTEGER PARAMETERS
 396 357 2 63 600   1 4 -1 1 0   1 0 30 1 150   0 1 0 1 22  1 0 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
2.4D-1  0.0D00  2.4D-1  1.0D03  1.0   1.0  1.0  1.0  1.0D-5  1.0D0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
20000000000000000000000000000000000000000000000000200000000000000000000000000000
00000000000000000000200000000000000000000000000000000000000000000000002000000000
00000000000000000000000000000000000000002000000000000000000000000000000000000000
00000000002000000000000000000000000000000000000000000000000020000000000000000000
00000000000000000000000000000020000000000000000000000000000000000000000000000000
20000000000000000000000000000000000000000000000000200000000000000000000000000000
00000000000000000000200000000000000000000000000000000000000000000000002000000000
00000000000000000000000000000000000000002
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001000010000100001000010000100001000010000
10000100001000010000100001000010000100001
1.0D38
C ******* DATA SET 5: CHEMICAL OUTPUT
 4
 23  44  131  141
C ******* DATA SET 6: MATERIAL PROPERTIES
 7.6D00  0.0D00  3.6D-5  1.7D00    Matrix
 7.6D00  0.0D00  3.6D-4  1.0D-20   Fracture
C ******* DATA SET 7: NODAL POINT COORDINATES
   1   21    1    0.0        0.0     0.0
  23   21    1    1.2D-4     0.0     0.0
  45   21    1    3.6D-4     0.0     0.0
  67   21    1    6.0D-4     0.0     0.0
  89   21    1    8.4D-4     0.0     0.0
 111   21    1    1.2D-3     0.0     0.0
 133   21    1    1.8D-3     0.0     0.0
 155   21    1    3.0D-3     0.0     0.0
 177   21    1    5.0D-3     0.0     0.0
 199   21    1    1.0D-2     0.0     0.0
 221   21    1    1.8D-2     0.0     0.0
 243   21    1    3.0D-2     0.0     0.0
 265   21    1    4.5D-2     0.0     0.0
 287   21    1    6.5D-2     0.0     0.0
 309   21    1    1.0D-1     0.0     0.0
 331   21    1    1.5D-1     0.0     0.0
 353   21    1    2.25D-1    0.0     0.0
 375   21    1    3.25D-1    0.0     0.0
   0    0    0    0.0        0.0     0.0    END OF X-COORD
   1   17   22    0          0.0     0.0
   2   17   22    0.8        0.0     0.0
```

Table 6.3 Input Data Sets for Problem 3 (continued)

```
   3   17   22    1.6        0.0     0.0
   4   17   22    2.4        0.0     0.0
   5   17   22    3.2        0.0     0.0
   6   17   22    4          0.0     0.0
   7   17   22    4.8        0.0     0.0
   8   17   22    5.5        0.0     0.0
   9   17   22    6.1        0.0     0.0
  10   17   22    6.6        0.0     0.0
  11   17   22    7          0.0     0.0
  12   17   22    7.3        0.0     0.0
  13   17   22    7.45       0.0     0.0
  14   17   22    7.523      0.0     0.0
  15   17   22    7.5616     0.0     0.0
  16   17   22    7.5808     0.0     0.0
  17   17   22    7.5904     0.0     0.0
  18   17   22    7.5952     0.0     0.0
  19   17   22    7.5976     0.0     0.0
  20   17   22    7.5988     0.0     0.0
  21   17   22    7.5994     0.0     0.0
  22   17   22    7.6        0.0     0.0
   0    0    0    0.0        0.0     0.0    END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1   23   24    2    1   21    17
C ******* DATA SET 9: MATERIAL TYPE CORRECTION
   1  62  1  2  0
   0   0  0  0  0
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 1   0  0 0 0 0  0 0
  TRACER
  1    0
C ******* DATA SET 11: INITIAL CONDITIONS
    1   20    1    1.0D-20    0.0D0    0.0D0   Fracture centerline (left boundary)
   22    2   22    1.0D00     0.0D0    0.0D0   Nodes along top of fracture
   88    0    0    0.675D0    0.0D0    0.0D0   Node at top of interface fract/matr
  110   13   22    0.35D00    0.0D0    0.0D0   Nodes along top of matrix
   23   20    1    1.0D-20    0.0D0    0.0D0   Nodes in fracture
   45   20    1    1.0D-20    0.0D0    0.0D0
   67   20    1    0.675D-20  0.0D0    0.0D0   Nodes along interface
   89   20    1    0.35D-20   0.0D0    0.0D0   Nodes in matrix
  111   20    1    0.35D-20   0.0D0    0.0D0
  133   20    1    0.35D-20   0.0D0    0.0D0
  155   20    1    0.35D-20   0.0D0    0.0D0
  177   20    1    0.35D-20   0.0D0    0.0D0
  199   20    1    0.35D-20   0.0D0    0.0D0
  221   20    1    0.35D-20   0.0D0    0.0D0
  243   20    1    0.35D-20   0.0D0    0.0D0
  265   20    1    0.35D-20   0.0D0    0.0D0
  287   20    1    0.35D-20   0.0D0    0.0D0
  309   20    1    0.35D-20   0.0D0    0.0D0
  331   20    1    0.35D-20   0.0D0    0.0D0
  353   20    1    0.35D-20   0.0D0    0.0D0
  375   20    1    0.35D-20   0.0D0    0.0D0
    0    0    0    0.0D00     0.0D0    0.0D0
```

Table 6.3 Input Data Sets for Problem 3 (concluded)

```
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
  0  0  0    0  0  0   18 3  2      0  0  1   2
C ******* DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
  0.0D0  1.0D0    1.0D38  1.0D0    BC for top of fracture
  0.0D0  0.675D0  1.0D38  0.675D0  BC for top of fracture/matrix interface
  0.0D0  0.35D0   1.0D38  0.35D0   BC for top of matrix
    1    2    1    1    0          DIR nodes along top of fracture
    4    0    0    2    0          DIR nodes at top of fracture/matrix interface
    5   13    1    3    0          DIR nodes along top of matrix
    0    0    0    0    0                      END OF B.C. SOLUTE
    1   17    1   22   22
    0    0    0    0    0                      END OF NDNP
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
    1   21    1    0.0  -0.469      0.0  0.0
   23   21    1    0.0  -0.450      0.0  0.0
   45   21    1    0.0  -0.300      0.0  0.0
   67  329    1    0.0   0.0D00     0.0  0.0
    0    0    0    0.0   0.0        0.0  0.0      END OF VELOCITY
    1   62    1    1.0   0.0
   64  293    1    0.35  0.0
    0    0    0    0.0   0.0                      END OF TH
    1  395    1    1.0   0.0  0.0  0.0
    0    0    0    0.0   0.0  0.0  0.0            END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
  1  0       0  0  0  0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
    0.0   0    0  0  0
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
  298.0   1.0
  -20.0  20.0  0.0  20.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
  1  1 50 1.0d-6  2.0D0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
  TRACER
  1  0
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
  FREE TRACER
    0    0.0     0
C ******* DATA SET 28: REACTIONS
0
          END OF JOB
```

6.4 Problem 4: Test Hydrologic Transport and Simple Adsorption

This problem involves transport in a 1 dm long, one-dimensional column. The flow velocity is -1.0 x 10^{-2} dm/hr (flow is from top to bottom). The effective porosity is 0.3, the bulk density is 1.2 kg/dm^3, and the dispersivity is 2 x 10^{-3} dm. The transport involves four chemical components. The initial condition is a total analytical concentration of 10^{-4} M, or 0.3 x 10^{-4} mol/dm^3 media, for all four chemical components. The boundary conditions are as follows: at the top of the column (z = 1.0 dm), the total analytical concentrations are 10^{-3} M, or 0.3 x 10^{-3} mol/dm^3 media; at z = 0.0 dm, variable boundary conditions with zero concentration gradients specified for all four components.

To mimic the hydrologic transport without interaction among four chemical components, we assume that each chemical component has two species: a free species and an adsorbed species. The ratios of the adsorbed species to the free species are assumed to be 0, 1/9, 1, and 9, respectively, for chemical components 1, 2, 3, and 4 (i.e., 0%, 10%, 50%, and 90% adsorption, respectively). To apply the no-interaction scenario among four components, the adsorbing site is not a constraint for the equilibrium between free species and adsorbed species for each component. In the original LEHGC problem formulation, which treats all concentrations as mol/L, the geochemical equilibrium constants for the formation of the four adsorbed species were 0 (log K = -38), 1/9, 1, and 9, respectively. These reactions are of the form:

$$C \leftrightarrow S \; , \qquad \text{with } K = \frac{[\text{S mol/L}]}{[\text{C mol/L}]} \tag{6.4.1}$$

For HYDROBIOGEOCHEM, all individual species concentrations are in units of mol/mass of phase. The adsorption/desorption reactions are of the form:

$$C \leftrightarrow S \; , \qquad \text{with } K' = \frac{[\text{S mol/mass of solid}]}{[\text{C mol/mass of liquid}]}$$

$$\text{where} \quad K' = K * \frac{1}{\rho_b} * \rho_\ell \theta \tag{6.4.2}$$

As noted above, $\theta = 0.3$, $\rho_b = 1.2$ kg/dm^3, and ρ_ℓ is assumed equal to 1.0 kg/dm^3. For the HYDROBIOGEOCHEM input, the equilibrium constants for the formation of the four adsorbed species were therefore 0, 0.027778, 0.25, and 2.25, respectively.

For numerical simulation, the column is discretized into 1 x 40 elements of size 0.025 dm by 0.025 dm, resulting in 82 nodes; the horizontal axis is the z-axis. The simulation is conducted for three time steps only because the purpose of this simulation is to verify the hydrologic module against LEHGC. The time-step size is 0.5 hr. The input data sets are prepared according to Appendix A and are given in Table 6.4. With the adjustments noted above, the results computed by HYDROBIOGEOCHEM are in agreement with those of LEHGC.

Table 6.4   Input Data Sets for Problem 4

```
    1 TEST OF LEHGC: TRANSPORT MODULE - FOUR COMPONENTS units in (dm-kg-hr) **logK's
  0 0 0 1 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 82 40 1 0 3   1 4 -1 1 0   1 0 30 1 150   0 1 0 1 12   1 0 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.50D0 0.0D0 0.50D00 15.0D0 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ******* DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
4444
0001
1.0D38
C ******* DATA SET 5: CHEMICAL PRINTOUT AND CHEMICAL PROPERTY TYPE INDICATOR
 3
 1 41 82        NODEP
C ******* DATA SET 6: MATERIAL PROPERTIES
 2.0D-3 0.0D0 0.0D0 1.2D0 AL AT AM RHOB
C ******* DATA SET 7: NODE COORDINATES
    1   40    2      0.0          0.0      0.0
    2   40    2      0.025D0    0.0D0      0.0D0
    0    0    0      0.0          0.0      0.0             END OF X-COORD
    1   40    2      0.0D0    0.025D0      0.0D0
    2   40    2      0.0D0    0.025D0      0.0
    0    0    0      0.0D0      0.0D0      0.0D0         END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1   40                 IE
C ******* DATA SET 10: CHEMICAL COMPONENT INFORMATION
 4 0  0 0 0 0  0 0
  CHEM 1
  1    0
  CHEM 2
  2    1
  CHEM 3
  3    1
  CHEM 4
  4    1
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 81 1  0.3D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0               END OF I.C. FIRST CHEMICAL
  1 81 1  0.3D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0               END OF I.C. SECOND CHEMICAL
  1 81 1  0.3D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0               END OF I.C. THIRD CHEMICAL
  1 81 1  0.3D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0               END OF I.C. FOURTH CHEMICAL
C ******* DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
  0 0 0  0 0 0  2 1 2  2 1 1 2  NSEL NSPR NSDP  NWNP NWPR NWDP  NDNP NDPR NDDP
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
     0.0D0   0.00D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. FIRST CHEMICAL
     0.0D0  0.000D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. SECOND CHEMICAL
```

Table 6.4 Input Data Sets for Problem 4 (continued)

```
     0.0D0    0.0D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. THIRD CHEMICAL
     0.0D0     0.0D0    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C.  FOURTH CHEMICAL
    1    1    1    1    1
    0    0    0    0    0                          END NPVB
    1    0    1    1    2    0    0    0    0
    0    0    0    0    0    0    0    0    0     END OF ISV
C ******* DATA SET 15:  DIRICHLET BOUNDARY CONDITIONS
   0.0D0 0.3D-3  1.0D38 0.3D-3
    1    1    1    1    0
    0    0    0    0    0                  END OF B.C.  FIRST CHEMICAL
   0.0D0 0.3D-3  1.0D38 0.3D-3
    1    1    1    1    0
    0    0    0    0    0                  END OF B. C. SECOND CHEMICAL
   0.0D0 0.3D-3  1.0D38 0.3D-3
    1    1    1    1    0
    0    0    0    0    0                  END OF B.C. THIRD CHEMICAL
   0.0D0 0.3D-3  1.0D38 0.3D-3
    1    1    1    1    0
    0    0    0    0    0                  END OF B.C.  FOURTH CHEMICAL
   1 1 1  81 1
   0 0 0 0 0                              END OF NPDB
C ******* DATA SET 16: HYDROLOGICAL VARIABLES
   1 81 1  0.0  -1.000D-2  0.0    0.0
   0  0 0  0.0   0.0       0.0    0.0   END OF VELOCITY
   1 39 1  0.3   0.0
   0  0 0  0.0   0.0                    END OF TH
   1 81 1  1.0   0.0       0.0
   0  0 0  0.0   0.0       0.0          END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 4 0 0 4 0 0
C ******* DATA SET 18: H+, E-, IONIC STRENGTH correction INFORMATION
 0.0 0 0 0 0 0
c ******* Data Set 19:  Temperature, pressure, and expected pe and ph
 298.0 1.0
 -20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
c ******* Data Set 22:  Basic real and integer information
 1.0  1  50  1.0d-6  2.0d0  1.0d38
c ******* Date Set 23:  Name of chemical components and type of component species
  CHEM 1
  1  0
  CHEM 2
  1  0
  CHEM 3
  1  0
  CHEM 4
  1  0
```

Table 6.4 Input Data Sets for Problem 4 (concluded)

```
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FREE CHEMICAL 1
  0 0 0  ISCN VJ IONEX
FREE CHEMICAL 2
  0 0 0  ISCN VJ IONEX
FREE CHEMICAL 3
  0 0 0  ISCN VJ IONEX
FREE CHEMICAL 4
  0 0 0  ISCN VJ IONEX
C ******** DATA SET 25:  ADSORBED SPECIES
SORBED CHEMICAL 1
 0       1 0 0 0   1 0 0 0
SORBED CHEMICAL 2
 0       0 1 0 0   0 1 0 0
SORBED CHEMICAL 3
 0       0 0 1 0   0 0 1 0
SORBED CHEMICAL 4
 0       0 0 0 1   0 0 0 1
C ******** DATA SET 28:  REACTIONS
4
 1 1  0         NRTS   NPDS   KRTYP  - RXN1
 -38.0          LOGKEQ
 1 1            CXYZP  DXYZP
 1 5            IGSNRT IGSNPD
 1 1  0         NRTS   NPDS   KRTYP - RXN2 (log k for conc in mol/mass phase)
 -1.5563025     LOGKEQ
 1 1            CXYZP  DXYZP
 2 6            IGSNRT IGSNPD
 1 1  0         NRTS   NPDS   KRTYP  - RXN3
 -0.60206       LOGKEQ
 1 1            CXYZP  DXYZP
 3 7            IGSNRT IGSNPD
 1 1  0         NRTS   NPDS   KRTYP  - RXN4
 0.352182518    LOGKEQ
 1 1            CXYZP  DXYZP
 4 8            IGSNRT IGSNPD
                                 END OF JOB
```

6.5 Problem 5: Biodegradation Coupled with Transport

This example addresses bioremediation in a hypothetical aquifer system. The physical system is represented using one dimensional transport through a region 100 dm long. Initially, a zone located at 20 dm $\leq x \leq$ 30 dm contains a biodegradable substrate and the microorganism capable of doing so. The initial concentration of substrate and biomass are S_0 = 200 mg/L and b_0 = 0.001 U.O.D., respectively. The biodegradation reaction parameters are K_S = 7.5 mg/L, Y_S = 0.130E-3, and μ_{max} = 0.0387 hr^{-1}. The substrate is present in the aqueous phase and its mobility is assumed not to be retarded by interactions with the porous media. The physical parameters selected to describe the system are porosity = 0.2, bulk density = 1.5 kg/dm^3, pore water velocity = 0.1 dm/hr, and longitudinal dispersivity = 0.5 dm. Eighty-one nodes and fifty-two elements (two rows of twenty-six elements) were used to discretize the region of interest. A uniform time step of 0.1 hours is used.

Three cases are considered in which different assumptions are made about the mobility of the biomass. Case A is transport of a non reactive tracer through the media; this represents the migration of the contaminant either when microorganisms are not present or are present but not acclimated to the substrate. Case B reflects the condition that biomass colonies have become established only in the zone in which the substrate is initially present and are adsorbed to the porous media (i.e. the biomass is immobile). Case C is when the biomass is present initially only in the zone in which the substrate is initially present and the biomass exists in the aqueous phase (i.e. the biomass is subject to transport). The input data sets for Case C are given in Table 6.5; the input files for all cases can be obtained on floppy disk.

Figure 6.1 compares the transported substrate concentration when the different assumptions are made about the mobility of the biomass. The progress of a non reactive tracer through the column is shown in Figure 6.1a for comparison. If biomass colonies have become established only in the zone in which the substrate was initially present and are assumed to be adsorbed to the porous media, there is significant reduction in contaminant levels throughout the column due to the degradation which is able to occur within the bioactive zone (Figure 6.1b). If the biomass is assumed to exist in the aqueous phase, additional removal of the pollutant is achieved as biodegradation of the substrate continues to occur as both it and the microorganisms are transported through the entire region of interest (Figure 6.1c). Figure 6.2 contrasts the substrate levels encountered at a location 20 dm down gradient from the initial edge of the plume (x = 50 dm). Over 40% removal is predicted when the biomass is present only in the original zone of contamination, over 90% removal is predicted if the biomass is mobile.

It is interesting to note that Case C is equivalent to the bioremoval of the contaminant that would be achieved in a batch system, regardless of whether the biomass exists in the aqueous or adsorbed phase in such a system (assuming the rate at which the microorganisms can degrade the substrate is the same when the microorganism is associated with either phase). This is equivalent to saying that achieving 90% removal in a batch experiment does not necessarily imply the same percentage of removal at a field site under transport conditions.

Table 6.5 Input Data Sets for Problem 5, Case C

```
    5  N. winogradski on N-NO2 + Transport (Units: m,kg,hr) *** S(aq),B(aq) ***
 1 0 0 10 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 81 52 1 0 8000   1 4 -1 1 0   1 0 30 1 150   0 1 0 1 22   1 0 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.10 0.0D0 0.10 800D0 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
44000000004000000000400000000040000000004000000000400000000040000000004000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
```

Table 6.5 Input Data Sets for Problem 5, Case C (continued)

```
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
```

Table 6.5 Input Data Sets for Problem 5, Case C (continued)

```
00000000000000000000000000000000000000000000000000000000000000000000000000000000
4
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
```

Table 6.5 Input Data Sets for Problem 5, Case C (continued)

```
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
1
1.0D38
```

Table 6.5 Input Data Sets for Problem 5, Case C (continued)

```
C ******* DATA SET 5: CHEMICAL PRINTOUT
 4
 20  26  32  38
C ******* DATA SET 6: MATERIAL PROPERTIES
 5.0D-3 0.0D0 0.00D0  1.5D0
C ******* DATA SET 7: NODAL POINT COORDINATES
    1    2    1       0.0D0      0.0D0      0.0D0          DEFINE X
    4    2    1       0.5D0      0.0D0      0.0D0          DEFINE X
    7    2    1       1.0D0      0.0D0      0.0D0          DEFINE X
   10    2    1       1.5D0      0.0D0      0.0D0          DEFINE X
   13    2    1       1.75D0     0.0D0      0.0D0          DEFINE X
   16    2    1       1.875D0    0.0D0      0.0D0          DEFINE X
   19    2    1       2.0D0      0.0D0      0.0D0          DEFINE X
   22    2    1       2.25D0     0.0D0      0.0D0          DEFINE X
   25    2    1       2.5D0      0.0D0      0.0D0          DEFINE X
   28    2    1       2.75D0     0.0D0      0.0D0          DEFINE X
   31    2    1       3.0D0      0.0D0      0.0D0          DEFINE X
   34    2    1       3.125D0    0.0D0      0.0D0          DEFINE X
   37    2    1       3.25D0     0.0D0      0.0D0          DEFINE X
   40   13    3       3.5D0      0.5D0      0.0D0          DEFINE X
   41   13    3       3.5D0      0.5D0      0.0D0          DEFINE X
   42   13    3       3.5D0      0.5D0      0.0D0          DEFINE X
    0    0    0       0.0        0.0        0.0            END OF X-COORD
    1   26    3       0.0D0      0.0D0      0.0D0          DEFINE Z FOR ALL NODES
    2   26    3       0.25D0     0.0D0      0.0D0          DEFINE Z FOR ALL NODES
    3   26    3       0.5D0      0.0D0      0.0D0          DEFINE Z FOR ALL NODES
    0    0    0       0.0D0      0.0D0      0.0D0          END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    4    5    2    1    2   26                 IE
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 1 0 0 0 0 0 1 0
Na-NO2
 1    0
C ******* DATA SET 11:  INITIAL CONDITIONS
  1   18   1  0.0D0   0.0D0 0.0D0
  19  14   1  40.0D0 0.0D0 0.0D0
  34  46   1  0.0D0   0.0D0 0.0D0
  0   0    0  0.0      0.0   0.0             END OF I.C. SUBSTRATE
  1   18   1  0.0D0   0.0D0 0.0D0
  19  14   1  2.0D-4 0.0D0 0.0D0
  34  46   1  0.0D0   0.0D0 0.0D0
  0   0    0  0.0      0.0   0.0             END OF I.C. MICROBE
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
  0 0 0  0 0 0  0 0 0  6 4 1 2
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
    0.0D0    0.00D00    1.0D38   0.00D00
    1    3    1    1    0
    0    0    0    0    0                 END OF B.C. SUBSTRATE
    0.0D0    0.00D00    1.0D38   0.00D00
    1    3    1    1    0
    0    0    0    0    0                 END OF B.C. MICROBE
    1    2    1    1    1
    4    2    1   79    1
```

Table 6.5   Input Data Sets for Problem 5, Case C (concluded)

```
    0    0    0    0    0                          END NVNP
    1    1    1    1    2    1    1    1    1
    3    1   51    4    5    1    1    1    1
    0    0    0    0    0    0    0    0    0     END OF NVES
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   1  80 1  0.002  0.0  0.0  0.0
   0   0 0  0.0    0.0  0.0  0.0        END OF VELOCITY
   1  51 1  0.20   0.0  0.0
   0  0  0  0.0    0.0  0.0             END OF TH
   1  80 1  1.0    0.0  0.0  0.0
   0   0 0  0.0    0.0  0.0  0.0        END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 1 0 0 0 0 0 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0    0 0 0
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 310.15 1.0
 -20.0 20.0 0.0 20.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0 1 100 1.0D-6 2.0  2.0
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Na-NO2
 1 0
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Na-NO2
0 0 0
C ******* DATA SET 28:  Microbial Species
NITROBACTER
0 -38.00 0
C ******* DATA SET 28: REACTIONS
1
1 1 2
0.0387 7.5 0.0 0.0   1 0 0  0 0
1  0.130D-3
1  2
0 0.0 0.0 0.0 0.0
                              END OF JOB
```

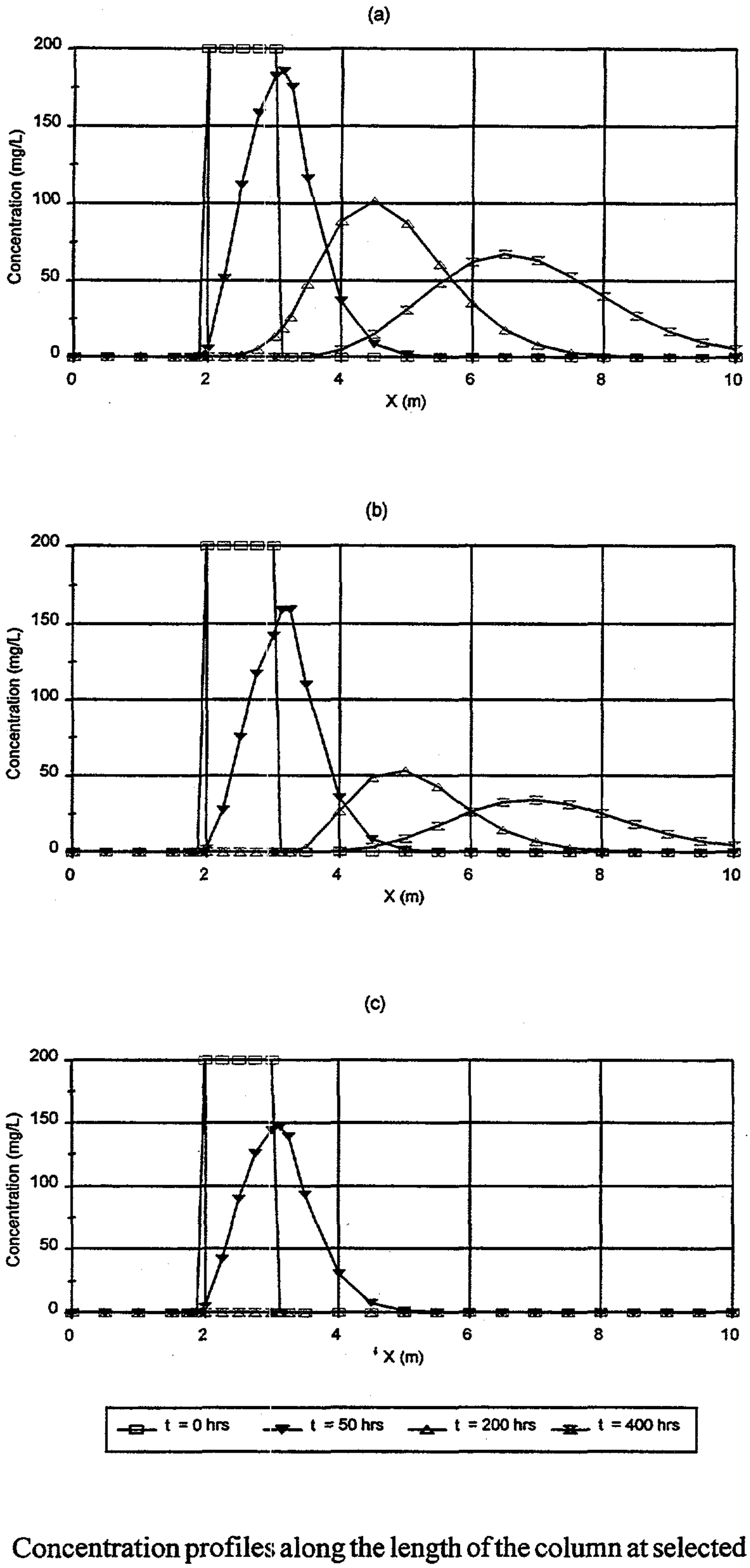


Figure 6.1. Concentration profiles along the length of the column at selected times for example problem 6.5. (a) Non reactive tracer, (b) Substrate, when the biomass is adsorbed within the original zone of contamination, (c) Substrate, when the biomass exists in the aqueous phase.

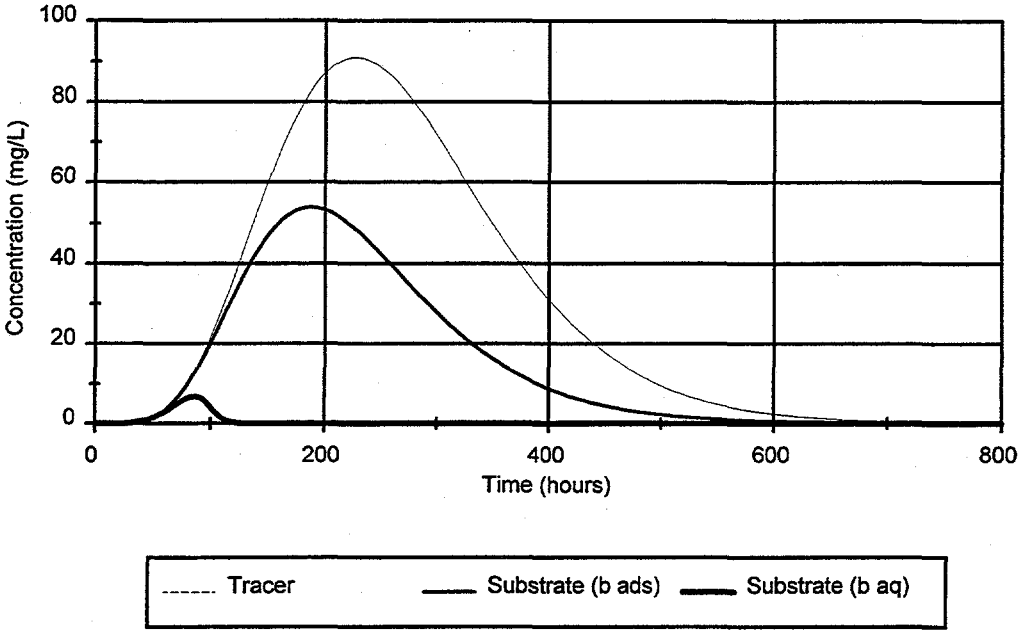


Figure 6.2 Concentration profiles versus time at location x = 5 m for example problem 6.5.

6.6 Problem 6: Microbiological and Chemical Reactions Coupled with Transport

This example is a benchmark problem for the simulation of reactive transport developed by Valocchi and Tebes (1997). It includes kinetic adsorption/desorption, equilibrium aqueous complexation and biodegradation as well as advective-dispersive transport. The problem description is directly from the formulation of Valocchi and Tebes, except as noted.

This problem involves one dimensional transport of multiple reacting species through a 100 dm long column over a seventy-five hour period. The physical parameters describing the system are porosity = 0.4, bulk density = 1.5 kg/dm^3, pore water velocity = 10 dm/hr, and longitudinal dispersivity = 0.5 dm. The domain was discretized using 100 elements and 202 nodes and a uniform time step size of 0.10 hours was used for all simulations. Activity corrections were not used.

Aqueous speciation is simulated using fourteen equilibrium chemical reactions (Table 6.6). Two of the aqueous species, Co^{2+} and $CoNTA^-$, may be removed from solution by adsorption to the media in the column. In addition, there is one kinetic biodegradation reaction affecting the chemical distribution within the column. Initially, the column is free from the biodegradation substrate, $HNTA^{2-}$, and the adsorbing species, then for a period of twenty hours a pulse containing Co^{2+} and

NTA^- is injected into the column. For the remaining fifty-five hours, the injection fluid has the same chemical composition as the fluid initially present in the column. Table 6.7 summarizes the concentrations initially present in the column and in the injected pulse. Three variations are simulated: (1) the adsorption reactions are kinetic and the pulse and the background solutions are buffered to keep pH =6, (2) the adsorption reactions are kinetic and the pH levels in both the pulse and the background solutions are allowed to vary, and (3) the adsorption reactions are fast, approximating an equilibrium rather than a kinetic process, and the pH levels in both the pulse and the background solutions are allowed to vary.

Table 6.6. Tableau for equilibrium reactions included in example problem 6.6.

	H^+	NTA^{3-}	Co^{2+}	$H_2CO_3^*$	NH_4^+	O_2	Buffer	log K_{eq}
H_3NTA	3	1	0	0	0	0	0	14.9
H_2NTA^-	2	1	0	0	0	0	0	13.3
$HNTA^{2-}$	1	1	0	0	0	0	0	10.3
$CoNTA^-$	0	1	1	0	0	0	0	11.7
$Co(NTA)_2^{4-}$	0	2	1	0	0	0	0	14.5
$CoOHNTA^{2-}$	-1	1	1	0	0	0	0	0.5
$CoOH^+$	-1	0	1	0	0	0	0	-9.7
$Co(OH)_2$	-2	0	1	0	0	0	0	-22.9
$Co(OH)_3^-$	-3	0	1	0	0	0	0	-31.5
HCO_3^-	-1	0	0	1	0	0	0	-6.35
CO_3^{2-}	-2	0	0	1	0	0	0	-16.68
OH^-	-1	0	0	0	0	0	0	-14.0
NH_3	-1	0	0	0	1	0	0	-9.3
HBuffer	1	0	0	0	0	0	1	6.0

Table 6.7. Concentration of component species in the column and in the incoming pulse for example problem 6.6.

Component	Type	Background Concentration	Pulse Concentration
H^+	Aqueous	pH = 6	pH = 6
NTA^{3-}	Aqueous	0.0	5.23E-6 mol/L
Co^{2+}	Aqueous	0.0	5.23E-6 mol/L
$H_2CO_3^*$	Aqueous	4.9E-7 mol/L	4.9E-7 mol/L
NH_4^+	Aqueous	0.0	0.0
O_2	Aqueous	3.125E-5 mol/L	3.125E-5 mol/L
Buffer	Aqueous	1.0E-3 mol/L or 0.0	1.0E-3 mol/L or 0.0
Biomass	Adsorbed	5.44E-5 g/dm^3 media	N/A
$CoNTA_{(ads)}$	Adsorbed	0.0	N/A

$Co_{(ads)}$	Adsorbed	0.0	N/A

Transport of the free cobalt species, Co^{2+}, and $CoNTA^-$ through the column is retarded due to adsorption. The availability of adsorbent sites is considered nonlimiting and the adsorption process is assumed to be kinetic. Valocchi and Tebes use a linear kinetic model to represent the adsorption process; the reactions and reaction rates have been reformulated to express adsorption in terms of forward and backward rate constants for use in HYDROBIOGEOCHEM. The parameters describing adsorption were selected by Valocchi and Tebes to make adsorption a significant kinetic process in the system; they do not necessarily represent realistic adsorption behavior for Co^{2+} or $CoNTA^-$. The two adsorption reactions simulated are:

$$\mathrm{CoNTA}^{-}_{(aq)} \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} \mathrm{CoNTA}_{(ads)} \tag{6.6.1}$$

$$\mathrm{Co}^{2+}_{(aq)} \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} \mathrm{Co}_{(ads)} \tag{6.6.2}$$

where $k_{f1} = 0.26667\ hr^{-1}$, $k_{b1} = 0.5003127\ hr^{-1}$, and $k_{f2} = 0.26667\ hr^{-1}$, $k_{b2} = 0.05259697\ hr^{-1}$ for simulations (1) and (2), and where the forward and backward rate constants are all increased by a factor of 10^3 for simulation (3) to approximate adsorption as an equilibrium process.

Biodegradation of $HNTA^-$ removes NTA from the system through the following reaction:

$$\begin{aligned} &\mathrm{HNTA}^{2-} + 1.620\ \mathrm{O_2} + 1.272\ \mathrm{H_2O} + 2.424\ \mathrm{H^+} \rightarrow \\ &17.3707\ \mathrm{C_5H_7O_2N} + 3.120\ \mathrm{H_2CO_3^*} + 0.424\ \mathrm{NH_4^+} \end{aligned} \tag{6.6.3}$$

where $K_S = 7.64E\text{-}7$ mol/L, $K_O = 6.25E\text{-}6$ mol/L, $\mu_{max} = 0.0916519\ hr^{-1}$, $b_0 = 5.44E\text{-}5$ gram/dm^3 of media, and $K_d = 0.00208\ hr^{-1}$.

The HYDROBIOGEOCHEM results compare well with those supplied by Valocchi and Tebes (Figure 6.3). In Figure 6.3, the solid lines denote the results supplied by Valocchi and Tebes, the symbols denote the HYDROBIOGEOCHEM results. The input data sets for Case A are provided in Table 6.8; the input data files for all three cases can be obtained on floppy disk.

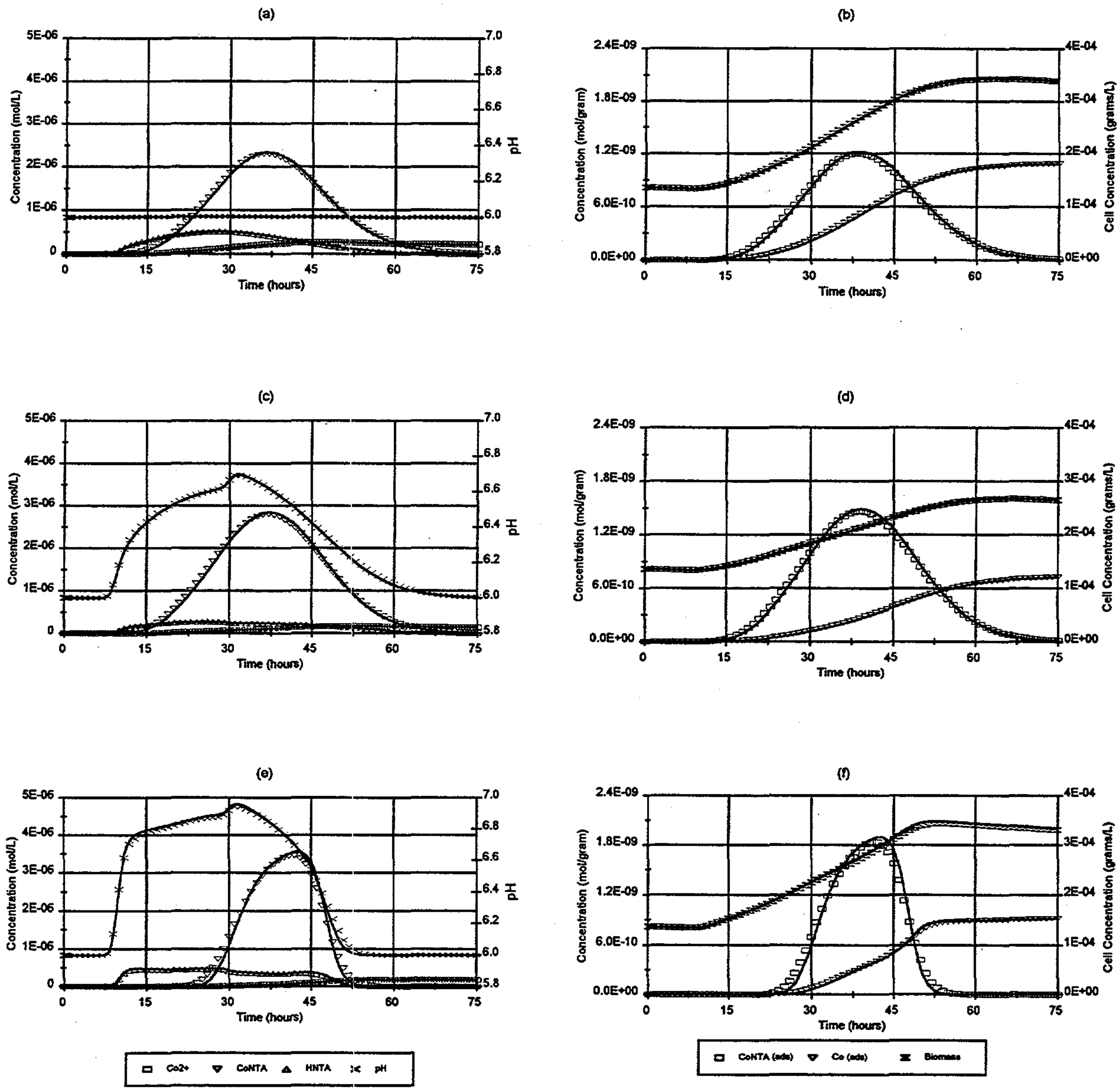


Figure 6.3. Concentration profiles at the end of the column (100 dm) versus time for example problem 6.6. (a) Major aqueous species and pH under conditions of kinetic adsorption and buffered pH, (b) Adsorbed species under conditions of kinetic adsorption and buffered pH, (c) Major aqueous species and pH under conditions of kinetic adsorption and variable pH, (d) Adsorbed species under conditions of kinetic adsorption and variable pH, (e) Major aqueous species and pH under conditions of equilibrium adsorption and variable pH, (f) Adsorbed species under conditions of equilibrium adsorption and variable pH.

Table 6.8 Input Data Sets for Problem 6, Case A, buffered pH

```
   1  BENCHMARK PROBLEM - CASE A - BUFFERED PH (IOPTRS=1)
 1 0 0 0 1
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 202 100 1 0 750   1 4 -1 1 0   0 0 40 1 50   0 1 0 1 11   2 1 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.1 0.0D0 0.1 75 0.0D0   1.0D0 1.0D0 1.0D00 1.0D-6 1.0D0
C ******* DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
40000000000000000000000000000000000000000000000000000000000000000000000000000000
4000000000000000000000000000004
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001000000000100000000010000000001000000000
1000000000100000000010000000001
1.0D38
C ******* DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR
 2
 1  201 NODEP

C ******* DATA SET 6: MATERIAL PROPERTIES
 0.5D-0 0.0D0 0.0D0 1.5D0 AL AT AM RHOB
C ******* DATA SET 7: NODE COORDINATES
    1   100    2      0.0D0   1.0D0  0.0
    2   100    2      0.0D0   1.0D0  0.0D0
    0     0    0      0.0     0.0    0.0           END OF X-COORD
    1   100    2      0.0D0   0.0D0  0.0D0
    2   100    2      1.0D0   0.0D0  0.0
    0     0    0      0.0D0   0.0D0  0.0D0         END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    3    4    2    1    1   100          IE
C ******* DATA SET 10: CHEMICAL COMPONENT INFORMATION
 7 0 0 2 0 0 0 1   NOhA NOhS NOKX KY KZ KP mb ma
    H+
  1   1
 H2CO3*
  2   1
 NH4+
  3   1
 O2
  4   1
```

Table 6.8   Input Data Sets for Problem 6, Case A, (continued)

```
 NTA3-
  5   1
 Co 2+
  6   1
 Buffer
  7   1
C ******* DATA SET 11:  INITIAL CONDITIONS (MASS/MEDIA VOLUME)
    1   201    1     2.0034d-4 0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. H+ - variable PH
    1   201    1     1.96d-7    0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. H2CO3(g)
    1   201    1     0.00d-14   0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. NH4+
    1   201    1     1.25d-5    0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. O2
    1   201    1     0.00d-14   0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. NTA3-
    1   201    1     0.00d-14   0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. Co2+
    1   201    1     4.00d-4    0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. Buffer
    1   201    1     0.00d-20   0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. CoNTA(ads) = Ky1
    1   201    1     0.00d-20   0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. Co(ads) = Ky2
    1   201    1     5.44d-5    0.0D0      0.0D0

    0    0     0     0.0         0.0        0.0          END OF I.C. Cells
C ******* DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
    0  0   0     0  0  0    0  0  0    4    2    2    4
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS (MASS/LIQUID VOLUME)
  0.0D0    5.01275D-4  20.0D0    5.01275D-4  20.01D0  5.0085D-4  75.0D0  5.0085D-4
  0.0D0    0.00D0      20.0D0    0.00D0      20.01D0  0.00D0     75.0D0  0.00D0
    1    1    1    1    1
    0    0    0    0    0                             END OF B.C. H+
  0.0D0    4.90D-7   20.0D0   4.90D-7   20.01D0  4.90D-7   75.0D0  4.90D-7
  0.0D0    0.00D0    20.0D0   0.00D0    20.01D0  0.00D0    75.0D0  0.00D0
    1    1    1    1    1
    0    0    0    0    0                             END OF B.C. H2CO3(g)
  0.0D0    0.00D0     20.0D0    0.00D0     20.01D0  0.00D0     75.0D0  0.00D0
  0.0D0    0.00D0     20.0D0    0.00D0     20.01D0  0.00D0     75.0D0  0.00D0
    1    1    1    1    1
    0    0    0    0    0                             END OF B.C. NH4+
```

Table 6.8 Input Data Sets for Problem 6, Case A, (continued)

```
  0.0D0   3.125D-5  20.0D0  3.125D-5  20.01D0  3.125D-5 75.0D0  3.125D-5
  0.0D0   0.00D0    20.0D0   0.00D0   20.01D0  0.00D0   75.0D0  0.00D0
    1     1    1    1    1
    0     0    0    0    0                          END OF B.C. O2
  0.0D0   5.23D-6  20.0D0   5.23D-6  20.01D0  0.00D0   75.0D0  0.00D0
  0.0D0   0.00D0   20.0D0   0.00D0   20.01D0  0.00D0   75.0D0  0.00D0
    1     1    1    1    1
    0     0    0    0    0                          END OF B.C. NTA3-
  0.0D0   5.23D-6  20.0D0   5.23D-6  20.01D0  0.00D0   75.0D0  0.00D0
  0.0D0   0.00D0   20.0D0   0.00D0   20.01D0  0.00D0   75.0D0  0.00D0
    1     1    1    1    1
    0     0    0    0    0                          END OF B.C. Co2+
  0.0D0   1.00D-3  20.0D0   1.00D-3  20.01D0  1.00D-3  75.0D0  1.00D-3
  0.0D0   0.00D0   20.0D0   0.00D0   20.01D0  0.00D0   75.0D0  0.00D0
    1     1    1    1    1
    0     0    0    0    0                          END OF B.C. Buffer
    1     1    1    1    1
    3     1    1    201  1
    0     0    0    0    0                          END NPVB
    1     1    1    1    2    1    99   2    2
    0     0    0    0    0    0    0    0    0      END OF ISV
C ******* DATA SET 16: HYDROLOGICAL VARIABLES
    1   201   1     4.0    0.0    0.0    0.0
    0     0   0     0.0    0.0    0.0    0.0      END OF VELOCITY
    1    99   1     0.4    0.0
    0     0   0     0.0    0.0    0.0             END OF TH
    1   201   1     1.0    0.0    0.0
    0     0   0     0.0    0.0    0.0             END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
7 0 14 2 0 0                            NONA NONS NOMX NOMY NOMZ NOMP
C ******* DATA SET 18: H+, E-, IONIC STRENGTH correction INFORMATION
 0.0 0 1 0 0   SICOR ICOR LNH LNG LNE

c ******* DATA SET 19:  temperature, pressure and expected pe and pH
 298.3 1.0   TEMP PRESSU
 -20.0 20.0 -20.0 20.0   PEMN PEMX PHMN PHMX

c ******* DATA SET 22: Basic real and integer parameters
  1.0 1 1000 1.0d-6 1.0d00 1.0d00 omegac npcyl niterc epsc cnstrx cnstry

c ******* DATA SET 23: Component name and component species types
 H+
  1 0
 H2CO3*
  1 0
 NH4+
  1 0
 O2
  1 0
 NTA-
  1 0
 Co 2+
  1 0
 Buffer
  1 0
```

Table 6.8 Input Data Sets for Problem 6, Case A, (continued)

```
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
H+
  0  1 0  iscn VJ IONEX
H2CO3*
  0  0 0  iscn VJ IONEX
NH4+
  0  1 0  iscn VJ IONEX
O2
  0  0 0  iscn VJ IONEX
NTA3-
  0 -3 0  iscn VJ IONEX
Co2+
  0  2 0  iscn VJ IONEX
Buffer
  0 -1 0  iscn VJ IONEX
C ******** DATA SET 25:  COMPLEXED SPECIES
H3NTA
0    3  0  0  0  1  0  0   0   3  0  0  0  1  0  0
H2NTA-
0    2  0  0  0  1  0  0   0   2  0  0  0  1  0  0
HNTA2-
0    1  0  0  0  1  0  0   0   1  0  0  0  1  0  0
CoNTA-
0    0  0  0  0  1  1  0   0   0  0  0  0  1  1  0
CoNTA2 4-
0    0  0  0  0  2  1  0   0   0  0  0  0  2  1  0
CoOHNTA 2-
0   -1  0  0  0  1  1  0   0  -1  0  0  0  1  1  0
CoOH+
0   -1  0  0  0  0  1  0   0  -1  0  0  0  0  1  0
Co(OH)2
0   -2  0  0  0  0  1  0   0  -2  0  0  0  0  1  0
Co(OH)3-
0   -3  0  0  0  0  1  0   0  -3  0  0  0  0  1  0
HCO3-
0   -1  1  0  0  0  0  0   0  -1  1  0  0  0  0  0
CO3 2-
0   -2  1  0  0  0  0  0   0  -2  1  0  0  0  0  0
NH3
0   -1  0  1  0  0  0  0   0  -1  0  1  0  0  0  0
OH-
0   -1  0  0  0  0  0  0   0  -1  0  0  0  0  0  0
HBuffer
0    1  0  0  0  0  0  1   0   1  0  0  0  0  0  1
C ******** DATA SET 26:  ADSORBED SPECIES
CoNTA(ads)
0    0  0  0  0  1  1  0       0  0  0  0  1  1  0
Co(ads)
0    0  0  0  0  0  1  0       0  0  0  0  0  1  0
C ******** DATA SET 28:  MICROBIAL SPECIES
C5H7O2N(cells)
  0  -2.681936665037 0
```

Table 6.8 Input Data Sets for Problem 6, Case A, (continued)

```
C ******** DATA SET 29:  reaction data
17

2 1 0     NRTS NPDS KRTYP            REACTION 1 - H3NTA
14.9      LOGKEQ
3  1  1
1  5  8
2 1 0     NRTS NPDS KRTYP            REACTION 2 - H2NTA
13.3      LOGKEQ
2  1  1
1  5  9
2 1 0     NRTS NPDS KRTYP            REACTION 3 - HNTA
10.3      LOGKEQ
1  1  1
1  5  10
2 1 0     NRTS NPDS KRTYP            REACTION 4 - CoNTA
11.7      LOGKEQ
1  1  1
5  6  11
2 1 0     NRTS NPDS KRTYP            REACTION 5 - CoNTA2
14.5      LOGKEQ
2  1  1
5  6  12
3 1 0     NRTS NPDS KRTYP            REACTION 6 - CoOHNTA
0.5      LOGKEQ
-1  1  1  1
1   5  6  13
2 1 0     NRTS NPDS KRTYP            REACTION 7 - CoOH
-9.7      LOGKEQ
 -1  1  1
 1  6  14
2 1 0     NRTS NPDS KRTYP            REACTION 8 - CoOH2
-22.9      LOGKEQ
 -2  1  1
 1  6  15
2 1 0     NRTS NPDS KRTYP            REACTION 9 - CoOH3
-31.5      LOGKEQ
 -3  1  1
 1  6  16
2 1 0     NRTS NPDS KRTYP            REACTION 10 - HCO3
-6.35      LOGKEQ
 -1  1  1
 1  2  17
2 1 0     NRTS NPDS KRTYP            REACTION 11 - CO3
-16.68     LOGKEQ
 -2  1  1
 1  2  18
2 1 0     NRTS NPDS KRTYP            REACTION 12 - NH3
-9.3       LOGKEQ
 -1  1  1
 1  3  19
```

Table 6.8 Input Data Sets for Problem 6, Case A, (concluded)

```
1 1 0    NRTS NPDS KRTYP             REACTION 13 - OH
-14.0      LOGKEQ
 -1  1
 1   20
2 1 0    NRTS NPDS KRTYP             REACTION 14 - HBuffer
6.0      LOGKEQ
 1  1  1
 1  7  21
1 1 1           NRTS NPDS KRTYP      REACTION 15 - CoNTA (ads)
-0.30075847675 -0.574031267728  LOGKB  LOGKF
 1    1
 11   22
1 1 1           NRTS NPDS KRTYP      REACTION 16 - Co(ads)
-1.279039227   -0.574031267728  LOGKB  LOGKF
 1    1
 6   23
3 3 2           NRTS NPDS KRTYP      REACTION 18 - Microbial rxn
0.0916519  7.64D-7 6.25D-6 0.0 1 2 0 0.0 0.0 grmax ks ks kn locs loca locn taul taue
1  1.620  2.424    17.370666  3.120  0.424
10 4      1        24         2      3
0 0 0 0 0              inhib hscinh hscinh p q
                                END OF JOB
```

6.7 Problem 7: Copper Leaching from a Five-Spot Well Pattern

This application involves the kinetic dissolution and formation of ten mineral species. It simulates the leaching of copper from an ore deposit using an acidic injection solution and is a benchmark reactive transport problem developed by Lichtner (1997). The region of interest is assumed to be homogeneous, having porosity of 5 % and a permeability of 1.5E-13 m^2. One central injection well and four evenly placed extraction wells are screened over 1200 dm and flow is distributed evenly over this depth. The injection and extraction rates are 2.52 L/s. Because of symmetry of the flow field, only one quarter of the entire region is simulated using one quarter of the total injection and extraction rates. This quarter region is 150 dm on each side and is discretized using 30 x 30 uniformly sized elements. An impervious boundary condition is imposed on each side of the region. The simulation is performed in two dimensions using a unit thickness of the 1200 dm depth and a steady state flow field. Figure 6.4 shows the flow field. The injection and extraction wells are at the lower left (x = 0, y = 0) and upper right (x = 150, y = 150) corners of the region, respectively.

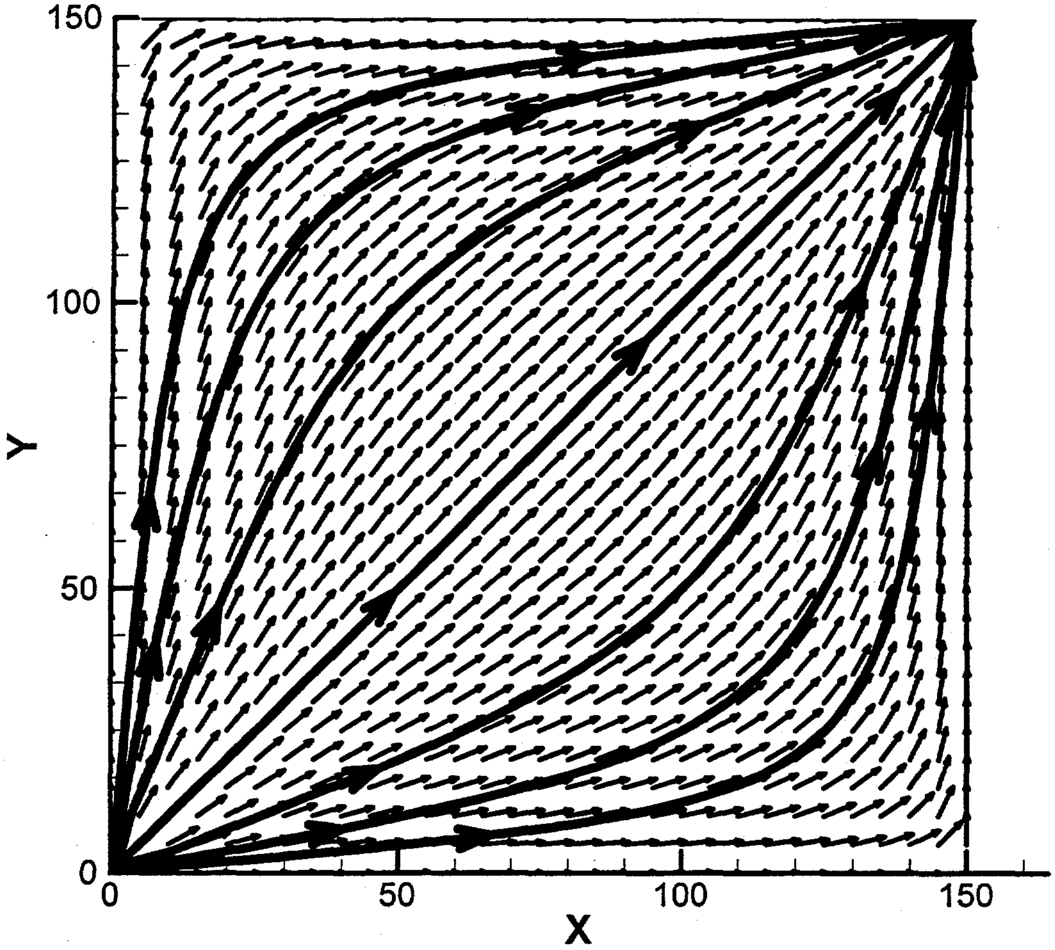


Figure 6.4. Steady State Flow Field

The injection and extraction wells are for the mining of copper from the deposit. The initial mineral composition based on volume is 0.5% chrysocolla, 2.5% goethite, 5% kaolinite, 5% muscovite, and 82% quartz. The copper containing ore is chrysocolla.

Twelve chemical components are included in the simulation: Na^+, K^+, Ca^{2+}, H^+, Cu^{2+}, Al^{3+}, Fe^{2+}, $SiO_{2\,(aq)}$, HCO_3^-, SO_4^{2-}, Cl^-, and $O_{2\,(aq)}$. In addition to the five primary minerals which exist at the start of the simulation, five secondary minerals may form as the geochemical conditions change within the region. The reactions governing the formation and dissolution of all minerals are simulated as kinetic and are listed below. The rates of these reactions and the molar volumes of these minerals are summarized in Table 6.9.

$$\text{Chrysocolla} + 0.39\,H^{+} \rightleftharpoons -1.61\,H^{+} + Cu^{2+} + SiO_{2(aq)} + 3\,H_2O \tag{6.7.1}$$

$$\text{Jurbanite} \rightleftharpoons Al^{3+} - H^{+} + SO_4^{2-} + 6\,H_2O \tag{6.7.2}$$

$$\text{Alunite} \rightleftharpoons 3\,Al^{3+} - 6\,H^{+} + K^{+} + 2\,SO_4^{2-} + 6\,H_2O \tag{6.7.3}$$

$$\text{Goethite} \rightleftharpoons Fe^{2+} - 2\,H^{+} + 0.25\,O_2 + 1.5\,H_2O \tag{6.7.4}$$

$$\text{Gypsum} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2\,H_2O \tag{6.7.5}$$

$$\text{Jarosite} \rightleftharpoons K^{+} - 3\,H^{+} + 3\,Fe^{2+} + 2\,SO_4^{2-} + 0.75\,O_2 + 4.5\,H_2O \tag{6.7.6}$$

$$\text{Kaolinite} \rightleftharpoons 2\,Al^{3+} - 6\,H^{+} + 2\,SiO_{2(aq)} + 5\,H_2O \tag{6.7.7}$$

$$\text{Muscovite} \rightleftharpoons 3\,Al^{3+} + K^{+} - 10\,H^{+} + 3\,SiO_{2(aq)} + 6\,H_2O \tag{6.7.8}$$

$$\text{Quartz} \rightleftharpoons SiO_{2(aq)} \tag{6.7.9}$$

$$SiO_{2(am)} \rightleftharpoons SiO_{2(aq)} \tag{6.7.10}$$

Table 6.9. Molar Volumes, Initial Conditions and Kinetic Rates for Precipitated Species.

Mineral	Molar Volume (dm^3/mol)	Initial Volume Fraction	Initial Concentration (mol/dm^3)	log k_f (yr^{-1})	log k_b (yr^{-1})
Chyrsocolla	0.07319	0.005	6.83153E-2	0.49881	-3.42919
Jurbanite	0.1260	0.000	0.00000D00	-0.50119	2.72881
Alunite	0.29360	0.000	0.00000D00	-0.50119	-0.15329
Goethite	0.02082	0.025	1.20077E+0	-0.50119	7.45381
Gypsum	0.07469	0.000	0.00000E00	0.49881	4.98081
Jarosite	0.15675	0.000	0.00000E00	-0.50119	34.33881
Kaolinite	0.09952	0.050	5.02412E-1	-2.50119	- 9.31119
Muscovite	0.14071	0.050	3.55341E-1	-2.50119	-16.09119
Quartz	0.022688	0.820	3.61425E+1	-3.50119	0.49781

Amorphous Silica	0.0290	0.000	0.00000E00	-0.50119	2.21281

The fluid composition is simulated using thirty-four soluble product species as well as the twelve aqueous component species. The formation of all aqueous complexed species is assumed to be equilibrium. Table 6.10 lists the reaction tableau for these aqueous species and the equilibrium constants for their formation. Table 6.11 summarizes the total initial concentration of each of the twelve chemical components present in solution in the matrix. The program determines the initial equilibrium aqueous speciation and the activity coefficients for all aqueous species. The pH of the fluid initially in the matrix is 8. The initial conditions in the matrix reflect a partial pressure of $CO_{2(g)}$ and $O_{2(g)}$ of 1E-3 and 0.20 atm, respectively. The density of the initial matrix fluid is 1.0005 kg/dm^3.

Table 6.10. Tableau of Equilibrium Aqueous Reactions for Copper Leaching Application.

	Na^+	K^+	Ca^{2+}	H^+	Cu^{2+}	Al^{3+}	Fe^{2+}	$SiO_{2\,(aq)}$	HCO_3^-	SO_4^{2-}	Cl^-	$O_{2\,(aq)}$	log K
OH-	0	0	0	-1	0	0	0	0	0	0	0	0	-13.995
Fe^{3+}	0	0	0	1	0	0	1	0	0	0	0	0.25	8.490
$Al(OH)_2^+$	0	0	0	-2	0	1	0	0	0	0	0	0	-10.595
$Al(OH)_{3\,(aq)}$	0	0	0	-3	0	1	0	0	0	0	0	0	-16.158
$Al(OH)_4^-$	0	0	0	-4	0	1	0	0	0	0	0	0	-22.883
$Al(SO4)_2^-$	0	0	0	0	0	1	0	0	0	2	0	0	4.9
$AlOH^{2+}$	0	0	0	-1	0	1	0	0	0	0	0	0	-4.9571
$AlSO_4^+$	0	0	0	0	0	1	0	0	0	1	0	0	3.01
H_2CO3^*	0	0	0	1	0	0	0	0	1	0	0	0	6.3447
CO_3^{-2}	0	0	0	-1	0	0	0	0	1	0	0	0	-10.329
$CaCO_{3\,(aq)}$	0	0	1	-1	0	0	0	0	1	0	0	0	-7.0017
$CaHCO_3^+$	0	0	1	0	0	0	0	0	1	0	0	0	1.0467
$CaOH^+$	0	0	1	-1	0	0	0	0	0	0	0	0	-12.8500
$CaSO_{4(aq)}$	0	0	1	0	0	0	0	0	0	1	0	0	2.1111
$CuOH^+$	0	0	0	-1	1	0	0	0	0	0	0	0	-7.2875
$CuSO_{4(aq)}$	0	0	0	0	1	0	0	0	0	1	0	0	2.31
$Fe[II](OH)_{2\,(aq)}$	0	0	0	-2	0	0	1	0	0	0	0	0	-20.6000
$Fe[III](OH)_2^+$	0	0	0	-1	0	0	1	0	0	0	0	0.25	2.820
$Fe[III](OH)_{3\,(aq)}$	0	0	0	-2	0	0	1	0	0	0	0	0.25	-3.51
$Fe[II](OH)_3^-$	0	0	0	-3	0	0	1	0	0	0	0	0	-31.000
$Fe[III](OH)_4^-$	0	0	0	-3	0	0	1	0	0	0	0	0.25	-13.110
$Fe[III](SO_4)_2^-$	0	0	0	1	0	0	1	0	0	2	0	0.25	11.704
$Fe[III]HSO_4^{2+}$	0	0	0	2	0	0	1	0	0	1	0	0.25	10.030
$Fe[II]SO_{4\,(aq)}$	0	0	0	0	0	0	1	0	0	1	0	0	2.2
$Fe[III]SO_4^+$	0	0	0	1	0	0	1	0	0	1	0	0.25	10.418
$H2SO_{4\,(aq)}$	0	0	0	2	0	0	0	0	0	1	0	0	-1.0209
HSO_4^-	0	0	0	1	0	0	0	0	0	1	0	0	1.9791
$Cu[II]Cl^+$	0	0	0	0	1	0	0	0	0	0	1	0	0.437
$Cu[II]Cl_{2\,(aq)}$	0	0	0	0	1	0	0	0	0	0	2	0	0.1585
$Cu[II]Cl_4^{2-}$	0	0	0	0	1	0	0	0	0	0	4	0	-4.5681
Cu^+	0	0	0	-1	1	0	0	0	0	0	0	-0.25	-18.77

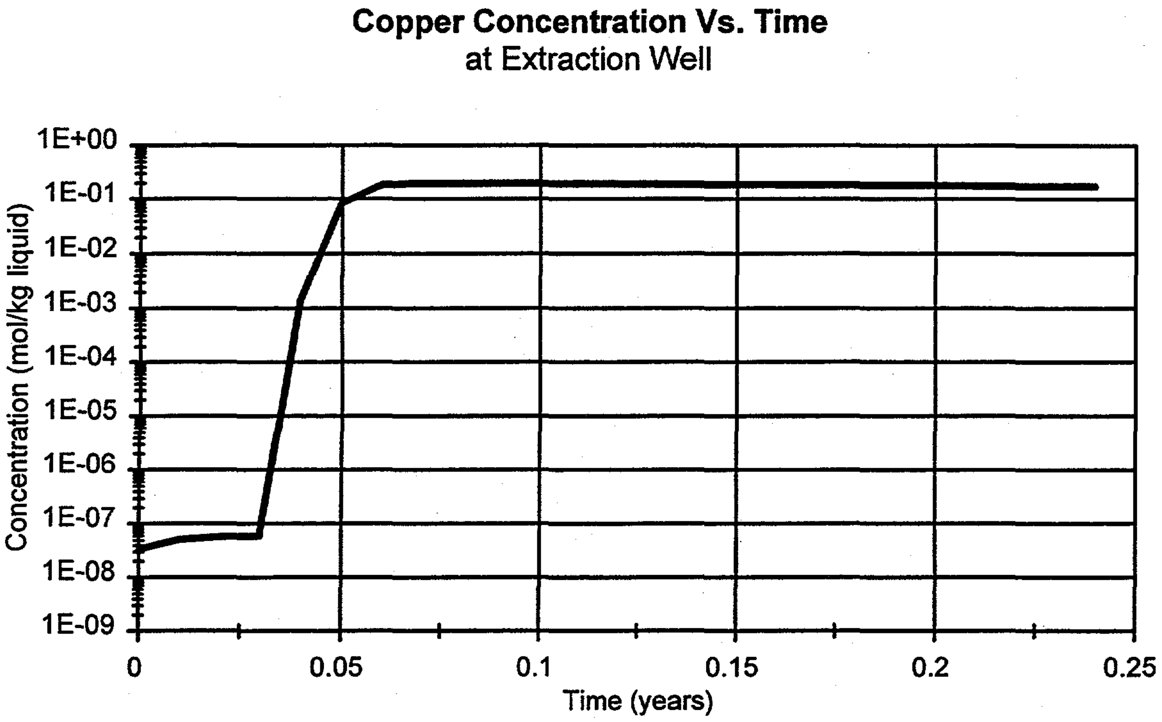
$Cu[I]Cl_2^-$	0	0 0	-1	1 0 0	0	0 0	2	-0.25	-13.949
$Cu[I]Cl_3^{-2}$	0	0 0	-1	1 0 0	0	0 0	3	-0.25	-13.141
$Cu[IIO_2^{-2}$	0	0 0	-4	1 0 0	0	0 0	0	0	-39.45

Table 6.11. Total Concentration of Components Initially in the Matrix Fluid and in the Injection Fluid.

Component	Initial Concentration (mol/dm^3 liquid)	Injection Fluid Concentration (mol/dm^3 liquid)
Na^+	5.00250E-3	5.2600E-3
K^+	2.57809E-5	1.3305E-4
Ca^{2+}	6.86031E-4	1.6086E-2
H^+	1.54064E-5	3.4649E-1
Cu^{2+}	3.23586E-8	1.0520E-8
Al^{3+}	2.04237E-8	2.6300E-2
Fe^{2+}	3.59984E-12	4.5694E-2
$SiO_{2\,(aq)}$	1.87124E-4	2.0243E-3
HCO_3^-	1.74271E-3	3.5737E-4
SO_4^{2-}	5.00246E-4	2.7435E-1
Cl^-	3.67274E-3	5.2600E-3
$O_{2\,(aq)}$	2.52896E-4	1.1689E-2
pH	8.0	1.0

The injection fluid has a pH of 1.0 and density of 1.0520 kg/dm^3. Its composition remains constant throughout the simulation. The total concentration of the aqueous components in the injection fluid is detailed in Table 6.11. The dissolution of the copper ore is pH dependent; as can be seen from reaction **(6.7.1)**, the dissolution rate is proportional to the activity of H^+ to the 0.39 power.

The simulation was run for a period of 0.25 years using a uniform time step of 1E-3 years. The same time step is used for both hydrologic transport and for the geochemical reactions. The operator splitting solution method was implemented. Figure 6.5 depicts the projected copper recovery and the pH and pe at the extraction well over time. Figures 6.6 and 6.7 show the spatial distribution of chrysocolla and the five secondary minerals at the end of the 0.25 year simulation. The results compare well with those provided by Lichtner (1997). The input data sets for this example are given in Table 6.12.



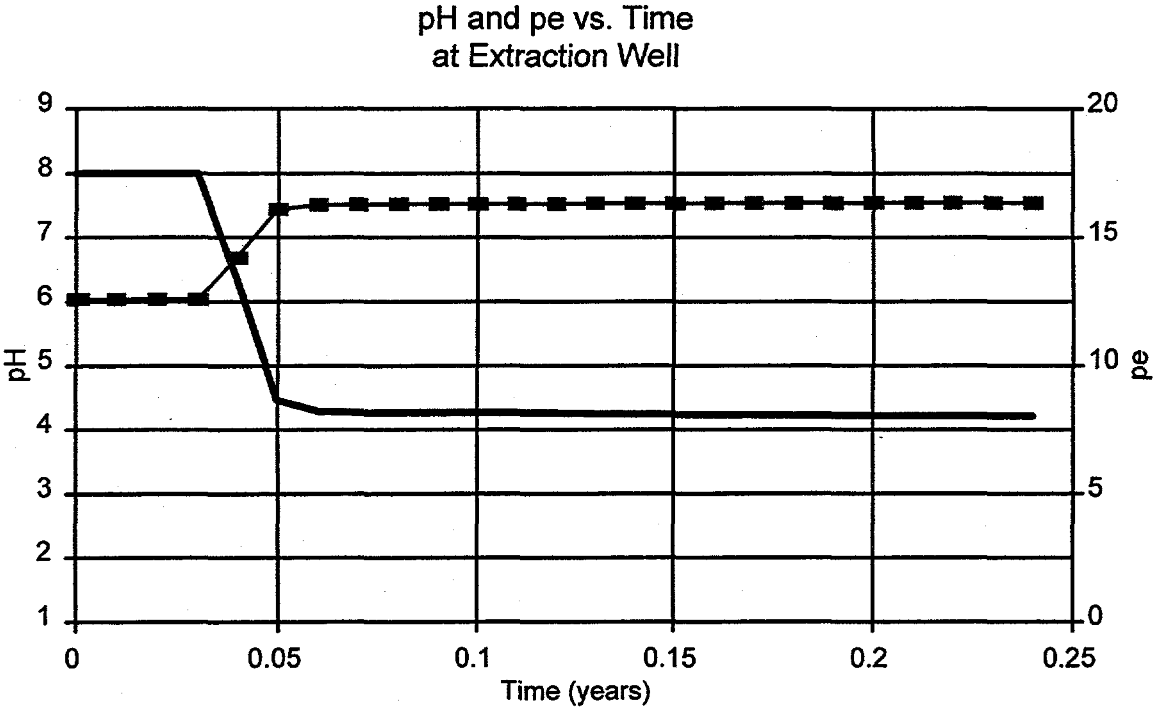


Figure 6.5. Copper Concentration and pe-pH at Extraction Well.

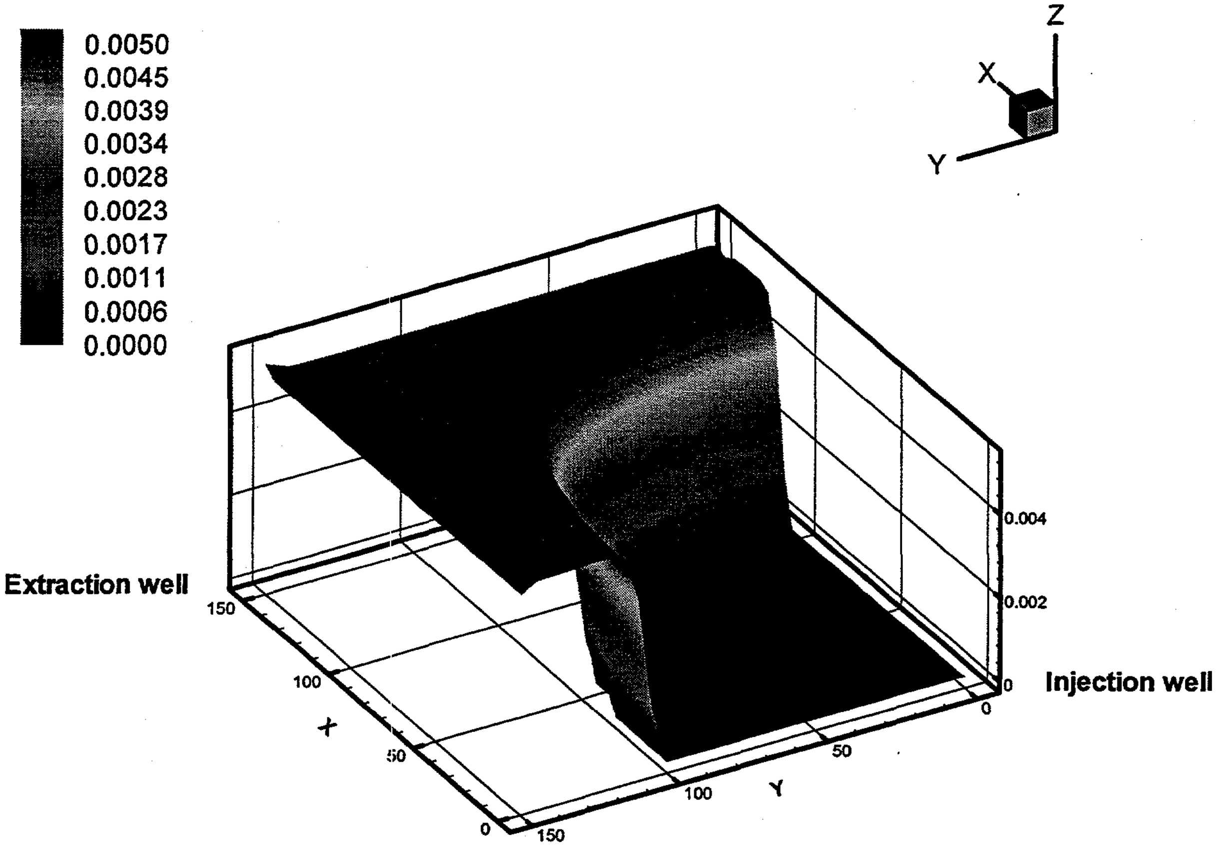


Figure 6.6. Volume Fraction of Chrysocolla after 0.25 years of Copper Leaching.

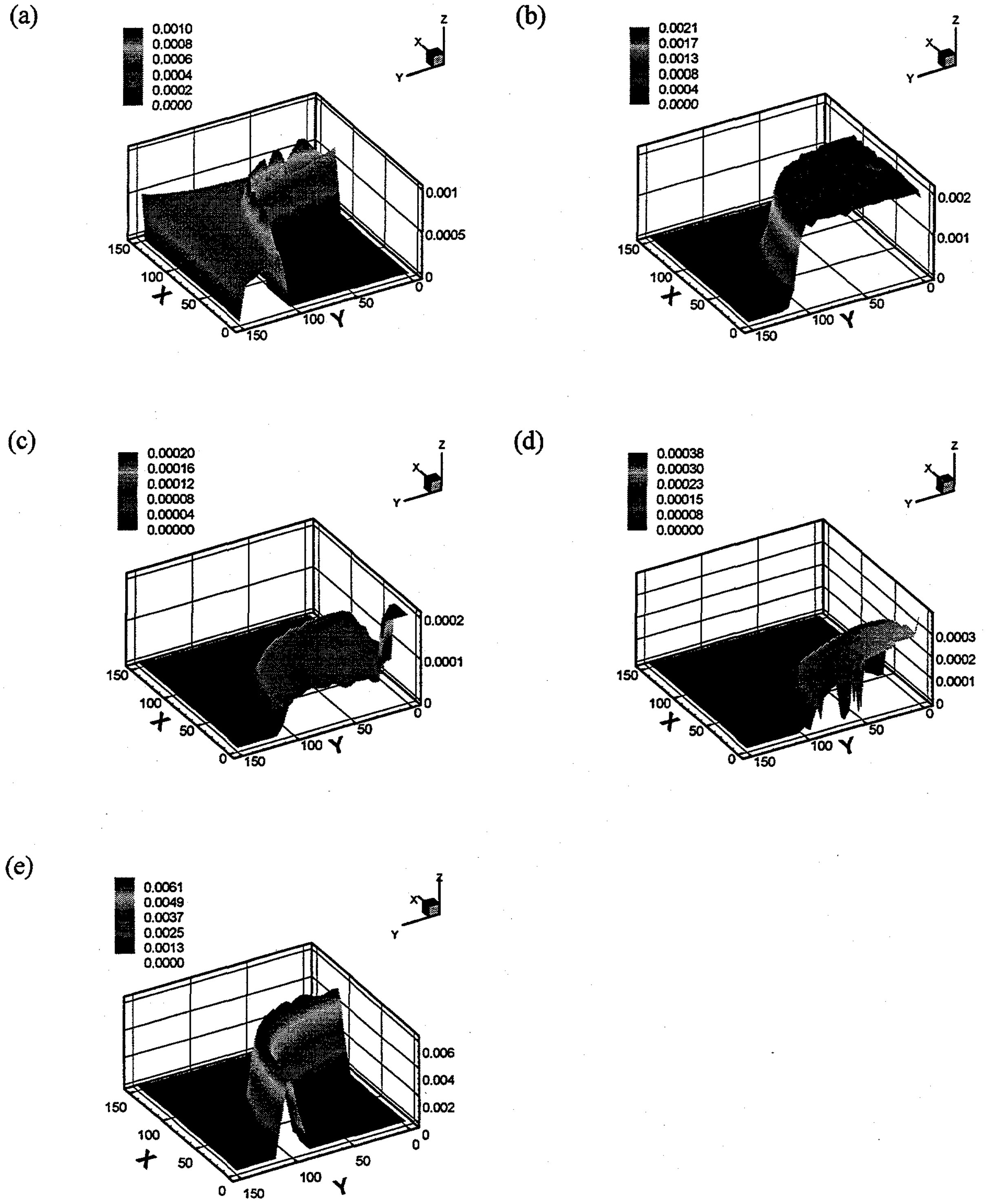


Figure 6.7. Volume Fraction of Secondary Minerals after 0.25 years of Copper Leaching. (a) Alunite, (b) Amorphous Silica, (c) Gypsum, (d) Jarosite, (e) Jurbanite. All figures are oriented so that the injection well (x = 0, y = 0) is at the right.

Table 6.12 Input Data Sets for Problem 7

```
   1  Copper Leaching from 5 Well Pattern (P. Lichtner Benchmark) (kg,dm,years)
 1 0 0 0 1
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 961 900 1 0 25   1 4 -1 1 0   0 0 40 1 50   0 1 0 1 11   1 1 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 1.0D-2 0.0D0 1.0D-2 0.25D0 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-6 1.0D0

C ******* DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
4400000000400000000400004
1111111111111111111111111
1.0D38
C ******* DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PROPERTY TYPE INDICATOR
 3
 1 481 961 NODEP

C ******* DATA SET 6: MATERIAL PROPERTIES
 0.0D0 0.0D0 0.0D0 2.56D0 AL AT AM RHOB
C ******* DATA SET 7: NODE COORDINATES
     1   30     1       0.0D0    0.0D0   0.0
    32   30     1       5.0D0    0.0D0   0.0
    63   30     1      10.0D0    0.0D0   0.0
    94   30     1      15.0D0    0.0D0   0.0
   125   30     1      20.0D0    0.0D0   0.0
   156   30     1      25.0D0    0.0D0   0.0
   187   30     1      30.0D0    0.0D0   0.0
   218   30     1      35.0D0    0.0D0   0.0
   249   30     1      40.0D0    0.0D0   0.0
   280   30     1      45.0D0    0.0D0   0.0
   311   30     1      50.0D0    0.0D0   0.0
   342   30     1      55.0D0    0.0D0   0.0
   373   30     1      60.0D0    0.0D0   0.0
   404   30     1      65.0D0    0.0D0   0.0
   435   30     1      70.0D0    0.0D0   0.0
   466   30     1      75.0D0    0.0D0   0.0
   497   30     1      80.0D0    0.0D0   0.0
   528   30     1      85.0D0    0.0D0   0.0
   559   30     1      90.0D0    0.0D0   0.0
   590   30     1      95.0D0    0.0D0   0.0
   621   30     1     100.0D0    0.0D0   0.0
   652   30     1     105.0D0    0.0D0   0.0
   683   30     1     110.0D0    0.0D0   0.0
   714   30     1     115.0D0    0.0D0   0.0
   745   30     1     120.0D0    0.0D0   0.0
   776   30     1     125.0D0    0.0D0   0.0
   807   30     1     130.0D0    0.0D0   0.0
   838   30     1     135.0D0    0.0D0   0.0
   869   30     1     140.0D0    0.0D0   0.0
   900   30     1     145.0D0    0.0D0   0.0
   931   30     1     150.0D0    0.0D0   0.0
     0    0     0      0.0      0.0     0.0           END OF X-COORD
     1   30     1      0.0D0    5.0D0   0.0
    32   30     1      0.0D0    5.0D0   0.0
    63   30     1      0.0D0    5.0D0   0.0
    94   30     1      0.0D0    5.0D0   0.0
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
  125   30     1      0.0D0   5.0D0  0.0
  156   30     1      0.0D0   5.0D0  0.0
  187   30     1      0.0D0   5.0D0  0.0
  218   30     1      0.0D0   5.0D0  0.0
  249   30     1      0.0D0   5.0D0  0.0
  280   30     1      0.0D0   5.0D0  0.0
  311   30     1      0.0D0   5.0D0  0.0
  342   30     1      0.0D0   5.0D0  0.0
  373   30     1      0.0D0   5.0D0  0.0
  404   30     1      0.0D0   5.0D0  0.0
  435   30     1      0.0D0   5.0D0  0.0
  466   30     1      0.0D0   5.0D0  0.0
  497   30     1      0.0D0   5.0D0  0.0
  528   30     1      0.0D0   5.0D0  0.0
  559   30     1      0.0D0   5.0D0  0.0
  590   30     1      0.0D0   5.0D0  0.0
  621   30     1      0.0D0   5.0D0  0.0
  652   30     1      0.0D0   5.0D0  0.0
  683   30     1      0.0D0   5.0D0  0.0
  714   30     1      0.0D0   5.0D0  0.0
  745   30     1      0.0D0   5.0D0  0.0
  776   30     1      0.0D0   5.0D0  0.0
  807   30     1      0.0D0   5.0D0  0.0
  838   30     1      0.0D0   5.0D0  0.0
  869   30     1      0.0D0   5.0D0  0.0
  900   30     1      0.0D0   5.0D0  0.0
  931   30     1      0.0D0   5.0D0  0.0
    0    0     0      0.0D0   0.0D0  0.0D0         END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1   32   33    2    1   30   30           IE
C ******* DATA SET 10: CHEMICAL COMPONENT INFORMATION
 12 0    0 0 0 10    0 0    NOHA HS   NOKX KY KZ KP  NOMB MA
 Na +
  1   1
 K+
  2   1
 Ca +2
  3   1
 H+
  4   1
 Cu +2
  5   1
 Al +3
  6   1
 Fe +2
  7   1
 SiO2 (aq)
  8   1
 HCO3 -
  9   1
 SO4 -2
 10   1
 Cl -
 11   1
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 O2  (aq)
 12    1
C ******* DATA SET 11:  INITIAL CONDITIONS (MASS/MEDIA VOLUME)
    1    960    1     2.50125D-4   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Na+
    1    960    1     1.28904D-6   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. K+
    1    960    1     3.43016D-5   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Ca+2
    1    960    1     7.70319D-7   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. H+
    1    960    1     1.61793D-9   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Cu+2
    1    960    1     1.02118D-9   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Al+3
    1    960    1     1.79992D-13  0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Fe+2
    1    960    1     9.35618D-6   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. SiO2(aq)
    1    960    1     8.71354D-5   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. HCO3-
    1    960    1     2.50123D-5   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. SO4 -2
    1    960    1     1.83637D-4   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Cl -
    1    960    1     1.26448D-5   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. O2 (aq)
    1    960    1     6.83153D-2   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0         END OF I.C. Chrysocolla - P1
    1    960    1     0.00000D00   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Jurbanite - P2
    1    960    1     0.00000D00   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Alunite   - P3
    1    960    1     1.20077D00   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Goethite  - P4
    1    960    1     0.00000D00   0.0D0      0.0D0

    0     0     0     0.0          0.0        0.0          END OF I.C. Gypsum    - P5
    1    960    1     0.00000D00   0.0D0      0.0D0
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
     0    0    0    0.0          0.0        0.0          END OF I.C. Jarosite   - P6
     1   960   1    5.02412D-1   0.0D0      0.0D0

     0    0    0    0.0          0.0        0.0          END OF I.C. Kaolinite - P7
     1   960   1    3.55341D-1   0.0D0      0.0D0

     0    0    0    0.0          0.0        0.0          END OF I.C. Muscovite - P8
     1   960   1    3.61425D+1   0.0D0      0.0D0

     0    0    0    0.0          0.0        0.0          END OF I.C. Quartz    - P9
     1   960   1    0.00000D00   0.0D0      0.0D0

     0    0    0    0.0          0.0        0.0          END OF I.C. SiO2 (am) - P10
C ******* DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
     0  0  0    2  2  2    0  0  0    0  0  0  0
C ******* DATA SET 13: WELL SOURCE/SINK (MASS/LIQUID VOLUME)
   1  961
   0.0D0   5.2600D-3   2.0D0   5.260D-3
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S Na+
   0.0D0   1.3305D-4   2.0D0   1.3305D-4
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S K+
   0.0D0   1.6086D-2   2.0D0   1.6086D-2
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S Ca+2
   0.0D0   3.4649D-1   2.0D0   3.4649D-1
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S H+
   0.0D0   1.0520D-8   2.0D0   1.0520D-8
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S Cu+2
   0.0D0   2.6300D-2   2.0D0   2.6300D-2
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S Al+3
   0.0D0   4.5694D-2   2.0D0   4.5694D-2
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S Fe+2
   0.0D0   2.0343D-3   2.0D0   2.0343D-3
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S SiO2(aq)
   0.0D0   3.5737D-4   2.0D0   3.5737D-4
   0.0D0   0.00D0      2.0D0   0.00D0
     1    1    1    1    1
     0    0    0    0    0                         END OF S/S HCO3-
   0.0D0   2.7435D-1   2.0D0   2.7435D-1
   0.0D0   0.00D0      2.0D0   0.00D0
```

Table 6.12   Input Data Sets for Problem 7 (continued)

```
    1     1     1     1     1
    0     0     0     0     0                       END OF S/S SO4 -2
  0.0D0   5.2600D-3   2.0D0   5.2600D-3
  0.0D0   0.00D0      2.0D0   0.00D0
    1     1     1     1     1
    0     0     0     0     0                       END OF S/S Cl-
  0.0D0   1.1689D-2   2.0D0   1.1689D-2
  0.0D0   0.00D0      2.0D0   0.00D0
    1     1     1     1     1
    0     0     0     0     0                       END OF S/S O2(aq)
  0.0D0   1.6556D4    2.0D0   1.6556D4
  0.0D0  -1.6556D4    2.0D0  -1.6556D4
    1     1     1     1     1
    0     0     0     0     0                       Q (dm^3/year per dm depth)
  0.0D0   1.0520D0    2.0D0   1.0520D0
  0.0D0   1.0005D0    2.0D0   1.0005D0
    1     1     1     1     1
    0     0     0     0     0                       END OF RHOL S/S
C ******* DATA SET 16: HYDROLOGICAL VARIABLES
    1     0     0   .4727141D+04   .4727141D+04   .00D+00   .00D+00
    2     0     0   .0000000D+00   .2159275D+04   .00D+00   .00D+00
    3     0     0   .0000000D+00   .1176175D+04   .00D+00   .00D+00
    4     0     0   .0000000D+00   .7639950D+03   .00D+00   .00D+00
    5     0     0   .0000000D+00   .5577350D+03   .00D+00   .00D+00
    6     0     0   .0000000D+00   .4381750D+03   .00D+00   .00D+00
    7     0     0   .0000000D+00   .3608200D+03   .00D+00   .00D+00
    8     0     0   .0000000D+00   .3066300D+03   .00D+00   .00D+00
    9     0     0   .0000000D+00   .2663950D+03   .00D+00   .00D+00
   10     0     0   .0000000D+00   .2351750D+03   .00D+00   .00D+00
   11     0     0   .0000000D+00   .2101000D+03   .00D+00   .00D+00
   12     0     0   .0000000D+00   .1893600D+03   .00D+00   .00D+00
   13     0     0   .0000000D+00   .1717950D+03   .00D+00   .00D+00
   14     0     0   .0000000D+00   .1565750D+03   .00D+00   .00D+00
   15     0     0   .0000000D+00   .1431200D+03   .00D+00   .00D+00
   16     0     0   .0000000D+00   .1310350D+03   .00D+00   .00D+00
   17     0     0   .0000000D+00   .1199650D+03   .00D+00   .00D+00
   18     0     0   .0000000D+00   .1097050D+03   .00D+00   .00D+00
   19     0     0   .0000000D+00   .1000525D+03   .00D+00   .00D+00
   20     0     0   .0000000D+00   .9086150D+02   .00D+00   .00D+00
   21     0     0   .0000000D+00   .8201650D+02   .00D+00   .00D+00
   22     0     0   .0000000D+00   .7342650D+02   .00D+00   .00D+00
   23     0     0   .0000000D+00   .6502000D+02   .00D+00   .00D+00
   24     0     0   .0000000D+00   .5674350D+02   .00D+00   .00D+00
   25     0     0   .0000000D+00   .4855300D+02   .00D+00   .00D+00
   26     0     0   .0000000D+00   .4041700D+02   .00D+00   .00D+00
   27     0     0   .0000000D+00   .3231400D+02   .00D+00   .00D+00
   28     0     0   .0000000D+00   .2422750D+02   .00D+00   .00D+00
   29     0     0   .0000000D+00   .1614950D+02   .00D+00   .00D+00
   30     0     0   .0000000D+00   .8074600D+01   .00D+00   .00D+00
   31     0     0   .0000000D+00   .0000000D+00   .00D+00   .00D+00
   32     0     0   .2159275D+04   .0000000D+00   .00D+00   .00D+00
   33     0     0   .1156725D+04   .1156725D+04   .00D+00   .00D+00
   34     0     0   .4818800D+03   .8290250D+03   .00D+00   .00D+00
   35     0     0   .2385950D+03   .6245650D+03   .00D+00   .00D+00
   36     0     0   .1365450D+03   .4930650D+03   .00D+00   .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
  37     0     0   .8722150D+02   .4042050D+03   .00D+00    .00D+00
  38     0     0   .6037350D+02   .3411000D+03   .00D+00    .00D+00
  39     0     0   .4433700D+02   .2942700D+03   .00D+00    .00D+00
  40     0     0   .3405950D+02   .2581850D+03   .00D+00    .00D+00
  41     0     0   .2711500D+02   .2294850D+03   .00D+00    .00D+00
  42     0     0   .2223200D+02   .2060200D+03   .00D+00    .00D+00
  43     0     0   .1869450D+02   .1863600D+03   .00D+00    .00D+00
  44     0     0   .1607350D+02   .1695450D+03   .00D+00    .00D+00
  45     0     0   .1409900D+02   .1548650D+03   .00D+00    .00D+00
  46     0     0   .1259500D+02   .1418200D+03   .00D+00    .00D+00
  47     0     0   .1144250D+02   .1300250D+03   .00D+00    .00D+00
  48     0     0   .1055700D+02   .1191950D+03   .00D+00    .00D+00
  49     0     0   .9877400D+01   .1091150D+03   .00D+00    .00D+00
  50     0     0   .9359300D+01   .9960550D+02   .00D+00    .00D+00
  51     0     0   .8968350D+01   .9052650D+02   .00D+00    .00D+00
  52     0     0   .8677850D+01   .8176950D+02   .00D+00    .00D+00
  53     0     0   .8466600D+01   .7324950D+02   .00D+00    .00D+00
  54     0     0   .8317250D+01   .6489800D+02   .00D+00    .00D+00
  55     0     0   .8215650D+01   .5666250D+02   .00D+00    .00D+00
  56     0     0   .8150000D+01   .4850300D+02   .00D+00    .00D+00
  57     0     0   .8110450D+01   .4038900D+02   .00D+00    .00D+00
  58     0     0   .8088950D+01   .3230000D+02   .00D+00    .00D+00
  59     0     0   .8078950D+01   .2422250D+02   .00D+00    .00D+00
  60     0     0   .8075350D+01   .1614850D+02   .00D+00    .00D+00
  61     0     0   .8074600D+01   .8074600D+01   .00D+00    .00D+00
  62     0     0   .8074600D+01   .0000000D+00   .00D+00    .00D+00
  63     0     0   .1176175D+04   .0000000D+00   .00D+00    .00D+00
  64     0     0   .8290250D+03   .4818800D+03   .00D+00    .00D+00
  65     0     0   .5321850D+03   .5321850D+03   .00D+00    .00D+00
  66     0     0   .3359600D+03   .4818850D+03   .00D+00    .00D+00
  67     0     0   .2203600D+03   .4180950D+03   .00D+00    .00D+00
  68     0     0   .1519650D+03   .3614650D+03   .00D+00    .00D+00
  69     0     0   .1099365D+03   .3149650D+03   .00D+00    .00D+00
  70     0     0   .8291450D+02   .2773400D+03   .00D+00    .00D+00
  71     0     0   .6478500D+02   .2467000D+03   .00D+00    .00D+00
  72     0     0   .5216800D+02   .2214050D+03   .00D+00    .00D+00
  73     0     0   .4311950D+02   .2001650D+03   .00D+00    .00D+00
  74     0     0   .3647300D+02   .1820300D+03   .00D+00    .00D+00
  75     0     0   .3149950D+02   .1662800D+03   .00D+00    .00D+00
  76     0     0   .2772700D+02   .1523800D+03   .00D+00    .00D+00
  77     0     0   .2483950D+02   .1399150D+03   .00D+00    .00D+00
  78     0     0   .2261800D+02   .1285550D+03   .00D+00    .00D+00
  79     0     0   .2090700D+02   .1180700D+03   .00D+00    .00D+00
  80     0     0   .1959350D+02   .1082500D+03   .00D+00    .00D+00
  81     0     0   .1859150D+02   .9895000D+02   .00D+00    .00D+00
  82     0     0   .1783600D+02   .9003600D+02   .00D+00    .00D+00
  83     0     0   .1727650D+02   .8140950D+02   .00D+00    .00D+00
  84     0     0   .1687150D+02   .7299250D+02   .00D+00    .00D+00
  85     0     0   .1658700D+02   .6472150D+02   .00D+00    .00D+00
  86     0     0   .1639550D+02   .5654650D+02   .00D+00    .00D+00
  87     0     0   .1627400D+02   .4843200D+02   .00D+00    .00D+00
  88     0     0   .1620300D+02   .4034950D+02   .00D+00    .00D+00
  89     0     0   .1616650D+02   .3228150D+02   .00D+00    .00D+00
  90     0     0   .1615150D+02   .2421600D+02   .00D+00    .00D+00
  91     0     0   .1614800D+02   .1614800D+02   .00D+00    .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

92	0	0	.1614850D+02	.8075350D+01	.00D+00	.00D+00
93	0	0	.1614950D+02	.0000000D+00	.00D+00	.00D+00
94	0	0	.7639950D+03	.0000000D+00	.00D+00	.00D+00
95	0	0	.6245650D+03	.2385950D+03	.00D+00	.00D+00
96	0	0	.4818850D+03	.3359600D+03	.00D+00	.00D+00
97	0	0	.3526900D+03	.3526900D+03	.00D+00	.00D+00
98	0	0	.2569650D+03	.3359600D+03	.00D+00	.00D+00
99	0	0	.1903500D+03	.3085900D+03	.00D+00	.00D+00
100	0	0	.1444950D+03	.2799600D+03	.00D+00	.00D+00
101	0	0	.1125990D+03	.2534300D+03	.00D+00	.00D+00
102	0	0	.8999850D+02	.2298800D+03	.00D+00	.00D+00
103	0	0	.7365300D+02	.2092650D+03	.00D+00	.00D+00
104	0	0	.6160450D+02	.1912100D+03	.00D+00	.00D+00
105	0	0	.5257700D+02	.1753150D+03	.00D+00	.00D+00
106	0	0	.4572400D+02	.1611750D+03	.00D+00	.00D+00
107	0	0	.4047050D+02	.1484650D+03	.00D+00	.00D+00
108	0	0	.3641800D+02	.1368900D+03	.00D+00	.00D+00
109	0	0	.3328350D+02	.1262250D+03	.00D+00	.00D+00
110	0	0	.3086100D+02	.1162750D+03	.00D+00	.00D+00
111	0	0	.2899750D+02	.1068750D+03	.00D+00	.00D+00
112	0	0	.2757700D+02	.9790550D+02	.00D+00	.00D+00
113	0	0	.2650900D+02	.8925650D+02	.00D+00	.00D+00
114	0	0	.2572100D+02	.8084100D+02	.00D+00	.00D+00
115	0	0	.2515500D+02	.7259000D+02	.00D+00	.00D+00
116	0	0	.2476300D+02	.6444800D+02	.00D+00	.00D+00
117	0	0	.2450500D+02	.5637100D+02	.00D+00	.00D+00
118	0	0	.2434750D+02	.4832800D+02	.00D+00	.00D+00
119	0	0	.2426100D+02	.4029550D+02	.00D+00	.00D+00
120	0	0	.2422200D+02	.3226000D+02	.00D+00	.00D+00
121	0	0	.2421200D+02	.2421200D+02	.00D+00	.00D+00
122	0	0	.2421600D+02	.1615150D+02	.00D+00	.00D+00
123	0	0	.2422250D+02	.8078950D+01	.00D+00	.00D+00
124	0	0	.2422750D+02	.0000000D+00	.00D+00	.00D+00
125	0	0	.5577350D+03	.0000000D+00	.00D+00	.00D+00
126	0	0	.4930650D+03	.1365450D+03	.00D+00	.00D+00
127	0	0	.4180950D+03	.2203600D+03	.00D+00	.00D+00
128	0	0	.3359600D+03	.2569650D+03	.00D+00	.00D+00
129	0	0	.2644600D+03	.2644600D+03	.00D+00	.00D+00
130	0	0	.2079600D+03	.2569650D+03	.00D+00	.00D+00
131	0	0	.1650900D+03	.2428600D+03	.00D+00	.00D+00
132	0	0	.1329950D+03	.2265450D+03	.00D+00	.00D+00
133	0	0	.1089590D+03	.2101350D+03	.00D+00	.00D+00
134	0	0	.9084150D+02	.1945500D+03	.00D+00	.00D+00
135	0	0	.7706950D+02	.1801050D+03	.00D+00	.00D+00
136	0	0	.6650800D+02	.1668350D+03	.00D+00	.00D+00
137	0	0	.5834900D+02	.1546450D+03	.00D+00	.00D+00
138	0	0	.5201300D+02	.1434050D+03	.00D+00	.00D+00
139	0	0	.4707850D+02	.1329600D+03	.00D+00	.00D+00
140	0	0	.4323650D+02	.1231750D+03	.00D+00	.00D+00
141	0	0	.4025550D+02	.1139200D+03	.00D+00	.00D+00
142	0	0	.3795900D+02	.1050700D+03	.00D+00	.00D+00
143	0	0	.3621050D+02	.9654050D+02	.00D+00	.00D+00
144	0	0	.3490100D+02	.8824350D+02	.00D+00	.00D+00
145	0	0	.3394300D+02	.8010850D+02	.00D+00	.00D+00
146	0	0	.3326450D+02	.7207850D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 147    0    0   .3280550D+02   .6410850D+02   .00D+00   .00D+00
 148    0    0   .3251500D+02   .5616200D+02   .00D+00   .00D+00
 149    0    0   .3234900D+02   .4821350D+02   .00D+00   .00D+00
 150    0    0   .3227100D+02   .4024600D+02   .00D+00   .00D+00
 151    0    0   .3225000D+02   .3225000D+02   .00D+00   .00D+00
 152    0    0   .3226000D+02   .2422200D+02   .00D+00   .00D+00
 153    0    0   .3228150D+02   .1616650D+02   .00D+00   .00D+00
 154    0    0   .3230000D+02   .8088950D+01   .00D+00   .00D+00
 155    0    0   .3231400D+02   .0000000D+00   .00D+00   .00D+00
 156    0    0   .4381750D+03   .0000000D+00   .00D+00   .00D+00
 157    0    0   .4042050D+03   .8722150D+02   .00D+00   .00D+00
 158    0    0   .3614650D+03   .1519650D+03   .00D+00   .00D+00
 159    0    0   .3085900D+03   .1903500D+03   .00D+00   .00D+00
 160    0    0   .2569650D+03   .2079600D+03   .00D+00   .00D+00
 161    0    0   .2119500D+03   .2119500D+03   .00D+00   .00D+00
 162    0    0   .1749150D+03   .2079650D+03   .00D+00   .00D+00
 163    0    0   .1453200D+03   .1997500D+03   .00D+00   .00D+00
 164    0    0   .1219900D+03   .1895650D+03   .00D+00   .00D+00
 165    0    0   .1036850D+03   .1786950D+03   .00D+00   .00D+00
 166    0    0   .8932250D+02   .1678200D+03   .00D+00   .00D+00
 167    0    0   .7803550D+02   .1572700D+03   .00D+00   .00D+00
 168    0    0   .6915150D+02   .1471650D+03   .00D+00   .00D+00
 169    0    0   .6215350D+02   .1375450D+03   .00D+00   .00D+00
 170    0    0   .5664650D+02   .1283750D+03   .00D+00   .00D+00
 171    0    0   .5232850D+02   .1195950D+03   .00D+00   .00D+00
 172    0    0   .4896500D+02   .1111500D+03   .00D+00   .00D+00
 173    0    0   .4637250D+02   .1029500D+03   .00D+00   .00D+00
 174    0    0   .4440400D+02   .9494350D+02   .00D+00   .00D+00
 175    0    0   .4294050D+02   .8706800D+02   .00D+00   .00D+00
 176    0    0   .4188500D+02   .7927100D+02   .00D+00   .00D+00
 177    0    0   .4115500D+02   .7150800D+02   .00D+00   .00D+00
 178    0    0   .4068000D+02   .6374500D+02   .00D+00   .00D+00
 179    0    0   .4040000D+02   .5595450D+02   .00D+00   .00D+00
 180    0    0   .4026350D+02   .4811800D+02   .00D+00   .00D+00
 181    0    0   .4022500D+02   .4022500D+02   .00D+00   .00D+00
 182    0    0   .4024600D+02   .3227100D+02   .00D+00   .00D+00
 183    0    0   .4029550D+02   .2426100D+02   .00D+00   .00D+00
 184    0    0   .4034950D+02   .1620300D+02   .00D+00   .00D+00
 185    0    0   .4038900D+02   .8110450D+01   .00D+00   .00D+00
 186    0    0   .4041700D+02   .0000000D+00   .00D+00   .00D+00
 187    0    0   .3608200D+03   .0000000D+00   .00D+00   .00D+00
 188    0    0   .3411000D+03   .6037350D+02   .00D+00   .00D+00
 189    0    0   .3149650D+03   .1099365D+03   .00D+00   .00D+00
 190    0    0   .2799600D+03   .1444950D+03   .00D+00   .00D+00
 191    0    0   .2428600D+03   .1650900D+03   .00D+00   .00D+00
 192    0    0   .2079650D+03   .1749150D+03   .00D+00   .00D+00
 193    0    0   .1772950D+03   .1772950D+03   .00D+00   .00D+00
 194    0    0   .1513900D+03   .1749150D+03   .00D+00   .00D+00
 195    0    0   .1300050D+03   .1696800D+03   .00D+00   .00D+00
 196    0    0   .1125850D+03   .1628500D+03   .00D+00   .00D+00
 197    0    0   .9850100D+02   .1552150D+03   .00D+00   .00D+00
 198    0    0   .8716150D+02   .1472500D+03   .00D+00   .00D+00
 199    0    0   .7806800D+02   .1392050D+03   .00D+00   .00D+00
 200    0    0   .7080200D+02   .1312400D+03   .00D+00   .00D+00
 201    0    0   .6502550D+02   .1234000D+03   .00D+00   .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 202    0    0   .6046600D+02   .1156950D+03   .00D+00   .00D+00
 203    0    0   .5690400D+02   .1081250D+03   .00D+00   .00D+00
 204    0    0   .5416200D+02   .1006420D+03   .00D+00   .00D+00
 205    0    0   .5209250D+02   .9321600D+02   .00D+00   .00D+00
 206    0    0   .5057350D+02   .8581350D+02   .00D+00   .00D+00
 207    0    0   .4950250D+02   .7839850D+02   .00D+00   .00D+00
 208    0    0   .4879000D+02   .7093800D+02   .00D+00   .00D+00
 209    0    0   .4835900D+02   .6340900D+02   .00D+00   .00D+00
 210    0    0   .4814200D+02   .5579300D+02   .00D+00   .00D+00
 211    0    0   .4807900D+02   .4807900D+02   .00D+00   .00D+00
 212    0    0   .4811800D+02   .4026350D+02   .00D+00   .00D+00
 213    0    0   .4821350D+02   .3234900D+02   .00D+00   .00D+00
 214    0    0   .4832800D+02   .2434750D+02   .00D+00   .00D+00
 215    0    0   .4843200D+02   .1627400D+02   .00D+00   .00D+00
 216    0    0   .4850300D+02   .8150000D+01   .00D+00   .00D+00
 217    0    0   .4855300D+02   .0000000D+00   .00D+00   .00D+00
 218    0    0   .3066300D+03   .0000000D+00   .00D+00   .00D+00
 219    0    0   .2942700D+03   .4433700D+02   .00D+00   .00D+00
 220    0    0   .2773400D+03   .8291450D+02   .00D+00   .00D+00
 221    0    0   .2534300D+03   .1125990D+03   .00D+00   .00D+00
 222    0    0   .2265450D+03   .1329950D+03   .00D+00   .00D+00
 223    0    0   .1997500D+03   .1453200D+03   .00D+00   .00D+00
 224    0    0   .1749150D+03   .1513900D+03   .00D+00   .00D+00
 225    0    0   .1529350D+03   .1529350D+03   .00D+00   .00D+00
 226    0    0   .1340550D+03   .1513900D+03   .00D+00   .00D+00
 227    0    0   .1181500D+03   .1478100D+03   .00D+00   .00D+00
 228    0    0   .1049275D+03   .1429450D+03   .00D+00   .00D+00
 229    0    0   .9404350D+02   .1372950D+03   .00D+00   .00D+00
 230    0    0   .8515750D+02   .1311800D+03   .00D+00   .00D+00
 231    0    0   .7796150D+02   .1248050D+03   .00D+00   .00D+00
 232    0    0   .7218750D+02   .1182850D+03   .00D+00   .00D+00
 233    0    0   .6760600D+02   .1116750D+03   .00D+00   .00D+00
 234    0    0   .6402400D+02   .1050050D+03   .00D+00   .00D+00
 235    0    0   .6127850D+02   .9827150D+02   .00D+00   .00D+00
 236    0    0   .5923000D+02   .9146700D+02   .00D+00   .00D+00
 237    0    0   .5775900D+02   .8457300D+02   .00D+00   .00D+00
 238    0    0   .5676100D+02   .7757000D+02   .00D+00   .00D+00
 239    0    0   .5614400D+02   .7043700D+02   .00D+00   .00D+00
 240    0    0   .5582500D+02   .6316050D+02   .00D+00   .00D+00
 241    0    0   .5573000D+02   .5573000D+02   .00D+00   .00D+00
 242    0    0   .5579300D+02   .4814200D+02   .00D+00   .00D+00
 243    0    0   .5595450D+02   .4040000D+02   .00D+00   .00D+00
 244    0    0   .5616200D+02   .3251500D+02   .00D+00   .00D+00
 245    0    0   .5637100D+02   .2450500D+02   .00D+00   .00D+00
 246    0    0   .5654650D+02   .1639550D+02   .00D+00   .00D+00
 247    0    0   .5666250D+02   .8215650D+01   .00D+00   .00D+00
 248    0    0   .5674350D+02   .0000000D+00   .00D+00   .00D+00
 249    0    0   .2663950D+03   .0000000D+00   .00D+00   .00D+00
 250    0    0   .2581850D+03   .3405950D+02   .00D+00   .00D+00
 251    0    0   .2467000D+03   .6478500D+02   .00D+00   .00D+00
 252    0    0   .2298800D+03   .8999850D+02   .00D+00   .00D+00
 253    0    0   .2101350D+03   .1089590D+03   .00D+00   .00D+00
 254    0    0   .1895650D+03   .1219900D+03   .00D+00   .00D+00
 255    0    0   .1696800D+03   .1300050D+03   .00D+00   .00D+00
 256    0    0   .1513900D+03   .1340550D+03   .00D+00   .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

257	0	0	.1351350D+03	.1351350D+03	.00D+00	.00D+00
258	0	0	.1210350D+03	.1340600D+03	.00D+00	.00D+00
259	0	0	.1090150D+03	.1314600D+03	.00D+00	.00D+00
260	0	0	.9892400D+02	.1278000D+03	.00D+00	.00D+00
261	0	0	.9055700D+02	.1234150D+03	.00D+00	.00D+00
262	0	0	.8369950D+02	.1185150D+03	.00D+00	.00D+00
263	0	0	.7815600D+02	.1132550D+03	.00D+00	.00D+00
264	0	0	.7374600D+02	.1077150D+03	.00D+00	.00D+00
265	0	0	.7030750D+02	.1019450D+03	.00D+00	.00D+00
266	0	0	.6769800D+02	.9597450D+02	.00D+00	.00D+00
267	0	0	.6579050D+02	.8980800D+02	.00D+00	.00D+00
268	0	0	.6447150D+02	.8344250D+02	.00D+00	.00D+00
269	0	0	.6363900D+02	.7687000D+02	.00D+00	.00D+00
270	0	0	.6319900D+02	.7008000D+02	.00D+00	.00D+00
271	0	0	.6306600D+02	.6306600D+02	.00D+00	.00D+00
272	0	0	.6316050D+02	.5582500D+02	.00D+00	.00D+00
273	0	0	.6340900D+02	.4835900D+02	.00D+00	.00D+00
274	0	0	.6374500D+02	.4068000D+02	.00D+00	.00D+00
275	0	0	.6410850D+02	.3280550D+02	.00D+00	.00D+00
276	0	0	.6444800D+02	.2476300D+02	.00D+00	.00D+00
277	0	0	.6472150D+02	.1658700D+02	.00D+00	.00D+00
278	0	0	.6489800D+02	.8317250D+01	.00D+00	.00D+00
279	0	0	.6502000D+02	.0000000D+00	.00D+00	.00D+00
280	0	0	.2351750D+03	.0000000D+00	.00D+00	.00D+00
281	0	0	.2294850D+03	.2711500D+02	.00D+00	.00D+00
282	0	0	.2214050D+03	.5216800D+02	.00D+00	.00D+00
283	0	0	.2092650D+03	.7365300D+02	.00D+00	.00D+00
284	0	0	.1945500D+03	.9084150D+02	.00D+00	.00D+00
285	0	0	.1786950D+03	.1036850D+03	.00D+00	.00D+00
286	0	0	.1628500D+03	.1125850D+03	.00D+00	.00D+00
287	0	0	.1478100D+03	.1181500D+03	.00D+00	.00D+00
288	0	0	.1340600D+03	.1210350D+03	.00D+00	.00D+00
289	0	0	.1218300D+03	.1218300D+03	.00D+00	.00D+00
290	0	0	.1111850D+03	.1210350D+03	.00D+00	.00D+00
291	0	0	.1020890D+03	.1190400D+03	.00D+00	.00D+00
292	0	0	.9444350D+02	.1161600D+03	.00D+00	.00D+00
293	0	0	.8812350D+02	.1125950D+03	.00D+00	.00D+00
294	0	0	.8299250D+02	.1085050D+03	.00D+00	.00D+00
295	0	0	.7891500D+02	.1039800D+03	.00D+00	.00D+00
296	0	0	.7576250D+02	.9908950D+02	.00D+00	.00D+00
297	0	0	.7341550D+02	.9387300D+02	.00D+00	.00D+00
298	0	0	.7176200D+02	.8834800D+02	.00D+00	.00D+00
299	0	0	.7069750D+02	.8251900D+02	.00D+00	.00D+00
300	0	0	.7012350D+02	.7638650D+02	.00D+00	.00D+00
301	0	0	.6994700D+02	.6994700D+02	.00D+00	.00D+00
302	0	0	.7008000D+02	.6319900D+02	.00D+00	.00D+00
303	0	0	.7043700D+02	.5614400D+02	.00D+00	.00D+00
304	0	0	.7093800D+02	.4879000D+02	.00D+00	.00D+00
305	0	0	.7150800D+02	.4115500D+02	.00D+00	.00D+00
306	0	0	.7207850D+02	.3326450D+02	.00D+00	.00D+00
307	0	0	.7259000D+02	.2515500D+02	.00D+00	.00D+00
308	0	0	.7299250D+02	.1687150D+02	.00D+00	.00D+00
309	0	0	.7324950D+02	.8466600D+01	.00D+00	.00D+00
310	0	0	.7342650D+02	.0000000D+00	.00D+00	.00D+00
311	0	0	.2101000D+03	.0000000D+00	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

312	0	0	.2060200D+03	.2223200D+02	.00D+00	.00D+00
313	0	0	.2001650D+03	.4311950D+02	.00D+00	.00D+00
314	0	0	.1912100D+03	.6160450D+02	.00D+00	.00D+00
315	0	0	.1801050D+03	.7706950D+02	.00D+00	.00D+00
316	0	0	.1678200D+03	.8932250D+02	.00D+00	.00D+00
317	0	0	.1552150D+03	.9850100D+02	.00D+00	.00D+00
318	0	0	.1429450D+03	.1049275D+03	.00D+00	.00D+00
319	0	0	.1314600D+03	.1090150D+03	.00D+00	.00D+00
320	0	0	.1210350D+03	.1111850D+03	.00D+00	.00D+00
321	0	0	.1118000D+03	.1118000D+03	.00D+00	.00D+00
322	0	0	.1038000D+03	.1111800D+03	.00D+00	.00D+00
323	0	0	.9700800D+02	.1095900D+03	.00D+00	.00D+00
324	0	0	.9135950D+02	.1072050D+03	.00D+00	.00D+00
325	0	0	.8677450D+02	.1041800D+03	.00D+00	.00D+00
326	0	0	.8315750D+02	.1006095D+03	.00D+00	.00D+00
327	0	0	.8041150D+02	.9656150D+02	.00D+00	.00D+00
328	0	0	.7843950D+02	.9208150D+02	.00D+00	.00D+00
329	0	0	.7714450D+02	.8719100D+02	.00D+00	.00D+00
330	0	0	.7643200D+02	.8189900D+02	.00D+00	.00D+00
331	0	0	.7621000D+02	.7621000D+02	.00D+00	.00D+00
332	0	0	.7638650D+02	.7012350D+02	.00D+00	.00D+00
333	0	0	.7687000D+02	.6363900D+02	.00D+00	.00D+00
334	0	0	.7757000D+02	.5676100D+02	.00D+00	.00D+00
335	0	0	.7839850D+02	.4950250D+02	.00D+00	.00D+00
336	0	0	.7927100D+02	.4188500D+02	.00D+00	.00D+00
337	0	0	.8010850D+02	.3394300D+02	.00D+00	.00D+00
338	0	0	.8084100D+02	.2572100D+02	.00D+00	.00D+00
339	0	0	.8140950D+02	.1727650D+02	.00D+00	.00D+00
340	0	0	.8176950D+02	.8677850D+01	.00D+00	.00D+00
341	0	0	.8201650D+02	.0000000D+00	.00D+00	.00D+00
342	0	0	.1893600D+03	.0000000D+00	.00D+00	.00D+00
343	0	0	.1863600D+03	.1869450D+02	.00D+00	.00D+00
344	0	0	.1820300D+03	.3647300D+02	.00D+00	.00D+00
345	0	0	.1753150D+03	.5257700D+02	.00D+00	.00D+00
346	0	0	.1668350D+03	.6650800D+02	.00D+00	.00D+00
347	0	0	.1572700D+03	.7803550D+02	.00D+00	.00D+00
348	0	0	.1472500D+03	.8716150D+02	.00D+00	.00D+00
349	0	0	.1372950D+03	.9404350D+02	.00D+00	.00D+00
350	0	0	.1278000D+03	.9892400D+02	.00D+00	.00D+00
351	0	0	.1190400D+03	.1020890D+03	.00D+00	.00D+00
352	0	0	.1111800D+03	.1038000D+03	.00D+00	.00D+00
353	0	0	.1043000D+03	.1043000D+03	.00D+00	.00D+00
354	0	0	.9842250D+02	.1038000D+03	.00D+00	.00D+00
355	0	0	.9353300D+02	.1024550D+03	.00D+00	.00D+00
356	0	0	.8958850D+02	.1003970D+03	.00D+00	.00D+00
357	0	0	.8653000D+02	.9771300D+02	.00D+00	.00D+00
358	0	0	.8428800D+02	.9446800D+02	.00D+00	.00D+00
359	0	0	.8278600D+02	.9070100D+02	.00D+00	.00D+00
360	0	0	.8194350D+02	.8643450D+02	.00D+00	.00D+00
361	0	0	.8167700D+02	.8167700D+02	.00D+00	.00D+00
362	0	0	.8189900D+02	.7643200D+02	.00D+00	.00D+00
363	0	0	.8251900D+02	.7069750D+02	.00D+00	.00D+00
364	0	0	.8344250D+02	.6447150D+02	.00D+00	.00D+00
365	0	0	.8457300D+02	.5775900D+02	.00D+00	.00D+00
366	0	0	.8581350D+02	.5057350D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 367     0    0   .8706800D+02    .4294050D+02    .00D+00    .00D+00
 368     0    0   .8824350D+02    .3490100D+02    .00D+00    .00D+00
 369     0    0   .8925650D+02    .2650900D+02    .00D+00    .00D+00
 370     0    0   .9003600D+02    .1783600D+02    .00D+00    .00D+00
 371     0    0   .9052650D+02    .8968350D+01    .00D+00    .00D+00
 372     0    0   .9086150D+02    .0000000D+00    .00D+00    .00D+00
 373     0    0   .1717950D+03    .0000000D+00    .00D+00    .00D+00
 374     0    0   .1695450D+03    .1607350D+02    .00D+00    .00D+00
 375     0    0   .1662800D+03    .3149950D+02    .00D+00    .00D+00
 376     0    0   .1611750D+03    .4572400D+02    .00D+00    .00D+00
 377     0    0   .1546450D+03    .5834900D+02    .00D+00    .00D+00
 378     0    0   .1471650D+03    .6915150D+02    .00D+00    .00D+00
 379     0    0   .1392050D+03    .7806800D+02    .00D+00    .00D+00
 380     0    0   .1311800D+03    .8515750D+02    .00D+00    .00D+00
 381     0    0   .1234150D+03    .9055700D+02    .00D+00    .00D+00
 382     0    0   .1161600D+03    .9444350D+02    .00D+00    .00D+00
 383     0    0   .1095900D+03    .9700800D+02    .00D+00    .00D+00
 384     0    0   .1038000D+03    .9842250D+02    .00D+00    .00D+00
 385     0    0   .9885100D+02    .9885100D+02    .00D+00    .00D+00
 386     0    0   .9476100D+02    .9842100D+02    .00D+00    .00D+00
 387     0    0   .9151650D+02    .9724000D+02    .00D+00    .00D+00
 388     0    0   .8908650D+02    .9538050D+02    .00D+00    .00D+00
 389     0    0   .8742400D+02    .9289600D+02    .00D+00    .00D+00
 390     0    0   .8647300D+02    .8981950D+02    .00D+00    .00D+00
 391     0    0   .8616800D+02    .8616800D+02    .00D+00    .00D+00
 392     0    0   .8643450D+02    .8194350D+02    .00D+00    .00D+00
 393     0    0   .8719100D+02    .7714450D+02    .00D+00    .00D+00
 394     0    0   .8834800D+02    .7176200D+02    .00D+00    .00D+00
 395     0    0   .8980800D+02    .6579050D+02    .00D+00    .00D+00
 396     0    0   .9146700D+02    .5923000D+02    .00D+00    .00D+00
 397     0    0   .9321600D+02    .5209250D+02    .00D+00    .00D+00
 398     0    0   .9494350D+02    .4440400D+02    .00D+00    .00D+00
 399     0    0   .9654050D+02    .3621050D+02    .00D+00    .00D+00
 400     0    0   .9790550D+02    .2757700D+02    .00D+00    .00D+00
 401     0    0   .9895000D+02    .1859150D+02    .00D+00    .00D+00
 402     0    0   .9960550D+02    .9359300D+01    .00D+00    .00D+00
 403     0    0   .1000525D+03    .0000000D+00    .00D+00    .00D+00
 404     0    0   .1565750D+03    .0000000D+00    .00D+00    .00D+00
 405     0    0   .1548650D+03    .1409900D+02    .00D+00    .00D+00
 406     0    0   .1523800D+03    .2772700D+02    .00D+00    .00D+00
 407     0    0   .1484650D+03    .4047050D+02    .00D+00    .00D+00
 408     0    0   .1434050D+03    .5201300D+02    .00D+00    .00D+00
 409     0    0   .1375450D+03    .6215350D+02    .00D+00    .00D+00
 410     0    0   .1312400D+03    .7080200D+02    .00D+00    .00D+00
 411     0    0   .1248050D+03    .7796150D+02    .00D+00    .00D+00
 412     0    0   .1185150D+03    .8369950D+02    .00D+00    .00D+00
 413     0    0   .1125950D+03    .8812350D+02    .00D+00    .00D+00
 414     0    0   .1072050D+03    .9135950D+02    .00D+00    .00D+00
 415     0    0   .1024550D+03    .9353300D+02    .00D+00    .00D+00
 416     0    0   .9842100D+02    .9476100D+02    .00D+00    .00D+00
 417     0    0   .9514400D+02    .9514400D+02    .00D+00    .00D+00
 418     0    0   .9263100D+02    .9476100D+02    .00D+00    .00D+00
 419     0    0   .9087450D+02    .9367250D+02    .00D+00    .00D+00
 420     0    0   .8984850D+02    .9191600D+02    .00D+00    .00D+00
 421     0    0   .8951400D+02    .8951400D+02    .00D+00    .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

422	0	0	.8981950D+02	.8647300D+02	.00D+00	.00D+00
423	0	0	.9070100D+02	.8278600D+02	.00D+00	.00D+00
424	0	0	.9208150D+02	.7843950D+02	.00D+00	.00D+00
425	0	0	.9387300D+02	.7341550D+02	.00D+00	.00D+00
426	0	0	.9597450D+02	.6769800D+02	.00D+00	.00D+00
427	0	0	.9827150D+02	.6127850D+02	.00D+00	.00D+00
428	0	0	.1006420D+03	.5416200D+02	.00D+00	.00D+00
429	0	0	.1029500D+03	.4637250D+02	.00D+00	.00D+00
430	0	0	.1050700D+03	.3795900D+02	.00D+00	.00D+00
431	0	0	.1068750D+03	.2899750D+02	.00D+00	.00D+00
432	0	0	.1082500D+03	.1959350D+02	.00D+00	.00D+00
433	0	0	.1091150D+03	.9877400D+01	.00D+00	.00D+00
434	0	0	.1097050D+03	.0000000D+00	.00D+00	.00D+00
435	0	0	.1431200D+03	.0000000D+00	.00D+00	.00D+00
436	0	0	.1418200D+03	.1259500D+02	.00D+00	.00D+00
437	0	0	.1399150D+03	.2483950D+02	.00D+00	.00D+00
438	0	0	.1368900D+03	.3641800D+02	.00D+00	.00D+00
439	0	0	.1329600D+03	.4707850D+02	.00D+00	.00D+00
440	0	0	.1283750D+03	.5664650D+02	.00D+00	.00D+00
441	0	0	.1234000D+03	.6502550D+02	.00D+00	.00D+00
442	0	0	.1182850D+03	.7218750D+02	.00D+00	.00D+00
443	0	0	.1132550D+03	.7815600D+02	.00D+00	.00D+00
444	0	0	.1085050D+03	.8299250D+02	.00D+00	.00D+00
445	0	0	.1041800D+03	.8677450D+02	.00D+00	.00D+00
446	0	0	.1003970D+03	.8958850D+02	.00D+00	.00D+00
447	0	0	.9724000D+02	.9151650D+02	.00D+00	.00D+00
448	0	0	.9476100D+02	.9263100D+02	.00D+00	.00D+00
449	0	0	.9298850D+02	.9298850D+02	.00D+00	.00D+00
450	0	0	.9193150D+02	.9263100D+02	.00D+00	.00D+00
451	0	0	.9158200D+02	.9158200D+02	.00D+00	.00D+00
452	0	0	.9191600D+02	.8984850D+02	.00D+00	.00D+00
453	0	0	.9289600D+02	.8742400D+02	.00D+00	.00D+00
454	0	0	.9446800D+02	.8428800D+02	.00D+00	.00D+00
455	0	0	.9656150D+02	.8041150D+02	.00D+00	.00D+00
456	0	0	.9908950D+02	.7576250D+02	.00D+00	.00D+00
457	0	0	.1019450D+03	.7030750D+02	.00D+00	.00D+00
458	0	0	.1050050D+03	.6402400D+02	.00D+00	.00D+00
459	0	0	.1081250D+03	.5690400D+02	.00D+00	.00D+00
460	0	0	.1111500D+03	.4896500D+02	.00D+00	.00D+00
461	0	0	.1139200D+03	.4025550D+02	.00D+00	.00D+00
462	0	0	.1162750D+03	.3086100D+02	.00D+00	.00D+00
463	0	0	.1180700D+03	.2090700D+02	.00D+00	.00D+00
464	0	0	.1191950D+03	.1055700D+02	.00D+00	.00D+00
465	0	0	.1199650D+03	.0000000D+00	.00D+00	.00D+00
466	0	0	.1310350D+03	.0000000D+00	.00D+00	.00D+00
467	0	0	.1300250D+03	.1144250D+02	.00D+00	.00D+00
468	0	0	.1285550D+03	.2261800D+02	.00D+00	.00D+00
469	0	0	.1262250D+03	.3328350D+02	.00D+00	.00D+00
470	0	0	.1231750D+03	.4323650D+02	.00D+00	.00D+00
471	0	0	.1195950D+03	.5232850D+02	.00D+00	.00D+00
472	0	0	.1156950D+03	.6046600D+02	.00D+00	.00D+00
473	0	0	.1116750D+03	.6760600D+02	.00D+00	.00D+00
474	0	0	.1077150D+03	.7374600D+02	.00D+00	.00D+00
475	0	0	.1039800D+03	.7891500D+02	.00D+00	.00D+00
476	0	0	.1006095D+03	.8315750D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

477	0	0	.9771300D+02	.8653000D+02	.00D+00	.00D+00
478	0	0	.9538050D+02	.8908650D+02	.00D+00	.00D+00
479	0	0	.9367250D+02	.9087450D+02	.00D+00	.00D+00
480	0	0	.9263100D+02	.9193150D+02	.00D+00	.00D+00
481	0	0	.9228100D+02	.9228100D+02	.00D+00	.00D+00
482	0	0	.9263100D+02	.9193150D+02	.00D+00	.00D+00
483	0	0	.9367250D+02	.9087450D+02	.00D+00	.00D+00
484	0	0	.9538050D+02	.8908650D+02	.00D+00	.00D+00
485	0	0	.9771300D+02	.8653000D+02	.00D+00	.00D+00
486	0	0	.1006095D+03	.8315750D+02	.00D+00	.00D+00
487	0	0	.1039800D+03	.7891500D+02	.00D+00	.00D+00
488	0	0	.1077150D+03	.7374600D+02	.00D+00	.00D+00
489	0	0	.1116750D+03	.6760600D+02	.00D+00	.00D+00
490	0	0	.1156950D+03	.6046600D+02	.00D+00	.00D+00
491	0	0	.1195950D+03	.5232850D+02	.00D+00	.00D+00
492	0	0	.1231750D+03	.4323650D+02	.00D+00	.00D+00
493	0	0	.1262250D+03	.3328350D+02	.00D+00	.00D+00
494	0	0	.1285550D+03	.2261800D+02	.00D+00	.00D+00
495	0	0	.1300250D+03	.1144250D+02	.00D+00	.00D+00
496	0	0	.1310350D+03	.0000000D+00	.00D+00	.00D+00
497	0	0	.1199650D+03	.0000000D+00	.00D+00	.00D+00
498	0	0	.1191950D+03	.1055700D+02	.00D+00	.00D+00
499	0	0	.1180700D+03	.2090700D+02	.00D+00	.00D+00
500	0	0	.1162750D+03	.3086100D+02	.00D+00	.00D+00
501	0	0	.1139200D+03	.4025550D+02	.00D+00	.00D+00
502	0	0	.1111500D+03	.4896500D+02	.00D+00	.00D+00
503	0	0	.1081250D+03	.5690400D+02	.00D+00	.00D+00
504	0	0	.1050050D+03	.6402400D+02	.00D+00	.00D+00
505	0	0	.1019450D+03	.7030750D+02	.00D+00	.00D+00
506	0	0	.9908950D+02	.7576250D+02	.00D+00	.00D+00
507	0	0	.9656150D+02	.8041150D+02	.00D+00	.00D+00
508	0	0	.9446800D+02	.8428800D+02	.00D+00	.00D+00
509	0	0	.9289600D+02	.8742400D+02	.00D+00	.00D+00
510	0	0	.9191600D+02	.8984850D+02	.00D+00	.00D+00
511	0	0	.9158200D+02	.9158200D+02	.00D+00	.00D+00
512	0	0	.9193150D+02	.9263100D+02	.00D+00	.00D+00
513	0	0	.9298850D+02	.9298850D+02	.00D+00	.00D+00
514	0	0	.9476100D+02	.9263100D+02	.00D+00	.00D+00
515	0	0	.9724000D+02	.9151650D+02	.00D+00	.00D+00
516	0	0	.1003970D+03	.8958850D+02	.00D+00	.00D+00
517	0	0	.1041800D+03	.8677450D+02	.00D+00	.00D+00
518	0	0	.1085050D+03	.8299250D+02	.00D+00	.00D+00
519	0	0	.1132550D+03	.7815600D+02	.00D+00	.00D+00
520	0	0	.1182850D+03	.7218750D+02	.00D+00	.00D+00
521	0	0	.1234000D+03	.6502550D+02	.00D+00	.00D+00
522	0	0	.1283750D+03	.5664650D+02	.00D+00	.00D+00
523	0	0	.1329600D+03	.4707850D+02	.00D+00	.00D+00
524	0	0	.1368900D+03	.3641800D+02	.00D+00	.00D+00
525	0	0	.1399150D+03	.2483950D+02	.00D+00	.00D+00
526	0	0	.1418200D+03	.1259500D+02	.00D+00	.00D+00
527	0	0	.1431200D+03	.0000000D+00	.00D+00	.00D+00
528	0	0	.1097050D+03	.0000000D+00	.00D+00	.00D+00
529	0	0	.1091150D+03	.9877400D+01	.00D+00	.00D+00
530	0	0	.1082500D+03	.1959350D+02	.00D+00	.00D+00
531	0	0	.1068750D+03	.2899750D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

532	0	0	.1050700D+03	.3795900D+02	.00D+00	.00D+00
533	0	0	.1029500D+03	.4637250D+02	.00D+00	.00D+00
534	0	0	.1006420D+03	.5416200D+02	.00D+00	.00D+00
535	0	0	.9827150D+02	.6127850D+02	.00D+00	.00D+00
536	0	0	.9597450D+02	.6769800D+02	.00D+00	.00D+00
537	0	0	.9387300D+02	.7341550D+02	.00D+00	.00D+00
538	0	0	.9208150D+02	.7843950D+02	.00D+00	.00D+00
539	0	0	.9070100D+02	.8278600D+02	.00D+00	.00D+00
540	0	0	.8981950D+02	.8647300D+02	.00D+00	.00D+00
541	0	0	.8951400D+02	.8951400D+02	.00D+00	.00D+00
542	0	0	.8984850D+02	.9191600D+02	.00D+00	.00D+00
543	0	0	.9087450D+02	.9367250D+02	.00D+00	.00D+00
544	0	0	.9263100D+02	.9476100D+02	.00D+00	.00D+00
545	0	0	.9514400D+02	.9514400D+02	.00D+00	.00D+00
546	0	0	.9842100D+02	.9476100D+02	.00D+00	.00D+00
547	0	0	.1024550D+03	.9353300D+02	.00D+00	.00D+00
548	0	0	.1072050D+03	.9135950D+02	.00D+00	.00D+00
549	0	0	.1125950D+03	.8812350D+02	.00D+00	.00D+00
550	0	0	.1185150D+03	.8369950D+02	.00D+00	.00D+00
551	0	0	.1248050D+03	.7796150D+02	.00D+00	.00D+00
552	0	0	.1312400D+03	.7080200D+02	.00D+00	.00D+00
553	0	0	.1375450D+03	.6215350D+02	.00D+00	.00D+00
554	0	0	.1434050D+03	.5201300D+02	.00D+00	.00D+00
555	0	0	.1484650D+03	.4047050D+02	.00D+00	.00D+00
556	0	0	.1523800D+03	.2772700D+02	.00D+00	.00D+00
557	0	0	.1548650D+03	.1409900D+02	.00D+00	.00D+00
558	0	0	.1565750D+03	.0000000D+00	.00D+00	.00D+00
559	0	0	.1000525D+03	.0000000D+00	.00D+00	.00D+00
560	0	0	.9960550D+02	.9359300D+01	.00D+00	.00D+00
561	0	0	.9895000D+02	.1859150D+02	.00D+00	.00D+00
562	0	0	.9790550D+02	.2757700D+02	.00D+00	.00D+00
563	0	0	.9654050D+02	.3621050D+02	.00D+00	.00D+00
564	0	0	.9494350D+02	.4440400D+02	.00D+00	.00D+00
565	0	0	.9321600D+02	.5209250D+02	.00D+00	.00D+00
566	0	0	.9146700D+02	.5923000D+02	.00D+00	.00D+00
567	0	0	.8980800D+02	.6579050D+02	.00D+00	.00D+00
568	0	0	.8834800D+02	.7176200D+02	.00D+00	.00D+00
569	0	0	.8719100D+02	.7714450D+02	.00D+00	.00D+00
570	0	0	.8643450D+02	.8194350D+02	.00D+00	.00D+00
571	0	0	.8616800D+02	.8616800D+02	.00D+00	.00D+00
572	0	0	.8647300D+02	.8981950D+02	.00D+00	.00D+00
573	0	0	.8742400D+02	.9289600D+02	.00D+00	.00D+00
574	0	0	.8908650D+02	.9538050D+02	.00D+00	.00D+00
575	0	0	.9151650D+02	.9724000D+02	.00D+00	.00D+00
576	0	0	.9476100D+02	.9842100D+02	.00D+00	.00D+00
577	0	0	.9885100D+02	.9885100D+02	.00D+00	.00D+00
578	0	0	.1038000D+03	.9842250D+02	.00D+00	.00D+00
579	0	0	.1095900D+03	.9700800D+02	.00D+00	.00D+00
580	0	0	.1161600D+03	.9444350D+02	.00D+00	.00D+00
581	0	0	.1234150D+03	.9055700D+02	.00D+00	.00D+00
582	0	0	.1311800D+03	.8515750D+02	.00D+00	.00D+00
583	0	0	.1392050D+03	.7806800D+02	.00D+00	.00D+00
584	0	0	.1471650D+03	.6915150D+02	.00D+00	.00D+00
585	0	0	.1546450D+03	.5834900D+02	.00D+00	.00D+00
586	0	0	.1611750D+03	.4572400D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

```
587    0    0    .1662800D+03    .3149950D+02    .00D+00    .00D+00
588    0    0    .1695450D+03    .1607350D+02    .00D+00    .00D+00
589    0    0    .1717950D+03    .0000000D+00    .00D+00    .00D+00
590    0    0    .9086150D+02    .0000000D+00    .00D+00    .00D+00
591    0    0    .9052650D+02    .8968350D+01    .00D+00    .00D+00
592    0    0    .9003600D+02    .1783600D+02    .00D+00    .00D+00
593    0    0    .8925650D+02    .2650900D+02    .00D+00    .00D+00
594    0    0    .8824350D+02    .3490100D+02    .00D+00    .00D+00
595    0    0    .8706800D+02    .4294050D+02    .00D+00    .00D+00
596    0    0    .8581350D+02    .5057350D+02    .00D+00    .00D+00
597    0    0    .8457300D+02    .5775900D+02    .00D+00    .00D+00
598    0    0    .8344250D+02    .6447150D+02    .00D+00    .00D+00
599    0    0    .8251900D+02    .7069750D+02    .00D+00    .00D+00
600    0    0    .8189900D+02    .7643200D+02    .00D+00    .00D+00
601    0    0    .8167700D+02    .8167700D+02    .00D+00    .00D+00
602    0    0    .8194350D+02    .8643450D+02    .00D+00    .00D+00
603    0    0    .8278600D+02    .9070100D+02    .00D+00    .00D+00
604    0    0    .8428800D+02    .9446800D+02    .00D+00    .00D+00
605    0    0    .8653000D+02    .9771300D+02    .00D+00    .00D+00
606    0    0    .8958850D+02    .1003970D+03    .00D+00    .00D+00
607    0    0    .9353300D+02    .1024550D+03    .00D+00    .00D+00
608    0    0    .9842250D+02    .1038000D+03    .00D+00    .00D+00
609    0    0    .1043000D+03    .1043000D+03    .00D+00    .00D+00
610    0    0    .1111800D+03    .1038000D+03    .00D+00    .00D+00
611    0    0    .1190400D+03    .1020890D+03    .00D+00    .00D+00
612    0    0    .1278000D+03    .9892400D+02    .00D+00    .00D+00
613    0    0    .1372950D+03    .9404350D+02    .00D+00    .00D+00
614    0    0    .1472500D+03    .8716150D+02    .00D+00    .00D+00
615    0    0    .1572700D+03    .7803550D+02    .00D+00    .00D+00
616    0    0    .1668350D+03    .6650800D+02    .00D+00    .00D+00
617    0    0    .1753150D+03    .5257700D+02    .00D+00    .00D+00
618    0    0    .1820300D+03    .3647300D+02    .00D+00    .00D+00
619    0    0    .1863600D+03    .1869450D+02    .00D+00    .00D+00
620    0    0    .1893600D+03    .0000000D+00    .00D+00    .00D+00
621    0    0    .8201650D+02    .0000000D+00    .00D+00    .00D+00
622    0    0    .8176950D+02    .8677850D+01    .00D+00    .00D+00
623    0    0    .8140950D+02    .1727650D+02    .00D+00    .00D+00
624    0    0    .8084100D+02    .2572100D+02    .00D+00    .00D+00
625    0    0    .8010850D+02    .3394300D+02    .00D+00    .00D+00
626    0    0    .7927100D+02    .4188500D+02    .00D+00    .00D+00
627    0    0    .7839850D+02    .4950250D+02    .00D+00    .00D+00
628    0    0    .7757000D+02    .5676100D+02    .00D+00    .00D+00
629    0    0    .7687000D+02    .6363900D+02    .00D+00    .00D+00
630    0    0    .7638650D+02    .7012350D+02    .00D+00    .00D+00
631    0    0    .7621000D+02    .7621000D+02    .00D+00    .00D+00
632    0    0    .7643200D+02    .8189900D+02    .00D+00    .00D+00
633    0    0    .7714450D+02    .8719100D+02    .00D+00    .00D+00
634    0    0    .7843950D+02    .9208150D+02    .00D+00    .00D+00
635    0    0    .8041150D+02    .9656150D+02    .00D+00    .00D+00
636    0    0    .8315750D+02    .1006095D+03    .00D+00    .00D+00
637    0    0    .8677450D+02    .1041800D+03    .00D+00    .00D+00
638    0    0    .9135950D+02    .1072050D+03    .00D+00    .00D+00
639    0    0    .9700800D+02    .1095900D+03    .00D+00    .00D+00
640    0    0    .1038000D+03    .1111800D+03    .00D+00    .00D+00
641    0    0    .1118000D+03    .1118000D+03    .00D+00    .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

642	0	0	.1210350D+03	.1111850D+03	.00D+00	.00D+00
643	0	0	.1314600D+03	.1090150D+03	.00D+00	.00D+00
644	0	0	.1429450D+03	.1049275D+03	.00D+00	.00D+00
645	0	0	.1552150D+03	.9850100D+02	.00D+00	.00D+00
646	0	0	.1678200D+03	.8932250D+02	.00D+00	.00D+00
647	0	0	.1801050D+03	.7706950D+02	.00D+00	.00D+00
648	0	0	.1912100D+03	.6160450D+02	.00D+00	.00D+00
649	0	0	.2001650D+03	.4311950D+02	.00D+00	.00D+00
650	0	0	.2060200D+03	.2223200D+02	.00D+00	.00D+00
651	0	0	.2101000D+03	.0000000D+00	.00D+00	.00D+00
652	0	0	.7342650D+02	.0000000D+00	.00D+00	.00D+00
653	0	0	.7324950D+02	.8466600D+01	.00D+00	.00D+00
654	0	0	.7299250D+02	.1687150D+02	.00D+00	.00D+00
655	0	0	.7259000D+02	.2515500D+02	.00D+00	.00D+00
656	0	0	.7207850D+02	.3326450D+02	.00D+00	.00D+00
657	0	0	.7150800D+02	.4115500D+02	.00D+00	.00D+00
658	0	0	.7093800D+02	.4879000D+02	.00D+00	.00D+00
659	0	0	.7043700D+02	.5614400D+02	.00D+00	.00D+00
660	0	0	.7008000D+02	.6319900D+02	.00D+00	.00D+00
661	0	0	.6994700D+02	.6994700D+02	.00D+00	.00D+00
662	0	0	.7012350D+02	.7638650D+02	.00D+00	.00D+00
663	0	0	.7069750D+02	.8251900D+02	.00D+00	.00D+00
664	0	0	.7176200D+02	.8834800D+02	.00D+00	.00D+00
665	0	0	.7341550D+02	.9387300D+02	.00D+00	.00D+00
666	0	0	.7576250D+02	.9908950D+02	.00D+00	.00D+00
667	0	0	.7891500D+02	.1039800D+03	.00D+00	.00D+00
668	0	0	.8299250D+02	.1085050D+03	.00D+00	.00D+00
669	0	0	.8812350D+02	.1125950D+03	.00D+00	.00D+00
670	0	0	.9444350D+02	.1161600D+03	.00D+00	.00D+00
671	0	0	.1020890D+03	.1190400D+03	.00D+00	.00D+00
672	0	0	.1111850D+03	.1210350D+03	.00D+00	.00D+00
673	0	0	.1218300D+03	.1218300D+03	.00D+00	.00D+00
674	0	0	.1340600D+03	.1210350D+03	.00D+00	.00D+00
675	0	0	.1478100D+03	.1181500D+03	.00D+00	.00D+00
676	0	0	.1628500D+03	.1125850D+03	.00D+00	.00D+00
677	0	0	.1786950D+03	.1036850D+03	.00D+00	.00D+00
678	0	0	.1945500D+03	.9084150D+02	.00D+00	.00D+00
679	0	0	.2092650D+03	.7365300D+02	.00D+00	.00D+00
680	0	0	.2214050D+03	.5216800D+02	.00D+00	.00D+00
681	0	0	.2294850D+03	.2711500D+02	.00D+00	.00D+00
682	0	0	.2351750D+03	.0000000D+00	.00D+00	.00D+00
683	0	0	.6502000D+02	.0000000D+00	.00D+00	.00D+00
684	0	0	.6489800D+02	.8317250D+01	.00D+00	.00D+00
685	0	0	.6472150D+02	.1658700D+02	.00D+00	.00D+00
686	0	0	.6444800D+02	.2476300D+02	.00D+00	.00D+00
687	0	0	.6410850D+02	.3280550D+02	.00D+00	.00D+00
688	0	0	.6374500D+02	.4068000D+02	.00D+00	.00D+00
689	0	0	.6340900D+02	.4835900D+02	.00D+00	.00D+00
690	0	0	.6316050D+02	.5582500D+02	.00D+00	.00D+00
691	0	0	.6306600D+02	.6306600D+02	.00D+00	.00D+00
692	0	0	.6319900D+02	.7008000D+02	.00D+00	.00D+00
693	0	0	.6363900D+02	.7687000D+02	.00D+00	.00D+00
694	0	0	.6447150D+02	.8344250D+02	.00D+00	.00D+00
695	0	0	.6579050D+02	.8980800D+02	.00D+00	.00D+00
696	0	0	.6769800D+02	.9597450D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

697	0	0	.7030750D+02	.1019450D+03	.00D+00	.00D+00
698	0	0	.7374600D+02	.1077150D+03	.00D+00	.00D+00
699	0	0	.7815600D+02	.1132550D+03	.00D+00	.00D+00
700	0	0	.8369950D+02	.1185150D+03	.00D+00	.00D+00
701	0	0	.9055700D+02	.1234150D+03	.00D+00	.00D+00
702	0	0	.9892400D+02	.1278000D+03	.00D+00	.00D+00
703	0	0	.1090150D+03	.1314600D+03	.00D+00	.00D+00
704	0	0	.1210350D+03	.1340600D+03	.00D+00	.00D+00
705	0	0	.1351350D+03	.1351350D+03	.00D+00	.00D+00
706	0	0	.1513900D+03	.1340550D+03	.00D+00	.00D+00
707	0	0	.1696800D+03	.1300050D+03	.00D+00	.00D+00
708	0	0	.1895650D+03	.1219900D+03	.00D+00	.00D+00
709	0	0	.2101350D+03	.1089590D+03	.00D+00	.00D+00
710	0	0	.2298800D+03	.8999850D+02	.00D+00	.00D+00
711	0	0	.2467000D+03	.6478500D+02	.00D+00	.00D+00
712	0	0	.2581850D+03	.3405950D+02	.00D+00	.00D+00
713	0	0	.2663950D+03	.0000000D+00	.00D+00	.00D+00
714	0	0	.5674350D+02	.0000000D+00	.00D+00	.00D+00
715	0	0	.5666250D+02	.8215650D+01	.00D+00	.00D+00
716	0	0	.5654650D+02	.1639550D+02	.00D+00	.00D+00
717	0	0	.5637100D+02	.2450500D+02	.00D+00	.00D+00
718	0	0	.5616200D+02	.3251500D+02	.00D+00	.00D+00
719	0	0	.5595450D+02	.4040000D+02	.00D+00	.00D+00
720	0	0	.5579300D+02	.4814200D+02	.00D+00	.00D+00
721	0	0	.5573000D+02	.5573000D+02	.00D+00	.00D+00
722	0	0	.5582500D+02	.6316050D+02	.00D+00	.00D+00
723	0	0	.5614400D+02	.7043700D+02	.00D+00	.00D+00
724	0	0	.5676100D+02	.7757000D+02	.00D+00	.00D+00
725	0	0	.5775900D+02	.8457300D+02	.00D+00	.00D+00
726	0	0	.5923000D+02	.9146700D+02	.00D+00	.00D+00
727	0	0	.6127850D+02	.9827150D+02	.00D+00	.00D+00
728	0	0	.6402400D+02	.1050050D+03	.00D+00	.00D+00
729	0	0	.6760600D+02	.1116750D+03	.00D+00	.00D+00
730	0	0	.7218750D+02	.1182850D+03	.00D+00	.00D+00
731	0	0	.7796150D+02	.1248050D+03	.00D+00	.00D+00
732	0	0	.8515750D+02	.1311800D+03	.00D+00	.00D+00
733	0	0	.9404350D+02	.1372950D+03	.00D+00	.00D+00
734	0	0	.1049275D+03	.1429450D+03	.00D+00	.00D+00
735	0	0	.1181500D+03	.1478100D+03	.00D+00	.00D+00
736	0	0	.1340550D+03	.1513900D+03	.00D+00	.00D+00
737	0	0	.1529350D+03	.1529350D+03	.00D+00	.00D+00
738	0	0	.1749150D+03	.1513900D+03	.00D+00	.00D+00
739	0	0	.1997500D+03	.1453200D+03	.00D+00	.00D+00
740	0	0	.2265450D+03	.1329950D+03	.00D+00	.00D+00
741	0	0	.2534300D+03	.1125990D+03	.00D+00	.00D+00
742	0	0	.2773400D+03	.8291450D+02	.00D+00	.00D+00
743	0	0	.2942700D+03	.4433700D+02	.00D+00	.00D+00
744	0	0	.3066300D+03	.0000000D+00	.00D+00	.00D+00
745	0	0	.4855300D+02	.0000000D+00	.00D+00	.00D+00
746	0	0	.4850300D+02	.8150000D+01	.00D+00	.00D+00
747	0	0	.4843200D+02	.1627400D+02	.00D+00	.00D+00
748	0	0	.4832800D+02	.2434750D+02	.00D+00	.00D+00
749	0	0	.4821350D+02	.3234900D+02	.00D+00	.00D+00
750	0	0	.4811800D+02	.4026350D+02	.00D+00	.00D+00
751	0	0	.4807900D+02	.4807900D+02	.00D+00	.00D+00

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 752    0    0   .4814200D+02   .5579300D+02   .00D+00    .00D+00
 753    0    0   .4835900D+02   .6340900D+02   .00D+00    .00D+00
 754    0    0   .4879000D+02   .7093800D+02   .00D+00    .00D+00
 755    0    0   .4950250D+02   .7839850D+02   .00D+00    .00D+00
 756    0    0   .5057350D+02   .8581350D+02   .00D+00    .00D+00
 757    0    0   .5209250D+02   .9321600D+02   .00D+00    .00D+00
 758    0    0   .5416200D+02   .1006420D+03   .00D+00    .00D+00
 759    0    0   .5690400D+02   .1081250D+03   .00D+00    .00D+00
 760    0    0   .6046600D+02   .1156950D+03   .00D+00    .00D+00
 761    0    0   .6502550D+02   .1234000D+03   .00D+00    .00D+00
 762    0    0   .7080200D+02   .1312400D+03   .00D+00    .00D+00
 763    0    0   .7806800D+02   .1392050D+03   .00D+00    .00D+00
 764    0    0   .8716150D+02   .1472500D+03   .00D+00    .00D+00
 765    0    0   .9850100D+02   .1552150D+03   .00D+00    .00D+00
 766    0    0   .1125850D+03   .1628500D+03   .00D+00    .00D+00
 767    0    0   .1300050D+03   .1696800D+03   .00D+00    .00D+00
 768    0    0   .1513900D+03   .1749150D+03   .00D+00    .00D+00
 769    0    0   .1772950D+03   .1772950D+03   .00D+00    .00D+00
 770    0    0   .2079650D+03   .1749150D+03   .00D+00    .00D+00
 771    0    0   .2428600D+03   .1650900D+03   .00D+00    .00D+00
 772    0    0   .2799600D+03   .1444950D+03   .00D+00    .00D+00
 773    0    0   .3149650D+03   .1099365D+03   .00D+00    .00D+00
 774    0    0   .3411000D+03   .6037350D+02   .00D+00    .00D+00
 775    0    0   .3608200D+03   .0000000D+00   .00D+00    .00D+00
 776    0    0   .4041700D+02   .0000000D+00   .00D+00    .00D+00
 777    0    0   .4038900D+02   .8110450D+01   .00D+00    .00D+00
 778    0    0   .4034950D+02   .1620300D+02   .00D+00    .00D+00
 779    0    0   .4029550D+02   .2426100D+02   .00D+00    .00D+00
 780    0    0   .4024600D+02   .3227100D+02   .00D+00    .00D+00
 781    0    0   .4022500D+02   .4022500D+02   .00D+00    .00D+00
 782    0    0   .4026350D+02   .4811800D+02   .00D+00    .00D+00
 783    0    0   .4040000D+02   .5595450D+02   .00D+00    .00D+00
 784    0    0   .4068000D+02   .6374500D+02   .00D+00    .00D+00
 785    0    0   .4115500D+02   .7150800D+02   .00D+00    .00D+00
 786    0    0   .4188500D+02   .7927100D+02   .00D+00    .00D+00
 787    0    0   .4294050D+02   .8706800D+02   .00D+00    .00D+00
 788    0    0   .4440400D+02   .9494350D+02   .00D+00    .00D+00
 789    0    0   .4637250D+02   .1029500D+03   .00D+00    .00D+00
 790    0    0   .4896500D+02   .1111500D+03   .00D+00    .00D+00
 791    0    0   .5232850D+02   .1195950D+03   .00D+00    .00D+00
 792    0    0   .5664650D+02   .1283750D+03   .00D+00    .00D+00
 793    0    0   .6215350D+02   .1375450D+03   .00D+00    .00D+00
 794    0    0   .6915150D+02   .1471650D+03   .00D+00    .00D+00
 795    0    0   .7803550D+02   .1572700D+03   .00D+00    .00D+00
 796    0    0   .8932250D+02   .1678200D+03   .00D+00    .00D+00
 797    0    0   .1036850D+03   .1786950D+03   .00D+00    .00D+00
 798    0    0   .1219900D+03   .1895650D+03   .00D+00    .00D+00
 799    0    0   .1453200D+03   .1997500D+03   .00D+00    .00D+00
 800    0    0   .1749150D+03   .2079650D+03   .00D+00    .00D+00
 801    0    0   .2119500D+03   .2119500D+03   .00D+00    .00D+00
 802    0    0   .2569650D+03   .2079600D+03   .00D+00    .00D+00
 803    0    0   .3085900D+03   .1903500D+03   .00D+00    .00D+00
 804    0    0   .3614650D+03   .1519650D+03   .00D+00    .00D+00
 805    0    0   .4042050D+03   .8722150D+02   .00D+00    .00D+00
 806    0    0   .4381750D+03   .0000000D+00   .00D+00    .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
  807    0    0   .3231400D+02    .0000000D+00    .00D+00    .00D+00
  808    0    0   .3230000D+02    .8088950D+01    .00D+00    .00D+00
  809    0    0   .3228150D+02    .1616650D+02    .00D+00    .00D+00
  810    0    0   .3226000D+02    .2422200D+02    .00D+00    .00D+00
  811    0    0   .3225000D+02    .3225000D+02    .00D+00    .00D+00
  812    0    0   .3227100D+02    .4024600D+02    .00D+00    .00D+00
  813    0    0   .3234900D+02    .4821350D+02    .00D+00    .00D+00
  814    0    0   .3251500D+02    .5616200D+02    .00D+00    .00D+00
  815    0    0   .3280550D+02    .6410850D+02    .00D+00    .00D+00
  816    0    0   .3326450D+02    .7207850D+02    .00D+00    .00D+00
  817    0    0   .3394300D+02    .8010850D+02    .00D+00    .00D+00
  818    0    0   .3490100D+02    .8824350D+02    .00D+00    .00D+00
  819    0    0   .3621050D+02    .9654050D+02    .00D+00    .00D+00
  820    0    0   .3795900D+02    .1050700D+03    .00D+00    .00D+00
  821    0    0   .4025550D+02    .1139200D+03    .00D+00    .00D+00
  822    0    0   .4323650D+02    .1231750D+03    .00D+00    .00D+00
  823    0    0   .4707850D+02    .1329600D+03    .00D+00    .00D+00
  824    0    0   .5201300D+02    .1434050D+03    .00D+00    .00D+00
  825    0    0   .5834900D+02    .1546450D+03    .00D+00    .00D+00
  826    0    0   .6650800D+02    .1668350D+03    .00D+00    .00D+00
  827    0    0   .7706950D+02    .1801050D+03    .00D+00    .00D+00
  828    0    0   .9084150D+02    .1945500D+03    .00D+00    .00D+00
  829    0    0   .1089590D+03    .2101350D+03    .00D+00    .00D+00
  830    0    0   .1329950D+03    .2265450D+03    .00D+00    .00D+00
  831    0    0   .1650900D+03    .2428600D+03    .00D+00    .00D+00
  832    0    0   .2079600D+03    .2569650D+03    .00D+00    .00D+00
  833    0    0   .2644600D+03    .2644600D+03    .00D+00    .00D+00
  834    0    0   .3359600D+03    .2569650D+03    .00D+00    .00D+00
  835    0    0   .4180950D+03    .2203600D+03    .00D+00    .00D+00
  836    0    0   .4930650D+03    .1365450D+03    .00D+00    .00D+00
  837    0    0   .5577350D+03    .0000000D+00    .00D+00    .00D+00
  838    0    0   .2422750D+02    .0000000D+00    .00D+00    .00D+00
  839    0    0   .2422250D+02    .8078950D+01    .00D+00    .00D+00
  840    0    0   .2421600D+02    .1615150D+02    .00D+00    .00D+00
  841    0    0   .2421200D+02    .2421200D+02    .00D+00    .00D+00
  842    0    0   .2422200D+02    .3226000D+02    .00D+00    .00D+00
  843    0    0   .2426100D+02    .4029550D+02    .00D+00    .00D+00
  844    0    0   .2434750D+02    .4832800D+02    .00D+00    .00D+00
  845    0    0   .2450500D+02    .5637100D+02    .00D+00    .00D+00
  846    0    0   .2476300D+02    .6444800D+02    .00D+00    .00D+00
  847    0    0   .2515500D+02    .7259000D+02    .00D+00    .00D+00
  848    0    0   .2572100D+02    .8084100D+02    .00D+00    .00D+00
  849    0    0   .2650900D+02    .8925650D+02    .00D+00    .00D+00
  850    0    0   .2757700D+02    .9790550D+02    .00D+00    .00D+00
  851    0    0   .2899750D+02    .1068750D+03    .00D+00    .00D+00
  852    0    0   .3086100D+02    .1162750D+03    .00D+00    .00D+00
  853    0    0   .3328350D+02    .1262250D+03    .00D+00    .00D+00
  854    0    0   .3641800D+02    .1368900D+03    .00D+00    .00D+00
  855    0    0   .4047050D+02    .1484650D+03    .00D+00    .00D+00
  856    0    0   .4572400D+02    .1611750D+03    .00D+00    .00D+00
  857    0    0   .5257700D+02    .1753150D+03    .00D+00    .00D+00
  858    0    0   .6160450D+02    .1912100D+03    .00D+00    .00D+00
  859    0    0   .7365300D+02    .2092650D+03    .00D+00    .00D+00
  860    0    0   .8999850D+02    .2298800D+03    .00D+00    .00D+00
  861    0    0   .1125990D+03    .2534300D+03    .00D+00    .00D+00
```

Table 6.12 Input Data Sets for Problem 7 (continued)

862	0	0	.1444950D+03	.2799600D+03	.00D+00	.00D+00
863	0	0	.1903500D+03	.3085900D+03	.00D+00	.00D+00
864	0	0	.2569650D+03	.3359600D+03	.00D+00	.00D+00
865	0	0	.3526900D+03	.3526900D+03	.00D+00	.00D+00
866	0	0	.4818850D+03	.3359600D+03	.00D+00	.00D+00
867	0	0	.6245650D+03	.2385950D+03	.00D+00	.00D+00
868	0	0	.7639950D+03	.0000000D+00	.00D+00	.00D+00
869	0	0	.1614950D+02	.0000000D+00	.00D+00	.00D+00
870	0	0	.1614850D+02	.8075350D+01	.00D+00	.00D+00
871	0	0	.1614800D+02	.1614800D+02	.00D+00	.00D+00
872	0	0	.1615150D+02	.2421600D+02	.00D+00	.00D+00
873	0	0	.1616650D+02	.3228150D+02	.00D+00	.00D+00
874	0	0	.1620300D+02	.4034950D+02	.00D+00	.00D+00
875	0	0	.1627400D+02	.4843200D+02	.00D+00	.00D+00
876	0	0	.1639550D+02	.5654650D+02	.00D+00	.00D+00
877	0	0	.1658700D+02	.6472150D+02	.00D+00	.00D+00
878	0	0	.1687150D+02	.7299250D+02	.00D+00	.00D+00
879	0	0	.1727650D+02	.8140950D+02	.00D+00	.00D+00
880	0	0	.1783600D+02	.9003600D+02	.00D+00	.00D+00
881	0	0	.1859150D+02	.9895000D+02	.00D+00	.00D+00
882	0	0	.1959350D+02	.1082500D+03	.00D+00	.00D+00
883	0	0	.2090700D+02	.1180700D+03	.00D+00	.00D+00
884	0	0	.2261800D+02	.1285550D+03	.00D+00	.00D+00
885	0	0	.2483950D+02	.1399150D+03	.00D+00	.00D+00
886	0	0	.2772700D+02	.1523800D+03	.00D+00	.00D+00
887	0	0	.3149950D+02	.1662800D+03	.00D+00	.00D+00
888	0	0	.3647300D+02	.1820300D+03	.00D+00	.00D+00
889	0	0	.4311950D+02	.2001650D+03	.00D+00	.00D+00
890	0	0	.5216800D+02	.2214050D+03	.00D+00	.00D+00
891	0	0	.6478500D+02	.2467000D+03	.00D+00	.00D+00
892	0	0	.8291450D+02	.2773400D+03	.00D+00	.00D+00
893	0	0	.1099365D+03	.3149650D+03	.00D+00	.00D+00
894	0	0	.1519650D+03	.3614650D+03	.00D+00	.00D+00
895	0	0	.2203600D+03	.4180950D+03	.00D+00	.00D+00
896	0	0	.3359600D+03	.4818850D+03	.00D+00	.00D+00
897	0	0	.5321850D+03	.5321850D+03	.00D+00	.00D+00
898	0	0	.8290250D+03	.4818800D+03	.00D+00	.00D+00
899	0	0	.1176175D+04	.0000000D+00	.00D+00	.00D+00
900	0	0	.8074600D+01	.0000000D+00	.00D+00	.00D+00
901	0	0	.8074600D+01	.8074600D+01	.00D+00	.00D+00
902	0	0	.8075350D+01	.1614850D+02	.00D+00	.00D+00
903	0	0	.8078950D+01	.2422250D+02	.00D+00	.00D+00
904	0	0	.8088950D+01	.3230000D+02	.00D+00	.00D+00
905	0	0	.8110450D+01	.4038900D+02	.00D+00	.00D+00
906	0	0	.8150000D+01	.4850300D+02	.00D+00	.00D+00
907	0	0	.8215650D+01	.5666250D+02	.00D+00	.00D+00
908	0	0	.8317250D+01	.6489800D+02	.00D+00	.00D+00
909	0	0	.8466600D+01	.7324950D+02	.00D+00	.00D+00
910	0	0	.8677850D+01	.8176950D+02	.00D+00	.00D+00
911	0	0	.8968350D+01	.9052650D+02	.00D+00	.00D+00
912	0	0	.9359300D+01	.9960550D+02	.00D+00	.00D+00
913	0	0	.9877400D+01	.1091150D+03	.00D+00	.00D+00
914	0	0	.1055700D+02	.1191950D+03	.00D+00	.00D+00
915	0	0	.1144250D+02	.1300250D+03	.00D+00	.00D+00
916	0	0	.1259500D+02	.1418200D+03	.00D+00	.00D+00

Table 6.12   Input Data Sets for Problem 7 (continued)

```
  917    0    0   .1409900D+02   .1548650D+03   .00D+00   .00D+00
  918    0    0   .1607350D+02   .1695450D+03   .00D+00   .00D+00
  919    0    0   .1869450D+02   .1863600D+03   .00D+00   .00D+00
  920    0    0   .2223200D+02   .2060200D+03   .00D+00   .00D+00
  921    0    0   .2711500D+02   .2294850D+03   .00D+00   .00D+00
  922    0    0   .3405950D+02   .2581850D+03   .00D+00   .00D+00
  923    0    0   .4433700D+02   .2942700D+03   .00D+00   .00D+00
  924    0    0   .6037350D+02   .3411000D+03   .00D+00   .00D+00
  925    0    0   .8722150D+02   .4042050D+03   .00D+00   .00D+00
  926    0    0   .1365450D+03   .4930650D+03   .00D+00   .00D+00
  927    0    0   .2385950D+03   .6245650D+03   .00D+00   .00D+00
  928    0    0   .4818800D+03   .8290250D+03   .00D+00   .00D+00
  929    0    0   .1156725D+04   .1156725D+04   .00D+00   .00D+00
  930    0    0   .2159275D+04   .0000000D+00   .00D+00   .00D+00
  931    0    0   .0000000D+00   .0000000D+00   .00D+00   .00D+00
  932    0    0   .0000000D+00   .8074600D+01   .00D+00   .00D+00
  933    0    0   .0000000D+00   .1614950D+02   .00D+00   .00D+00
  934    0    0   .0000000D+00   .2422750D+02   .00D+00   .00D+00
  935    0    0   .0000000D+00   .3231400D+02   .00D+00   .00D+00
  936    0    0   .0000000D+00   .4041700D+02   .00D+00   .00D+00
  937    0    0   .0000000D+00   .4855300D+02   .00D+00   .00D+00
  938    0    0   .0000000D+00   .5674350D+02   .00D+00   .00D+00
  939    0    0   .0000000D+00   .6502000D+02   .00D+00   .00D+00
  940    0    0   .0000000D+00   .7342650D+02   .00D+00   .00D+00
  941    0    0   .0000000D+00   .8201650D+02   .00D+00   .00D+00
  942    0    0   .0000000D+00   .9086150D+02   .00D+00   .00D+00
  943    0    0   .0000000D+00   .1000525D+03   .00D+00   .00D+00
  944    0    0   .0000000D+00   .1097050D+03   .00D+00   .00D+00
  945    0    0   .0000000D+00   .1199650D+03   .00D+00   .00D+00
  946    0    0   .0000000D+00   .1310350D+03   .00D+00   .00D+00
  947    0    0   .0000000D+00   .1431200D+03   .00D+00   .00D+00
  948    0    0   .0000000D+00   .1565750D+03   .00D+00   .00D+00
  949    0    0   .0000000D+00   .1717950D+03   .00D+00   .00D+00
  950    0    0   .0000000D+00   .1893600D+03   .00D+00   .00D+00
  951    0    0   .0000000D+00   .2101000D+03   .00D+00   .00D+00
  952    0    0   .0000000D+00   .2351750D+03   .00D+00   .00D+00
  953    0    0   .0000000D+00   .2663950D+03   .00D+00   .00D+00
  954    0    0   .0000000D+00   .3066300D+03   .00D+00   .00D+00
  955    0    0   .0000000D+00   .3608200D+03   .00D+00   .00D+00
  956    0    0   .0000000D+00   .4381750D+03   .00D+00   .00D+00
  957    0    0   .0000000D+00   .5577350D+03   .00D+00   .00D+00
  958    0    0   .0000000D+00   .7639950D+03   .00D+00   .00D+00
  959    0    0   .0000000D+00   .1176175D+04   .00D+00   .00D+00
  960    0    0   .0000000D+00   .2159275D+04   .00D+00   .00D+00
  961    0    0   .4727141D+04   .4727141D+04   .00D+00   .00D+00
    0    0    0     0.0     0.0    0.0     0.0     END OF VELOCITY
    1  899    1     0.05    0.0
    0    0    0     0.0     0.0    0.0             END OF TH
    1  960    1     1.0005  0.0    0.0
    0    0    0     0.0     0.0    0.0             END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
12 0 34 0 0 10                        NONA NONS NOMX NOMY NOMZ NOMP

C ******* DATA SET 18: H+, E-, IONIC STRENGTH correction INFORMATION
 0.0 2 4 0 0   SICOR ICOR LNH LNG LNE
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
c ******* DATA SET 19:  temperature, pressure and expected pe and pH
 298.3 1.0    TEMP PRESSU
 -20.0 20.0 -20.0 20.0    PEMN PEMX PHMN PHMX
c ******* DATA SET 22: Basic real and integer parameters
1.0 10 500 1.0d-8 1.0d00 1.0d00 1 omegac npcyl niterc epsc cnstrx y ipiv
c ******* DATA SET 23: Component name and component species types
 Na +
  1 0      INDTC(J,2)   IFCS
 K +
  1 0      INDTC(J,2)   IFCS
 Ca +2
  1 0      INDTC(J,2)   IFCS
 H +
  1 0      INDTC(J,2)   IFCS
 Cu +2
  1 0      INDTC(J,2)   IFCS
 Al +3
  1 0      INDTC(J,2)   IFCS
 Fe +2
  1 0      INDTC(J,2)   IFCS
 SiO2(aq)
  1 0      INDTC(J,2)   IFCS
 HCO3 -
  1 0      INDTC(J,2)   IFCS
 SO4 -2
  1 0      INDTC(J,2)   IFCS
 Cl -
  1 0      INDTC(J,2)   IFCS
 O2(aq)
  1 0      INDTC(J,2)   IFCS
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
 Na +
  0  1 0   ISCN   VJ   IONEX
 K +
  0  1 0   ISCN   VJ   IONEX
 Ca +2
  0  2 0   ISCN   VJ   IONEX
 H +
  0  1 0   ISCN   VJ   IONEX
 Cu +2
  0  2 0   ISCN   VJ   IONEX
 Al +3
  0  3 0   ISCN   VJ   IONEX
 Fe +2
  0  2 0   ISCN   VJ   IONEX
 SiO2(aq)
  0  0 0   ISCN   VJ   IONEX
 HCO3 -
  0 -1 0   ISCN   VJ   IONEX
 SO4 -2
  0 -2 0   ISCN   VJ   IONEX
 Cl -
  0 -1 0   ISCN   VJ   IONEX
 O2(aq)
  0  0 0   ISCN   VJ   IONEX
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
C ******** DATA SET 25:  COMPLEXED SPECIES
OH-
0     0 0 0 -1 0 0 0 0 0 0 0 0     0     0 0 0 -1 0 0 0 0 0 0 0 0
Fe +3
0     0 0 0  1 0 0 1 0 0 0 0 0.25 0     0 0 0  1 0 0 1 0 0 0 0 0.25
Al(OH)2 +
0     0 0 0 -2 0 1 0 0 0 0 0 0     0     0 0 0 -2 0 1 0 0 0 0 0 0
Al(OH)3 (aq)
0     0 0 0 -3 0 1 0 0 0 0 0 0     0     0 0 0 -3 0 1 0 0 0 0 0 0
Al(OH)4 -
0     0 0 0 -4 0 1 0 0 0 0 0 0     0     0 0 0 -4 0 1 0 0 0 0 0 0
Al(SO4)2 -
0     0 0 0  0 0 1 0 0 0 2 0 0     0     0 0 0  0 0 1 0 0 0 2 0 0
AlOH +2
0     0 0 0 -1 0 1 0 0 0 0 0 0     0     0 0 0 -1 0 1 0 0 0 0 0 0
AlSO4 +
0     0 0 0  0 0 1 0 0 0 1 0 0     0     0 0 0  0 0 1 0 0 0 1 0 0
H2CO3*
0     0 0 0  1 0 0 0 0 1 0 0 0     0     0 0 0  1 0 0 0 0 1 0 0 0
CO3 -2
0     0 0 0 -1 0 0 0 0 1 0 0 0     0     0 0 0 -1 0 0 0 0 1 0 0 0
CaCO3 (aq)
0     0 0 1 -1 0 0 0 0 1 0 0 0     0     0 0 1 -1 0 0 0 0 1 0 0 0
CaHCO3 +
0     0 0 1  0 0 0 0 0 1 0 0 0     0     0 0 1  0 0 0 0 0 1 0 0 0
CaOH +
0     0 0 1 -1 0 0 0 0 0 0 0 0     0     0 0 1 -1 0 0 0 0 0 0 0 0
CaSO4(aq)
0     0 0 1  0 0 0 0 0 0 1 0 0     0     0 0 1  0 0 0 0 0 0 1 0 0
CuOH +
0     0 0 0 -1 1 0 0 0 0 0 0 0     0     0 0 0 -1 1 0 0 0 0 0 0 0
CuSO4(aq)
0     0 0 0  0 1 0 0 0 0 1 0 0     0     0 0 0  0 1 0 0 0 0 1 0 0
Fe[II](OH)2 (aq)
0     0 0 0 -2 0 0 1 0 0 0 0 0     0     0 0 0 -2 0 0 1 0 0 0 0 0
Fe[III](OH)2 +
0     0 0 0 -1 0 0 1 0 0 0 0 0.25 0     0 0 0 -1 0 0 1 0 0 0 0 0.25
Fe[III](OH)3 (aq)
0     0 0 0 -2 0 0 1 0 0 0 0 0.25 0     0 0 0 -2 0 0 1 0 0 0 0 0.25
Fe[II](OH)3 -
0     0 0 0 -3 0 0 1 0 0 0 0 0     0     0 0 0 -3 0 0 1 0 0 0 0 0
Fe[III](OH)4 -
0     0 0 0 -3 0 0 1 0 0 0 0 0.25 0     0 0 0 -3 0 0 1 0 0 0 0 0.25
Fe[III](SO4)2 -
0     0 0 0  1 0 0 1 0 0 2 0 0.25 0     0 0 0  1 0 0 1 0 0 2 0 0.25
Fe[III]HSO4 +2
0     0 0 0  2 0 0 1 0 0 1 0 0.25 0     0 0 0  2 0 0 1 0 0 1 0 0.25
Fe[II]SO4 (aq)
0     0 0 0  0 0 0 1 0 0 1 0 0     0     0 0 0  0 0 0 1 0 0 1 0 0
Fe[III]SO4 +
0     0 0 0  1 0 0 1 0 0 1 0 0.25 0     0 0 0  1 0 0 1 0 0 1 0 0.25
H2SO4 (aq)
0     0 0 0  2 0 0 0 0 0 1 0 0     0     0 0 0  2 0 0 0 0 0 1 0 0
HSO4 -
0     0 0 0  1 0 0 0 0 0 1 0 0     0     0 0 0  1 0 0 0 0 0 1 0 0
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
Cu[II]Cl +
0    0 0 0  0 1 0 0 0 0 0 1 0    0    0 0 0  0 1 0 0 0 0 0 1 0
Cu[II]Cl2 (aq)
0    0 0 0  0 1 0 0 0 0 0 2 0    0    0 0 0  0 1 0 0 0 0 0 2 0
Cu[II]Cl4 -2
0    0 0 0  0 1 0 0 0 0 0 4 0    0    0 0 0  0 1 0 0 0 0 0 4 0
Cu +
0    0 0 0 -1 1 0 0 0 0 0 0 -0.25 0   0 0 0 -1 1 0 0 0 0 0 0 -0.25
Cu[I]Cl2 -
0    0 0 0 -1 1 0 0 0 0 0 2 -0.25 0   0 0 0 -1 1 0 0 0 0 0 2 -0.25
Cu[I]Cl3 -2
0    0 0 0 -1 1 0 0 0 0 0 3 -0.25 0   0 0 0 -1 1 0 0 0 0 0 3 -0.25
Cu[IIO2 -2
0    0 0 0 -4 1 0 0 0 0 0 0 0    0    0 0 0 -4 1 0 0 0 0 0 0 0
C ******** DATA SET 27:  PRECIPITATED SPECIES
Chrysocolla
0  -3.928     0 0 0 -2 1 0 0 1 0 0 0 0    0 0 0 -2 1 0 0 1 0 0 0 0
Jurbanite
0   3.23      0 0 0 -1 0 1 0 0 0 1 0 0    0 0 0 -1 0 1 0 0 0 1 0 0
Alunite
0   0.3479    0 1 0 -6 0 3 0 0 0 2 0 0    0 1 0 -6 0 3 0 0 0 2 0 0
Goethite
0   7.955     0 0 0 -2 0 0 1 0 0 0 0 0.25 0 0 0 -2 0 0 1 0 0 0 0 0.25
Gypsum
0   4.482     0 0 1  0 0 0 0 0 0 1 0 0    0 0 1  0 0 0 0 0 0 1 0 0
Jarosite
0  34.84      0 1 0 -3 0 0 3 0 0 2 0 0.75 0 1 0 -3 0 0 3 0 0 2 0 0.75
Kaolinite
0  -6.810     0 0 0 -6 0 2 0 2 0 0 0 0    0 0 0 -6 0 2 0 2 0 0 0 0
Muscovite
0 -13.59      0 1 0 -10 0 3 0 3 0 0 0 0    0 1 0 -10 0 3 0 3 0 0 0 0
Quartz
0   3.999     0 0 0  0 0 0 0 1 0 0 0 0    0 0 0  0 0 0 0 1 0 0 0 0
SiO2 (am)
0   2.714     0 0 0  0 0 0 0 1 0 0 0 0    0 0 0  0 0 0 0 1 0 0 0 0
C ******** DATA SET 29:  reaction data
44
 1  1  0                NRTS NPDS KRTYP           RXN 1: OH -
-13.995                 LOGKEQ
-1  1                   STOICHIOMETRY           (Reactants, Products)
 4  13                  GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  0                NRTS NPDS KRTYP           RXN 2: Fe +3
  8.490                 LOGKEQ
 1  1  0.25 1           STOICHIOMETRY           (Reactants, Products)
 4  7  12   14          GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                NRTS NPDS KRTYP           RXN 3: Al(OH)2 +
-10.595                 LOGKEQ
-2  1  1                STOICHIOMETRY           (Reactants, Products)
 4  6  15               GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                NRTS NPDS KRTYP           RXN 4: Al(OH)3 (aq)
-16.158                 LOGKEQ
-3  1  1                STOICHIOMETRY           (Reactants, Products)
 4  6  16               GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                NRTS NPDS KRTYP           RXN 5:Al(OH)4 -
-22.883                 LOGKEQ
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
-4  1  1              STOICHIOMETRY           (Reactants, Products)
 4  6  17             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 6: Al(SO4)2 -
  4.9                 LOGKEQ
 1  2  1              STOICHIOMETRY           (Reactants, Products)
 6  10 18             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 7: AlOH +
 -4.9571              LOGKEQ
-1  1  1              STOICHIOMETRY           (Reactants, Products)
 4  6  19             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 8: AlSO4 +
  3.01                LOGKEQ
 1  1  1              STOICHIOMETRY           (Reactants, Products)
 6  10 20             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 9: H2CO3*
  6.3447              LOGKEQ
 1  1  1              STOICHIOMETRY           (Reactants, Products)
 4  9  21             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 10: CO3 -
-10.329               LOGKEQ
-1  1  1              STOICHIOMETRY           (Reactants, Products)
 4  9  22             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 3  1  0              NRTS NPDS KRTYP            RXN 11: CaCO3 (aq)
 -7.0017              LOGKEQ
 1 -1  1  1           STOICHIOMETRY           (Reactants, Products)
 3  4  9  23          GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 12: CaHCO3 +
  1.0467              LOGKEQ
 1  1  1              STOICHIOMETRY           (Reactants, Products)
 3  9  24             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 13: CaOH +
-12.8500              LOGKEQ
 1 -1  1              STOICHIOMETRY           (Reactants, Products)
 3  4  25             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 14: CaSO4(aq)
  2.1111              LOGKEQ
 1  1  1              STOICHIOMETRY           (Reactants, Products)
 3  10 26             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 15: CuOH +
 -7.2875              LOGKEQ
-1  1  1              STOICHIOMETRY           (Reactants, Products)
 4  5  27             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2 1 0                NRTS NPDS KRTYP            RXN 16: CuSO4(aq)
  2.31                LOGKEQ
 1  1  1              STOICHIOMETRY           (Reactants, Products)
 5  10 28             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP            RXN 17: Fe[II](OH)2 (aq)
-20.6000              LOGKEQ
-2  1  1              STOICHIOMETRY           (Reactants, Products)
 4  7  29             GLOBAL SPECIES NUMBERS  (Reactants, Products)
 3  1  0              NRTS NPDS KRTYP            RXN 18: Fe[III](OH)2 +
  2.820               LOGKEQ
-1  1  0.25 1         STOICHIOMETRY           (Reactants, Products)
 4  7  12   30        GLOBAL SPECIES NUMBERS  (Reactants, Products)
 3  1  0              NRTS NPDS KRTYP            RXN 19: Fe[III](OH)3 (aq)
```

Table 6.12 Input Data Sets for Problem 7 (continued)

```
 -3.51                   LOGKEQ
-2  1  0.25 1            STOICHIOMETRY           (Reactants, Products)
 4  7  12   31                 GLOBAL SPECIES NUMBERS (Reactants, Products)
 2 1 0                   NRTS NPDS KRTYP            RXN 20: Fe[II](OH)3 -
-31.000                  LOGKEQ
-3  1  1                 STOICHIOMETRY           (Reactants, Products)
 4  7  32                GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  0                 NRTS NPDS KRTYP            RXN 21: Fe[III](OH)4 -
-13.110                  LOGKEQ
-3  1  0.25 1            STOICHIOMETRY           (Reactants, Products)
 4  7  12   33           GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  0                 NRTS NPDS KRTYP         RXN 22: Fe[III](SO4)2 -
 11.704                  LOGKEQ
 1  1  2  0.25 1         STOICHIOMETRY           (Reactants, Products)
 4  7  10 12   34        GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  0                 NRTS NPDS KRTYP         RXN 23: Fe[III]HSO4 +2
 10.030                  LOGKEQ
 2  1  1  0.25 1         STOICHIOMETRY           (Reactants, Products)
 4  7  10 12   35        GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 24: Fe[II]SO4 (aq)
 2.2                     LOGKEQ
 1  1    1               STOICHIOMETRY           (Reactants, Products)
 7  10   36              GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  0                 NRTS NPDS KRTYP         RXN 25: Fe[III]SO4 +
 10.4180                 LOGKEQ
 1  1  1  0.25 1         STOICHIOMETRY           (Reactants, Products)
 4  7  10 12   37        GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 26: H2SO4 (aq)
-1.0209                  LOGKEQ
 2  1    1               STOICHIOMETRY           (Reactants, Products)
 4  10   38              GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 27: HSO4 -
 1.9791                  LOGKEQ
 1  1    1               STOICHIOMETRY           (Reactants, Products)
 4  10   39              GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 28: Cu[II]Cl +
 0.437                   LOGKEQ
 1  1    1               STOICHIOMETRY           (Reactants, Products)
 5  11   40              GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 29: Cu[II]Cl2 (aq)
 0.1585                  LOGKEQ
 1  2    1               STOICHIOMETRY           (Reactants, Products)
 5  11   41              GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0                 NRTS NPDS KRTYP            RXN 30: Cu[II]Cl4 -2
-4.5681                  LOGKEQ
 1  4    1               STOICHIOMETRY           (Reactants, Products)
 5  11   42              GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  0                 NRTS NPDS KRTYP            RXN 31: Cu +
-18.77                   LOGKEQ
-1  1 -0.25 1            STOICHIOMETRY           (Reactants, Products)
 4  5 12     43          GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  0                 NRTS NPDS KRTYP            RXN 32: Cu[I]Cl2 -
-13.949                  LOGKEQ
-1  1  2 -0.25 1         STOICHIOMETRY           (Reactants, Products)
 4  5  11 12   44        GLOBAL SPECIES NUMBERS (Reactants, Products)
```

Table 6.12 Input Data Sets for Problem 7 (concluded)

```
 4  1  0              NRTS NPDS KRTYP           RXN 33: Cu[I]Cl3 -2
-13.141               LOGKEQ
-1  1  3 -0.25 1      STOICHIOMETRY          (Reactants, Products)
 4  5  11 12   45     GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  0              NRTS NPDS KRTYP           RXN 34: Cu[IIO2 -2
-39.45                LOGKEQ
-4  1    1            STOICHIOMETRY          (Reactants, Products)
 4  5    46           GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  3  1              NRTS NPDS KRTYP ***dissol*** RXN 35: Chrysocolla
-3.42919  0.49881     LOG(kb) LOG(kf)
1  0.39 -1.61  1  1   STOICHIOMETRY          (Reactants, Products)
47 4    4      5  8   GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  1              NRTS NPDS KRTYP           RXN 36: Jurbanite
-0.50119  2.72881     LOG(kb) LOG(kf)
-1  1  1  1           STOICHIOMETRY          (Reactants, Products)
 4  6  10 48          GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  1              NRTS NPDS KRTYP           RXN 37: Alunite
-0.50119 -0.15329     LOG(kb) LOG(kf)
 1 -6  3  2  1        STOICHIOMETRY          (Reactants, Products)
 2  4  6  10 49       GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  1              NRTS NPDS KRTYP           RXN 38: Goethite
-0.50119  7.45381     LOG(kb) LOG(kf)
-2  1  0.25 1         STOICHIOMETRY          (Reactants, Products)
 4  7  12   50        GLOBAL SPECIES NUMBERS (Reactants, Products)
 2  1  1              NRTS NPDS KRTYP           RXN 39: Gypsum
 0.49881   4.98081    LOG(kb) LOG(kf)
 1  1  1              STOICHIOMETRY          (Reactants, Products)
 3  10 51             GLOBAL SPECIES NUMBERS (Reactants, Products)
 5  1  1              NRTS NPDS KRTYP     RXN 40: Jarosite
-0.50119  34.33881    LOG(kb) LOG(kf)
 1 -3  3  2  0.75 1   STOICHIOMETRY          (Reactants, Products)
 2  4  7  10 12   52  GLOBAL SPECIES NUMBERS (Reactants, Products)
 3  1  1              NRTS NPDS KRTYP           RXN 41: Kaolinite
-2.50119  -9.31119    LOG(kb) LOG(kf)
-6  2  2  1           STOICHIOMETRY          (Reactants, Products)
 4  6  8  53          GLOBAL SPECIES NUMBERS (Reactants, Products)
 4  1  1              NRTS NPDS KRTYP           RXN 42: Muscovite
-2.50119 -16.09119    LOG(kb) LOG(kf)
 1 -10 3  3  1        STOICHIOMETRY          (Reactants, Products)
 2  4  6  8  54       GLOBAL SPECIES NUMBERS (Reactants, Products)
 1  1  1              NRTS NPDS KRTYP           RXN 43: Quartz
-3.50119  0.49781     LOG(kb) LOG(kf)
 1  1                 STOICHIOMETRY          (Reactants, Products)
 8  55                GLOBAL SPECIES NUMBERS (Reactants, Products)
 1  1  1              NRTS NPDS KRTYP           RXN 44: SiO2 (am)
-0.50119  2.21281     LOG(kb) LOG(kf)
 1  1                 STOICHIOMETRY          (Reactants, Products)
 8  56                GLOBAL SPECIES NUMBERS (Reactants, Products)
                                 END OF JOB
```

6.8 Problem 8: Kinetic Adsorption and Biodegradation

This application simulates bioremediation of a contaminated soil through the supply of an appropriate microorganism at the injection well. The biogeochemical reaction system for this application is adapted from the one dimensional reactive transport benchmark problem developed by Valocchi and Tebes (1997), and simulated in Problem 6. The steady state flow field for this example is identical to the one used in Problem 7 (See Figure 6.4). The injection and extraction wells in this case serve as a means of bioremediating this hypothetical field site.

A 50 x 50 dm region adjacent to the injection well is assumed to be initially contaminated with cobalt and nitrilotriacetate (NTA), a chelating agent. The remainder of the region is initially free from these species. Seven components are used to characterize the system: H^+, $H_2CO_3^*$, NH_4^+, O_2, NTA^{3-}, Co^{2+}, and an adsorbent surface site >SOH. Table 6.13 summarizes the total concentrations of these components present initially in the region. The fluid composition is simulated using fourteen soluble complexed species. Formation of all are assumed to be equilibrium. Table 6.14 summarizes the reaction tableau for these aqueous species and the equilibrium constants for their formation.

Table 6.13. Total Concentration of Components and Kinetic Species Initially in the Matrix Fluid and in the Injection Fluid. All chemical species concentrations are expressed in mol/dm^3 of media. Biomass concentration is expressed in kg/dm^3 of media.

Species	Contaminated Zone Initially	Non-Contaminated Zone Initially	Injection Fluid ≤ 48 hours	Injection Fluid > 48 hours
pH	6.3	6.5	6	6
$H_2CO_3^*$	2.45E-8	2.45E-8	2.45E-8	2.45E-8
NH_4^+	0	0	0	0
O_2	1.5625E-6	1.5625E-6	1.5625E-6	1.5625E-6
NTA3-	2.6150E-7	0	0	0
Co2+	2.6150E-7	0	0	0
>SOH	1.4000E-3	1.4000E-3	NA	NA
>SOH_2-CoNTA	0	0	NA	NA
>$(SO)_2$-Co	0	0	NA	NA
Cells $_{(aq)}$	0	0	6.8000E-9	0
Cells $_{(ads)}$	0	0	NA	NA

Table 6.14. Tableau of Equilibrium Aqueous Speciation Reactions for Bioremediation Application.

	H^+	NTA^{3-}	Co^{2+}	$H_2CO_3^*$	NH_4^+	O_2	log K_{eq}
H_3NTA	3	1	0	0	0	0	14.9
H_2NTA^-	2	1	0	0	0	0	13.3
$HNTA^{2-}$	1	1	0	0	0	0	10.3
$CoNTA^-$	0	1	1	0	0	0	11.7
$Co(NTA)_2^{4-}$	0	2	1	0	0	0	14.5
$CoOHNTA^{2-}$	-1	1	1	0	0	0	0.5
$CoOH^+$	-1	0	1	0	0	0	-9.7
$Co(OH)_2$	-2	0	1	0	0	0	-22.9
$Co(OH)_3$	-3	0	1	0	0	0	-31.5
OH^-	-1	0	0	0	0	0	-14.0
HCO_3^-	-1	0	0	1	0	0	-6.3
CO_3^{2-}	-2	0	0	1	0	0	-16.5
NH_3	1	0	0	0	1	0	-9.3

The mobility of two aqueous species, Co^{2+} and $CoNTA^-$, is retarded due to kinetic adsorption to an oxide coating on the porous media. The distribution and charge of the adsorption sites on the oxide coating is pH dependent as given by reactions **(6.8.1)** and **(6.8.2)**. The two kinetic chemical adsorption reactions are given by **(6.8.3)** and **(6.8.4)**.

$$>SOH + H^+ \rightleftharpoons >SOH_2^+ , \quad \log K_{eq} = 5.6 \tag{6.8.1}$$

$$>SOH - H^+ \rightleftharpoons >SO^- , \quad \log K_{eq} = -11.6 \tag{6.8.2}$$

$$>SOH_2^+ + CoNTA^-_{(aq)} \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} >SOH_2\text{-}CoNTA_{(ads)} \tag{6.8.3}$$

$$2(>SO^-) + Co^{2+}_{(aq)} \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} (>SO)_2\text{-}Co_{(ads)} \tag{6.8.4}$$

where $k_{f1} = 0.8000$ hr^{-1}, $k_{b1} = 0.005260$ hr^{-1}, and $k_{f2} = 0.2667$ hr^{-1}, $k_{b2} = 0.05260$ hr^{-1}. The adsorption parameters were selected to make this a significant kinetic process in the system; they do not necessarily represent the true adsorption behavior for Co^{2+} or $CoNTA^-$.

A preliminary simulation was performed without flow due to pumping to allow for this adsorption process to occur until a steady state distribution of Co^{2+} and NTA^{3-} between the aqueous and adsorbed phases occurred. The purpose was to approximate a preremediation condition in which some species' mobility is hindered by adsorption to the matrix. Figure 6.8 shows the results of this kinetic adsorption process. Because of the pH of the system, the reactive adsorbent sites are primarily positively charged, and $>SOH_2\text{-}CoNTA_{(ads)}$ is the primary surface species. Negligible amounts of $>(SO)_2\text{-}Co_{(ads)}$ are formed. By approximately 1000 hours, a steady state condition is reached with 40% of the total Co^{2+} and NTA^{3-} adsorbed to the media.

After the adsorption process was allowed to reach steady state, the pumping wells were activated. For a period of 48 hours, the injection fluid contains a microorganism capable of degrading NTA. After that initial period, injection of water continues to maintain flow through the region but supply of the microorganism is ceased. The simulation is run for a total of 2500 hours. Table 6.13 summarizes the chemical and microbial concentrations in the injection solution. Both the matrix fluid and the injection fluid are assumed to have a density of 1 kg/dm^3.

Biodegradation can alter the chemical distribution in this system. It is assumed that the microorganisms can use nitroltriacetate as a growth substrate but can degrade only one of the aqueous complexed forms, $HNTA^{2-}$. The biodegradation reaction is:

$$\begin{aligned} HNTA^{2-} + 1.620\ O_2 + 1.272\ H_2O + 2.424\ H^+ &\rightarrow \\ \underset{\text{(cells)}}{17.3707\ C_5H_7O_2N} + 3.120\ H_2CO_3^* + 0.424\ NH_4^+ & \end{aligned} \qquad \textbf{(6.8.5)}$$

where $K_S = 7.64E\text{-}7$ mol/L, $K_O = 6.25E\text{-}6$ mol/L, $\mu_{max} = 0.0916519\ hr^{-1}$, $b_0 = 5.44E\text{-}5$ gram/dm^3 of media, and $K_d = 0.00208\ hr^{-1}$ (Valocchi and Tebes, 1997). It is assumed that the microorganisms are in the aqueous phase in the injection solution, but that they may adsorb to the porous media once in the matrix. A kinetic reaction is used to describe this adsorption process:

$$C_5H_7O_2N\ (aq) \rightleftharpoons C_5H_7O_2N\ (ads) \qquad \textbf{(6.8.6)}$$

where $k_f = 0.2667\ hr^{-1}$ and $k_{b2} = 0.05260\ hr^{-1}$. Microorganisms both in solution and adsorbed to the media are assumed capable of degrading HNTA by reaction **(6.8.5)** and at the same rate.

Figure 6.9 depicts the total aqueous Co^{2+} and $>SOH_2\text{-}CoNTA_{(ads)}$ in the system after 44 hours and 304 hours of pumping. Transport of the aqueous species is apparent. A portion of the adsorbed species is removed from the originally contaminated zone, and some is formed in the initially clean

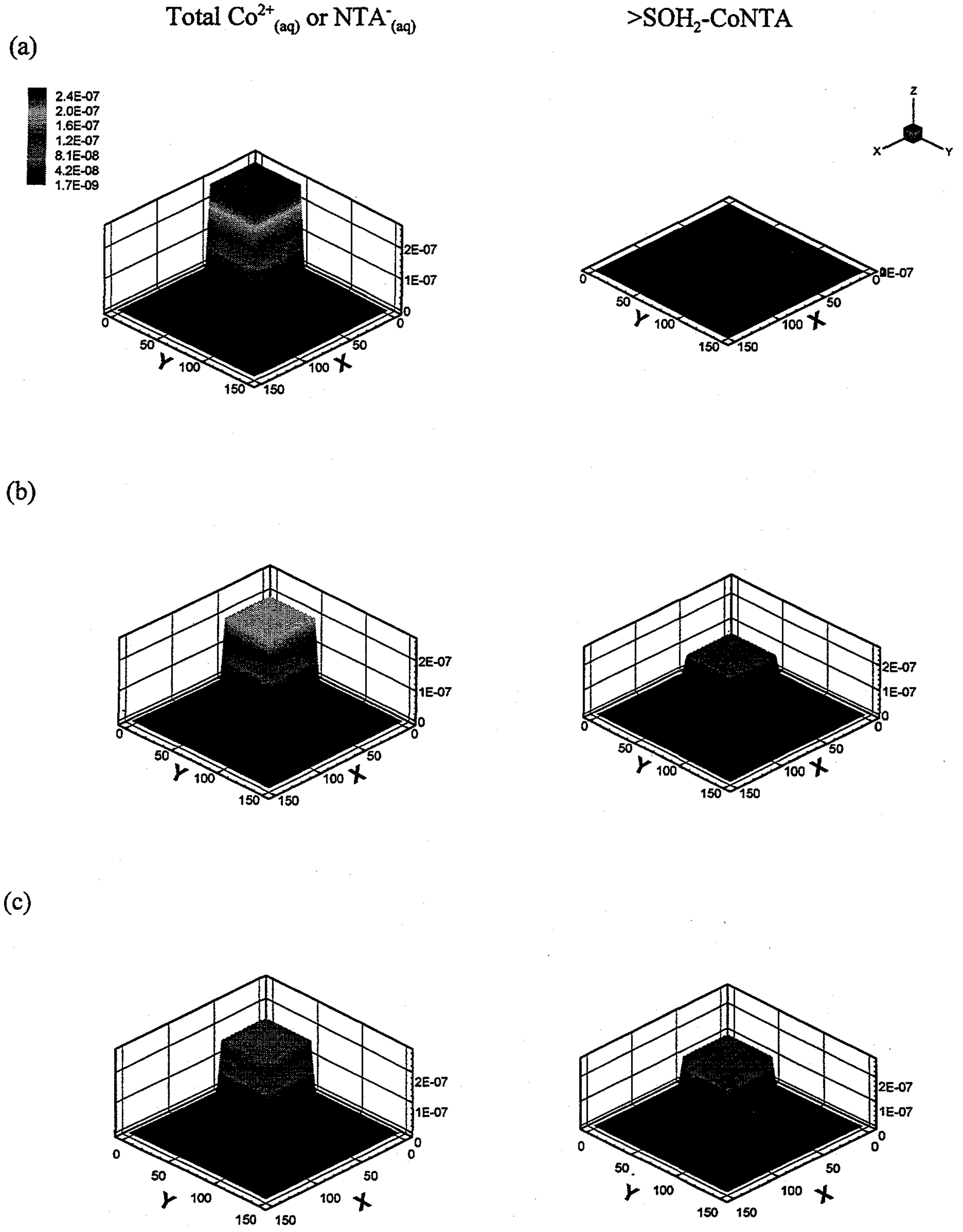
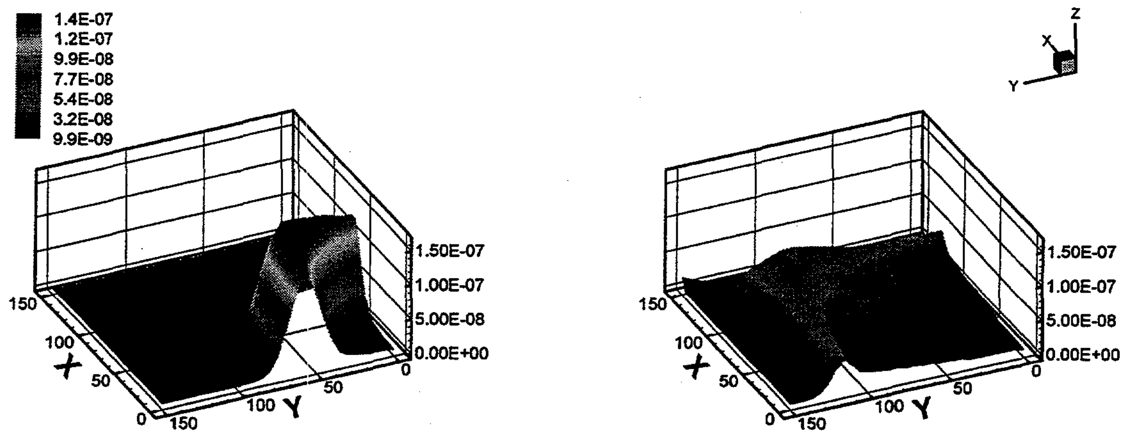


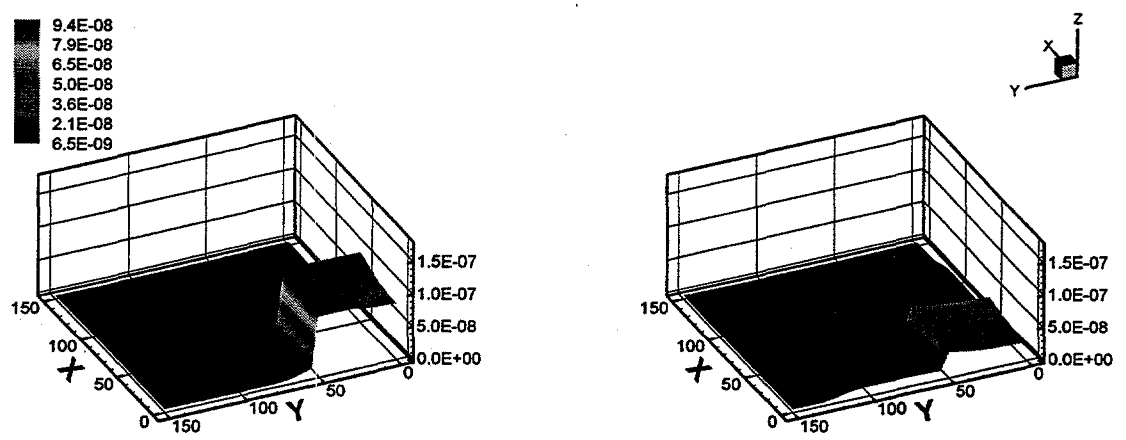
Figure 6.8. Adsorption of Co^{2+} and NTA^{3-} to the media surface at various times. (a) t = 0 hours, (b) t = 116 hours, (c) t = 1015 hours. On left, total concentration of Co^{2+} or NTA^{3-} in solution. On right, >SOH_2-CoNTA.

(a) Total aqueous Co^{2+}


At 44 hours

At 303 hours

(b) >SOH_2-CoNTA


At 44 hours

At 303 hours

Figure 6.9. Concentration of (a) total aqueous Co^{2+} and (b) >SOH_2-CoNTA in the region after 44 and after 303 hours of pumping. All figures are oriented so that the injection well (x = 0, y = 0) is at the right.

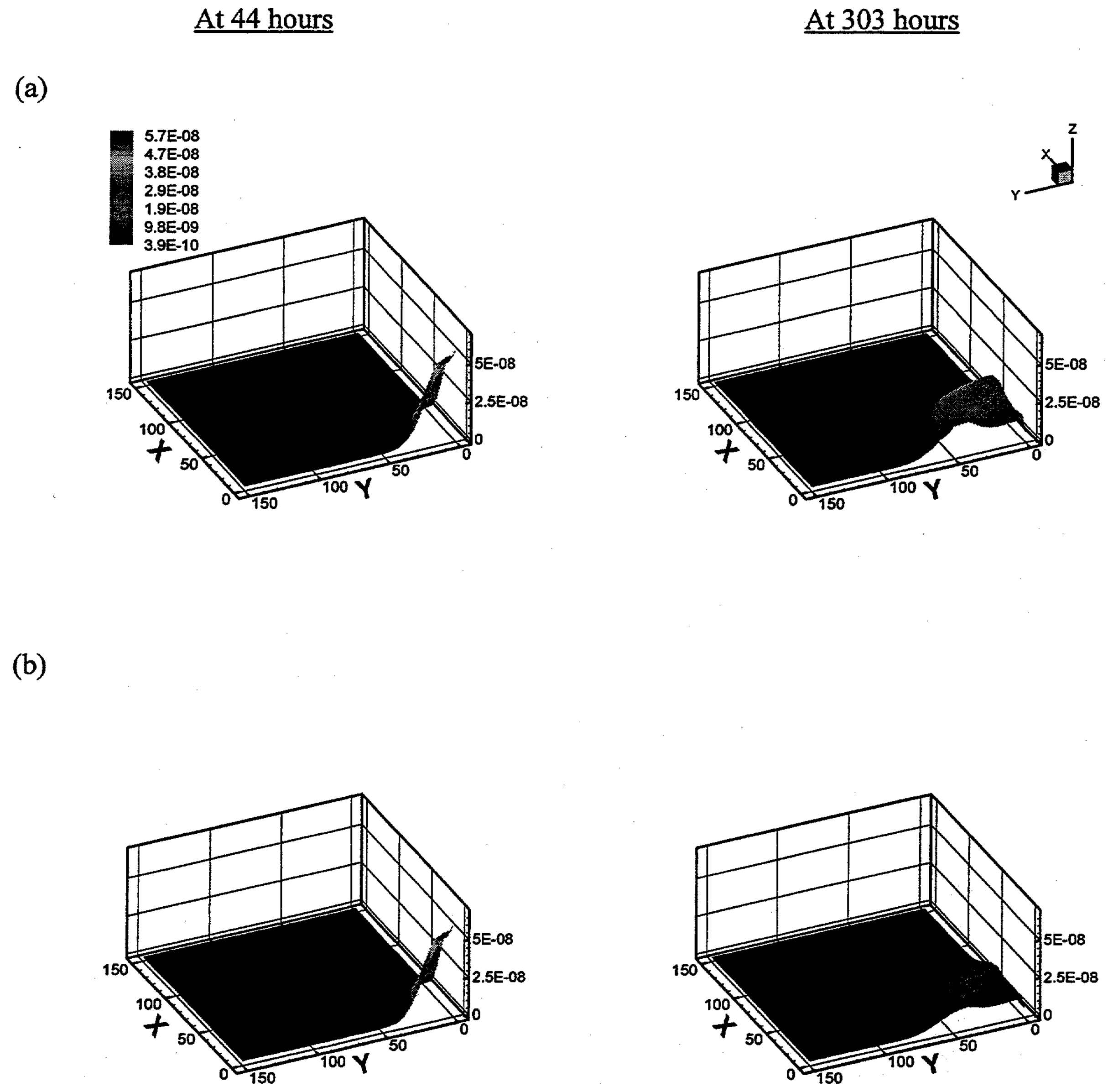


Figure 6.10. Concentration of aqueous biomass in the region after 44 and after 303 hours of pumping. (a) growth condition, (b) no growth condition. All figures are oriented so that the injection well ($x = 0$, $y = 0$) is at the right.

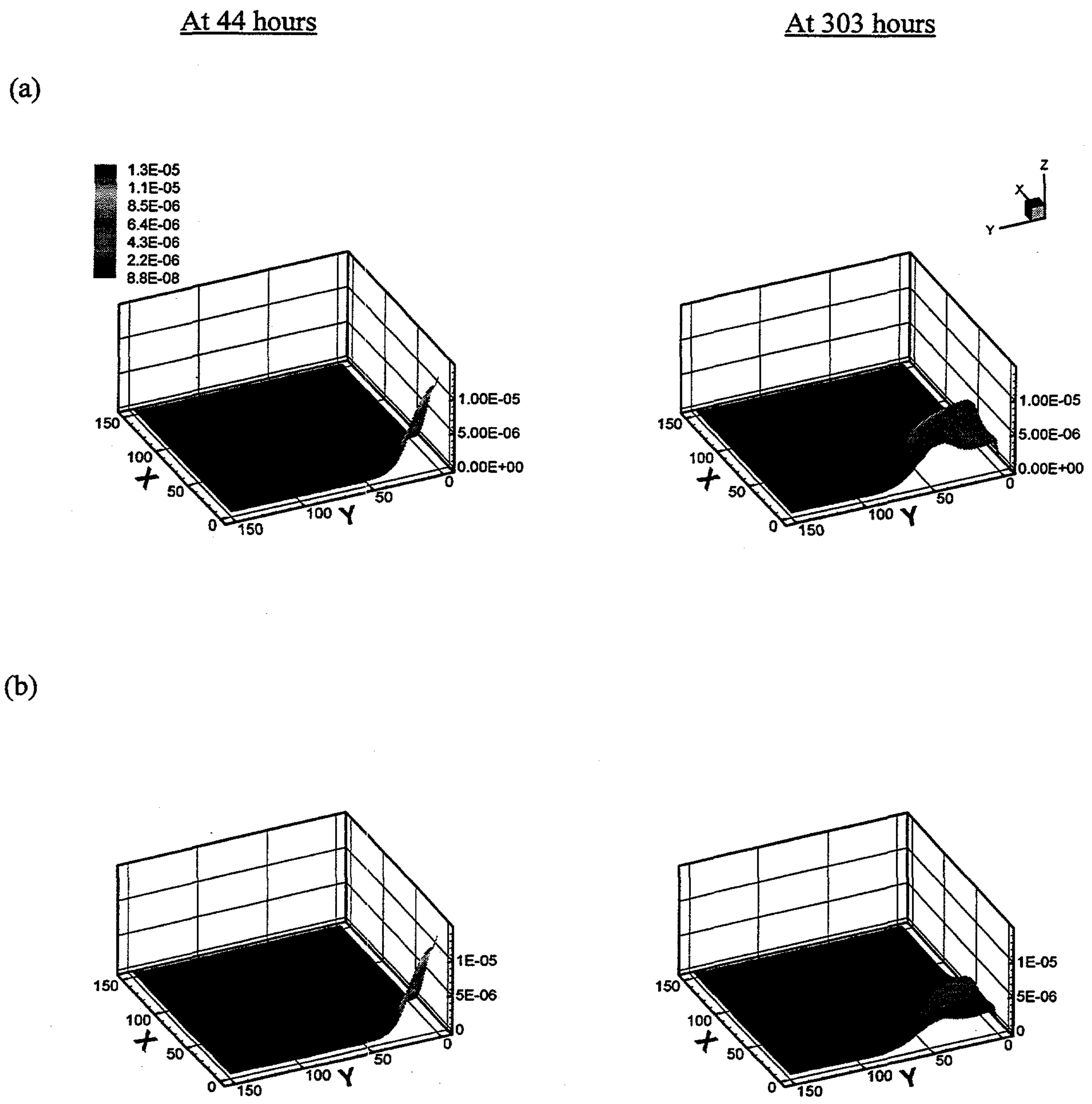


Figure 6.11. Concentration of adsorbed biomass in the region after 44 and after 303 hours of pumping. (a) growth condition, (b) no growth condition. All figures are oriented so that the injection well (x = 0, y = 0) is at the right.

region as aqueous Co^{2+} and NTA^{3-} are transported toward the extraction well. Figures 6.10 and 6.11 show the aqueous and adsorbed microbial species concentrations at these same times and contrasts them to a "no growth" condition. This "no growth condition" reflects a separate simulation performed with injection of the aqueous microorganism and its subsequent transport through and adsorption to the porous media; biodegradation reaction **(6.8.5)** was not included. Enhanced levels of biomass both in solution and adsorbed to the media result when reaction **(6.8.5)** is allowed to proceed.

Figure 6.12 shows the concentration of total aqueous Co^{2+} and NTA^{3-} over time at the recovery well. Three conditions are contrasted to allow the impact of different processes to be assessed: (1) recovery of a non-reactive tracer present initially in the same amount and spatial distribution as Co^{2+} and NTA^{3-}, (2) recovery of Co^{2+} and NTA^{3-} when flow is maintained through the region but microorganisms are not injected into the system, and (3) recovery of Co^{2+} and NTA^{3-} when microorganisms are injected into the contaminated zone and biodegradation can proceed. Contrasting conditions 1 and 2 shows the retardation of Co^{2+} and NTA^{3-} due to their adsorption to the oxide coating, and indicates that flushing of the contaminated zone with clean water will achieve cleanup under the conditions simulated. Contrasting conditions 2 and 3 helps make evident the slight acceleration of remediation that can be achieved with biodegradation in this system. NTA is removed from the system resulting in less recovered at the extraction well. Co^{2+} arrives slightly earlier as a result. Cobalt is retained in the media because of the combined effects of its equilibrium aqueous complexation with NTA^{3-} and its subsequent kinetic adsorption to the porous media surface as $>SOH_2\text{-}CoNTA_{(ads)}$. As biodegradation removes NTA from the system, less is available to complex with Co^{2+} and adsorb to the surface. Cobalt's mobility is enhanced as a result when biodegradation occurs. Though the impact is small for the particular parameters chosen for this example, this result helps to illustrate the value of the capability of simulating kinetic geochemical and microbiological effects simultaneously.

The input data sets for Problem 8 are prepared according to Appendix A and are given in Table 6.15.

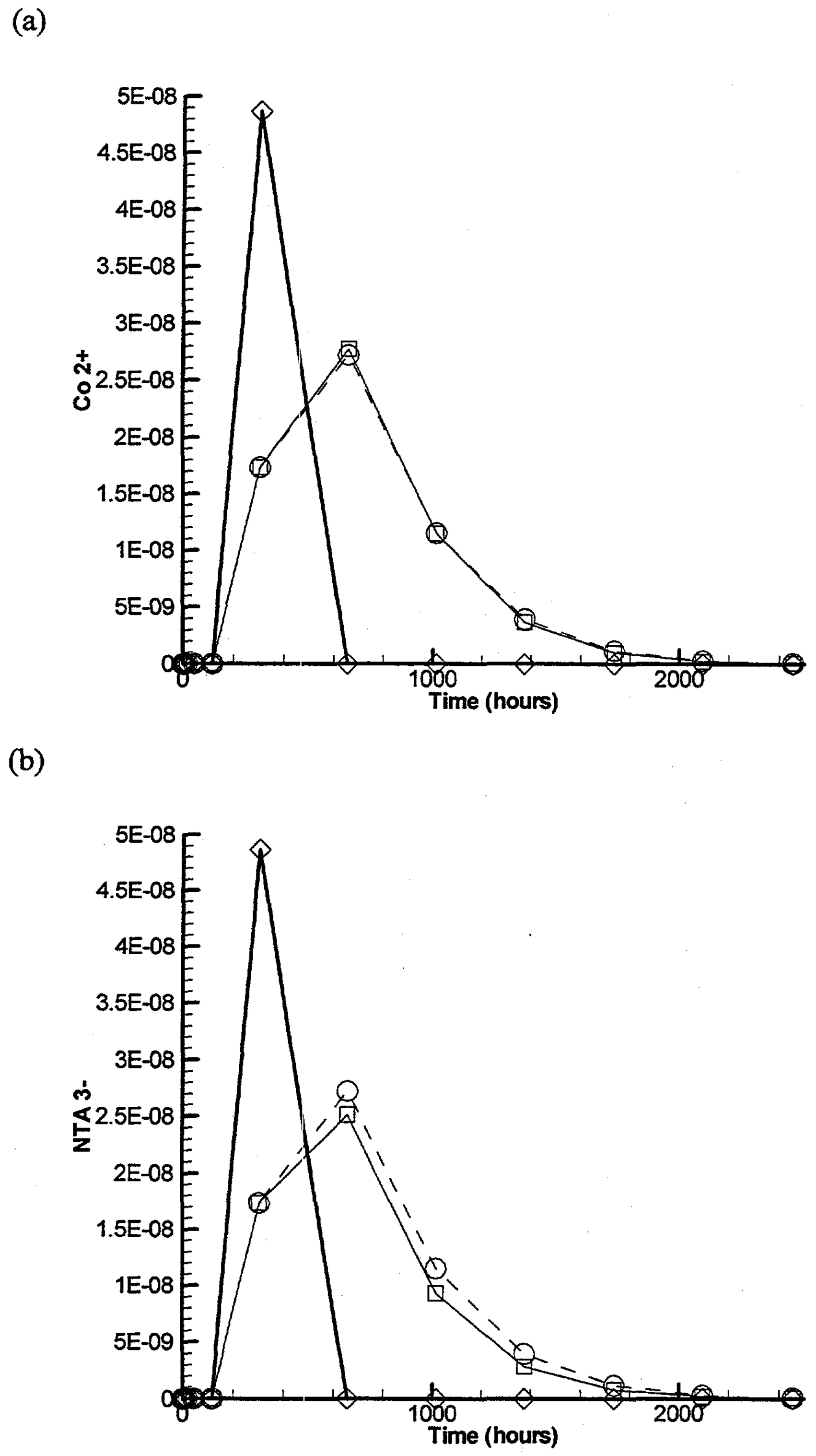


Figure 6.12. Total aqueous (a) Co^{2+} and (b) NTA^{3-} at the extraction well over time when subjected to flushing of adsorbed species (○ / dashed line) versus flushing plus biodegradation (□ / solid line). A nonreactive tracer is plotted (◇ / bold line) for comparison.

Table 6.15 Input Data Sets for Problem 8

```
   1  MICROBIAL BENCHMARK PROBLEM (PART B) + 2D FLOW (KG,DM,HR)
 1 0 0 0 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 961 900 1 0 200   1 4 -1 1 0   0 0 40 1 50   0 1 0 1 11   1 1 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
0.1 0.1D0 36.0 17520 1.0D0   1.0D0 1.0D0 1.0D00 1.0D-6 1.0D0
C ******* DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
44444444440000000000400000000040000000004000000000400000000040000000004000000000
40000000004000000000400000000040000000004000000000400000000040000000004000000000
40000000004000000000400000000040000000004
10100010101000000000100000000010000100001000010000100001000010000100001000010000
10000100001000010000100000000010000000001000000000100000000010000000001000000000
10000000001000000000100000000010000000001
1.0D38
C ******* DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PROPERTY TYPE INDICATOR
 3
 1 481 961 NODEP

C ******* DATA SET 6: MATERIAL PROPERTIES
 0.0D0 0.0D0 0.0D0 2.56D0 AL AT AM RHOB
C ******* DATA SET 7: NODE COORDINATES
    1   30     1       0.0D0   0.0D0  0.0
   32   30     1       5.0D0   0.0D0  0.0
   63   30     1      10.0D0   0.0D0  0.0
   94   30     1      15.0D0   0.0D0  0.0
  125   30     1      20.0D0   0.0D0  0.0
  156   30     1      25.0D0   0.0D0  0.0
  187   30     1      30.0D0   0.0D0  0.0
  218   30     1      35.0D0   0.0D0  0.0
  249   30     1      40.0D0   0.0D0  0.0
  280   30     1      45.0D0   0.0D0  0.0
  311   30     1      50.0D0   0.0D0  0.0
  342   30     1      55.0D0   0.0D0  0.0
  373   30     1      60.0D0   0.0D0  0.0
  404   30     1      65.0D0   0.0D0  0.0
  435   30     1      70.0D0   0.0D0  0.0
  466   30     1      75.0D0   0.0D0  0.0
  497   30     1      80.0D0   0.0D0  0.0
  528   30     1      85.0D0   0.0D0  0.0
  559   30     1      90.0D0   0.0D0  0.0
  590   30     1      95.0D0   0.0D0  0.0
  621   30     1     100.0D0   0.0D0  0.0
  652   30     1     105.0D0   0.0D0  0.0
  683   30     1     110.0D0   0.0D0  0.0
  714   30     1     115.0D0   0.0D0  0.0
  745   30     1     120.0D0   0.0D0  0.0
  776   30     1     125.0D0   0.0D0  0.0
  807   30     1     130.0D0   0.0D0  0.0
  838   30     1     135.0D0   0.0D0  0.0
  869   30     1     140.0D0   0.0D0  0.0
  900   30     1     145.0D0   0.0D0  0.0
  931   30     1     150.0D0   0.0D0  0.0
    0    0     0       0.0      0.0     0.0          END OF X-COORD
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
     1   30      1      0.0D0    5.0D0   0.0
    32   30      1      0.0D0    5.0D0   0.0
    63   30      1      0.0D0    5.0D0   0.0
    94   30      1      0.0D0    5.0D0   0.0
   125   30      1      0.0D0    5.0D0   0.0
   156   30      1      0.0D0    5.0D0   0.0
   187   30      1      0.0D0    5.0D0   0.0
   218   30      1      0.0D0    5.0D0   0.0
   249   30      1      0.0D0    5.0D0   0.0
   280   30      1      0.0D0    5.0D0   0.0
   311   30      1      0.0D0    5.0D0   0.0
   342   30      1      0.0D0    5.0D0   0.0
   373   30      1      0.0D0    5.0D0   0.0
   404   30      1      0.0D0    5.0D0   0.0
   435   30      1      0.0D0    5.0D0   0.0
   466   30      1      0.0D0    5.0D0   0.0
   497   30      1      0.0D0    5.0D0   0.0
   528   30      1      0.0D0    5.0D0   0.0
   559   30      1      0.0D0    5.0D0   0.0
   590   30      1      0.0D0    5.0D0   0.0
   621   30      1      0.0D0    5.0D0   0.0
   652   30      1      0.0D0    5.0D0   0.0
   683   30      1      0.0D0    5.0D0   0.0
   714   30      1      0.0D0    5.0D0   0.0
   745   30      1      0.0D0    5.0D0   0.0
   776   30      1      0.0D0    5.0D0   0.0
   807   30      1      0.0D0    5.0D0   0.0
   838   30      1      0.0D0    5.0D0   0.0
   869   30      1      0.0D0    5.0D0   0.0
   900   30      1      0.0D0    5.0D0   0.0
   931   30      1      0.0D0    5.0D0   0.0
     0    0      0      0.0D0    0.0D0   0.0D0          END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
     1    1    32   33     2     1    30    30           IE
C ******* DATA SET 10: CHEMICAL COMPONENT INFORMATION
 6 1 0 2 0 0 1 1   NOHA NOHS NOKX KY KZ KP MB MA
 H+
  1   1
 H2CO3*
  2   1
 NH4+
  3   1
 O2
  4   1
 NTA3-
  5   1
 Co 2+
  6   1
 >SOH
  7   2
C ******* DATA SET 11:  INITIAL CONDITIONS (MASS/MEDIA VOLUME)
     1     10    1    2.3289d-4 0.0D0      0.0D0
    32     10    1    2.3289d-4 0.0D0      0.0D0
    63     10    1    2.3289d-4 0.0D0      0.0D0
    94     10    1    2.3289d-4 0.0D0      0.0D0
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 125     10    1     2.3289d-4 0.0D0       0.0D0
 156     10    1     2.3289d-4 0.0D0       0.0D0
 187     10    1     2.3289d-4 0.0D0       0.0D0
 218     10    1     2.3289d-4 0.0D0       0.0D0
 249     10    1     2.3289d-4 0.0D0       0.0D0
 280     10    1     2.3289d-4 0.0D0       0.0D0
 311     10    1     2.3289d-4 0.0D0       0.0D0
  12     19    1     1.5653d-4 0.0D0       0.0D0
  43     19    1     1.5653d-4 0.0D0       0.0D0
  74     19    1     1.5653d-4 0.0D0       0.0D0
 105     19    1     1.5653d-4 0.0D0       0.0D0
 136     19    1     1.5653d-4 0.0D0       0.0D0
 167     19    1     1.5653d-4 0.0D0       0.0D0
 198     19    1     1.5653d-4 0.0D0       0.0D0
 229     19    1     1.5653d-4 0.0D0       0.0D0
 260     19    1     1.5653d-4 0.0D0       0.0D0
 291     19    1     1.5653d-4 0.0D0       0.0D0
 322     639   1     1.5653d-4 0.0D0       0.0D0
   0     0     0     0.0       0.0         0.0           END OF I.C. H+ - variable PH
   1     960   1     2.45d-8   0.0D0       0.0D0
   0     0     0.0   0.0       0.0         0.0D0         END OF I.C. H2CO3(g)
   1     960   1     0.00d-14  0.0D0       0.0D0
   0     0     0     0.0       0.0         0.0           END OF I.C. NH4+
   1     960   1     1.5625d-6 0.0D0       0.0D0
   0     0     0     0.0       0.0         0.0           END OF I.C. O2
   1     10    1     1.5810d-7 0.0D0       0.0D0
  32     10    1     1.5810d-7 0.0D0       0.0D0
  63     10    1     1.5810d-7 0.0D0       0.0D0
  94     10    1     1.5810d-7 0.0D0       0.0D0
 125     10    1     1.5810d-7 0.0D0       0.0D0
 156     10    1     1.5810d-7 0.0D0       0.0D0
 187     10    1     1.5810d-7 0.0D0       0.0D0
 218     10    1     1.5810d-7 0.0D0       0.0D0
 249     10    1     1.5810d-7 0.0D0       0.0D0
 280     10    1     1.5810d-7 0.0D0       0.0D0
 311     10    1     1.5810d-7 0.0D0       0.0D0
  12     19    1     0.0000d-7 0.0D0       0.0D0
  43     19    1     0.0000d-7 0.0D0       0.0D0
  74     19    1     0.0000d-7 0.0D0       0.0D0
 105     19    1     0.0000d-7 0.0D0       0.0D0
 136     19    1     0.0000d-7 0.0D0       0.0D0
 167     19    1     0.0000d-7 0.0D0       0.0D0
 198     19    1     0.0000d-7 0.0D0       0.0D0
 229     19    1     0.0000d-7 0.0D0       0.0D0
 260     19    1     0.0000d-7 0.0D0       0.0D0
 291     19    1     0.0000d-7 0.0D0       0.0D0
 322     639   1     0.0000d-7 0.0D0       0.0D0
   0     0     0     0.0       0.0         0.0           END OF I.C. NTA3-
   1     10    1     1.5810d-7 0.0D0       0.0D0
  32     10    1     1.5810d-7 0.0D0       0.0D0
  63     10    1     1.5810d-7 0.0D0       0.0D0
  94     10    1     1.5810d-7 0.0D0       0.0D0
 125     10    1     1.5810d-7 0.0D0       0.0D0
 156     10    1     1.5810d-7 0.0D0       0.0D0
 187     10    1     1.5810d-7 0.0D0       0.0D0
```

Table 6.15   Input Data Sets for Problem 8 (continued)

```
  218    10   1    1.5810d-7 0.0D0      0.0D0
  249    10   1    1.5810d-7 0.0D0      0.0D0
  280    10   1    1.5810d-7 0.0D0      0.0D0
  311    10   1    1.5810d-7 0.0D0      0.0D0
   12    19   1    0.0000d-7 0.0D0      0.0D0
   43    19   1    0.0000d-7 0.0D0      0.0D0
   74    19   1    0.0000d-7 0.0D0      0.0D0
  105    19   1    0.0000d-7 0.0D0      0.0D0
  136    19   1    0.0000d-7 0.0D0      0.0D0
  167    19   1    0.0000d-7 0.0D0      0.0D0
  198    19   1    0.0000d-7 0.0D0      0.0D0
  229    19   1    0.0000d-7 0.0D0      0.0D0
  260    19   1    0.0000d-7 0.0D0      0.0D0
  291    19   1    0.0000d-7 0.0D0      0.0D0
  322    639  1    0.0000d-7 0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. Co2+
    1    960  1    1.40d-3   0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. >SOH
    1    960  1    0.00d-5   0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. Cells (aq)
    1    10   1    1.0340d-7 0.0D0      0.0D0
   32    10   1    1.0340d-7 0.0D0      0.0D0
   63    10   1    1.0340d-7 0.0D0      0.0D0
   94    10   1    1.0340d-7 0.0D0      0.0D0
  125    10   1    1.0340d-7 0.0D0      0.0D0
  156    10   1    1.0340d-7 0.0D0      0.0D0
  187    10   1    1.0340d-7 0.0D0      0.0D0
  218    10   1    1.0340d-7 0.0D0      0.0D0
  249    10   1    1.0340d-7 0.0D0      0.0D0
  280    10   1    1.0340d-7 0.0D0      0.0D0
  311    10   1    1.0340d-7 0.0D0      0.0D0
   12    19   1    0.0000d-7 0.0D0      0.0D0
   43    19   1    0.0000d-7 0.0D0      0.0D0
   74    19   1    0.0000d-7 0.0D0      0.0D0
  105    19   1    0.0000d-7 0.0D0      0.0D0
  136    19   1    0.0000d-7 0.0D0      0.0D0
  167    19   1    0.0000d-7 0.0D0      0.0D0
  198    19   1    0.0000d-7 0.0D0      0.0D0
  229    19   1    0.0000d-7 0.0D0      0.0D0
  260    19   1    0.0000d-7 0.0D0      0.0D0
  291    19   1    0.0000d-7 0.0D0      0.0D0
  322    639  1    0.0000d-7 0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. CoNTA(ads) = Ky1
    1    960  1    0.00d-20  0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. Co(ads) = Ky2
    1    960  1    0.00d-5   0.0D0      0.0D0
    0    0    0    0.0       0.0        0.0           END OF I.C. Cells (ads)
C ******* DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
    0  0  0    2  2  4    0  0  0    0  0  0  0
C ******* DATA SET 13: WELL SOURCE/SINK (MASS/LIQUID VOLUME)
  1  961
0.0D0 8.387D-7  48.0D0 8.387D-7  48.01D0 8.387D-7 17520.0D0 8.387d-7
0.0D0 0.00D0    48.0D0 0.00D0    48.01D0 0.00D0   17520.0D0 0.00D0
    1    1    1    1    1
    0    0    0    0    0                          END OF B.C. H+
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
0.0D0 4.90D-7    48.0D0 4.90D-7    48.01D0 4.90D-7  17520.0D0 4.90d-7
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF B.C. H2CO3(g)
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF B.C. NH4+
0.0D0 3.125D-5   48.0D0 3.125D-5   48.01D0 3.125D-5 17520.0D0 3.125D-5
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF B.C. O2
0.0D0 0.00D-6    48.0D0 0.00D-6    48.01D0 0.00D0   17520.0D0 0.00D0
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF B.C. NTA3-
0.0D0 0.00D-6    48.0D0 0.00D-6    48.01D0 0.00D0   17520.0D0 0.00D0
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF B.C. Co2+
0.0D0 1.36D-6    48.0D0 1.36D-6    48.01D0 0.00D0   17520.0D0 0.00D0
0.0D0 0.00D0     48.0D0 0.00D0     48.01D0 0.00D0   17520.0D0 0.00D0
    1     1    1     1     1
    0     0    0     0     0             Cells(aq) kg/dm^3 liq *** rev
0.0D0   1.9D0  48.0D0   1.9D0  48.01D0   1.90D0  17520.0D0  1.90D0
0.0D0  -1.9D0  48.0D0  -1.9D0  48.01D0  -1.90D0  17520.0D0 -1.90D0
    1     1    1     1     1
    0     0    0     0     0                        Q (dm^3/hr per dm depth)
0.0D0 1.0000D0   48.0D0 1.0000D0   48.01D0 1.00D0   17520.0D0 1.00D0
0.0D0 1.0000D0   48.0D0 1.0000D0   48.01D0 1.00D0   17520.0D0 1.00D0
    1     1    1     1     1
    0     0    0     0     0                        END OF RHOL S/S
C ******* DATA SET 16: HYDROLOGICAL VARIABLES
    1     0    0   .5396279D+00   .5396279D+00   .00D+00   .00D+00
    2     0    0   .0000000D+00   .2464926D+00   .00D+00   .00D+00
    3     0    0   .0000000D+00   .1342666D+00   .00D+00   .00D+00
    4     0    0   .0000000D+00   .8721404D-01   .00D+00   .00D+00
    5     0    0   .0000000D+00   .6366838D-01   .00D+00   .00D+00
    6     0    0   .0000000D+00   .5001998D-01   .00D+00   .00D+00
    7     0    0   .0000000D+00   .4118950D-01   .00D+00   .00D+00
    8     0    0   .0000000D+00   .3500342D-01   .00D+00   .00D+00
    9     0    0   .0000000D+00   .3041039D-01   .00D+00   .00D+00
   10     0    0   .0000000D+00   .2684646D-01   .00D+00   .00D+00
   11     0    0   .0000000D+00   .2398402D-01   .00D+00   .00D+00
   12     0    0   .0000000D+00   .2161644D-01   .00D+00   .00D+00
   13     0    0   .0000000D+00   .1961130D-01   .00D+00   .00D+00
   14     0    0   .0000000D+00   .1787386D-01   .00D+00   .00D+00
   15     0    0   .0000000D+00   .1633790D-01   .00D+00   .00D+00
   16     0    0   .0000000D+00   .1495833D-01   .00D+00   .00D+00
   17     0    0   .0000000D+00   .1369463D-01   .00D+00   .00D+00
   18     0    0   .0000000D+00   .1252340D-01   .00D+00   .00D+00
   19     0    0   .0000000D+00   .1142152D-01   .00D+00   .00D+00
   20     0    0   .0000000D+00   .1037232D-01   .00D+00   .00D+00
   21     0    0   .0000000D+00   .9362614D-02   .00D+00   .00D+00
   22     0    0   .0000000D+00   .8382021D-02   .00D+00   .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 23   0   0  .0000000D+00   .7422374D-02   .00D+00   .00D+00
 24   0   0  .0000000D+00   .6477568D-02   .00D+00   .00D+00
 25   0   0  .0000000D+00   .5542580D-02   .00D+00   .00D+00
 26   0   0  .0000000D+00   .4613813D-02   .00D+00   .00D+00
 27   0   0  .0000000D+00   .3688813D-02   .00D+00   .00D+00
 28   0   0  .0000000D+00   .2765696D-02   .00D+00   .00D+00
 29   0   0  .0000000D+00   .1843550D-02   .00D+00   .00D+00
 30   0   0  .0000000D+00   .9217580D-03   .00D+00   .00D+00
 31   0   0  .0000000D+00   .0000000D+00   .00D+00   .00D+00
 32   0   0  .2464926D+00   .0000000D+00   .00D+00   .00D+00
 33   0   0  .1320462D+00   .1320462D+00   .00D+00   .00D+00
 34   0   0  .5500913D-01   .9463756D-01   .00D+00   .00D+00
 35   0   0  .2723687D-01   .7129737D-01   .00D+00   .00D+00
 36   0   0  .1558733D-01   .5628596D-01   .00D+00   .00D+00
 37   0   0  .9956792D-02   .4614212D-01   .00D+00   .00D+00
 38   0   0  .6891952D-02   .3893836D-01   .00D+00   .00D+00
 39   0   0  .5061301D-02   .3359247D-01   .00D+00   .00D+00
 40   0   0  .3888071D-02   .2947317D-01   .00D+00   .00D+00
 41   0   0  .3095320D-02   .2619692D-01   .00D+00   .00D+00
 42   0   0  .2537900D-02   .2351826D-01   .00D+00   .00D+00
 43   0   0  .2134075D-02   .2127397D-01   .00D+00   .00D+00
 44   0   0  .1834874D-02   .1935445D-01   .00D+00   .00D+00
 45   0   0  .1609475D-02   .1767865D-01   .00D+00   .00D+00
 46   0   0  .1437785D-02   .1618950D-01   .00D+00   .00D+00
 47   0   0  .1306221D-02   .1484304D-01   .00D+00   .00D+00
 48   0   0  .1205137D-02   .1360674D-01   .00D+00   .00D+00
 49   0   0  .1127557D-02   .1245605D-01   .00D+00   .00D+00
 50   0   0  .1068413D-02   .1137049D-01   .00D+00   .00D+00
 51   0   0  .1023784D-02   .1033408D-01   .00D+00   .00D+00
 52   0   0  .9906221D-03   .9334418D-02   .00D+00   .00D+00
 53   0   0  .9665068D-03   .8361815D-02   .00D+00   .00D+00
 54   0   0  .9494578D-03   .7408447D-02   .00D+00   .00D+00
 55   0   0  .9378596D-03   .6468322D-02   .00D+00   .00D+00
 56   0   0  .9303653D-03   .5536872D-02   .00D+00   .00D+00
 57   0   0  .9258505D-03   .4610616D-02   .00D+00   .00D+00
 58   0   0  .9233961D-03   .3687215D-02   .00D+00   .00D+00
 59   0   0  .9222546D-03   .2765126D-02   .00D+00   .00D+00
 60   0   0  .9218436D-03   .1843436D-02   .00D+00   .00D+00
 61   0   0  .9217580D-03   .9217580D-03   .00D+00   .00D+00
 62   0   0  .9217580D-03   .0000000D+00   .00D+00   .00D+00
 63   0   0  .1342666D+00   .0000000D+00   .00D+00   .00D+00
 64   0   0  .9463756D-01   .5500913D-01   .00D+00   .00D+00
 65   0   0  .6075171D-01   .6075171D-01   .00D+00   .00D+00
 66   0   0  .3835160D-01   .5500970D-01   .00D+00   .00D+00
 67   0   0  .2515525D-01   .4772774D-01   .00D+00   .00D+00
 68   0   0  .1734760D-01   .4126313D-01   .00D+00   .00D+00
 69   0   0  .1254983D-01   .3595491D-01   .00D+00   .00D+00
 70   0   0  .9465126D-02   .3165982D-01   .00D+00   .00D+00
 71   0   0  .7395548D-02   .2816210D-01   .00D+00   .00D+00
 72   0   0  .5955251D-02   .2527454D-01   .00D+00   .00D+00
 73   0   0  .4922317D-02   .2284989D-01   .00D+00   .00D+00
 74   0   0  .4163584D-02   .2077968D-01   .00D+00   .00D+00
 75   0   0  .3595833D-02   .1898174D-01   .00D+00   .00D+00
 76   0   0  .3165183D-02   .1739498D-01   .00D+00   .00D+00
 77   0   0  .2835559D-02   .1597203D-01   .00D+00   .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

78	0	0	.2581963D-02	.1467523D-01	.00D+00	.00D+00
79	0	0	.2386644D-02	.1347831D-01	.00D+00	.00D+00
80	0	0	.2236701D-02	.1235731D-01	.00D+00	.00D+00
81	0	0	.2122317D-02	.1129566D-01	.00D+00	.00D+00
82	0	0	.2036073D-02	.1027808D-01	.00D+00	.00D+00
83	0	0	.1972203D-02	.9293322D-02	.00D+00	.00D+00
84	0	0	.1925970D-02	.8332477D-02	.00D+00	.00D+00
85	0	0	.1893493D-02	.7388299D-02	.00D+00	.00D+00
86	0	0	.1871632D-02	.6455080D-02	.00D+00	.00D+00
87	0	0	.1857763D-02	.5528767D-02	.00D+00	.00D+00
88	0	0	.1849658D-02	.4606107D-02	.00D+00	.00D+00
89	0	0	.1845491D-02	.3685103D-02	.00D+00	.00D+00
90	0	0	.1843779D-02	.2764384D-02	.00D+00	.00D+00
91	0	0	.1843379D-02	.1843379D-02	.00D+00	.00D+00
92	0	0	.1843436D-02	.9218436D-03	.00D+00	.00D+00
93	0	0	.1843550D-02	.0000000D+00	.00D+00	.00D+00
94	0	0	.8721404D-01	.0000000D+00	.00D+00	.00D+00
95	0	0	.7129737D-01	.2723687D-01	.00D+00	.00D+00
96	0	0	.5500970D-01	.3835160D-01	.00D+00	.00D+00
97	0	0	.4026142D-01	.4026142D-01	.00D+00	.00D+00
98	0	0	.2933390D-01	.3835160D-01	.00D+00	.00D+00
99	0	0	.2172945D-01	.3522717D-01	.00D+00	.00D+00
100	0	0	.1649486D-01	.3195890D-01	.00D+00	.00D+00
101	0	0	.1285377D-01	.2893037D-01	.00D+00	.00D+00
102	0	0	.1027380D-01	.2624201D-01	.00D+00	.00D+00
103	0	0	.8407877D-02	.2388870D-01	.00D+00	.00D+00
104	0	0	.7032477D-02	.2182763D-01	.00D+00	.00D+00
105	0	0	.6001941D-02	.2001313D-01	.00D+00	.00D+00
106	0	0	.5219635D-02	.1839897D-01	.00D+00	.00D+00
107	0	0	.4619920D-02	.1694806D-01	.00D+00	.00D+00
108	0	0	.4157306D-02	.1562671D-01	.00D+00	.00D+00
109	0	0	.3799486D-02	.1440925D-01	.00D+00	.00D+00
110	0	0	.3522945D-02	.1327340D-01	.00D+00	.00D+00
111	0	0	.3310217D-02	.1220034D-01	.00D+00	.00D+00
112	0	0	.3148059D-02	.1117643D-01	.00D+00	.00D+00
113	0	0	.3026142D-02	.1018910D-01	.00D+00	.00D+00
114	0	0	.2936187D-02	.9228425D-02	.00D+00	.00D+00
115	0	0	.2871575D-02	.8286530D-02	.00D+00	.00D+00
116	0	0	.2826826D-02	.7357078D-02	.00D+00	.00D+00
117	0	0	.2797374D-02	.6435046D-02	.00D+00	.00D+00
118	0	0	.2779395D-02	.5516895D-02	.00D+00	.00D+00
119	0	0	.2769521D-02	.4599943D-02	.00D+00	.00D+00
120	0	0	.2765068D-02	.3682648D-02	.00D+00	.00D+00
121	0	0	.2763927D-02	.2763927D-02	.00D+00	.00D+00
122	0	0	.2764384D-02	.1843779D-02	.00D+00	.00D+00
123	0	0	.2765126D-02	.9222546D-03	.00D+00	.00D+00
124	0	0	.2765696D-02	.0000000D+00	.00D+00	.00D+00
125	0	0	.6366838D-01	.0000000D+00	.00D+00	.00D+00
126	0	0	.5628596D-01	.1558733D-01	.00D+00	.00D+00
127	0	0	.4772774D-01	.2515525D-01	.00D+00	.00D+00
128	0	0	.3835160D-01	.2933390D-01	.00D+00	.00D+00
129	0	0	.3018950D-01	.3018950D-01	.00D+00	.00D+00
130	0	0	.2373973D-01	.2933390D-01	.00D+00	.00D+00
131	0	0	.1884589D-01	.2772374D-01	.00D+00	.00D+00
132	0	0	.1518208D-01	.2586130D-01	.00D+00	.00D+00

Table 6.15   Input Data Sets for Problem 8 (continued)

133	0	0	.1243824D-01	.2398801D-01	.00D+00	.00D+00
134	0	0	.1037003D-01	.2220890D-01	.00D+00	.00D+00
135	0	0	.8797888D-02	.2055993D-01	.00D+00	.00D+00
136	0	0	.7592237D-02	.1904509D-01	.00D+00	.00D+00
137	0	0	.6660845D-02	.1765354D-01	.00D+00	.00D+00
138	0	0	.5937557D-02	.1637043D-01	.00D+00	.00D+00
139	0	0	.5374258D-02	.1517808D-01	.00D+00	.00D+00
140	0	0	.4935674D-02	.1406107D-01	.00D+00	.00D+00
141	0	0	.4595377D-02	.1300457D-01	.00D+00	.00D+00
142	0	0	.4333219D-02	.1199429D-01	.00D+00	.00D+00
143	0	0	.4133619D-02	.1102061D-01	.00D+00	.00D+00
144	0	0	.3984132D-02	.1007346D-01	.00D+00	.00D+00
145	0	0	.3874772D-02	.9144806D-02	.00D+00	.00D+00
146	0	0	.3797317D-02	.8228139D-02	.00D+00	.00D+00
147	0	0	.3744920D-02	.7318322D-02	.00D+00	.00D+00
148	0	0	.3711758D-02	.6411187D-02	.00D+00	.00D+00
149	0	0	.3692808D-02	.5503824D-02	.00D+00	.00D+00
150	0	0	.3683904D-02	.4594292D-02	.00D+00	.00D+00
151	0	0	.3681507D-02	.3681507D-02	.00D+00	.00D+00
152	0	0	.3682648D-02	.2765068D-02	.00D+00	.00D+00
153	0	0	.3685103D-02	.1845491D-02	.00D+00	.00D+00
154	0	0	.3687215D-02	.9233961D-03	.00D+00	.00D+00
155	0	0	.3688813D-02	.0000000D+00	.00D+00	.00D+00
156	0	0	.5001998D-01	.0000000D+00	.00D+00	.00D+00
157	0	0	.4614212D-01	.9956792D-02	.00D+00	.00D+00
158	0	0	.4126313D-01	.1734760D-01	.00D+00	.00D+00
159	0	0	.3522717D-01	.2172945D-01	.00D+00	.00D+00
160	0	0	.2933390D-01	.2373973D-01	.00D+00	.00D+00
161	0	0	.2419521D-01	.2419521D-01	.00D+00	.00D+00
162	0	0	.1996747D-01	.2374030D-01	.00D+00	.00D+00
163	0	0	.1658904D-01	.2280251D-01	.00D+00	.00D+00
164	0	0	.1392580D-01	.2163984D-01	.00D+00	.00D+00
165	0	0	.1183619D-01	.2039897D-01	.00D+00	.00D+00
166	0	0	.1019663D-01	.1915753D-01	.00D+00	.00D+00
167	0	0	.8908162D-02	.1795320D-01	.00D+00	.00D+00
168	0	0	.7894007D-02	.1679966D-01	.00D+00	.00D+00
169	0	0	.7095148D-02	.1570148D-01	.00D+00	.00D+00
170	0	0	.6466495D-02	.1465468D-01	.00D+00	.00D+00
171	0	0	.5973573D-02	.1365240D-01	.00D+00	.00D+00
172	0	0	.5589612D-02	.1268836D-01	.00D+00	.00D+00
173	0	0	.5293664D-02	.1175228D-01	.00D+00	.00D+00
174	0	0	.5068950D-02	.1083830D-01	.00D+00	.00D+00
175	0	0	.4901884D-02	.9939269D-02	.00D+00	.00D+00
176	0	0	.4781393D-02	.9049201D-02	.00D+00	.00D+00
177	0	0	.4698059D-02	.8163014D-02	.00D+00	.00D+00
178	0	0	.4643836D-02	.7276826D-02	.00D+00	.00D+00
179	0	0	.4611872D-02	.6387500D-02	.00D+00	.00D+00
180	0	0	.4596290D-02	.5492922D-02	.00D+00	.00D+00
181	0	0	.4591895D-02	.4591895D-02	.00D+00	.00D+00
182	0	0	.4594292D-02	.3683904D-02	.00D+00	.00D+00
183	0	0	.4599943D-02	.2769521D-02	.00D+00	.00D+00
184	0	0	.4606107D-02	.1849658D-02	.00D+00	.00D+00
185	0	0	.4610616D-02	.9258505D-03	.00D+00	.00D+00
186	0	0	.4613813D-02	.0000000D+00	.00D+00	.00D+00
187	0	0	.4118950D-01	.0000000D+00	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 188     0    0   .3893836D-01    .6891952D-02    .00D+00    .00D+00
 189     0    0   .3595491D-01    .1254983D-01    .00D+00    .00D+00
 190     0    0   .3195890D-01    .1649486D-01    .00D+00    .00D+00
 191     0    0   .2772374D-01    .1884589D-01    .00D+00    .00D+00
 192     0    0   .2374030D-01    .1996747D-01    .00D+00    .00D+00
 193     0    0   .2023916D-01    .2023916D-01    .00D+00    .00D+00
 194     0    0   .1728196D-01    .1996747D-01    .00D+00    .00D+00
 195     0    0   .1484075D-01    .1936986D-01    .00D+00    .00D+00
 196     0    0   .1285217D-01    .1859018D-01    .00D+00    .00D+00
 197     0    0   .1124441D-01    .1771861D-01    .00D+00    .00D+00
 198     0    0   .9949943D-02    .1680936D-01    .00D+00    .00D+00
 199     0    0   .8911872D-02    .1589098D-01    .00D+00    .00D+00
 200     0    0   .8082420D-02    .1498174D-01    .00D+00    .00D+00
 201     0    0   .7423002D-02    .1408676D-01    .00D+00    .00D+00
 202     0    0   .6902511D-02    .1320719D-01    .00D+00    .00D+00
 203     0    0   .6495890D-02    .1234304D-01    .00D+00    .00D+00
 204     0    0   .6182877D-02    .1148881D-01    .00D+00    .00D+00
 205     0    0   .5946632D-02    .1064110D-01    .00D+00    .00D+00
 206     0    0   .5773231D-02    .9796062D-02    .00D+00    .00D+00
 207     0    0   .5650970D-02    .8949600D-02    .00D+00    .00D+00
 208     0    0   .5569635D-02    .8097945D-02    .00D+00    .00D+00
 209     0    0   .5520434D-02    .7238470D-02    .00D+00    .00D+00
 210     0    0   .5495662D-02    .6369064D-02    .00D+00    .00D+00
 211     0    0   .5488470D-02    .5488470D-02    .00D+00    .00D+00
 212     0    0   .5492922D-02    .4596290D-02    .00D+00    .00D+00
 213     0    0   .5503824D-02    .3692808D-02    .00D+00    .00D+00
 214     0    0   .5516895D-02    .2779395D-02    .00D+00    .00D+00
 215     0    0   .5528767D-02    .1857763D-02    .00D+00    .00D+00
 216     0    0   .5536872D-02    .9303653D-03    .00D+00    .00D+00
 217     0    0   .5542580D-02    .0000000D+00    .00D+00    .00D+00
 218     0    0   .3500342D-01    .0000000D+00    .00D+00    .00D+00
 219     0    0   .3359247D-01    .5061301D-02    .00D+00    .00D+00
 220     0    0   .3165982D-01    .9465126D-02    .00D+00    .00D+00
 221     0    0   .2893037D-01    .1285377D-01    .00D+00    .00D+00
 222     0    0   .2586130D-01    .1518208D-01    .00D+00    .00D+00
 223     0    0   .2280251D-01    .1658904D-01    .00D+00    .00D+00
 224     0    0   .1996747D-01    .1728196D-01    .00D+00    .00D+00
 225     0    0   .1745833D-01    .1745833D-01    .00D+00    .00D+00
 226     0    0   .1530308D-01    .1728196D-01    .00D+00    .00D+00
 227     0    0   .1348744D-01    .1687329D-01    .00D+00    .00D+00
 228     0    0   .1197803D-01    .1631792D-01    .00D+00    .00D+00
 229     0    0   .1073556D-01    .1567295D-01    .00D+00    .00D+00
 230     0    0   .9721176D-02    .1497489D-01    .00D+00    .00D+00
 231     0    0   .8899715D-02    .1424715D-01    .00D+00    .00D+00
 232     0    0   .8240582D-02    .1350285D-01    .00D+00    .00D+00
 233     0    0   .7717580D-02    .1274829D-01    .00D+00    .00D+00
 234     0    0   .7308676D-02    .1198687D-01    .00D+00    .00D+00
 235     0    0   .6995263D-02    .1121821D-01    .00D+00    .00D+00
 236     0    0   .6761416D-02    .1044144D-01    .00D+00    .00D+00
 237     0    0   .6593493D-02    .9654452D-02    .00D+00    .00D+00
 238     0    0   .6479566D-02    .8855023D-02    .00D+00    .00D+00
 239     0    0   .6409132D-02    .8040753D-02    .00D+00    .00D+00
 240     0    0   .6372717D-02    .7210103D-02    .00D+00    .00D+00
 241     0    0   .6361872D-02    .6361872D-02    .00D+00    .00D+00
 242     0    0   .6369064D-02    .5495662D-02    .00D+00    .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

243	0	0	.6387500D-02	.4611872D-02	.00D+00	.00D+00
244	0	0	.6411187D-02	.3711758D-02	.00D+00	.00D+00
245	0	0	.6435046D-02	.2797374D-02	.00D+00	.00D+00
246	0	0	.6455080D-02	.1871632D-02	.00D+00	.00D+00
247	0	0	.6468322D-02	.9378596D-03	.00D+00	.00D+00
248	0	0	.6477568D-02	.0000000D+00	.00D+00	.00D+00
249	0	0	.3041039D-01	.0000000D+00	.00D+00	.00D+00
250	0	0	.2947317D-01	.3888071D-02	.00D+00	.00D+00
251	0	0	.2816210D-01	.7395548D-02	.00D+00	.00D+00
252	0	0	.2624201D-01	.1027380D-01	.00D+00	.00D+00
253	0	0	.2398801D-01	.1243824D-01	.00D+00	.00D+00
254	0	0	.2163984D-01	.1392580D-01	.00D+00	.00D+00
255	0	0	.1936986D-01	.1484075D-01	.00D+00	.00D+00
256	0	0	.1728196D-01	.1530308D-01	.00D+00	.00D+00
257	0	0	.1542637D-01	.1542637D-01	.00D+00	.00D+00
258	0	0	.1381678D-01	.1530365D-01	.00D+00	.00D+00
259	0	0	.1244463D-01	.1500685D-01	.00D+00	.00D+00
260	0	0	.1129269D-01	.1458904D-01	.00D+00	.00D+00
261	0	0	.1033756D-01	.1408847D-01	.00D+00	.00D+00
262	0	0	.9554737D-02	.1352911D-01	.00D+00	.00D+00
263	0	0	.8921918D-02	.1292865D-01	.00D+00	.00D+00
264	0	0	.8418493D-02	.1229623D-01	.00D+00	.00D+00
265	0	0	.8025970D-02	.1163756D-01	.00D+00	.00D+00
266	0	0	.7728082D-02	.1095599D-01	.00D+00	.00D+00
267	0	0	.7510331D-02	.1025205D-01	.00D+00	.00D+00
268	0	0	.7359760D-02	.9525400D-02	.00D+00	.00D+00
269	0	0	.7264726D-02	.8775114D-02	.00D+00	.00D+00
270	0	0	.7214498D-02	.8000000D-02	.00D+00	.00D+00
271	0	0	.7199315D-02	.7199315D-02	.00D+00	.00D+00
272	0	0	.7210103D-02	.6372717D-02	.00D+00	.00D+00
273	0	0	.7238470D-02	.5520434D-02	.00D+00	.00D+00
274	0	0	.7276826D-02	.4643836D-02	.00D+00	.00D+00
275	0	0	.7318322D-02	.3744920D-02	.00D+00	.00D+00
276	0	0	.7357078D-02	.2826826D-02	.00D+00	.00D+00
277	0	0	.7388299D-02	.1893493D-02	.00D+00	.00D+00
278	0	0	.7408447D-02	.9494578D-03	.00D+00	.00D+00
279	0	0	.7422374D-02	.0000000D+00	.00D+00	.00D+00
280	0	0	.2684646D-01	.0000000D+00	.00D+00	.00D+00
281	0	0	.2619692D-01	.3095320D-02	.00D+00	.00D+00
282	0	0	.2527454D-01	.5955251D-02	.00D+00	.00D+00
283	0	0	.2388870D-01	.8407877D-02	.00D+00	.00D+00
284	0	0	.2220890D-01	.1037003D-01	.00D+00	.00D+00
285	0	0	.2039897D-01	.1183619D-01	.00D+00	.00D+00
286	0	0	.1859018D-01	.1285217D-01	.00D+00	.00D+00
287	0	0	.1687329D-01	.1348744D-01	.00D+00	.00D+00
288	0	0	.1530365D-01	.1381678D-01	.00D+00	.00D+00
289	0	0	.1390753D-01	.1390753D-01	.00D+00	.00D+00
290	0	0	.1269235D-01	.1381678D-01	.00D+00	.00D+00
291	0	0	.1165400D-01	.1358904D-01	.00D+00	.00D+00
292	0	0	.1078122D-01	.1326027D-01	.00D+00	.00D+00
293	0	0	.1005976D-01	.1285331D-01	.00D+00	.00D+00
294	0	0	.9474030D-02	.1238642D-01	.00D+00	.00D+00
295	0	0	.9008562D-02	.1186986D-01	.00D+00	.00D+00
296	0	0	.8648687D-02	.1131159D-01	.00D+00	.00D+00
297	0	0	.8380765D-02	.1071610D-01	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

298	0	0	.8192009D-02	.1008539D-01	.00D+00	.00D+00
299	0	0	.8070491D-02	.9419977D-02	.00D+00	.00D+00
300	0	0	.8004966D-02	.8719920D-02	.00D+00	.00D+00
301	0	0	.7984817D-02	.7984817D-02	.00D+00	.00D+00
302	0	0	.8000000D-02	.7214498D-02	.00D+00	.00D+00
303	0	0	.8040753D-02	.6409132D-02	.00D+00	.00D+00
304	0	0	.8097945D-02	.5569635D-02	.00D+00	.00D+00
305	0	0	.8163014D-02	.4698059D-02	.00D+00	.00D+00
306	0	0	.8228139D-02	.3797317D-02	.00D+00	.00D+00
307	0	0	.8286530D-02	.2871575D-02	.00D+00	.00D+00
308	0	0	.8332477D-02	.1925970D-02	.00D+00	.00D+00
309	0	0	.8361815D-02	.9665068D-03	.00D+00	.00D+00
310	0	0	.8382021D-02	.0000000D+00	.00D+00	.00D+00
311	0	0	.2398402D-01	.0000000D+00	.00D+00	.00D+00
312	0	0	.2351826D-01	.2537900D-02	.00D+00	.00D+00
313	0	0	.2284989D-01	.4922317D-02	.00D+00	.00D+00
314	0	0	.2182763D-01	.7032477D-02	.00D+00	.00D+00
315	0	0	.2055993D-01	.8797888D-02	.00D+00	.00D+00
316	0	0	.1915753D-01	.1019663D-01	.00D+00	.00D+00
317	0	0	.1771861D-01	.1124441D-01	.00D+00	.00D+00
318	0	0	.1631792D-01	.1197803D-01	.00D+00	.00D+00
319	0	0	.1500685D-01	.1244463D-01	.00D+00	.00D+00
320	0	0	.1381678D-01	.1269235D-01	.00D+00	.00D+00
321	0	0	.1276256D-01	.1276256D-01	.00D+00	.00D+00
322	0	0	.1184932D-01	.1269178D-01	.00D+00	.00D+00
323	0	0	.1107397D-01	.1251027D-01	.00D+00	.00D+00
324	0	0	.1042917D-01	.1223801D-01	.00D+00	.00D+00
325	0	0	.9905765D-02	.1189269D-01	.00D+00	.00D+00
326	0	0	.9492865D-02	.1148510D-01	.00D+00	.00D+00
327	0	0	.9179395D-02	.1102300D-01	.00D+00	.00D+00
328	0	0	.8954281D-02	.1051159D-01	.00D+00	.00D+00
329	0	0	.8806450D-02	.9953311D-02	.00D+00	.00D+00
330	0	0	.8725114D-02	.9349201D-02	.00D+00	.00D+00
331	0	0	.8699772D-02	.8699772D-02	.00D+00	.00D+00
332	0	0	.8719920D-02	.8004966D-02	.00D+00	.00D+00
333	0	0	.8775114D-02	.7264726D-02	.00D+00	.00D+00
334	0	0	.8855023D-02	.6479566D-02	.00D+00	.00D+00
335	0	0	.8949600D-02	.5650970D-02	.00D+00	.00D+00
336	0	0	.9049201D-02	.4781393D-02	.00D+00	.00D+00
337	0	0	.9144806D-02	.3874772D-02	.00D+00	.00D+00
338	0	0	.9228425D-02	.2936187D-02	.00D+00	.00D+00
339	0	0	.9293322D-02	.1972203D-02	.00D+00	.00D+00
340	0	0	.9334418D-02	.9906221D-03	.00D+00	.00D+00
341	0	0	.9362614D-02	.0000000D+00	.00D+00	.00D+00
342	0	0	.2161644D-01	.0000000D+00	.00D+00	.00D+00
343	0	0	.2127397D-01	.2134075D-02	.00D+00	.00D+00
344	0	0	.2077968D-01	.4163584D-02	.00D+00	.00D+00
345	0	0	.2001313D-01	.6001941D-02	.00D+00	.00D+00
346	0	0	.1904509D-01	.7592237D-02	.00D+00	.00D+00
347	0	0	.1795320D-01	.8908162D-02	.00D+00	.00D+00
348	0	0	.1680936D-01	.9949943D-02	.00D+00	.00D+00
349	0	0	.1567295D-01	.1073556D-01	.00D+00	.00D+00
350	0	0	.1458904D-01	.1129269D-01	.00D+00	.00D+00
351	0	0	.1358904D-01	.1165400D-01	.00D+00	.00D+00
352	0	0	.1269178D-01	.1184932D-01	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

353	0	0	.1190639D-01	.1190639D-01	.00D+00	.00D+00
354	0	0	.1123545D-01	.1184932D-01	.00D+00	.00D+00
355	0	0	.1067728D-01	.1169578D-01	.00D+00	.00D+00
356	0	0	.1022700D-01	.1146084D-01	.00D+00	.00D+00
357	0	0	.9877854D-02	.1115445D-01	.00D+00	.00D+00
358	0	0	.9621918D-02	.1078402D-01	.00D+00	.00D+00
359	0	0	.9450457D-02	.1035400D-01	.00D+00	.00D+00
360	0	0	.9354281D-02	.9866952D-02	.00D+00	.00D+00
361	0	0	.9323858D-02	.9323858D-02	.00D+00	.00D+00
362	0	0	.9349201D-02	.8725114D-02	.00D+00	.00D+00
363	0	0	.9419977D-02	.8070491D-02	.00D+00	.00D+00
364	0	0	.9525400D-02	.7359760D-02	.00D+00	.00D+00
365	0	0	.9654452D-02	.6593493D-02	.00D+00	.00D+00
366	0	0	.9796062D-02	.5773231D-02	.00D+00	.00D+00
367	0	0	.9939269D-02	.4901884D-02	.00D+00	.00D+00
368	0	0	.1007346D-01	.3984132D-02	.00D+00	.00D+00
369	0	0	.1018910D-01	.3026142D-02	.00D+00	.00D+00
370	0	0	.1027808D-01	.2036073D-02	.00D+00	.00D+00
371	0	0	.1033408D-01	.1023784D-02	.00D+00	.00D+00
372	0	0	.1037232D-01	.0000000D+00	.00D+00	.00D+00
373	0	0	.1961130D-01	.0000000D+00	.00D+00	.00D+00
374	0	0	.1935445D-01	.1834874D-02	.00D+00	.00D+00
375	0	0	.1898174D-01	.3595833D-02	.00D+00	.00D+00
376	0	0	.1839897D-01	.5219635D-02	.00D+00	.00D+00
377	0	0	.1765354D-01	.6660845D-02	.00D+00	.00D+00
378	0	0	.1679966D-01	.7894007D-02	.00D+00	.00D+00
379	0	0	.1589098D-01	.8911872D-02	.00D+00	.00D+00
380	0	0	.1497489D-01	.9721176D-02	.00D+00	.00D+00
381	0	0	.1408847D-01	.1033756D-01	.00D+00	.00D+00
382	0	0	.1326027D-01	.1078122D-01	.00D+00	.00D+00
383	0	0	.1251027D-01	.1107397D-01	.00D+00	.00D+00
384	0	0	.1184932D-01	.1123545D-01	.00D+00	.00D+00
385	0	0	.1128436D-01	.1128436D-01	.00D+00	.00D+00
386	0	0	.1081747D-01	.1123527D-01	.00D+00	.00D+00
387	0	0	.1044709D-01	.1110046D-01	.00D+00	.00D+00
388	0	0	.1016969D-01	.1088818D-01	.00D+00	.00D+00
389	0	0	.9979909D-02	.1060457D-01	.00D+00	.00D+00
390	0	0	.9871347D-02	.1025337D-01	.00D+00	.00D+00
391	0	0	.9836530D-02	.9836530D-02	.00D+00	.00D+00
392	0	0	.9866952D-02	.9354281D-02	.00D+00	.00D+00
393	0	0	.9953311D-02	.8806450D-02	.00D+00	.00D+00
394	0	0	.1008539D-01	.8192009D-02	.00D+00	.00D+00
395	0	0	.1025205D-01	.7510331D-02	.00D+00	.00D+00
396	0	0	.1044144D-01	.6761416D-02	.00D+00	.00D+00
397	0	0	.1064110D-01	.5946632D-02	.00D+00	.00D+00
398	0	0	.1083830D-01	.5068950D-02	.00D+00	.00D+00
399	0	0	.1102061D-01	.4133619D-02	.00D+00	.00D+00
400	0	0	.1117643D-01	.3148059D-02	.00D+00	.00D+00
401	0	0	.1129566D-01	.2122317D-02	.00D+00	.00D+00
402	0	0	.1137049D-01	.1068413D-02	.00D+00	.00D+00
403	0	0	.1142152D-01	.0000000D+00	.00D+00	.00D+00
404	0	0	.1787386D-01	.0000000D+00	.00D+00	.00D+00
405	0	0	.1767865D-01	.1609475D-02	.00D+00	.00D+00
406	0	0	.1739498D-01	.3165183D-02	.00D+00	.00D+00
407	0	0	.1694806D-01	.4619920D-02	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

408	0	0	.1637043D-01	.5937557D-02	.00D+00	.00D+00
409	0	0	.1570148D-01	.7095148D-02	.00D+00	.00D+00
410	0	0	.1498174D-01	.8082420D-02	.00D+00	.00D+00
411	0	0	.1424715D-01	.8899715D-02	.00D+00	.00D+00
412	0	0	.1352911D-01	.9554737D-02	.00D+00	.00D+00
413	0	0	.1285331D-01	.1005976D-01	.00D+00	.00D+00
414	0	0	.1223801D-01	.1042917D-01	.00D+00	.00D+00
415	0	0	.1169578D-01	.1067728D-01	.00D+00	.00D+00
416	0	0	.1123527D-01	.1081747D-01	.00D+00	.00D+00
417	0	0	.1086119D-01	.1086119D-01	.00D+00	.00D+00
418	0	0	.1057432D-01	.1081747D-01	.00D+00	.00D+00
419	0	0	.1037380D-01	.1069321D-01	.00D+00	.00D+00
420	0	0	.1025668D-01	.1049269D-01	.00D+00	.00D+00
421	0	0	.1021849D-01	.1021849D-01	.00D+00	.00D+00
422	0	0	.1025337D-01	.9871347D-02	.00D+00	.00D+00
423	0	0	.1035400D-01	.9450457D-02	.00D+00	.00D+00
424	0	0	.1051159D-01	.8954281D-02	.00D+00	.00D+00
425	0	0	.1071610D-01	.8380765D-02	.00D+00	.00D+00
426	0	0	.1095599D-01	.7728082D-02	.00D+00	.00D+00
427	0	0	.1121821D-01	.6995263D-02	.00D+00	.00D+00
428	0	0	.1148881D-01	.6182877D-02	.00D+00	.00D+00
429	0	0	.1175228D-01	.5293664D-02	.00D+00	.00D+00
430	0	0	.1199429D-01	.4333219D-02	.00D+00	.00D+00
431	0	0	.1220034D-01	.3310217D-02	.00D+00	.00D+00
432	0	0	.1235731D-01	.2236701D-02	.00D+00	.00D+00
433	0	0	.1245605D-01	.1127557D-02	.00D+00	.00D+00
434	0	0	.1252340D-01	.0000000D+00	.00D+00	.00D+00
435	0	0	.1633790D-01	.0000000D+00	.00D+00	.00D+00
436	0	0	.1618950D-01	.1437785D-02	.00D+00	.00D+00
437	0	0	.1597203D-01	.2835559D-02	.00D+00	.00D+00
438	0	0	.1562671D-01	.4157306D-02	.00D+00	.00D+00
439	0	0	.1517808D-01	.5374258D-02	.00D+00	.00D+00
440	0	0	.1465468D-01	.6466495D-02	.00D+00	.00D+00
441	0	0	.1408676D-01	.7423002D-02	.00D+00	.00D+00
442	0	0	.1350285D-01	.8240582D-02	.00D+00	.00D+00
443	0	0	.1292865D-01	.8921918D-02	.00D+00	.00D+00
444	0	0	.1238642D-01	.9474030D-02	.00D+00	.00D+00
445	0	0	.1189269D-01	.9905765D-02	.00D+00	.00D+00
446	0	0	.1146084D-01	.1022700D-01	.00D+00	.00D+00
447	0	0	.1110046D-01	.1044709D-01	.00D+00	.00D+00
448	0	0	.1081747D-01	.1057432D-01	.00D+00	.00D+00
449	0	0	.1061513D-01	.1061513D-01	.00D+00	.00D+00
450	0	0	.1049446D-01	.1057432D-01	.00D+00	.00D+00
451	0	0	.1045457D-01	.1045457D-01	.00D+00	.00D+00
452	0	0	.1049269D-01	.1025668D-01	.00D+00	.00D+00
453	0	0	.1060457D-01	.9979909D-02	.00D+00	.00D+00
454	0	0	.1078402D-01	.9621918D-02	.00D+00	.00D+00
455	0	0	.1102300D-01	.9179395D-02	.00D+00	.00D+00
456	0	0	.1131159D-01	.8648687D-02	.00D+00	.00D+00
457	0	0	.1163756D-01	.8025970D-02	.00D+00	.00D+00
458	0	0	.1198687D-01	.7308676D-02	.00D+00	.00D+00
459	0	0	.1234304D-01	.6495890D-02	.00D+00	.00D+00
460	0	0	.1268836D-01	.5589612D-02	.00D+00	.00D+00
461	0	0	.1300457D-01	.4595377D-02	.00D+00	.00D+00
462	0	0	.1327340D-01	.3522945D-02	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

463	0	0	.1347831D-01	.2386644D-02	.00D+00	.00D+00
464	0	0	.1360674D-01	.1205137D-02	.00D+00	.00D+00
465	0	0	.1369463D-01	.0000000D+00	.00D+00	.00D+00
466	0	0	.1495833D-01	.0000000D+00	.00D+00	.00D+00
467	0	0	.1484304D-01	.1306221D-02	.00D+00	.00D+00
468	0	0	.1467523D-01	.2581963D-02	.00D+00	.00D+00
469	0	0	.1440925D-01	.3799486D-02	.00D+00	.00D+00
470	0	0	.1406107D-01	.4935674D-02	.00D+00	.00D+00
471	0	0	.1365240D-01	.5973573D-02	.00D+00	.00D+00
472	0	0	.1320719D-01	.6902511D-02	.00D+00	.00D+00
473	0	0	.1274829D-01	.7717580D-02	.00D+00	.00D+00
474	0	0	.1229623D-01	.8418493D-02	.00D+00	.00D+00
475	0	0	.1186986D-01	.9008562D-02	.00D+00	.00D+00
476	0	0	.1148510D-01	.9492865D-02	.00D+00	.00D+00
477	0	0	.1115445D-01	.9877854D-02	.00D+00	.00D+00
478	0	0	.1088818D-01	.1016969D-01	.00D+00	.00D+00
479	0	0	.1069321D-01	.1037380D-01	.00D+00	.00D+00
480	0	0	.1057432D-01	.1049446D-01	.00D+00	.00D+00
481	0	0	.1053436D-01	.1053436D-01	.00D+00	.00D+00
482	0	0	.1057432D-01	.1049446D-01	.00D+00	.00D+00
483	0	0	.1069321D-01	.1037380D-01	.00D+00	.00D+00
484	0	0	.1088818D-01	.1016969D-01	.00D+00	.00D+00
485	0	0	.1115445D-01	.9877854D-02	.00D+00	.00D+00
486	0	0	.1148510D-01	.9492865D-02	.00D+00	.00D+00
487	0	0	.1186986D-01	.9008562D-02	.00D+00	.00D+00
488	0	0	.1229623D-01	.8418493D-02	.00D+00	.00D+00
489	0	0	.1274829D-01	.7717580D-02	.00D+00	.00D+00
490	0	0	.1320719D-01	.6902511D-02	.00D+00	.00D+00
491	0	0	.1365240D-01	.5973573D-02	.00D+00	.00D+00
492	0	0	.1406107D-01	.4935674D-02	.00D+00	.00D+00
493	0	0	.1440925D-01	.3799486D-02	.00D+00	.00D+00
494	0	0	.1467523D-01	.2581963D-02	.00D+00	.00D+00
495	0	0	.1484304D-01	.1306221D-02	.00D+00	.00D+00
496	0	0	.1495833D-01	.0000000D+00	.00D+00	.00D+00
497	0	0	.1369463D-01	.0000000D+00	.00D+00	.00D+00
498	0	0	.1360674D-01	.1205137D-02	.00D+00	.00D+00
499	0	0	.1347831D-01	.2386644D-02	.00D+00	.00D+00
500	0	0	.1327340D-01	.3522945D-02	.00D+00	.00D+00
501	0	0	.1300457D-01	.4595377D-02	.00D+00	.00D+00
502	0	0	.1268836D-01	.5589612D-02	.00D+00	.00D+00
503	0	0	.1234304D-01	.6495890D-02	.00D+00	.00D+00
504	0	0	.1198687D-01	.7308676D-02	.00D+00	.00D+00
505	0	0	.1163756D-01	.8025970D-02	.00D+00	.00D+00
506	0	0	.1131159D-01	.8648687D-02	.00D+00	.00D+00
507	0	0	.1102300D-01	.9179395D-02	.00D+00	.00D+00
508	0	0	.1078402D-01	.9621918D-02	.00D+00	.00D+00
509	0	0	.1060457D-01	.9979909D-02	.00D+00	.00D+00
510	0	0	.1049269D-01	.1025668D-01	.00D+00	.00D+00
511	0	0	.1045457D-01	.1045457D-01	.00D+00	.00D+00
512	0	0	.1049446D-01	.1057432D-01	.00D+00	.00D+00
513	0	0	.1061513D-01	.1061513D-01	.00D+00	.00D+00
514	0	0	.1081747D-01	.1057432D-01	.00D+00	.00D+00
515	0	0	.1110046D-01	.1044709D-01	.00D+00	.00D+00
516	0	0	.1146084D-01	.1022700D-01	.00D+00	.00D+00
517	0	0	.1189269D-01	.9905765D-02	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

518	0	0	.1238642D-01	.9474030D-02	.00D+00	.00D+00
519	0	0	.1292865D-01	.8921918D-02	.00D+00	.00D+00
520	0	0	.1350285D-01	.8240582D-02	.00D+00	.00D+00
521	0	0	.1408676D-01	.7423002D-02	.00D+00	.00D+00
522	0	0	.1465468D-01	.6466495D-02	.00D+00	.00D+00
523	0	0	.1517808D-01	.5374258D-02	.00D+00	.00D+00
524	0	0	.1562671D-01	.4157306D-02	.00D+00	.00D+00
525	0	0	.1597203D-01	.2835559D-02	.00D+00	.00D+00
526	0	0	.1618950D-01	.1437785D-02	.00D+00	.00D+00
527	0	0	.1633790D-01	.0000000D+00	.00D+00	.00D+00
528	0	0	.1252340D-01	.0000000D+00	.00D+00	.00D+00
529	0	0	.1245605D-01	.1127557D-02	.00D+00	.00D+00
530	0	0	.1235731D-01	.2236701D-02	.00D+00	.00D+00
531	0	0	.1220034D-01	.3310217D-02	.00D+00	.00D+00
532	0	0	.1199429D-01	.4333219D-02	.00D+00	.00D+00
533	0	0	.1175228D-01	.5293664D-02	.00D+00	.00D+00
534	0	0	.1148881D-01	.6182877D-02	.00D+00	.00D+00
535	0	0	.1121821D-01	.6995263D-02	.00D+00	.00D+00
536	0	0	.1095599D-01	.7728082D-02	.00D+00	.00D+00
537	0	0	.1071610D-01	.8380765D-02	.00D+00	.00D+00
538	0	0	.1051159D-01	.8954281D-02	.00D+00	.00D+00
539	0	0	.1035400D-01	.9450457D-02	.00D+00	.00D+00
540	0	0	.1025337D-01	.9871347D-02	.00D+00	.00D+00
541	0	0	.1021849D-01	.1021849D-01	.00D+00	.00D+00
542	0	0	.1025668D-01	.1049269D-01	.00D+00	.00D+00
543	0	0	.1037380D-01	.1069321D-01	.00D+00	.00D+00
544	0	0	.1057432D-01	.1081747D-01	.00D+00	.00D+00
545	0	0	.1086119D-01	.1086119D-01	.00D+00	.00D+00
546	0	0	.1123527D-01	.1081747D-01	.00D+00	.00D+00
547	0	0	.1169578D-01	.1067728D-01	.00D+00	.00D+00
548	0	0	.1223801D-01	.1042917D-01	.00D+00	.00D+00
549	0	0	.1285331D-01	.1005976D-01	.00D+00	.00D+00
550	0	0	.1352911D-01	.9554737D-02	.00D+00	.00D+00
551	0	0	.1424715D-01	.8899715D-02	.00D+00	.00D+00
552	0	0	.1498174D-01	.8082420D-02	.00D+00	.00D+00
553	0	0	.1570148D-01	.7095148D-02	.00D+00	.00D+00
554	0	0	.1637043D-01	.5937557D-02	.00D+00	.00D+00
555	0	0	.1694806D-01	.4619920D-02	.00D+00	.00D+00
556	0	0	.1739498D-01	.3165183D-02	.00D+00	.00D+00
557	0	0	.1767865D-01	.1609475D-02	.00D+00	.00D+00
558	0	0	.1787386D-01	.0000000D+00	.00D+00	.00D+00
559	0	0	.1142152D-01	.0000000D+00	.00D+00	.00D+00
560	0	0	.1137049D-01	.1068413D-02	.00D+00	.00D+00
561	0	0	.1129566D-01	.2122317D-02	.00D+00	.00D+00
562	0	0	.1117643D-01	.3148059D-02	.00D+00	.00D+00
563	0	0	.1102061D-01	.4133619D-02	.00D+00	.00D+00
564	0	0	.1083830D-01	.5068950D-02	.00D+00	.00D+00
565	0	0	.1064110D-01	.5946632D-02	.00D+00	.00D+00
566	0	0	.1044144D-01	.6761416D-02	.00D+00	.00D+00
567	0	0	.1025205D-01	.7510331D-02	.00D+00	.00D+00
568	0	0	.1008539D-01	.8192009D-02	.00D+00	.00D+00
569	0	0	.9953311D-02	.8806450D-02	.00D+00	.00D+00
570	0	0	.9866952D-02	.9354281D-02	.00D+00	.00D+00
571	0	0	.9836530D-02	.9836530D-02	.00D+00	.00D+00
572	0	0	.9871347D-02	.1025337D-01	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

```
  573    0    0   .9979909D-02   .1060457D-01   .00D+00   .00D+00
  574    0    0   .1016969D-01   .1088818D-01   .00D+00   .00D+00
  575    0    0   .1044709D-01   .1110046D-01   .00D+00   .00D+00
  576    0    0   .1081747D-01   .1123527D-01   .00D+00   .00D+00
  577    0    0   .1128436D-01   .1128436D-01   .00D+00   .00D+00
  578    0    0   .1184932D-01   .1123545D-01   .00D+00   .00D+00
  579    0    0   .1251027D-01   .1107397D-01   .00D+00   .00D+00
  580    0    0   .1326027D-01   .1078122D-01   .00D+00   .00D+00
  581    0    0   .1408847D-01   .1033756D-01   .00D+00   .00D+00
  582    0    0   .1497489D-01   .9721176D-02   .00D+00   .00D+00
  583    0    0   .1589098D-01   .8911872D-02   .00D+00   .00D+00
  584    0    0   .1679966D-01   .7894007D-02   .00D+00   .00D+00
  585    0    0   .1765354D-01   .6660845D-02   .00D+00   .00D+00
  586    0    0   .1839897D-01   .5219635D-02   .00D+00   .00D+00
  587    0    0   .1898174D-01   .3595833D-02   .00D+00   .00D+00
  588    0    0   .1935445D-01   .1834874D-02   .00D+00   .00D+00
  589    0    0   .1961130D-01   .0000000D+00   .00D+00   .00D+00
  590    0    0   .1037232D-01   .0000000D+00   .00D+00   .00D+00
  591    0    0   .1033408D-01   .1023784D-02   .00D+00   .00D+00
  592    0    0   .1027808D-01   .2036073D-02   .00D+00   .00D+00
  593    0    0   .1018910D-01   .3026142D-02   .00D+00   .00D+00
  594    0    0   .1007346D-01   .3984132D-02   .00D+00   .00D+00
  595    0    0   .9939269D-02   .4901884D-02   .00D+00   .00D+00
  596    0    0   .9796062D-02   .5773231D-02   .00D+00   .00D+00
  597    0    0   .9654452D-02   .6593493D-02   .00D+00   .00D+00
  598    0    0   .9525400D-02   .7359760D-02   .00D+00   .00D+00
  599    0    0   .9419977D-02   .8070491D-02   .00D+00   .00D+00
  600    0    0   .9349201D-02   .8725114D-02   .00D+00   .00D+00
  601    0    0   .9323858D-02   .9323858D-02   .00D+00   .00D+00
  602    0    0   .9354281D-02   .9866952D-02   .00D+00   .00D+00
  603    0    0   .9450457D-02   .1035400D-01   .00D+00   .00D+00
  604    0    0   .9621918D-02   .1078402D-01   .00D+00   .00D+00
  605    0    0   .9877854D-02   .1115445D-01   .00D+00   .00D+00
  606    0    0   .1022700D-01   .1146084D-01   .00D+00   .00D+00
  607    0    0   .1067728D-01   .1169578D-01   .00D+00   .00D+00
  608    0    0   .1123545D-01   .1184932D-01   .00D+00   .00D+00
  609    0    0   .1190639D-01   .1190639D-01   .00D+00   .00D+00
  610    0    0   .1269178D-01   .1184932D-01   .00D+00   .00D+00
  611    0    0   .1358904D-01   .1165400D-01   .00D+00   .00D+00
  612    0    0   .1458904D-01   .1129269D-01   .00D+00   .00D+00
  613    0    0   .1567295D-01   .1073556D-01   .00D+00   .00D+00
  614    0    0   .1680936D-01   .9949943D-02   .00D+00   .00D+00
  615    0    0   .1795320D-01   .8908162D-02   .00D+00   .00D+00
  616    0    0   .1904509D-01   .7592237D-02   .00D+00   .00D+00
  617    0    0   .2001313D-01   .6001941D-02   .00D+00   .00D+00
  618    0    0   .2077968D-01   .4163584D-02   .00D+00   .00D+00
  619    0    0   .2127397D-01   .2134075D-02   .00D+00   .00D+00
  620    0    0   .2161644D-01   .0000000D+00   .00D+00   .00D+00
  621    0    0   .9362614D-02   .0000000D+00   .00D+00   .00D+00
  622    0    0   .9334418D-02   .9906221D-03   .00D+00   .00D+00
  623    0    0   .9293322D-02   .1972203D-02   .00D+00   .00D+00
  624    0    0   .9228425D-02   .2936187D-02   .00D+00   .00D+00
  625    0    0   .9144806D-02   .3874772D-02   .00D+00   .00D+00
  626    0    0   .9049201D-02   .4781393D-02   .00D+00   .00D+00
  627    0    0   .8949600D-02   .5650970D-02   .00D+00   .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

628	0	0	.8855023D-02	.6479566D-02	.00D+00	.00D+00
629	0	0	.8775114D-02	.7264726D-02	.00D+00	.00D+00
630	0	0	.8719920D-02	.8004966D-02	.00D+00	.00D+00
631	0	0	.8699772D-02	.8699772D-02	.00D+00	.00D+00
632	0	0	.8725114D-02	.9349201D-02	.00D+00	.00D+00
633	0	0	.8806450D-02	.9953311D-02	.00D+00	.00D+00
634	0	0	.8954281D-02	.1051159D-01	.00D+00	.00D+00
635	0	0	.9179395D-02	.1102300D-01	.00D+00	.00D+00
636	0	0	.9492865D-02	.1148510D-01	.00D+00	.00D+00
637	0	0	.9905765D-02	.1189269D-01	.00D+00	.00D+00
638	0	0	.1042917D-01	.1223801D-01	.00D+00	.00D+00
639	0	0	.1107397D-01	.1251027D-01	.00D+00	.00D+00
640	0	0	.1184932D-01	.1269178D-01	.00D+00	.00D+00
641	0	0	.1276256D-01	.1276256D-01	.00D+00	.00D+00
642	0	0	.1381678D-01	.1269235D-01	.00D+00	.00D+00
643	0	0	.1500685D-01	.1244463D-01	.00D+00	.00D+00
644	0	0	.1631792D-01	.1197803D-01	.00D+00	.00D+00
645	0	0	.1771861D-01	.1124441D-01	.00D+00	.00D+00
646	0	0	.1915753D-01	.1019663D-01	.00D+00	.00D+00
647	0	0	.2055993D-01	.8797888D-02	.00D+00	.00D+00
648	0	0	.2182763D-01	.7032477D-02	.00D+00	.00D+00
649	0	0	.2284989D-01	.4922317D-02	.00D+00	.00D+00
650	0	0	.2351826D-01	.2537900D-02	.00D+00	.00D+00
651	0	0	.2398402D-01	.0000000D+00	.00D+00	.00D+00
652	0	0	.8382021D-02	.0000000D+00	.00D+00	.00D+00
653	0	0	.8361815D-02	.9665068D-03	.00D+00	.00D+00
654	0	0	.8332477D-02	.1925970D-02	.00D+00	.00D+00
655	0	0	.8286530D-02	.2871575D-02	.00D+00	.00D+00
656	0	0	.8228139D-02	.3797317D-02	.00D+00	.00D+00
657	0	0	.8163014D-02	.4698059D-02	.00D+00	.00D+00
658	0	0	.8097945D-02	.5569635D-02	.00D+00	.00D+00
659	0	0	.8040753D-02	.6409132D-02	.00D+00	.00D+00
660	0	0	.8000000D-02	.7214498D-02	.00D+00	.00D+00
661	0	0	.7984817D-02	.7984817D-02	.00D+00	.00D+00
662	0	0	.8004966D-02	.8719920D-02	.00D+00	.00D+00
663	0	0	.8070491D-02	.9419977D-02	.00D+00	.00D+00
664	0	0	.8192009D-02	.1008539D-01	.00D+00	.00D+00
665	0	0	.8380765D-02	.1071610D-01	.00D+00	.00D+00
666	0	0	.8648687D-02	.1131159D-01	.00D+00	.00D+00
667	0	0	.9008562D-02	.1186986D-01	.00D+00	.00D+00
668	0	0	.9474030D-02	.1238642D-01	.00D+00	.00D+00
669	0	0	.1005976D-01	.1285331D-01	.00D+00	.00D+00
670	0	0	.1078122D-01	.1326027D-01	.00D+00	.00D+00
671	0	0	.1165400D-01	.1358904D-01	.00D+00	.00D+00
672	0	0	.1269235D-01	.1381678D-01	.00D+00	.00D+00
673	0	0	.1390753D-01	.1390753D-01	.00D+00	.00D+00
674	0	0	.1530365D-01	.1381678D-01	.00D+00	.00D+00
675	0	0	.1687329D-01	.1348744D-01	.00D+00	.00D+00
676	0	0	.1859018D-01	.1285217D-01	.00D+00	.00D+00
677	0	0	.2039897D-01	.1183619D-01	.00D+00	.00D+00
678	0	0	.2220890D-01	.1037003D-01	.00D+00	.00D+00
679	0	0	.2388870D-01	.8407877D-02	.00D+00	.00D+00
680	0	0	.2527454D-01	.5955251D-02	.00D+00	.00D+00
681	0	0	.2619692D-01	.3095320D-02	.00D+00	.00D+00
682	0	0	.2684646D-01	.0000000D+00	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 683    0    0   .7422374D-02   .0000000D+00   .00D+00   .00D+00
 684    0    0   .7408447D-02   .9494578D-03   .00D+00   .00D+00
 685    0    0   .7388299D-02   .1893493D-02   .00D+00   .00D+00
 686    0    0   .7357078D-02   .2826826D-02   .00D+00   .00D+00
 687    0    0   .7318322D-02   .3744920D-02   .00D+00   .00D+00
 688    0    0   .7276826D-02   .4643836D-02   .00D+00   .00D+00
 689    0    0   .7238470D-02   .5520434D-02   .00D+00   .00D+00
 690    0    0   .7210103D-02   .6372717D-02   .00D+00   .00D+00
 691    0    0   .7199315D-02   .7199315D-02   .00D+00   .00D+00
 692    0    0   .7214498D-02   .8000000D-02   .00D+00   .00D+00
 693    0    0   .7264726D-02   .8775114D-02   .00D+00   .00D+00
 694    0    0   .7359760D-02   .9525400D-02   .00D+00   .00D+00
 695    0    0   .7510331D-02   .1025205D-01   .00D+00   .00D+00
 696    0    0   .7728082D-02   .1095599D-01   .00D+00   .00D+00
 697    0    0   .8025970D-02   .1163756D-01   .00D+00   .00D+00
 698    0    0   .8418493D-02   .1229623D-01   .00D+00   .00D+00
 699    0    0   .8921918D-02   .1292865D-01   .00D+00   .00D+00
 700    0    0   .9554737D-02   .1352911D-01   .00D+00   .00D+00
 701    0    0   .1033756D-01   .1408847D-01   .00D+00   .00D+00
 702    0    0   .1129269D-01   .1458904D-01   .00D+00   .00D+00
 703    0    0   .1244463D-01   .1500685D-01   .00D+00   .00D+00
 704    0    0   .1381678D-01   .1530365D-01   .00D+00   .00D+00
 705    0    0   .1542637D-01   .1542637D-01   .00D+00   .00D+00
 706    0    0   .1728196D-01   .1530308D-01   .00D+00   .00D+00
 707    0    0   .1936986D-01   .1484075D-01   .00D+00   .00D+00
 708    0    0   .2163984D-01   .1392580D-01   .00D+00   .00D+00
 709    0    0   .2398801D-01   .1243824D-01   .00D+00   .00D+00
 710    0    0   .2624201D-01   .1027380D-01   .00D+00   .00D+00
 711    0    0   .2816210D-01   .7395548D-02   .00D+00   .00D+00
 712    0    0   .2947317D-01   .3888071D-02   .00D+00   .00D+00
 713    0    0   .3041039D-01   .0000000D+00   .00D+00   .00D+00
 714    0    0   .6477568D-02   .0000000D+00   .00D+00   .00D+00
 715    0    0   .6468322D-02   .9378596D-03   .00D+00   .00D+00
 716    0    0   .6455080D-02   .1871632D-02   .00D+00   .00D+00
 717    0    0   .6435046D-02   .2797374D-02   .00D+00   .00D+00
 718    0    0   .6411187D-02   .3711758D-02   .00D+00   .00D+00
 719    0    0   .6387500D-02   .4611872D-02   .00D+00   .00D+00
 720    0    0   .6369064D-02   .5495662D-02   .00D+00   .00D+00
 721    0    0   .6361872D-02   .6361872D-02   .00D+00   .00D+00
 722    0    0   .6372717D-02   .7210103D-02   .00D+00   .00D+00
 723    0    0   .6409132D-02   .8040753D-02   .00D+00   .00D+00
 724    0    0   .6479566D-02   .8855023D-02   .00D+00   .00D+00
 725    0    0   .6593493D-02   .9654452D-02   .00D+00   .00D+00
 726    0    0   .6761416D-02   .1044144D-01   .00D+00   .00D+00
 727    0    0   .6995263D-02   .1121821D-01   .00D+00   .00D+00
 728    0    0   .7308676D-02   .1198687D-01   .00D+00   .00D+00
 729    0    0   .7717580D-02   .1274829D-01   .00D+00   .00D+00
 730    0    0   .8240582D-02   .1350285D-01   .00D+00   .00D+00
 731    0    0   .8899715D-02   .1424715D-01   .00D+00   .00D+00
 732    0    0   .9721176D-02   .1497489D-01   .00D+00   .00D+00
 733    0    0   .1073556D-01   .1567295D-01   .00D+00   .00D+00
 734    0    0   .1197803D-01   .1631792D-01   .00D+00   .00D+00
 735    0    0   .1348744D-01   .1687329D-01   .00D+00   .00D+00
 736    0    0   .1530308D-01   .1728196D-01   .00D+00   .00D+00
 737    0    0   .1745833D-01   .1745833D-01   .00D+00   .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

738	0	0	.1996747D-01	.1728196D-01	.00D+00	.00D+00
739	0	0	.2280251D-01	.1658904D-01	.00D+00	.00D+00
740	0	0	.2586130D-01	.1518208D-01	.00D+00	.00D+00
741	0	0	.2893037D-01	.1285377D-01	.00D+00	.00D+00
742	0	0	.3165982D-01	.9465126D-02	.00D+00	.00D+00
743	0	0	.3359247D-01	.5061301D-02	.00D+00	.00D+00
744	0	0	.3500342D-01	.0000000D+00	.00D+00	.00D+00
745	0	0	.5542580D-02	.0000000D+00	.00D+00	.00D+00
746	0	0	.5536872D-02	.9303653D-03	.00D+00	.00D+00
747	0	0	.5528767D-02	.1857763D-02	.00D+00	.00D+00
748	0	0	.5516895D-02	.2779395D-02	.00D+00	.00D+00
749	0	0	.5503824D-02	.3692808D-02	.00D+00	.00D+00
750	0	0	.5492922D-02	.4596290D-02	.00D+00	.00D+00
751	0	0	.5488470D-02	.5488470D-02	.00D+00	.00D+00
752	0	0	.5495662D-02	.6369064D-02	.00D+00	.00D+00
753	0	0	.5520434D-02	.7238470D-02	.00D+00	.00D+00
754	0	0	.5569635D-02	.8097945D-02	.00D+00	.00D+00
755	0	0	.5650970D-02	.8949600D-02	.00D+00	.00D+00
756	0	0	.5773231D-02	.9796062D-02	.00D+00	.00D+00
757	0	0	.5946632D-02	.1064110D-01	.00D+00	.00D+00
758	0	0	.6182877D-02	.1148881D-01	.00D+00	.00D+00
759	0	0	.6495890D-02	.1234304D-01	.00D+00	.00D+00
760	0	0	.6902511D-02	.1320719D-01	.00D+00	.00D+00
761	0	0	.7423002D-02	.1408676D-01	.00D+00	.00D+00
762	0	0	.8082420D-02	.1498174D-01	.00D+00	.00D+00
763	0	0	.8911872D-02	.1589098D-01	.00D+00	.00D+00
764	0	0	.9949943D-02	.1680936D-01	.00D+00	.00D+00
765	0	0	.1124441D-01	.1771861D-01	.00D+00	.00D+00
766	0	0	.1285217D-01	.1859018D-01	.00D+00	.00D+00
767	0	0	.1484075D-01	.1936986D-01	.00D+00	.00D+00
768	0	0	.1728196D-01	.1996747D-01	.00D+00	.00D+00
769	0	0	.2023916D-01	.2023916D-01	.00D+00	.00D+00
770	0	0	.2374030D-01	.1996747D-01	.00D+00	.00D+00
771	0	0	.2772374D-01	.1884589D-01	.00D+00	.00D+00
772	0	0	.3195890D-01	.1649486D-01	.00D+00	.00D+00
773	0	0	.3595491D-01	.1254983D-01	.00D+00	.00D+00
774	0	0	.3893836D-01	.6891952D-02	.00D+00	.00D+00
775	0	0	.4118950D-01	.0000000D+00	.00D+00	.00D+00
776	0	0	.4613813D-02	.0000000D+00	.00D+00	.00D+00
777	0	0	.4610616D-02	.9258505D-03	.00D+00	.00D+00
778	0	0	.4606107D-02	.1849658D-02	.00D+00	.00D+00
779	0	0	.4599943D-02	.2769521D-02	.00D+00	.00D+00
780	0	0	.4594292D-02	.3683904D-02	.00D+00	.00D+00
781	0	0	.4591895D-02	.4591895D-02	.00D+00	.00D+00
782	0	0	.4596290D-02	.5492922D-02	.00D+00	.00D+00
783	0	0	.4611872D-02	.6387500D-02	.00D+00	.00D+00
784	0	0	.4643836D-02	.7276826D-02	.00D+00	.00D+00
785	0	0	.4698059D-02	.8163014D-02	.00D+00	.00D+00
786	0	0	.4781393D-02	.9049201D-02	.00D+00	.00D+00
787	0	0	.4901884D-02	.9939269D-02	.00D+00	.00D+00
788	0	0	.5068950D-02	.1083830D-01	.00D+00	.00D+00
789	0	0	.5293664D-02	.1175228D-01	.00D+00	.00D+00
790	0	0	.5589612D-02	.1268836D-01	.00D+00	.00D+00
791	0	0	.5973573D-02	.1365240D-01	.00D+00	.00D+00
792	0	0	.6466495D-02	.1465468D-01	.00D+00	.00D+00

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 793    0    0   .7095148D-02   .1570148D-01   .00D+00   .00D+00
 794    0    0   .7894007D-02   .1679966D-01   .00D+00   .00D+00
 795    0    0   .8908162D-02   .1795320D-01   .00D+00   .00D+00
 796    0    0   .1019663D-01   .1915753D-01   .00D+00   .00D+00
 797    0    0   .1183619D-01   .2039897D-01   .00D+00   .00D+00
 798    0    0   .1392580D-01   .2163984D-01   .00D+00   .00D+00
 799    0    0   .1658904D-01   .2280251D-01   .00D+00   .00D+00
 800    0    0   .1996747D-01   .2374030D-01   .00D+00   .00D+00
 801    0    0   .2419521D-01   .2419521D-01   .00D+00   .00D+00
 802    0    0   .2933390D-01   .2373973D-01   .00D+00   .00D+00
 803    0    0   .3522717D-01   .2172945D-01   .00D+00   .00D+00
 804    0    0   .4126313D-01   .1734760D-01   .00D+00   .00D+00
 805    0    0   .4614212D-01   .9956792D-02   .00D+00   .00D+00
 806    0    0   .5001998D-01   .0000000D+00   .00D+00   .00D+00
 807    0    0   .3688813D-02   .0000000D+00   .00D+00   .00D+00
 808    0    0   .3687215D-02   .9233961D-03   .00D+00   .00D+00
 809    0    0   .3685103D-02   .1845491D-02   .00D+00   .00D+00
 810    0    0   .3682648D-02   .2765068D-02   .00D+00   .00D+00
 811    0    0   .3681507D-02   .3681507D-02   .00D+00   .00D+00
 812    0    0   .3683904D-02   .4594292D-02   .00D+00   .00D+00
 813    0    0   .3692808D-02   .5503824D-02   .00D+00   .00D+00
 814    0    0   .3711758D-02   .6411187D-02   .00D+00   .00D+00
 815    0    0   .3744920D-02   .7318322D-02   .00D+00   .00D+00
 816    0    0   .3797317D-02   .8228139D-02   .00D+00   .00D+00
 817    0    0   .3874772D-02   .9144806D-02   .00D+00   .00D+00
 818    0    0   .3984132D-02   .1007346D-01   .00D+00   .00D+00
 819    0    0   .4133619D-02   .1102061D-01   .00D+00   .00D+00
 820    0    0   .4333219D-02   .1199429D-01   .00D+00   .00D+00
 821    0    0   .4595377D-02   .1300457D-01   .00D+00   .00D+00
 822    0    0   .4935674D-02   .1406107D-01   .00D+00   .00D+00
 823    0    0   .5374258D-02   .1517808D-01   .00D+00   .00D+00
 824    0    0   .5937557D-02   .1637043D-01   .00D+00   .00D+00
 825    0    0   .6660845D-02   .1765354D-01   .00D+00   .00D+00
 826    0    0   .7592237D-02   .1904509D-01   .00D+00   .00D+00
 827    0    0   .8797888D-02   .2055993D-01   .00D+00   .00D+00
 828    0    0   .1037003D-01   .2220890D-01   .00D+00   .00D+00
 829    0    0   .1243824D-01   .2398801D-01   .00D+00   .00D+00
 830    0    0   .1518208D-01   .2586130D-01   .00D+00   .00D+00
 831    0    0   .1884589D-01   .2772374D-01   .00D+00   .00D+00
 832    0    0   .2373973D-01   .2933390D-01   .00D+00   .00D+00
 833    0    0   .3018950D-01   .3018950D-01   .00D+00   .00D+00
 834    0    0   .3835160D-01   .2933390D-01   .00D+00   .00D+00
 835    0    0   .4772774D-01   .2515525D-01   .00D+00   .00D+00
 836    0    0   .5628596D-01   .1558733D-01   .00D+00   .00D+00
 837    0    0   .6366838D-01   .0000000D+00   .00D+00   .00D+00
 838    0    0   .2765696D-02   .0000000D+00   .00D+00   .00D+00
 839    0    0   .2765126D-02   .9222546D-03   .00D+00   .00D+00
 840    0    0   .2764384D-02   .1843779D-02   .00D+00   .00D+00
 841    0    0   .2763927D-02   .2763927D-02   .00D+00   .00D+00
 842    0    0   .2765068D-02   .3682648D-02   .00D+00   .00D+00
 843    0    0   .2769521D-02   .4599943D-02   .00D+00   .00D+00
 844    0    0   .2779395D-02   .5516895D-02   .00D+00   .00D+00
 845    0    0   .2797374D-02   .6435046D-02   .00D+00   .00D+00
 846    0    0   .2826826D-02   .7357078D-02   .00D+00   .00D+00
 847    0    0   .2871575D-02   .8286530D-02   .00D+00   .00D+00
```

Table 6.15   Input Data Sets for Problem 8 (continued)

```
 848     0     0   .2936187D-02    .9228425D-02    .00D+00     .00D+00
 849     0     0   .3026142D-02    .1018910D-01    .00D+00     .00D+00
 850     0     0   .3148059D-02    .1117643D-01    .00D+00     .00D+00
 851     0     0   .3310217D-02    .1220034D-01    .00D+00     .00D+00
 852     0     0   .3522945D-02    .1327340D-01    .00D+00     .00D+00
 853     0     0   .3799486D-02    .1440925D-01    .00D+00     .00D+00
 854     0     0   .4157306D-02    .1562671D-01    .00D+00     .00D+00
 855     0     0   .4619920D-02    .1694806D-01    .00D+00     .00D+00
 856     0     0   .5219635D-02    .1839897D-01    .00D+00     .00D+00
 857     0     0   .6001941D-02    .2001313D-01    .00D+00     .00D+00
 858     0     0   .7032477D-02    .2182763D-01    .00D+00     .00D+00
 859     0     0   .8407877D-02    .2388870D-01    .00D+00     .00D+00
 860     0     0   .1027380D-01    .2624201D-01    .00D+00     .00D+00
 861     0     0   .1285377D-01    .2893037D-01    .00D+00     .00D+00
 862     0     0   .1649486D-01    .3195890D-01    .00D+00     .00D+00
 863     0     0   .2172945D-01    .3522717D-01    .00D+00     .00D+00
 864     0     0   .2933390D-01    .3835160D-01    .00D+00     .00D+00
 865     0     0   .4026142D-01    .4026142D-01    .00D+00     .00D+00
 866     0     0   .5500970D-01    .3835160D-01    .00D+00     .00D+00
 867     0     0   .7129737D-01    .2723687D-01    .00D+00     .00D+00
 868     0     0   .8721404D-01    .0000000D+00    .00D+00     .00D+00
 869     0     0   .1843550D-02    .0000000D+00    .00D+00     .00D+00
 870     0     0   .1843436D-02    .9218436D-03    .00D+00     .00D+00
 871     0     0   .1843379D-02    .1843379D-02    .00D+00     .00D+00
 872     0     0   .1843779D-02    .2764384D-02    .00D+00     .00D+00
 873     0     0   .1845491D-02    .3685103D-02    .00D+00     .00D+00
 874     0     0   .1849658D-02    .4606107D-02    .00D+00     .00D+00
 875     0     0   .1857763D-02    .5528767D-02    .00D+00     .00D+00
 876     0     0   .1871632D-02    .6455080D-02    .00D+00     .00D+00
 877     0     0   .1893493D-02    .7388299D-02    .00D+00     .00D+00
 878     0     0   .1925970D-02    .8332477D-02    .00D+00     .00D+00
 879     0     0   .1972203D-02    .9293322D-02    .00D+00     .00D+00
 880     0     0   .2036073D-02    .1027808D-01    .00D+00     .00D+00
 881     0     0   .2122317D-02    .1129566D-01    .00D+00     .00D+00
 882     0     0   .2236701D-02    .1235731D-01    .00D+00     .00D+00
 883     0     0   .2386644D-02    .1347831D-01    .00D+00     .00D+00
 884     0     0   .2581963D-02    .1467523D-01    .00D+00     .00D+00
 885     0     0   .2835559D-02    .1597203D-01    .00D+00     .00D+00
 886     0     0   .3165183D-02    .1739498D-01    .00D+00     .00D+00
 887     0     0   .3595833D-02    .1898174D-01    .00D+00     .00D+00
 888     0     0   .4163584D-02    .2077968D-01    .00D+00     .00D+00
 889     0     0   .4922317D-02    .2284989D-01    .00D+00     .00D+00
 890     0     0   .5955251D-02    .2527454D-01    .00D+00     .00D+00
 891     0     0   .7395548D-02    .2816210D-01    .00D+00     .00D+00
 892     0     0   .9465126D-02    .3165982D-01    .00D+00     .00D+00
 893     0     0   .1254983D-01    .3595491D-01    .00D+00     .00D+00
 894     0     0   .1734760D-01    .4126313D-01    .00D+00     .00D+00
 895     0     0   .2515525D-01    .4772774D-01    .00D+00     .00D+00
 896     0     0   .3835160D-01    .5500970D-01    .00D+00     .00D+00
 897     0     0   .6075171D-01    .6075171D-01    .00D+00     .00D+00
 898     0     0   .9463756D-01    .5500913D-01    .00D+00     .00D+00
 899     0     0   .1342666D+00    .0000000D+00    .00D+00     .00D+00
 900     0     0   .9217580D-03    .0000000D+00    .00D+00     .00D+00
 901     0     0   .9217580D-03    .9217580D-03    .00D+00     .00D+00
 902     0     0   .9218436D-03    .1843436D-02    .00D+00     .00D+00
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
 903     0     0   .9222546D-03   .2765126D-02   .00D+00    .00D+00
 904     0     0   .9233961D-03   .3687215D-02   .00D+00    .00D+00
 905     0     0   .9258505D-03   .4610616D-02   .00D+00    .00D+00
 906     0     0   .9303653D-03   .5536872D-02   .00D+00    .00D+00
 907     0     0   .9378596D-03   .6468322D-02   .00D+00    .00D+00
 908     0     0   .9494578D-03   .7408447D-02   .00D+00    .00D+00
 909     0     0   .9665068D-03   .8361815D-02   .00D+00    .00D+00
 910     0     0   .9906221D-03   .9334418D-02   .00D+00    .00D+00
 911     0     0   .1023784D-02   .1033408D-01   .00D+00    .00D+00
 912     0     0   .1068413D-02   .1137049D-01   .00D+00    .00D+00
 913     0     0   .1127557D-02   .1245605D-01   .00D+00    .00D+00
 914     0     0   .1205137D-02   .1360674D-01   .00D+00    .00D+00
 915     0     0   .1306221D-02   .1484304D-01   .00D+00    .00D+00
 916     0     0   .1437785D-02   .1618950D-01   .00D+00    .00D+00
 917     0     0   .1609475D-02   .1767865D-01   .00D+00    .00D+00
 918     0     0   .1834874D-02   .1935445D-01   .00D+00    .00D+00
 919     0     0   .2134075D-02   .2127397D-01   .00D+00    .00D+00
 920     0     0   .2537900D-02   .2351826D-01   .00D+00    .00D+00
 921     0     0   .3095320D-02   .2619692D-01   .00D+00    .00D+00
 922     0     0   .3888071D-02   .2947317D-01   .00D+00    .00D+00
 923     0     0   .5061301D-02   .3359247D-01   .00D+00    .00D+00
 924     0     0   .6891952D-02   .3893836D-01   .00D+00    .00D+00
 925     0     0   .9956792D-02   .4614212D-01   .00D+00    .00D+00
 926     0     0   .1558733D-01   .5628596D-01   .00D+00    .00D+00
 927     0     0   .2723687D-01   .7129737D-01   .00D+00    .00D+00
 928     0     0   .5500913D-01   .9463756D-01   .00D+00    .00D+00
 929     0     0   .1320462D+00   .1320462D+00   .00D+00    .00D+00
 930     0     0   .2464926D+00   .0000000D+00   .00D+00    .00D+00
 931     0     0   .0000000D+00   .0000000D+00   .00D+00    .00D+00
 932     0     0   .0000000D+00   .9217580D-03   .00D+00    .00D+00
 933     0     0   .0000000D+00   .1843550D-02   .00D+00    .00D+00
 934     0     0   .0000000D+00   .2765696D-02   .00D+00    .00D+00
 935     0     0   .0000000D+00   .3688813D-02   .00D+00    .00D+00
 936     0     0   .0000000D+00   .4613813D-02   .00D+00    .00D+00
 937     0     0   .0000000D+00   .5542580D-02   .00D+00    .00D+00
 938     0     0   .0000000D+00   .6477568D-02   .00D+00    .00D+00
 939     0     0   .0000000D+00   .7422374D-02   .00D+00    .00D+00
 940     0     0   .0000000D+00   .8382021D-02   .00D+00    .00D+00
 941     0     0   .0000000D+00   .9362614D-02   .00D+00    .00D+00
 942     0     0   .0000000D+00   .1037232D-01   .00D+00    .00D+00
 943     0     0   .0000000D+00   .1142152D-01   .00D+00    .00D+00
 944     0     0   .0000000D+00   .1252340D-01   .00D+00    .00D+00
 945     0     0   .0000000D+00   .1369463D-01   .00D+00    .00D+00
 946     0     0   .0000000D+00   .1495833D-01   .00D+00    .00D+00
 947     0     0   .0000000D+00   .1633790D-01   .00D+00    .00D+00
 948     0     0   .0000000D+00   .1787386D-01   .00D+00    .00D+00
 949     0     0   .0000000D+00   .1961130D-01   .00D+00    .00D+00
 950     0     0   .0000000D+00   .2161644D-01   .00D+00    .00D+00
 951     0     0   .0000000D+00   .2398402D-01   .00D+00    .00D+00
 952     0     0   .0000000D+00   .2684646D-01   .00D+00    .00D+00
 953     0     0   .0000000D+00   .3041039D-01   .00D+00    .00D+00
 954     0     0   .0000000D+00   .3500342D-01   .00D+00    .00D+00
 955     0     0   .0000000D+00   .4118950D-01   .00D+00    .00D+00
 956     0     0   .0000000D+00   .5001998D-01   .00D+00    .00D+00
 957     0     0   .0000000D+00   .6366838D-01   .00D+00    .00D+00
```

Table 6.15   Input Data Sets for Problem 8 (continued)

```
  958    0    0   .0000000D+00   .8721404D-01   .00D+00   .00D+00
  959    0    0   .0000000D+00   .1342666D+00   .00D+00   .00D+00
  960    0    0   .0000000D+00   .2464926D+00   .00D+00   .00D+00
  961    0    0   .5396279D+00   .5396279D+00   .00D+00   .00D+00
    0    0    0     0.0     0.0     0.0     0.0      END OF VELOCITY (dm/hr)
    1  899    1     0.05    0.0
    0    0    0     0.0     0.0     0.0              END OF TH
    1  960    1     1.000   0.0     0.0
    0    0    0     0.0     0.0     0.0              END OF RHOL
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
6 1 13 4 0 0                          NONA NONS NOMX NOMY NOMZ NOMP
C ******* DATA SET 18: H+, E-, IONIC STRENGTH correction INFORMATION
 0.0 0 1 0 0   SICOR ICOR LNH LNG LNE
  c ******* DATA SET 19:  temperature, pressure and expected pe and pH
 298.3 1.0   TEMP PRESSU
 -20.0 20.0 -20.0 20.0   PEMN PEMX PHMN PHMX
c ******* DATA SET 20: Adsorption Information
 1 0
0 0
0 0 0
c ******* DATA SET 22: Basic real and integer parameters
1.0 1 1000 1.0d-6 1.0d0 1.0d0 1 omegac npcyl niterc epsc cnstrx,y ipiv
c ******* DATA SET 23: Component name and component species types
 H+
  1 0
 H2CO3*
  1 0
 NH4+
  1 0
 O2
  1 0
 NTA-
  1 0
 Co 2+
  1 0
 >SOH
  2 0
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
H+
  0  1 0  iscn VJ IONEX
H2CO3*
  0  0 0  iscn VJ IONEX
NH4+
  0  1 0  iscn VJ IONEX
O2
  0  0 0  iscn VJ IONEX
NTA3-
  0 -3 0  iscn VJ IONEX
Co2+
  0  2 0  iscn VJ IONEX
>SOH
  0  0 0  iscn VJ IONEX
C ******** DATA SET 25:  COMPLEXED SPECIES
H3NTA
0    3   0   0   0   1   0   0    0   3   0   0   0   1   0   0
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
H2NTA-
0    2  0  0  0  1  0  0   0   2  0  0  0  1  0  0
HNTA2-
0    1  0  0  0  1  0  0   0   1  0  0  0  1  0  0
CoNTA-
0    0  0  0  0  1  1  0   0   0  0  0  0  1  1  0
CoNTA2 4-
0    0  0  0  0  2  1  0   0   0  0  0  0  2  1  0
CoOHNTA 2-
0   -1  0  0  0  1  1  0   0  -1  0  0  0  1  1  0
CoOH+
0   -1  0  0  0  0  1  0   0  -1  0  0  0  0  1  0
Co(OH)2
0   -2  0  0  0  0  1  0   0  -2  0  0  0  0  1  0
Co(OH)3-
0   -3  0  0  0  0  1  0   0  -3  0  0  0  0  1  0
HCO3-
0   -1  1  0  0  0  0  0   0  -1  1  0  0  0  0  0
CO3 2-
0   -2  1  0  0  0  0  0   0  -2  1  0  0  0  0  0
NH3
0   -1  0  1  0  0  0  0   0  -1  0  1  0  0  0  0
OH-
0   -1  0  0  0  0  0  0   0  -1  0  0  0  0  0  0
C ******** DATA SET 26:  ADSORBED SPECIES
>SOH2+
0    1  0  0  0  0  0  1       1  0  0  0  0  0  1
>SO-
0   -1  0  0  0  0  0  1      -1  0  0  0  0  0  1
>SOH2-CoNTA(ads)
0    1  0  0  0  1  1  1       1  0  0  0  1  1  1
>SO-Co(ads)
0   -2  0  0  0  0  1  2      -2  0  0  0  0  1  2
C ******** DATA SET 28:  MICROBIAL SPECIES
C5H7O2N(aq cells)
  0  -2.681936665037 0
C5H7O2N(ads cells)
  0  -2.681936665037 0
C ******** DATA SET 29:  reaction data
20
2 1 0    NRTS NPDS KRTYP           REACTION 1 - H3NTA
14.9     LOGKEQ
3  1  1
1  5  8
2 1 0    NRTS NPDS KRTYP           REACTION 2 - H2NTA
13.3     LOGKEQ
2  1  1
1  5  9
2 1 0    NRTS NPDS KRTYP           REACTION 3 - HNTA
10.3     LOGKEQ
1  1  1
1  5  10
2 1 0    NRTS NPDS KRTYP           REACTION 4 - CoNTA
11.7     LOGKEQ
```

Table 6.15 Input Data Sets for Problem 8 (continued)

```
1  1  1
5  6  11
2 1 0    NRTS NPDS KRTYP           REACTION 5 - CoNTA2
14.5     LOGKEQ
2  1  1
5  6  12
3 1 0    NRTS NPDS KRTYP           REACTION 6 - CoOHNTA
0.5     LOGKEQ
-1  1  1  1
1   5  6  13
2 1 0    NRTS NPDS KRTYP           REACTION 7 - CoOH
-9.7     LOGKEQ
 -1  1  1
 1  6  14
2 1 0    NRTS NPDS KRTYP           REACTION 8 - CoOH2
-22.9     LOGKEQ
 -2  1  1
 1  6  15
2 1 0    NRTS NPDS KRTYP           REACTION 9 - CoOH3
-31.5     LOGKEQ
 -3  1  1
 1  6  16
2 1 0    NRTS NPDS KRTYP           REACTION 10 - HCO3
-6.35     LOGKEQ
 -1  1  1
 1  2  17
2 1 0    NRTS NPDS KRTYP           REACTION 11 - CO3
-16.68    LOGKEQ
 -2  1  1
 1  2  18
2 1 0    NRTS NPDS KRTYP           REACTION 12 - NH3
-9.3      LOGKEQ
 -1  1  1
 1  3  19
1 1 0    NRTS NPDS KRTYP           REACTION 13 - OH
-14.0      LOGKEQ
 -1  1
 1   20
2 1 0    NRTS NPDS KRTYP           REACTION 14 - >SOH2+
 5.6      LOGKEQ
 1   1  1
 7   1  21
2 1 0    NRTS NPDS KRTYP           REACTION 15 - >SO-
-11.6      LOGKEQ
 1  -1  1
 7   1  22
2 1 1            NRTS NPDS KRTYP    REACTION 16 - CoNTA (ads) * rates revised
-2.279039227   -0.09690     LOGKB  LOGKF
 1  1  1
 11 21  23
2 1 1            NRTS NPDS KRTYP    REACTION 16 - Co(ads)
-1.279039227   -0.574031267728     LOGKB  LOGKF
 1  2  1
 6  22 24
3 3 2            NRTS NPDS KRTYP    REACTION 17 - MB rxn - aq species
```

Table 6.15 Input Data Sets for Problem 8 (concluded)

```
0.0916519  7.64D-7 6.25D-6 0.0 1 2 0 0.0 0.0 grmax ks ka kn locsan taul taue
1  1.620  2.424    17.370666  3.120  0.424
10 4      1        25         2      3
0 0 0 0 0            inhib hscinh hscinh p q
3 3 2          NRTS NPDS KRTYP    REACTION 18 - MB rxn - ads species
0.0916519  7.64D-7 6.25D-6 0.0 1 2 0 0.0 0.0 grmax ks ka kn locsan taul taue
1  1.620  2.424    17.370666  3.120  0.424
10 4      1        26         2      3
0 0 0 0 0            inhib hscinh hscinh p q
1 1 3          NRTS NPDS KRTYP    REACTION 19 - MB phase transfer rxn
-1.279039227   -0.574031267728  LOGKB  LOGKF
 1    1
 25   26
                                 END OF JOB
```

7.0 REFERENCES

Bailey, J. E. and D. F. Olis, 1986. Biochemical Engineering Fundamentals, Second Edition. McGraw-Hill, Inc., New York.

Bjerrum, N., 1926. Ionic association: I. Influence of ionic association on the activity of ions at moderate degrees of association. Kgl. Danske Videnskab. Selskb. Math-fys. Medd. 7:1-48.

Carnahan, C. L., 1986. Simulation of Uranium Transport with Variable Temperature and Oxidation Potential: The Computer Program THCC. Report 21639. Lawrence Berkeley Laboratory, Berkeley, CA.

Clough, R. W., 1971. Analysis of structure vibrations and dynamic response. *In* R. H. Gallagher, Y. Yamada, and J. T. Oden (eds.), Recent Advances in Matrix Methods of Structural Analysis and Design. University of Alabama Press, Huntsville, Alabama.

Conte, S. D., 1965. Elementary Numerical Analysis. McGraw-Hill Book Company, New York, NY, 278 pp.

Davies, C. W., 1962. Ion Association. Butterworths, Washington, DC, 190 pp.

Davis, J. A., and J. O. Leckie, 1978. Surface ionization and complexation at oxide water interface: Part 2. J. Colloid Interface Sci. 67:90-107.

Dyhuizen, R. C. and W. H. Casey, 1989. An Analysis of Solute Diffusion in the Culebra Dolomite, SAND89-0750, Sandia National Laboratories, Albuquerque, NM.

Forsythe, G. E., and W. R. Wasow, 1960. Finite-Difference Methods for Partial Difference Equations. John Wiley & Sons, Inc., New York, NY, 444 pp.

Forsythe, G., M. A. Malcolm, and C. B. Moler, 1977. Computer Methods for Mathematical Computations. Prentice-Hall, Inc., Englewood Cliffs, NJ, 259 pp.

Freeze, R. A., 1972a. Role of subsurface flow in generating surface runoff: 1. Baseflow contributions to channel flow. Water Resour. Res. 8:609-623.

Freeze, R. A., 1972b. Role of subsurface flow in generating surface runoff: 2. Upstream Source Areas. Water Resour. Res. 8:1272-1283.

Fuoss, R. M., 1935. Properties of electrolyte solutions. Chem. Rev. 17:27-42.

Gartling, D. K., 1982. COYOTE – A Finite Element Computer Program for Nonlinear Heat Conduction Problems, SAND77-1332, Sandia National Laboratories, Albuquerque, NM.

Grisak, G. E. and J. F. Pickens, 1980. Solute Transport Through Fractured Media 1. The Effect of Matrix Diffusion, Water Resources Research, 16(4):719-730.

Grisak, G. E., J. F. Pickens, and J. C. Cherry, 1980. Solute Transport Through Fractured Media 2. Column Study of Fractured Till, Water Resources Research, 16(4):731-739.

Huebner, K. H., 1975. The Finite Element Methods for Engineers. John Wiley & Sons, Inc., New York, NY, 500 pp.

Huyakorn, P. S., J. W. Mercer, and D. S. Ward, 1985. Finite element matrix and mass balance computational schemes for transport in variably saturated porous media. Water Resour. Res. 21(3):346-358.

Kappeler, J. and W. Gujer, 1992. Estimation of Kinetic Parameters of Heterotrophic Biomass Under Aerobic Conditions and Characterization of Wastewater for Activated Sludge Modelling. Water Science and Technology, 25(6): 125-139.

Kincaid, C. T., J. R. Morrey, and J. E. Rogers, 1984. Geohydrochemical Models for Solute Migration Volume 1: Process Development and Computer Code Selection. EA-3417, Volume 1. Final Report. Battelle, Pacific Northwest Laboratory, Richland, WA.

Konikow, L. E., and J. D. Bredehoeft, 1978. Computer Model of Two-Dimensional Solute Transport and Dispersion in Ground Water. Chapter C, Book 7, Techniques of Water-Resources Investigations of the United States Geological Survey. USGS, Reston, VA, 90 pp.

Kono, T., 1968. Kinetics of Microbial Cell Growth. Biotechnology and Bioengineering, X:105-131.

Lapidus, L., and G. F. Pinder, 1982. Numerical Solution of Partial Differential Equations in Science and Engineering. John Wiley & Sons, Inc., New York, NY. 677 pp.

Lichtner, P. C., 1997. Benchmark Problems: A Workshop on Subsurface Reactive Transport Modeling, October 29 - November 1, 1997. Pacific Northwest Laboratory, Richland, WA.

Martinez, M. J. and N. E. Bixler, 1983. Radionuclide Transport Code Developmenr in Support of Nuclear Waste Storage Investigations, SAND83-0660, Sandia National Laboratories, Albuquerque, NM.

Miller, C. W., 1983. CHEMTRN User's Manual, LBL-16152. Lawrence Berkeley Laboratory, University of California, Berkeley, CA.

Morel, F., and J. Morgan, 1972. A numerical method for computing equilibria in aqueous chemical systems. Environ. Sci. Technol. 6(1):58-67.

Narasimhan, T. N., and P. A. Witherspoon, 1977. Numerical model for saturated-unsaturated flow in deformable porous media. Water Resour. Res. 13(3):657-664.

Nguyen V. V., W. G. Gray, G. F. Pinder, J. F. Botha, and D. A. Crerar, 1982. A Theoretical Investigation on the Transport of Chemicals in Reactive Porous Media. Water Resour. Res. 18(4):1149-1156.

Nordstrom, D. K., L. N. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerar, T. M. Florence, B. Fritz, M. Hoffman, G. R. Holdren, Jr., G. M. Lafon, S. V. Mattigod, R. E. McDuff, F. Morel, M. M. Reddy, G. Sposito, and J. Thrailkill, 1979. A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems. Proc. Chemical Modeling in Aqueous Systems, 176th Meeting of the American Chemical Society, Miami Beach, FL, September 11 through 13, 1978, ACS Symposium Series 93, American Chemical Society, Washington DC, pp. 857-894.

Parkhurst, D. L., D. C. Thorstenson, and L. N. Plummer, 1980. PHREEQE—A Computer Program for Geochemical Calculations. United States Geological Survey Water Resources Investigations 80-96, USGS, Reston, VA.

Reilly, P. J., R. H. Wood, and R. A. Robinson, 1971. Prediction of osmotic and activity coefficients in mixed-electrolyte solutions. J. Phys. Chem. 75:1305-1315.

Rubin, J., 1983. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. Water Resour. Res. 19(5):1231-1252.

Stumm, W., and J. J. Morgan, 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, New York, NY, 780 pp.

Truesdell, A. H., and B. F. Jones, 1974. WATEQ, A computer program for calculating chemical equilibria of natural waters. J. Res. U.S. Geol. Surv. 2(2): 233-248.

Valocchi, A. J. and C. Tebes, 1997. Benchmark Problems: A Workshop on Subsurface Reactive Transport Modeling, October 29 - November 1, 1997. Pacific Northwest Laboratory, Richland, WA.

Walsh, M. P., S. L. Bryant, and L. W. Lake, 1984. Precipitation and dissolution of solids attending flow through porous media. AIChE J. 30(2):317-328.

Wang, J. D., and J. J. Connor, 1975. Mathematical Modeling of Near Coastal Circulation. Report No. MITSG 75-13. Massachusetts Institute of Technology, Cambridge, MA.

Westall, J. C., J. L. Zachary, and F. M. M. Morel, 1976. MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous System. Technical Note 18, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA, 91 pp.

Wolery, T. J., 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals:The EQ3/6 Software Package. UCRL-52658, Lawrence Livermore Laboratory, Livermore, CA.

Wood, B. D., C. N. Dawson, J. E. Szecsody and G. P. Streile, 1994. Modeling Contaminant Transport and Biodegradation in a Layered Porous Media System. Water Resources Research, 30 (6): 1833-1845.

Yeh, G. T., 1985. Comparison of successive iteration and direct methods to solve finite element equations of aquifer contaminant transport. Water Resour. Res. 21(3):272-280.

Yeh, G. T., 1986. On orthogonal upstream finite element approach to modeling aquifer contaminant transport. Water Resour. Res. 22(6):952-964.

Yeh, G. T., 1987. FEMWATER: A Finite Element Model of WATER Flow through Saturated-Unsaturated Porous Media—First Revision. ORNL-5567/R1, Oak Ridge National Laboratory, Oak Ridge, TN.

Yeh, G. T., and D. S. Ward, 1980. FEMWATER: A Finite Element Model of WATER Flow through Saturated-Unsaturated Porous Media. ORNL-5567, Oak Ridge National Laboratory, Oak Ridge, TN.

Yeh, G. T., and D. S. Ward, 1981. FEMWASTE: A Finite Element Model of WASTE Transport through Saturated-Unsaturated Porous Media. ORNL-5601, Oak Ridge National Laboratory, Oak Ridge, TN.

Yeh, G. T., and R. J. Luxmoore, 1983. Modeling moisture and thermal transport in unsaturated porous media. J. Hydrol. 64:299-309.

Yeh, G. T., and V. S. Tripathi, 1989. A critical evaluation of recent developments of hydrogeochemical transport models of reactive multi-chemical components. Water Resour. Res. 25(1):93-108.

Yeh, G. T., and K. M. Salvage, 1995. Users' Manual for HYDROGEOCHEM2.0: A Coupled Model of Hydrologic Transport and Mixed Geochemical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media, The Pennsylvania State University.

Yeh, G. T., S. L. Carpenter, P. L. Hopkins, M. D. Siegel, 1995. Users' Manual for LEHGC: A Lagrangian-Eulerian Finite-Element Model of HydroGeoChemical Transport Through Saturated-Unsaturated Media - Version 1.1, SAND95-1121, Sandia National Laboratories, Albuquerque, NM.

Zienkiewicz, O. C., 1977. The Finite Element Methods in Engineering Science. McGraw-Hill Book Company, New York, NY, 521 pp.

APPENDIX A

Data Input Guide for HYDROBIOGEOCHEM

Data Input Guide for HYDROBIOGEOCHEM

UNITS OF MEASURE: The unit of mass and length used for the data input should be kilogram (kg) and decimeter (dm), respectively. Any units of time may be used as long as the same unit is used consistently throughout all data sets. All total analytical concentrations and all initial conditions should be specified in units of moles of chemical per unit total volume of media (mol/dm^3). All source/sink concentrations should be specified in units of moles of chemical per volume of liquid (mol/dm^3). All boundary condition concentrations should be specified in units of moles of chemical per mass of phase in which the chemical exists (mol/kg).

NOTE: All data sets except for Data Set 1 must be preceded by a data set name.

DATA SET 1: TITLE

Two lines are used per problem

Line 1: FORMAT(I5,7A10)

1. NPROB = Problem number.
2. TITLE = Array for the title of the problem. It may contain up to 70 characters from column 6 to column 75.

Line 2: Free format input contains 5 integers as follows:

1. IITR = Integer indicating if iteration table of convergence information to be printed:
   0 = no.
   1 = transport iteration table be printed.
   2 = both transport and chemical iteration tables printed.
2. INTER = Integer indicating if concentration field is to be printed for each hydrological-chemical interaction:
   1 = yes
   0 = no.
3. ICOND = Integer indicating if the condition number of the Jacobian matrix in biogeochemical computations is to be printed:
   1 = yes.
   0 = no.

4. NHGCI = Integer indicating if biogeochemical information is to be printed:
0 = no.
> 0 = print every NHGCI inter-hydro-geochem iterations.

5. IGEOM = Integer signifying if the geometric data are to be printed:
0 = no.
1 = yes.

DATA SET 2: BASIC INTEGER PARAMETERS

Free format input contains 23 integers as follows:

1. NNP = Number of nodal points.

2. NEL = Number of elements.

3. NMAT = Number of material types.

4. NCM = Number of elements with material property correction.

5. NTI = Number of time steps or time increments.

6. KSS = Steady-state simulation control:
0 = Steady-state solution desired.
± 1 = No steady-state solution desired.

NOTE: The combination of KSS and NTI will determine the type of simulation run:
If KSS = 0 and NTI = 0, a steady state simulation will be performed.
If KSS = 0 and NTI > 0, a transient simulation using the steady state solution as initial conditions will be performed.
If KSS = 1 and NTI > 0, a transient simulation using user supplied initial conditions will be performed. The program will equilibrate the user supplied initial conditions before the transient simulation is run.
If KSS = -1 and NTI > 0, a transient simulation using user supplied initial conditions will be performed. The user supplied initial conditions will **not** be equilibrated. The user is cautioned against using this option.

7. NMPPM = Number of material properties per material: must be 4 in the current program.

8. KVI = Velocity input control:
- 1 = Velocity and moisture content defined by Data Set 16.
1 = Steady-state velocity and moisture content read from Logical Unit 11.
2 = Transient velocity and moisture content read from Logical Unit 11.

9. ILUMP = Mass matrix lumping control:
0 = No lump.
1 = Lump.

10. IMID = Mid-difference control:
0 = No mid-difference.
1 = Mid-difference, and W in Data Set 3 should be 1.

11. IWET = Weighting function control:
0 = Galerkin weighting.
1 = Upstream weighting.

12. IOPTIM = Optimization factor computing indictor:
1 = Optimization factor is to be computed.
0 = Optimization factor is set to 1.0, 0.0, or -1.0.

13. NITER = Number of iterations allowed between hydrological-chemical iterations.

14. NDTCHG = Number of times to reset the time-step size to the initial value.

15. NPITER = Number of iterations allowed for solving the linear matrix equation with pointwise iteration.

16. IPNTS = Method to be used to solve the matrix equations:
0 = standard-banded Gaussian direct elimination procedure.
1 = pointwise iteration method.
2 = preconditioned conjugate gradient method, with polynomial as preconditioner.
3 = preconditioned conjugate gradient method, with incomplete Cholesky decomposition as preconditioner.
4 = preconditioned conjugate gradient method, with modified incomplete Cholesky decomposition as preconditioner.
5 = preconditioned conjugate gradient method, with symmetric successive over-relaxation as preconditioner

17. KSTR = Auxiliary storage output control:
0 = No storage.
1 = Output stored in Logical Unit 12.

18. NSTR = Number of logical records to be read from Logical Unit 13 for restarting the calculation:
0 = No restart.

19. LGRN = Is the Lagrangian-Eulerian approach to be used:
1 = Yes.
0 = No.

20. IQUAD = Indicator for quadrature integration:
11 = nodal quadrature for both surface integration and volume integration.
12 = nodal and Gaussian quadrature for surface and volume integration, respectively.
21 = Gaussian and nodal quadrature for surface and volume integration, respectively.
22 = Gaussian quadrature for both surface and volume integration.

21. IDETQ = Option for velocity for the Lagrangian step.
1 = average velocity approach.
2 = single velocity approach.

22. IOPTRS = Option for operator splitting.
0 = do not use operator splitting (use fully implicit scheme).
1 = use operator splitting.

23. IAIEF = Option for adaptive implicit-explicit handling of the reaction term in the transport equations.
0 = no. (reaction term on RHS of transport equation).
1 = yes. (reaction term adaptively adjusted to LHS or RHS depending on sign).

NOTE: NTI can be computed by NTI = I1 + 1 + I2 + 1, where

I1 = Largest integer not exceeding Log(DELMAX/DELT)/LOG(1+CHNG).

I2 = Largest integer not exceeding (RTIME-DELT*((1+CHNG)**(I1+1)-1)/CHNG)/DELMAX.

RTIME = Real simulation time.

(DELMAX, DELT, and CHNG are defined in Data Set 3).

If IPNTS is .GE.2 (i.e. if a preconditioned conjugate gradient method (PCG) is to be used), a second line is needed for the following 4 parameters:

1. IEIGEN = Signal of parameter estimation for GG in the polynomial PCG method:
0 = not requested.
1 = requested.

2. GG = The upper bound on the maximum eigenvalue of the coefficient matrix used in the polynomial PCG method.

3. ALPHA = Weighting factor for computing the diagonal element of the diagonal matrix used in the modified incomplete Cholesky PCG method.

4. OMEGA = Relaxation parameter used in the SSOR PCG method.

DATA SET 3: BASIC REAL PARAMETERS

Free-field format input contains 10 real numbers as follows:

1. DELT = Initial time-step size (T).

2. CHNG = Percent change in the time-step size in each of the subsequent time increments, (dimensionless in decimal fraction).

3. DELMAX = Maximum allowable time-step size (T).

4. TMAX = Maximum simulation time (T).

5. W = Time-derivative weighting factor for all terms except the velocity terms:
   0.5 = Crank-Nicolson central.
   1.0 = Backward difference and mid-difference.

6. WV = Time integration factor for the velocity terms:
   0.0 = Forward difference (explicit).
   0.5 = Central difference.
   1.0 = Backward difference (completely implicit).

7. OME = Relaxation parameter for solving the nonlinear equation:
   0.0 - 1.0 = Under-relaxation.
   1.0 = Exact relaxation.
   1.0 - 2.0 = Over-relaxation.

8. OMI = Relaxation parameter for pointwise solving the matrix equation:
   0.0 - 1.0 = Under-relaxation.
   1.0 = Exact relaxation.
   1.0-2.0 = Over-relaxation.

9. TOLA = Error tolerance for solving the nonlinear equations. Half of its value is used as the tolerance for solving the linearized matrix equation with pointwise iteration.

10. APHAG = Upstream weighting factor if IOPTIM = 0:
Values are between 0.0 and 1.50 when the advection form of the equation is used. If APHAG > 1.34D0, the program will choose appropriate values of weighting factor. When the conservative form of the equations is used or when IOPTIM = 1, this value is not used by the program.

DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL, AND TIMES FOR RESETTING STEP SIZE

The number of lines here depends on the number of time increments, NTI, and the number of times to reset the time step, NDTCHG. The number of lines is [(NTI/80+1)*2] + NLINE: (NTI/80+1) lines for printer output control, (NTI/80+1) lines for storage control, and NLINE lines for time-step-size resetting control, which depends on NDTCHG. NLINE lines are required to enter NDTCHG real numbers with free format.

Line 1 to Line [(NTI/80+1)]: FORMAT(80I1)

KPR0	KPR(1)	KPR(2)	...	KPR(NTI)
1	2	3	...	80

KPR0 = Printer control for initial and steady state conditions.
KPR(I) = Printer control for the I-th time step:

0 = Print nothing.
1 = Print chemical component data from within biogeochemical subroutine.
2 = Print above plus chemical component species data.
3 = Print above plus product species data.
4 = Print above plus stoichiometric coefficients and reaction data.
5 = Print above plus mass flow rates (FLOW, FRATE, and TFLOW).
6 = Print above plus velocities.

(Note: summary concentration values at each node are printed when a convergent solution is reached for each time step. Options 1 through 4 provide more detailed output on the chemical speciation in the system from within the biogeochemical portion of the program every NHGCI iterations. NHGCI is specified in Data Set 1).

Line [(NTI/80+1)+1] to Line [(NTI/80+1)*2]: FORMAT(80I1)

KDSK0	KDSK(1)	KDSK(2)	. . .	KDSK(NTI)
1	2	3	. . .	80

KDSK0 = Auxiliary storage control for steady-state and initial conditions.

KDSK(I) = Auxiliary storage control for the I-th time-step, the same allowable values as for KDSKO;
0 = No storage.
1 = Store on Logical Unit 12.

Line greater than line (NTI/80+1)*2: Free-field format input contains NDTCHG real numbers:

1. TDTCH(1) = The first time at which the time-step size is reset to its initial value.
2. TDTCH(2) = The second time at which the time-step size is reset to its initial value.
N. TDTCH(N) = The N-th time at which the time-step size is reset to its initial value.

DATA SET 5: PRINTOUT INDICATOR

The number of lines in this data set depends on NCPRT. Normally two lines are sufficient.

Line 1: Free-field format input containing one integer.

1. NCPRT = Number of nodes at which detailed biogeochemical information will be printed.

Line 2: Free-field format input contains NCPRT integers.

1. IWRK(1) = Global node number of the first node where detailed chemical information will be printed.

2. IWRK(2) = Global node number of the second node where detailed chemical information will be printed.

N. IWRK(N) = Global node number of the N-th node where detailed chemical information will be printed.

NOTE: IWRK(I), for 1 ≤ I ≤ NCPRT is used to temporarily store the node numbers where detailed chemical information is to be printed. These node numbers are then used to set NODEP(NP) =1 or 0. When NODEP(NP) = 1, detailed chemical information will be printed for the NP-th node. When NODEP(NP)= 0, detailed chemical information will not be printed for the NP-th node.

DATA SET 6: MATERIAL PROPERTIES

A total of NMAT lines are required for this data set.

Each line is free-field format input containing the following information:

1. PROP(1,I) = Longitudinal dispersivity (L).
2. PROP(2,I) = Lateral dispersivity (L).
3. PROP(3,I) = Effective molecular diffusion coefficient of the I-th medium (L**2/T).
4. PROP(4,I) = Bulk density of medium I (M/L**3).

***** NOTE: Data Sets 7 and 8 are not needed if Logical Unit 11 is used as input (i.e., if KVI > 0 in Data Set 2).**

DATA SET 7: NODAL POINT COORDINATES

Typically, a total of 2*NNP lines are required: NNP lines each for the x- and z-coordinates. However, if a group of nodes appear in regular pattern, automatic generation can be used.

Line 1 to Line NNP: Each line is free-field format input containing:

1. NI = Node number of the first node in the sequence.
2. NSEQ = NSEQ subsequent nodes to be automatically generated.
3. NAD = Increment of the node number for each of the NSEQ subsequent nodes.
4. XNI = x-coordinate of node NI (L).
5. XAD = Increment of the x-coordinate for each of the NSEQ subsequent nodes (L).
6. XRD = Percent increase of the increment over its preceding increment (decimal fraction):
   0 = All increments, XAD's, are the same.
   \> 0 = The first increment is XAD*(1+XRD), the second increment is XAD*(1+XRD)**2, the third increment is XAD*(1+XRD)**3, and so on.

NOTE: A line containing six zeros separated by spaces or commas must be used to signal the end of the x-coordinate data.

Line (NNP+1) to Line 2*NNP contain the same information as described above but for the z-coordinate.

NOTE: A line containing six zeros separated by spaces or commas must be used to signal the end of the z-coordinate data.

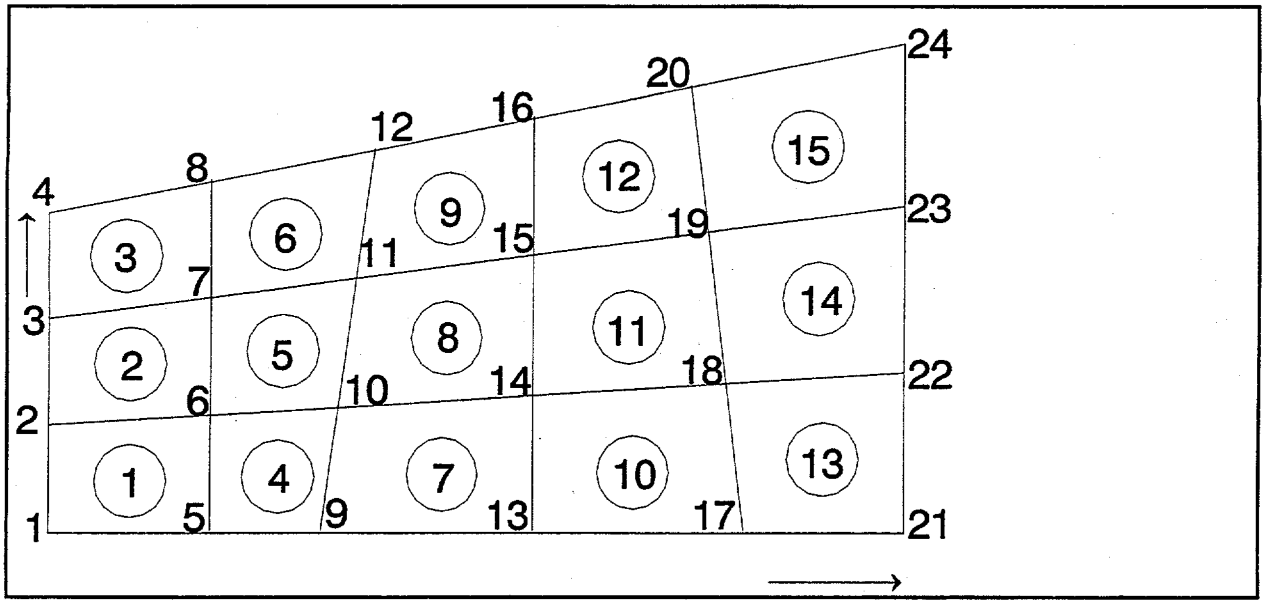
DATA SET 8: ELEMENT INCIDENCES

Typically, a total of NEL lines are needed, one for each element. However, only one line is needed if a group of elements appears in a regular pattern.

Free-field format input for each line contains the following information:

1. MI = Global element number.
2. IE(MI,1) = Global node number of the first node of element MI.
3. IE(MI,2) = Global node number of the second node of element MI.
4. IE(MI,3) = Global node number of the third node of element MI.
5. IE(MI,4) = Global node number of the fourth node of element MI.
6. IE(MI,5) = Material type to be applied to element MI.
7. MODL = Number of elements in the direction of the most rapid increase in node numbers.
8. NLAY = Number of elements in the direction of the least rapid increase in node numbers.

IE(MI,1) to IE(MI,4) are numbered beginning with the lower left corner and progressing around the element in a counterclockwise direction. For a rectangular block of elements, it is only necessary to specify the first element, the width MODL and the length NLAY, where MODL and NLAY are measured in elements. Element numbering proceeds most rapidly along the MODL dimension and least rapidly along the NLAY dimension. Figure A.1 provides an example. The object is considered to be rectangular because it has width MODL = 3 on two opposite sides and length NLAY = 5 on the other two opposite sides. To generate definitions of elements 2 through 15 automatically, including both the incidence and material type, only one line is necessary. Although all elements of this example will be assumed to contain the same material type, MITYP = 1, this situation can easily be changed by using the material-correction option in Data Set 9.



```
-------------------------------------------------------------
  1    1    5    6    2    1    3    5
-------------------------------------------------------------
```

Fig. A.1

DATA SET 9: MATERIAL TYPE CORRECTION

This data set is required only if NCM > 0. Normally NCM lines are required, but if the elements with different material properties appear in regular patterns, automatic generation can be used.

Free-field format input for each line contains the following information:

1. MI = Global element number of the first element in the sequence.

2. NSEQ = NSEQ subsequent elements will be generated automatically.

3. MAD = Increment of element number for each of the NSEQ subsequent elements.

4. MITYP = Material type to be applied to element MI.

5. MTYPAD = Increment of the type of material for each of the NSEQ subsequent elements.

NOTE: A line containing five zeros separated by spaces or commas must be used to signal the end of this data set.

DATA SET 10: CHEMICAL COMPONENT INFORMATION

Line 1: Free-field format input contains eight integers.

1. NOHA = Number of mobile components
2. NOHS = Number of immobile components
3. NOKX = Number of kinetic aqueous complexed species
4. NOKY = Number of kinetic adsorbed species
5. NOKZ = Number of kinetic ion-exchanged species
6. NOKP = Number of kinetic precipitated species
7. NOMB = Number of aqueous phase microbial species
8. NOMA = Number of adsorbed phase microbial species

Line 2 and Line 3 are repeated (NOHA + NOHS) times, once for each component in the simulation.

Line 2 FORMAT(A10) contains the following information:

1. CNAM(I) = component name of the I-th component

Line 3 FORMAT(2I5) contains the following information:

1. IDNTC(I,1) = Chemical component number of the I-th transport component

2. INDTC(I,1) = indicator of the I-the transport component,
   0 = conservative component
   1 = nonconservative mobile component
   2 = immobile component
   3 = component whose activity is fixed.

DATA SET 11: INPUT FOR INITIAL OR PRE-INITIAL CONDITIONS

This data set is needed only if NSTR = 0. (NSTR is specified in Data Set 2). When this data set is needed, typically a total of NNP lines is required for each chemical component, one each for each node. However, if the initial or pre-initial conditions appear in a regular pattern, automatic generation may be used. The following set of lines should be repeated for each of the NOHA + NOHS components, the NOKX + NOKY + NOKZ + NOKP kinetic chemical product species, and the NOMB + NOMA microbial species. (NOHA, NOHS, NOKX, NOKY, NOKZ, NOKP, NOMB, NOMA are specified in Data Set 10).

Each line is free-field format input containing the following information:

1. NI = Global node number of the first node in the sequence.
2. NSEQ = NSEQ subsequent nodes will be generated automatically.
3. NAD = Increment of the node number for each of the NSEQ nodes.
4. RNI = Initial or pre-initial total concentration at node NI (moles/total dm^3).
5. RAD = Increment of initial or pre-initial total concentration for each of the NSEQ nodes (moles/total dm^3).
6. RRD = Percent increase of the increment over its preceding increment (decimal fraction):
   0 = All increments, RAD's, are the same.
   > 0 = The first increment is RAD*(1+RRD), the second increment is RAD*(1+RRD)**2, the third increment is RAD*(1+RRD)**3, and so on.

NOTE: A line with six zeros separated by spaces or commas must be used to signal the end of this data set for each species.

NOTE: All initial concentrations are in moles per volume of media (= total volume of the solid and liquid phases).

NOTE: If the INDTC for any chemical component is equal to 3, then the log10 of its activity should be entered for initial or pre-initial values. (INDTC is specified in Data Set 10).

NOTE ON INITIAL CONDITIONS: The initial conditions for a transient calculation may be obtained in three different ways: from batch input, auxiliary storage input, or steady-state calculation using time-invariant boundary conditions. In the latter case, a batch input of the pre-initial conditions is required as the zero-th order iterate of the steady state solution. Auxiliary storage input is necessary whenever the restarting facility is being used. That is, concentration distribution for NSTR different times have been generated and written on disk or magnetic tape. If NSTR > 0, these distributions will be read from Logical Unit 13, and NSTR-th distribution will be used as the initial condition for current calculation. If KSTR > zero, the concentration values will be written on a different device as they are read from Logical Unit 13 so that a complete record of calculations may be kept on one device, Logical Unit 12. If either the first (batch input) or the last (steady-state) option is used, then NSTR = 0. (NSTR is specified in Data Set 2).

NOTE ON AUXILIARY UNITS: Logical Unit 11 is used to input hydrodynamic variables to HYDROGEOCHEM if KVI > 0. Logical Unit 12 is used to store output of HYDROGEOCHEM if KSTR > 0. Logical Unit 13 is used to input initial condition if NSTR > 0. Proper identification of these three units must be made if either of these options is used. The DSNAME for Logical Unit 13 of the current job should be the same as that for Logical Unit 12 of the previous job.

NOTE ON STEADY-STATE INPUT: A steady-state option may be used to provide either the final state of a system under study or the initial conditions for a transient state calculation. In former case KSS = 0 and NTI = 0, and in the latter case KSS = 0 and NTI > 0. If KSS ≠ 0, there will be no steady-state calculation.

DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS

Free-field format input contains 13 integers as follows:

1. NSEL = Number of source/sink elements.
2. NSPR = Number of source/sink profiles.
3. NSDP = Number of data points in each source/sink profile.

4. NWNP = Number of well or point source/sink nodes.
5. NWPR = Number of well or point source/sink strength profiles.
6. NWDP = Number of data points in each of the NWPR profiles.

7. NDNP = Number of Dirichlet nodes.
8. NDPR = Number of Dirichlet profiles (should be ≥ 1 if NDNP ≥ 1).
9. NDDP = Number of data points in each of the NDPR profiles (should be ≥ 2).

10. NVNP = Number of variable-boundary nodes.
11. NVES = Number of variable-boundary sides.
12. NVPR = Number of incoming fluid concentration profiles to be applied to variable-boundary element sides.
13. NVDP = Number of data points in each of the NVPR profiles.

DATA SET 13: ELEMENT (DISTRIBUTED) AND WELL (POINT) SOURCE/SINK

(13.1) Element Source/Sink: Subdata sets (13.1a, b, c) are needed if and only if NSEL > 0. When NSEL > 0, subdata sets (b) and (c) should be repeated (NOHA + NOHS + NOKX + NOMB + 2) times. (NSEL is specified in Data Set 12. NOHA, NOHS, NOKX, and NOMB are specified in Data Set 10).

(13.1a) Global element number of compressed source/sink element number: Free-field format input contains the following information:

1. LES(1) = Global element number of the first distributed source/sink element.

2. LES(2) = Global element number of the second distributed source/sink element.

N. LES(N) = Global element number of the N-th distributed source/sink element.

(13.1b) Element source/sink profile: Number of lines depends on NSPR, NSDP, and NON. Each line contains a number of data points = 2*NSDP numerical numbers. Each line is free-field format input.

For K =1, NOHA + NOHS + NOKX + NOMB + 2

For I = 1, NSPR

1. TSOSF(1,I,K) = Time of first data point in I-th profile for K-th component (T).

2. SOSF(1,I,K) = Source/sink value of first data point in I-th profile for K-th component:
= concentration (moles/dm^3 liquid) if K $\leq$ (NOHA+NOHS+NOKX+NOMB),
= flow rate of liquid (L**3/T) if K = (NOHA+NOHS+NOKX+NOMB+1), and
= density of incoming liquid (kg/dm^3) if K = (NOHA+NOHS+NOKX+NOMB+2).

3. TSOSF(2,I,K) = Time of second data point in I-th profile for K-th component (T).

4. SOSF(2,I,K) = Source/sink value of second data point in I-th profile for K-th component:

2N-1. TSOSF(N,I,K) = Time of N-th data point in I-th profile for K-th component (T).

2N. SOSF(N,I,K) = Source/sink value of N-th data point in I-th profile for K-th component:

(13.1c) Source/sink profile type in each source/sink element: Typically, one line per element is needed. However, automatic generation can be used.

Each line is free-field format input containing the following:

1. MI = Compressed source/sink element number of first element in the sequence.

2. NSEQ = NSEQ source/sink elements will have profile type MITYP.

3. MAD = Increment of MI for each of the NSEQ elements.

4. MITYP = Source/sink profile type for element MI.

5. MTYPAD = Increment of source profile type in each of the NSEQ subsequent elements.

NOTE: A line containing five zeros separated by spaces or commas must be used to end this data set.

(13.2) Point source/sink: Subdata sets (13.2a, b, c) are needed if and only if NWNP > 0. When NWNP > 0, subdata sets (b) and (c) should be repeated (NOHA + NOHS + NOKX + NOMB + 2) times. (NWNP is specified in Data Set 12. NOHA, NOHS, NOKX, and NOMB are specified in Data Set 10).

(13.2a) Global node number of compressed point source/sink number: Free-field format input contains the following information:

1. NPW(1) =Global node number of the first source/sink node.

2. NPW(2) =Global node number of the second source/sink node.

N. NPW(N) =Global node number of the N-th source/sink node.

(13.2b) Point source/sink profile: Number of lines depends on NWPR, NWDP, and NOHA + NOHS + NOKX + NOMB. Each line contains a number of data points = 2*NWDP numerical numbers. Each line is free-field format input.

For K =1, NOHA + NOHS + NOKX + NOMB + 2

For I = 1, NWPR

1.TWSSF(1,I,K) = Time of first data point in I-th profile for K-th component (T).

2. WSSF(1,I,K) = Source/sink value of first data point in I-th profile for K-th component:
= concentration (moles/dm^3 liquid) if K $\leq$ (NOHA+NOHS+NOKX+NOMB),
= flow rate of liquid (L**3/T) if K = (NOHA+NOHS+NOKX+NOMB+1), and
= density of incoming liquid (kg/dm^3) if K = (NOHA+NOHS+NOKX+NOMB+2).

3. TWSSF(2,I,K) = Time of second data point in I-th profile for K-th component (T).

4. WSSF(2,I,K) = Source/sink value of second data point in I-th profile for K-th component.

2N-1.TWSSF(N,I,K) = Time of N-th data point in I-th profile for K-th component (T).

2N. WSSF(N,I,K) = Source/sink value of N-th data point in I-th profile for K-th component.

(13.2c) Type of point source/sink nodes: Typically, one line per well node is needed. However, automatic generation may be used.

Each line is free-field format input containing the following:

1. NI = Compressed well node number of the first node in a sequence.
2. NSEQ = NSEQ subsequent well nodes will be generated automatically for the source profile type.
3. NIAD = Increment of compressed well node number for each of the NSEQ subsequent nodes.
4. NITYP = Type of well source/sink profile assigned to NI-th well node.
5. NITYPA = Increment of NITYP for each of the NSEQ subsequent nodes.

NOTE: A line containing five zeros separated by spaces or commas must be used to signal the end of this subdata set.

DATA SET 14: VARIABLE BOUNDARY CONDITIONS

This data set is required if and only if NVES > 0. Boundary conditions must be specified for all mobile components (i.e. those with INDTC(I,1) = 0 or 1), for all kinetic aqueous complexed chemical product species, and for all aqueous phase microbial species. (NVES is specified in Data Set 12; INDTC is specified in Data Set 10).

Four groups of lines are required for this data set: The first group is used to specify the incoming concentration profiles, the second group is used to assign the type of incoming concentration profile to each of the NVES boundary sides, the third group is used to read the global nodal number of NVNP in-flowing and out-flowing nodes, and the fourth group is used to specify the information of the NVES element sides. The first group and the second group should be repeated (NOHA + NOKX + NOMB) times, once for each of these species, followed by the third and fourth groups. For example: if there were three chemical components, the order of the groups would be a b a b a b c d, where the first, second, and third a and b would apply to the first, second, and third chemical components, respectively. The program checks INDTC(I,1) for each of the NOH components, and only reads a boundary condition if ≤ 1. (i.e. do not specify a boundary condition for fixed concentration or immobile components).

(a) Incoming concentration profiles: This subdata set is read in similarly to that of 13 (b).

For I = 1, NVPR

1.TCVBF(1,I,K) = Time of first data point in I-th incoming concentration versus time profile for K-th component (T).

2. CVBF(1,I,K) = Concentration of first data point in I-th incoming concentration versus time profile for K-th component: (moles/liter).

3. TCVBF(2,I,K) = Time of second data point in I-th incoming concentration versus time profile for K-th component (T).

4. CVBF(2,I,K) = Concentration of second data point in I-th incoming concentration versus time profile for K-th component: (moles/liter).

.

.

2N-1. TCVBF(N,I,K) = Time of the N-th data point in I-th incoming concentration versus time profile for K-th component (T).

2N. CVBF(N,I,K) = Concentration of the N-th data point in I-th incoming concentration versus time profile for K-th component: (moles/liter).

(b) Incoming concentration profile type assigned to variable-boundary sides: This subdata set is read in similarly to that in 13 (c).

1. MI = Compressed variable-boundary side number of the first side in a sequence.
2. NSEQ = NSEQ subsequent sides will be generated automatically.
3. MIAD = Increment of the compressed variable-boundary element side number for each of the NSEQ subsequent sides.
4. MITYP = Type of incoming concentration profile assigned to side MI.
5. MTYPAD = Increment of the type of incoming concentration profile for each of the NSEQ subsequent sides.

NOTE: A line containing five zeros separated by spaces or commas is used to end the input of this subdata set.

(c) Global nodal number of NVNP variable-boundary condition nodes: Typically, NVNP lines are needed. However, automatic generation can be used.

Each line is free-field format input containing the following:

1. NI = Compressed variable-boundary node number of the first node in a sequence.
2. NSEQ = NSEQ subsequent nodes will be generated automatically.
3. NIAD = Increment of the compressed variable-boundary node number for each of the NSEQ subsequent sides.
4. NODE = Global node of the compressed node NI.
5. NODEAD = Increment of NODE for each of the NSEQ subsequent nodes.

NOTE: A line containing five zeros separated by spaces or commas is used to end the input of this subdata set.

(d) Specification of variable-boundary sides: Typically, NVES lines are required, one each for a variable-boundary element side. However, if a group of variable-boundary element sides appears in a regular pattern, automatic generation may be used.

Each line is free-field format input containing the following:

1. MI = Compressed variable boundary element-side number of the first element side in a sequence.
2. NSEQ = NSEQ subsequent variable-boundary element sides will be generated automatically.
3. M = Global element number to which the MI-th element side belongs.
4. IS1 = Compressed variable-boundary nodal number of the first node of element side MI.
5. IS2 = Compressed variable-boundary nodal number of the second node of element side MI.
6. MIAD = Increment of MI for each of the NSEQ subsequent variable-boundary element sides.

7. MAD = Increment of M for each of the NSEQ subsequent variable-boundary element sides.

8. IS1AD = Increment of IS1 for each of the NSEQ subsequent variable-boundary element sides.

9. IS2AD = Increment of IS2 for each of the NSEQ subsequent variable-boundary element sides.

NOTE: A line with nine zeros separated by spaces or commas is used to end the input of this subdata set.

DATA SET 15: DIRICHLET BOUNDARY CONDITIONS

This data set is required if and only if NDNP > 0. Boundary conditions must be specified for all mobile components (i.e. those with INDTC(I,1) = 0 or 1), for all kinetic aqueous complexed product species, and for all aqueous phase microbial species. (NDNP is specified in Data Set 12; INDTC is specified in Data Set 10).

Subdata sets (a) and (b) should be repeated (NOHA + NOKX + NOMB) times, once for each of these species, followed by the third group. For example: if there were three chemical components, the order of the groups would be a b a b a b c, where the first, second and third a and b would apply to the first, second and third chemical components respectively. (The program checks INDTC(I,1) for each of the NOH components, and only reads a boundary condition if ≤ 1).

(a) Dirichlet concentration profile: This subdata set is read in similarly to that in 13 (b).

For I = 1, NDPR

1. TCDBF(1,I,K) =Time of first data point in I-th Dirichlet concentration versus time profile for K-th component (T).

2. CDBF(1,I,K) = Concentration of first data point in the I-th Dirichlet concentration versus time profile for K-th component: (moles/kg).

3. TCDBF(2,I,K) =Time of second data point in the I-th Dirichlet concentration versus time profile for K-th component (T).

4. CDBF(2,I,K) = Concentration of second data point in the I-th Dirichlet concentration versus time profile for K-th component: (moles/kg).

.

.

2N-1. TCDBF(N,I,K) =Time of the N-th data point in the I-th Dirichlet concentration versus time profile for K-th component (T).

2N. CDBF(N,I,K) = Concentration of the N-th data point in the I-th Dirichlet concentration versus time profile for K-th component: (moles/kg).

(b) Type of Dirichlet node: This subdata set is read in similarly to that of Data Set 14 (b).

Each line is free field format input containing five intergers:

1. NI = Compressed Dirichlet node number of the first node in the sequence.
2. NSEQ = NSEQ subsequent Dirichlet nodes will be generated automatically.
3. NAD = Increment of compressed Dirichlet node number for each of the NSEQ nodes.
4. NITYP = Type of Dirichlet concentration profile for node NI and the NSEQ subsequent nodes.
5. NTYPAD = Increment of NITYP for each of the NSEQ subsequent nodes.

NOTE: A line with five zeros separated by spaces or commas must be used to signal the end of this subdata set.

(c) Dirichlet nodes: This subdata set is read in similarly to that of Data Set 14 (c).

Each line is free-field format input containing five integers:

1. NI = Compressed Dirichlet boundary node number of the first node in a sequence.
2. NSEQ = NSEQ subsequent nodes will be generated automatically.
3. NIAD = Increment of the compressed Dirichlet boundary node number for each of the NSEQ subsequent sides.
4. NODE = Global node of the compressed node NI.
5. NODEAD= Increment of NODE for each of the NSEQ subsequent nodes.

NOTE: A line containing five zeros separated by spaces or commas is used to end the input of this subdata set.

DATA SET 16: VELOCITY, MOISTURE CONTENT, AND LIQUID DENSITY

If KVI > 0, the velocity and moisture data is not needed because they will be read via Logical Unit 11. (KVI is specified in Data Set 2).

(a) Velocity field: Normally, one line per node is needed. However, automatic generation can be used.

Each line is free-field format input containing seven variables:

1. NI = Node number of the first node in the sequence.
2. NSEQ = NSEQ subsequent nodes will be automatically generated.
3. NAD = Increment of node number in each of the NSEQ subsequent nodes.
4. VXNI = x-velocity component of node NI (L/T).
5. VZNI = z-velocity component of node NI (L/T).
6. VXAD = Increment of x-velocity for each of the NSEQ subsequent nodes (L/T).
7. VZAD = Increment of z-velocity for each of the NSEQ subsequent nodes (L/T).

NOTE: A line with seven zeros separated by spaces or commas signals the end of this subdata set.

(b) Moisture content field: Typically, one line per element is needed. However, automatic generation can be used.

Each line is free-field format input containing five variables:

1. NI = Element number of the first element in the sequence.
2. NSEQ = NSEQ subsequent elements will have the moisture content automatically generated.
3. NAD = Increment of element number for each of the NSEQ subsequent elements.
4. THNI = Moisture content of element NI (decimal point).
5. THNIAD = Increment of moisture content for each of the NSEQ subsequent elements (decimal point).

NOTE: A line with five zeros separated by spaces or commas signals the end of this subdata set.

(c) Liquid density field: Typically, one line per node is needed. However, automatic generation can be used.

Each line is free-field format input containing six variables:

1. NI = Node number of the first node in the sequence.

2. NSEQ = NSEQ subsequent nodes will have liquid density automatically generated.

3. NAD = Increment of the node number for each of the NSEQ subsequent nodes.

4. RHOLNI = Liquid density at node NI (M/L^3).

5. RHOLAD = Incremental increase of the liquid density for each of the NSEQ subsequent nodes (M/L^3).

6. RHOLRD = Percent increase of the increment over its preceding increment (decimal fraction).

NOTE: A line containing six zeros separated by spaces or commas must be used to signal the end of the this subdata set.

DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES

One line (FREE FORMAT) contains 6 variables as follows:

1. NONA = Number of aqueous components.
2. NONS = Number of adsorbent components.
3. NOMX = Number of complexed species.
4. NOMY = Number of adsorbed species.
5. NOMZ = Number of ion-exchanged species.
6. NOMP = Number of species subject to precipitation/dissolution.

DATA SET 18: H^+, e^-, AND IONIC STRENGTH CORRECTION INFORMATION

One line (FREE FORMAT) contains the following five variables:

1. SICOR = User's specified ionic strength for computing activity coefficients. (This will be used as a constant ionic strength if the user sets ICOR = 1 below).

2. ICOR = Is Ionic strength used to correct activity coefficient ?
    - 0 = no,
    - 1 = constant ionic strength is used (value specified by the user above),
    - 2 = variable ionic strength is used (as calculated by the program).

3. LNH = Location of the component H^+ among component list (in Data Sets 23 and 24).

4. LNG = Location of the gas component among component list (in Data Sets 23 and 24).

5. LNE = Location of the component e^- among component list (in Data Sets 23 and 24).

DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH

Two lines per problem are required.

Line 1 (FREE FORMAT) contains the following information:

1. TEMP = Absolute temperature in Kelvin.
2. PRESU = Pressure in ATM.

Line 2 (FREE FORMAT) contains the following information:

1. PEMN = Expected minimum pe.
2. PEMX = Expected maximum pe.
3. PHMN = Expected minimum pH.
4. PHMX = Expected maximum pH.

DATA SET 20: ADSORPTION INFORMATION

This data set is needed if and only if NONS .GT. 0. (NONS, the number of adsorbent components, is specified in Data Set 17). This set reads information for NSORB adsorbing sites.

Line 1 contains the following two variables:

1. NSORB = Number of adsorbing sites

2. IADS = Adsorption model index:
    - 0 = simple surface complexation,
    - 1 = constant capacitance model,
    - 2 = triple layer model.

Note: If IADS = 0, NONS = 1 x NSORB
If IADS = 1, NONS = 2 x NSORB
If IADS = 2, NONS = 3 x NSORB

Lines 2 to Record NSORB + 1:

Total number of lines in this subset is NSORB. Each record contains the following two variables.

1. LNOA(I) = Location of the exp(-e*psio/kt) component in the component list for the I-th adsorbing site. (Components are listed in Data Sets 23 and 24).

2. LNBA(I) = Location of the exp(-e*psib/kt) component in the component list for the I-th adsorbing site. (Components are listed in Data Sets 23 and 24).

Record NSORB+2 to Record NSORB+1+NMAT:
Total number of records in this subset is NMAT. Each record contains the following variables

1. CAP1M(1,I) = Capacitance between the surface and "o" plane, (Farady/L**2) for the first adsorbing site in material I,

2. CAP2M(1,I) = Capacitance between the "o" plane and "b" plane, (Farady/L**2) for the first adsorbing site in material I,

3. SREAM(1,I) = Surface area of the first adsorbing site in material I, (L**2/M of solid),

4. CAP1M(2,I) = Capacitance between the surface and "o" plane, (Farady/L**2) for the second adsorbing site in material I,

5. CAP2M(2,I) = Capacitance between the "o" plane and "b" plane, (Farady/L**2) for the second adsorbing site in material I,

6. SREAM(2,I) = Surface area of the second adsorbing site in material I, (L**2/M of solid),

.
.
.

3J-2. CAP1M(J,I) = Capacitance between the surface and "o" plane, (Farady/L**2) for the J-th adsorbing site in material I,

3J-1. CAP2M(J,I) = Capacitance between the "o" plane and "b" plane, (Farady/L**2) for the J-th adsorbing site in material I,

3J. SREAM(J,I) = Surface area of the J-th adsorbing site in material I, (L**2/M of solid),

.

.

3NSORB-2. CAP1M(NSORB,I) = Capacitance between the surface and "o" plane, (Farady/L**2) for the NSORB-th adsorbing site in material I,

3NSORB-1. CAP2M(NSORB,I) = Capacitance between the "o" plane and "b" plane, (Farady/L**2) for the NSORB-th adsorbing site in material I,

3NSROB. SREAM(NSORBI) = Surface area of the NSORB-th adsorbing site in material I, (L**2/M of solid).

DATA SET 21: ION-EXCHANGE INFORMATION

This data set is needed only if NOMZ .GT. 0. (NOMZ, the number of ion-exchanged species, is specified in Data Set 17). This set reads information of ion exchange information for NSITE exchange sites.

Record 1 contains the following variable

1. NSITE = Number of ion-exchange sites

Record 2 to Record NSITE + 1
Total number of records in this subset is NSITE. Each Record contains the following two variables for the I-th site

1. NOMZI(I) = Number of ion-exchanged species participating in reactions at the I-th exchanged site.

2. LNI(I) = Indicator for the "reference" ion-exchange species for the I-th site. It gives the location of this "reference" species on the ion-exchanged species list.

Record NSITE+2 to Record NSITE+1+NMAT
Total number of records in this subset is NMAT. Each record contains the following variables

1. CECM(1,I) = Ion-exchange capacity (equivalents per unit mass of solid) for the first site in material I.

2. CECM(2,I) = Ion-exchange capacity (equivalents per unit mass of solid) for the second site in material I.

.

.

J. CECM(J,I) = Ion-exchange capacity (equivalents per unit mss of solid) for the J-th site in material I,

.

.

NSITE. CECM(NSITE,I) = Ion-exchange capacity (equivalents per unit mass of solid) for the NSITE-th site in material I.

DATA SET 22: BASIC REAL AND INTEGER PARAMETERS

One line of unformatted input contain the following 6 variables.

1. OMEGAC = relaxation parameters for iteration:
   0 ~ 1 = under-relaxation,
   1 = exact relaxation,
   1 ~ 2 = over-relaxation.

2. NPCYL = number of cycles allowed for iterating precipitation-dissolution. (Set NPCYL = 1 if precipitation-dissolution is not in the simulation).

3. NITERC = number of iterations allowed.

4. EPSC = error tolerance for iteration.

5. CNSTRNX = a factor for the constraint on complexed species concentration. No complexed species concentration would yield a total component concentration greater than CNSTRNX times of the input total component concentration.

6. CNSTRNY = a factor for the constraint on adsorbed species concentration. No adsorbed species concentration would yield a total component concentration greater than CNSTRNY times of the input total component concentration.

7. IPIV = option for pivoting for solution of the Newton-Raphson matrix equations.
   1 = full pivoting.
   2 = partial pivoting.

DATA SET 23: NAMES AND TYPES OF CHEMICAL COMPONENT SPECIES

For each component, two lines are needed.

Line 1 - FORMAT(A20,*)

1. CNAM(J,2) = Component name of the J-th component.

Line 2 - free format.

1. INDTC(J,2) = Type of the J-th component species,
   1 = mobile aqueous species, e.g, Ca^{2+},
   2 = immobile adsorbent species, e.g., SOH
   3 = fictitious species, e.g., sigmao or sigmab
   4 = mobile adsorbent species, e.g. colloid component species

2. IFCS = Indicator for free component species:
   0 = free component species subject to transport.
   1 = free component species not subject to transport.

DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES

For each component species, either two lines or (2 + 3*IONEX) lines are needed, depending on whether the species participates in ion-exchange reactions. If the species does not participate in ion-exchange reaction, two lines are needed for the species. If the species is involved in IONEX sites of ion-exchanged reaction, (2+3*IONEX) lines are needed for the species.

Data for the NONA aqueous components should be listed first, then for the NONS adsorbent components. (NONA and NONS are specified in Data Set 17). All information relating to one component species is input (either 2 or (2+3*IONEX) lines), then the information for the next component species. Components should be described in the same order used in Data Set 23.

Line 1: FORMAT(A20)

1. SPECN(I) = Name of the I-th component species.

Line 2: Free format. This line contains three variables:

1. ISCN(I) = Indicator of the I-th species concentration:
   0 = Species concentration or activity will be computed.
   3 = Species concentration or activity is fixed.

2. VJ(I) = Charge of the I-the component species.

3. IONEX = Integer indicating the number of ion exchange sites to which this component species participates:
   0 = This component species does not participate in any ion exchange reaction.
   IONEX = This component species participates in IONEX ion exchange reactions.

The following sub-data set is needed for a component specie only if IONEX is not equal to zero. When IONEX is not equal to 0, this subdata set is repeated IONEX times. For each of the IONEX ion exchange sites on which this component specie is involved in ion-exchange reactions, the following three lines are needed.

For k = 1, IONEX

Line 3 - This line contains the following variable

1. J = This species participates in the J-th ion exchange site's reaction.

Line 4 - FORMAT(A20):

1. SPECN(II) = Name of the II-th ion-exchanged species resulted from the I-th component species involving in the J-th ion exchange site reaction.
   NOTE: II is internally arranged according to the order of ion exchange site.

Line 5 - Free Format. This line contains the following variables

1. ISCN(II) = Indicator of the II-th ion-exchanged species concentration:
   0 = species concentration is be computed,
   3 = species concentration is fixed.

2. AXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

3. AXYZP(I,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

4. AXYZP(I,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

.

.

NON+1. AXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

NON+2. BXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

NON+3. BXYZP(I,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

NON+4. BXYZP(I,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

.

.

2*NON+1. BXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

DATA SET 25: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

This data set is needed only if NOMX .GT. 0. If needed, it is read in similar to DATA SET 24. (NOMX, the number of aqueous complexed species, is specified in Data Set 17).

Line 1: FORMAT(A20)

1. SPECN(II) = Name of the II-th species or the I-th complexed species.

Line 2: Free format contains the following variables:

1. ISCN(II) = Indicator of the II-th species concentration:
   0 = Species concentrtion will be computed.
   3 = Species concentration is fixed.

2. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mass action equation.

3. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mass action equation.

4. AXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mass action equation.

.

.

NON+1. AXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the I-th complexed species, for use in mass action equation.

NON+2. IONEX = Integer indicating the number of ion exchange sites on which this complexed species participates in ion-exchange reactions:

0 = This complexed species does not participate in any ion exchange reaction.

IONEX = This complexed species participates in IONEX ion exchange reactions.

NON+3. BXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mole balance equation.

NON+4. BXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mole balance equation.

NON+5. BXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mole balance equation.

.

.

2*NON+1. BXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the I-th complexed species, for use in mole balance equation.

The following sub-data set is needed for this aqueous complexed species only if IONEX is not equal to zero. When IONEX is not equal to 0, this sub-data set is repeated IONEX times. For each of the IONEX ion exchange sites on which this aqueous complexed specie is involved in ion-exchange reactions, the following three lines are needed to read ion exchanged species information.

For k = 1, IONEX

Line 3 - This line contains the following variable

1. J = This complexed species participates in the J-th ion exchange site's reaction.

Line 4 - FORMAT(A20):

1. SPECN(II) = Name of the II-th ion-exchanged species resulted from the I-th complexed species involving in the J-th ion exchange site reaction.

NOTE: II is internally arranged according to the order of ion exchange site.

Line 5 - Free Format. This line contains the following variables

1. ISCN(II) = Indicator of the II-th ion-exchanged species concentration:
   0 = species concentration is be computed,
   3 = species concentration is fixed.

2. AXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange

species for use in mass action, where IPD=II-NON.

3. AXYZP(I,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

4. AXYZP(I,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

.

.

NON+1. AXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the II-th ion exchange species for use in mass action, where IPD=II-NON.

NON+2. BXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

NON+3. BXYZP(I,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

NON+4. BXYZP(I,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

.

.

2*NON+1. BXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the II-th ion exchange species for use in mole balance, where IPD=II-NON.

DATA SET 26: ADSORBED SPECIES

This data set is needed only if NOMY .GT. 0. Two lines per adsorbed species are needed. (NOMY, the number of adsorbed species, is specified in Data Set 17).

Line 1 - FORMAT(A20)

1. SPECN(II) = Name of the II-th species or the I-th adsorbed species.

Line 2 - Unformatted input containing the following variables

1. ISCN(II) = Indicator of the II-th species concentration:
   0 = species concentration is to be computed,
   3 = species concentration is fixed.

2. AXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th product species or in the I-th adsorbed species, for use in mass action equation.

3. AXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th product species or in the I-th adsorbed species, for use in mass action equation.

4. AXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th product species or in the I-th adsorbed species, for use in mass action equation.

.

.

.

NON+1. AXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th product species or in the I-th adsorbed species, for use in mass action equation.

NON+2. BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th product species or in the I-th adsorbed species, for use in mole balance equation.

NON+3. BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th product species or in the I-th adsorbed species, for use in mole balance equation.

NON+4. BXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th product species or in the I-th adsorbed species, for use in mole balance equation.

.

.

.

2*NON+1. BXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th product species or in the I-th adsorbed species, for use in mole balance equation.

DATA SET 27: PRECIPITATED/DISSOLVED SPECIES

This data set is needed only if NOMP .GT. 0. Two lines per precipitated species are needed. (NOMP, the number of precipitated species, is specified in Data Set 17).

Line 1 - FORMAT(A20)

1. SPECN(II) = Name of the II-th product species or the I-th precipipated/dissolved species.

Line 2 - Unformatted input containing the following variables

1. ISCN(II) = Indicator of the II-th species concentration:
   0 = species concentration is to be computed,
   3 = species concentration is fixed.

2. PKIPD = Log10 of the equilibrium formation constant for the I-th precipitated species.

3. AXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th product species or in the I-th precipitated/dissolved species, for use in mass action equation.

4. AXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th product species or in the I-th precipitated/dissolved species, for use in mass action equation.

5. AXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th product species or in the I-th precipitated/dissolved species, for use in mass action equation.

.

.

.

NON+2. AXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th product species or in the I-th precipitated/dissolved species, for use in mass action equation.

NON+3. BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th product species or in the I-th precipitated/dissolved species, for use in mole balance equation.

NON+4. BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th product species or in the I-th precipitated/dissolved species, for use in mole balance equation.

NON+5. BXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th product species or in the I-th precipitated/dissolved species, for use in mole balance equation.

.

.

.

2*NON+2. BXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th product species or in the I-th precipitated/dissolved species, for use in mole balance equation.

DATA SET 28: MICROBIAL SPECIES

This data set is needed only if NOMB or NOMA .GT. 0. For each species, two lines are needed. The NOMB aqueous microbial species should be listed first, then the NOMA adsorbed microbial components. (NOMB and NOMA are specified in Data Set 10).

Line 1 - FORMAT(A20, I5)

1. SPECN(II) = Name of the II-th species

Line 2 - (FREE FORMAT) contains the following variables

1. ISCN(II) = Indicator of the II-th species concentration
   0 = species concentration is to be computed.
   3 = species concentration is fixed.

2. PKD = Log10 of the death/decay constant of the I-th microbial species.

3. NER = Number of chemical species affected by endogenous respiration of this microbial species.

The following lines are needed only if NER .GT. 0. Two lines are needed for each of the NER species affected by endogenous respiration.

Line 3 - (FREE FORMAT) contains the following variable

1. IGER(II,J) = global species number of the J-th chemical species affected by endogenous respiration of the II-th microbial species.

Line 4 - (FREE FORMAT) contains the following variables

1. ERAIJ = stoichiometric coefficient for use of the J-th chemical species due to maintenance/decay processes of this microbial species.

2. ERKIJ = half saturation constant for the J-th chemical species in the maintenance/decay processes of this microbial species.

DATA SET 29: REACTION DATA

NOTE: Equilibrium chemical reactions involving aqueous complexation, adsorption or precipitation may involve as many reactants as necessary but must be written as the formation of only one equilibrium product species. Each equilibrium product species may participate in only one equilibrium reaction.

Ion exchange reactions, whether equilibrium or kinetic, must have one aqueous species and one ion exchanged species both as reactants and as products. The reactant ion exchanged species must be the reference ion exchange species for the site involved, i.e.:
Aqueous Species + Reference IE Species ↔ New Aqueous Species + New IE Species

All other kinetic chemical reactions may involve any species as reactants or products.

Microbiological reactions may involve any chemical species as reactants and products. One reactant may be identified as the substrate, one as the electron acceptor, one as the nutrient, and one as the inhibitor for use in the Monod kinetic expressions.

One line is needed specifying the number of mixed kinetic reactions in the simulation.

Line 1 - (FREE FORMAT) contains the following variable:

1. NRXN = The number of kinetic reactions in this simulation

The following subset is needed only if NRXN is greater than zero. For each of the NRXN kinetic reactions four lines are needed.

Line 1 - (FREE FORMAT) contains the following variables:

1. NRTS = The number of reactant species participating in this kinetic reaction.

2. NPDS = The number of product species participating in this kinetic reaction.

3. KRTYP(I) = Kinetic reaction type of the I-th reaction.
    0 = Equilibrium reaction.
    1 = Kinetic chemical reaction.
    2 = Monod kinetic microbial reaction.
    3 = Microbial phase transfer reaction.

Line 2 - (FREE FORMAT) contains the following variables:

If KRTYP(I) = 0,
1. PEQK = Log10 of the equilibrium constant for this reaction.

If KRTYP(I) = 1 or 3,

1. PBK = Log10 of the backward rate constant for this kinetic reaction.
2. PFK = Log10 of the forward rate constant for this kinetic reaction.

If KRTYP(I) = 2,

1. GRMAXK = maximum specific growth rate of the i-th reaction, μ_{max}, (1/T).

2. HSCS = half saturation constant for the substrate in the i-th reaction, K_S, , mass/mass of phase (M/M). (If the substrate availability is not to be incorporated in the Monod kinetic expressions for this reaction, set = 0).

3. HSCA = half saturation constant for the electron acceptor in the i-th reaction, K_A, , mass/mass of phase (M/M). (If electron acceptor availability is not to be incorporated in the Monod kinetic expressions for this reaction, set = 0).

4. HSCN = half saturation constant for the nutrient in the i-th reaction, K_N, , mass/mass of phase (M/M). (If nutrient availability is not to be incorporated in the Monod kinetic expressions for this reaction, set = 0).

5. LOCS = reactant which is the substrate in the i-th reaction. (Set = 0 if not used).

6. LOCA = reactant which is the electron acceptor in the i-th reaction. (Set = 0 if not used).

7. LOCN = reactant which is the nutrient in the i-th reaction. (Set = 0 if not used).

8. TAUL = lag time for the i-th reaction.

9. TAUE = time to reach exponential growth for the i-th reaction.

Line 3 - (FREE FORMAT) contains the following variables:

1. CXYZP(I,1) = stoichiometric coefficient of the 1st reactant species in the I-th reaction.

2. CXYZP(I,2) = stoichiometric coefficient of the 2nd reactant species in the I-th reaction.

.

.

.

NRTS. CXYZP(I,NRTS) = stoichiometric coefficient of the NRTS-th reactant species in the I-th reaction.

NRTS+1. DXYZP(I,1) = stoichiometric coefficient of the 1-st product species in the I-th reaction.

NRTS+2. DXYZP(I,2) = stoichiometric coefficient of the 2nd product species in the I-th reaction.

.
.
.

NRTS+NPDS. DXYZP(I,NPDS) = stoichiometric coefficient of the NPDS-th product species in the I-th reaction.

Line 4 - (FREE FORMAT) contains the following variables:

1. IGSNRT(I,1) = global species number of the 1-st reactant species in the I-th reaction.

2. IGSNRT(I,2) = global species number of the 2-nd reactant species in the I-th reaction.

.
.
.

NRTS. IGSNRT(I,NRTS) = global species number of the NRTS-th reactant species in the I-th reaction.

NRTS+1. IGSNPD(I,1) = global species number of the 1-st product species in the I-th reaction.

NRTS+2. IGSNPD(I,2) = global species number of the 2-nd product species in the I-th reaction.

.
.
.

NRTS+NPDS. IGSNPD(I,NPDS) = global species number of the NPDS-th product species in the I-th reaction.

NOTE: The total, or global, number of species in the simulation is NONA + NONS + NOMX + NOMY + NOMZ. + NOMP + NOMB + NOMA. (All specified in Data Set 17). These species are stored in the following order:

	<u>Global Species Number:</u>
NONA aqueous component species	1 through NONA
NONS adsorbent component species	(NONA+1) through (NONA+NONS)
NOMX aqueous complexed species	(NONA+NONS+1) through (NONA+NONS+NOMX)
NOMY adsorbed species	(NONA+NONS+NOMX+1) through (NONA+NONS+NOMX+NOMY)
NOMZ ion-exchange species	(NONA+NONS+NOMX+NOMY+1)

	through (NONA+NONS+NOMX+NOMY+NOMZ)
NOMP precipitated species	(NONA+NONS+NOMX+NOMY+NOMZ+1) through (NONA+NONS+NOMX+NOMY+NOMZ+NOMP)
NOMB aqueous phase microbial species	(NONA+NONS+NOMX+NOMY+NOMZ+NOMP) through (NONA+NONS+NOMX+NOMY+NOMZ +NOMP +NOMB)
NOMA adsorbed phase microbial species	(NONA+NONS+NOMX+NOMY+NOMZ+NOMP+NOMB) through (NONA+NONS+NOMX+NOMY+NOMZ+NOMP +NOMB+NOMA)

Within the NONA, NONS, NOMX, NOMY, NOMP, NOMB, and NOMA groups of species, the species are stored in the same order in which they are input. Within the NOMZ group of species, the ion exchanged species are internally rearranged and are stored in order first by ion exchange site and then by the order of the aqueous species corresponding to the ion exchange species at that site.

DATA SET 30: END-OF-JOB CARD LINE

A blank line must be used to signal the end of the job.

INTERNAL DISTRIBUTION

L. D. Bates, 9704-2, MS-8011
C. A. Bednarz, 7078D, MS-6402
B. A. Berven, 4500S, MS-6126
S. C. Brooks, 1505, MS-6038
E. F. D'Azevedo, 6012, MS-6367
S. B. Garland, 900TCB, MS-7606
(5) J. P. Gwo, 4500N, MS-6203
G. K. Jacobs, 1505, MS-6036
P. M. Jardine, 1505, MS-6038
R. J. Luxmoore, 1505, MS-6038
K. L. Kliewer, 4500N, MS-6203
G. Mahithakumar, 4500N, MS-6203
G. R. Moline, 1509, MS-6400
S. D. VanHoesen, 1000, MS-6338
(5) Central Research Library
ESD Library
Laboratory Records Dept.
Laboratory Records, ORNL-RC
ORNL Patent Section
ORNL Y-12 Technical Library

EXTERNAL DISTRIBUTION

Paul Bayer, U.S. Department of Energy, ER-74, GTN, 19901 Germantown Rd.,
Germantown, MD 20874

Sally M. Benson, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., MS
90-1116, Berkeley, CA 94720

John W. Bradbury, NMSS/DWM/ENGB, U.S. Nuclear Regulatory Comission,
Washington, DC 20555

Robert Carsel, NERL, Ecosystems Research Division, Athens, GA 30605-2700

Inn G. Choi, Westinghouse Savannah River Co., Savannah River Tech. Center
Aiken, SC 29808

James Davis, Bldg 15, McKelvey Building, 345 Middlefield Road, MS 465,
Menlo Park, CA 94025

Mark S Dortch, Waterways Experiment Station, 3909 Halls Ferry Road,
Vicksburg, Mississippi 39180

William E. Glassley, Lawrence Livermore National Laboratory, P.O. Box 808, L-202, Livermore, CA 94550

Jeff P. Holland, Waterways Experiment Station, Coastal And Hydraulics
Laboratory, 3909 Halls Ferry Road, Vicksburg, Mississippi 39180

George Hornberger, University of Virginia, Department of Environmental
Science, Charlottesville, VA 22903

David Janecky, Los Almos National Laboratory, Chemical Sciences and Technology Division, Environmental Sciences & Waste Technology Group, CST-7, MS J514, TA-48 Pajarito Road, Los Alamos, NM 87545

Wolfgan Kinzelbach, Professor, ETH Hoenggerberg, HIL G 37.3, CH-8093, Zurich, Switzerland

David R. Parker, Professor, University of California, Riverside, Department of Soil & Environ. Sci., Riverside, CA 92521

Jack C. Parker, ES&T Inc., 2608 Sheffield Dr., Blacksburg, VA 24060-8270

Robert W. Puls, USEPA Robert S. Kerr Environmental Research Center, Subsurface Protection & Remdiatn Div/ORD, P.O. Box # 1198, Ada, OK 74821-1198

(5) Karen M. Salvage, Department of Geological Sciences and Environmental Studies, State University of New York, PO Box 6000, Binghamton, NY 13902-6000

H. M. Selim, Louisiana State Unv., Agronomy Department, Baton Rouge, LA 70803

Thomas E. Short, USEPA Robert S. Kerr Environmental Research Center, Subsurface Protection & Remdiatn Div/ORD, P.O. Box # 1198, Ada, OK 74821-1198

Malcolm D. Siegel, Sandia National Laboratories, New Mexico, PO Box 5800, Albuquerque, NM 87185-0733

Kip Solomon, Department of Geology and Geophys., School of Mines and Earth Science, University of Utah, 717 WBB, Salt Lake City, UT 84112-1183

(5) Jim Szecsody, Pacific Northwest National Laboratory, P.O. Box 999, MS-K3-61, Richland, WA 99352

David Tomasko, Argonne National Laboratory, Bldg. 900, 9700 S. Case Ave., Argonne, IL 60439

Albert Valocchi, Department of Civil Engineering, University of Illinois, 208 N. Romine St., Urbana, IL 61801

Rein van Genuchten, U.S. Salinity Laboratory, 450 Big Springs Rd., Riverside, CA 92507-4617

Jim Weaver, NERL, Ecosystems Research Division, Athens, GA 30605-2700

Glenn V. Wilson, Desert Research Institute, P.O. Box 19040, Las Vegas, NV 89132

Frank J. Wobber, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585

(5) G. T. Yeh, Department of Civil and Environmental Engineering, Pennsylvania State University, 212 Sackett Building, University Park, PA 16802

(5) John Zachara, Pacific Northwest Laboratory, P.O. Box 999, MS K8-96, Richland, WA 99352

Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P.O. Box 2001, Oak Ridge, TN 37831-8600

(2) Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831