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Users' Manual for LEHGC: A Lagrangian-Eulerian Finite-Element Model of HydroGeoChemical Transport Through Saturated-Unsaturated Media – Version 1.1

Gour-Tsyh Yeh, Sharman L. Carpenter,
Polly L. Hopkins, Malcolm D. Siegel

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USERS' MANUAL FOR LEHGC: A LAGRANGIAN-EULERIAN FINITE-ELEMENT MODEL OF HYDROGEOCHEMICAL TRANSPORT THROUGH SATURATED-UNSATURATED MEDIA - VERSION 1.1

Gour-Tsyh Yeh
Department of Civil and Environmental Engineering
Pennsylvania State University
University Park, PA 16802

Sharman L. Carpenter
Department of Earth and Planetary Sciences
University of New Mexico
Albuquerque, NM 87131

Polly L. Hopkins
Computational Fluid Dynamics Department
Sandia National Laboratories
Albuquerque, NM 87185

Malcolm D. Siegel
WIPP Chemical and Disposal Room Processes Department
Sandia National Laboratories
Albuquerque, NM 87185

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ABSTRACT

The computer program LEHGC is a Hybrid Lagrangian-Eulerian Finite-Element Model of HydroGeo-Chemical (LEHGC) Transport Through Saturated-Unsaturated Media. LEHGC iteratively solves two-dimensional transport and geochemical equilibrium equations and is a descendant of HYDROGEOCHEM, a strictly Eulerian finite-element reactive transport code. The hybrid Lagrangian-Eulerian scheme improves on the Eulerian scheme by allowing larger time steps to be used in the advection-dominant transport calculations. This causes less numerical dispersion and alleviates the problem of calculated negative concentrations at sharp concentration fronts. The code also is more computationally efficient than the strictly Eulerian version.

LEHGC is designed for generic application to reactive transport problems associated with contaminant transport 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 reactions, and the initial and boundary conditions. Output includes the spatial distribution of chemical element concentrations as a function of time and space and the chemical speciation at user-specified nodes.

LEHGC Version 1.1 is a modification of LEHGC Version 1.0. The modification includes: (1) devising a tracking algorithm with the computational effort proportional to N where N is the number of computational grid nodes rather than N^2 as in LEHGC Version 1.0, (2) including multiple adsorbing sites and multiple ion-exchange sites, (3) using four preconditioned conjugate gradient methods for the solution of matrix equations, and (4) providing a model for some features of solute transport by colloids.

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LIST OF ACRONYMS

CPU	Central processing 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

1.0 INTRODUCTION

This document is the users' guide for the Lagrangian-Eulerian Finite Element Model of HydroGeo-Chemical (LEHGC) transport through saturated-unsaturated media - Version 1.1. LEHGC is a flexible and comprehensive package. It is designed to:

- Treat heterogeneous and anisotropic media.
- Consider spatially and temporally distributed chemical sources/sinks as well as point chemical sources/sinks.
- Accept the prescribed initial conditions or obtain initial conditions by simulating the steady-state version of the system under consideration.
- Accept steady-state or transient flow velocity and moisture content from HYDROFLOW or other hydrology code.
- 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.
- Reset automatically the time-step size when boundary conditions or source/sinks change abruptly.
- 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.

1.1 New Features in LEHGC 1.1

This version is a modification of LEHGC1.0 (Yeh, 1995), a general purpose computer program written in FORTRAN 77 which is designed to solve coupled hydrologic transport and geochemical equilibrium problems. The modification includes: (1) devising a tracking algorithm with the computational effort proportional to N where N is the number of computational grid nodes rather than N^2 as in LEHGC1.0, (2) including multiple adsorbing sites and multiple ion-exchange sites, (3) using four preconditioned conjugate gradient methods for the solution of matrix equations, and (4) providing the capability to model certain aspects of colloid transport.

To achieve the objectives of fast node tracking, six subroutines in LEHGC1.0 were completely replaced with ten new subroutines. The six old subroutines were NDTAU, ADVTRN, MPLOC, XSI2D, ADVBC, and Q2ADVB. The ten new subroutines are ADVWRK, BTGN, ELMTRC, TRACK1, TRACK2, BASE1, XSI2D, ALGBDY, ADVBC, and Q2ADVB. The function of these new subroutines are described in Chapter 4. To include the multiple adsorption sites and multiple ion-exchange sites, four subroutines were greatly modified: RADC, RIES, JADC, and JIES. Minor modifications were made throughout all subroutines. The governing equations and numerical implementation, respectively, for the description of multiple adsorbing sites and multiple ion-exchange sites are described in Chapter 2 and Chapter 3, respectively. To include four preconditioned conjugate gradient methods for the solution of matrix equations, nine subroutines were added. These are CONNEC, ILUCG, LLTINV, PPCG, POLYP, MICPCG, MICP, SSORCG, SSORP. The functions of these subroutines are described in Chapter 4.

1.2 Colloid Transport

LEHGC1.1 can be used to model some aspects of transport of solutes by colloids. Colloids are represented as mobile components that can adsorb other mobile components to form colloid complexes. The adsorption model used for the mobile adsorption sites is the same as that used for the immobile adsorption sites. Source and sinks can be defined for the colloid component (as they can for other aqueous components) to simulate capture or generation of the colloid component (but not colloid complexes).

To implement this model, it is necessary to classify the types of chemical components differently in the transport and geochemical modules. In the transport module, a component is classified either as a mobile or an immobile component. In the geochemical module, a chemical component is classified either as an aqueous component or as an adsorbent component. For example, a colloid component is considered a mobile component in the transport module but is considered as an adsorbent component in the geochemical module.

To make the model flexible and to simplify data input, the order of components in transport module is not necessarily the same order of those in the geochemical module. The number of components in the transport module is not necessarily the same as that in the geochemical

module. For example, the fictitious components SIGMA0 and SIGMAB do not have to be included as components in the transport module. Colloid complexes are described as aqueous complexes in the data input sets. The modification of the source code to accommodate this capability was done throughout all subroutines that contain the following FORTRAN variables: NOH, NOHA, NOHS, INDTC, and IDNTC. Sample Problem 9 illustrates the specification of problems involving colloid transport for LEHGC1.1.

1.3 Organization of Manual

This document is intended to assist modelers in using this code for site-specific applications. It is suggested that new users examine Chapter 6 to identify sample problems that are similar to their particular application, and then to review appropriate sections of the Data Input Guide in Appendix A to make modifications to the input deck that are needed to run their own problem. The manual is organized similar to LEHGC1.0 as follows:

- Chapter 2.0 derives the governing equations and initial and boundary conditions acceptable to and solved by LEHGC.

- Chapter 3.0 details the numerical method used in solving the transport equations and geochemical equilibria.

- Chapter 4.0 describes the program structure of LEHGC. 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 components and species). The chapter also describes the input-output format and specifications of LEHGC. This information is important for application of the code to problems that are not similar to the sample problems described in Chapter 6.0.

- Chapter 6.0 contains a set of sample problems designed to illustrate the use of the code for a variety of common applications. Four of the problems were previously presented in the HYDROGEOCHEM (Yeh and Tripathi, 1991) and LEHGC1.0 (Yeh, 1995) manuals. The six new sample problems either demonstrate new features of the code or benchmark LEHGC1.1 against analytical solutions, simulations by other computer codes or experimental results. The problem descriptions are designed to allow new users to run similar problems even if they have not read Chapters 2 through 5.

- Appendix A is a data input guide that contains a complete description of all the problem-specific input necessary for running a calculation. Users who read Chapter 6 and relevant sections of Appendix A will probably be able to run problems for many common applications.

- Appendix B contains a complete listing, with definitions, of all the symbols used in

this report.

- Appendix C contains a complete listing of the LEHGC1.1 code parameters, identifying the data set where each parameter is specified and indicating other data sets which will be affected by the value of that parameter.

1.4 Notes on Units

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 this version, the unit of length should be decimeter (dm), and the unit of mass for any chemical species should be mole. The density of water and solid should be expressed in kg/dm^3 (liter). The ion-exchange capacity is in equivalents/kg of solid. Surface area should be specified as dm^2/kg of the solid. The capacitances of the surface in the surface complexation models should be in units of $Farad/dm^2$. The corresponding concentration unit of all species (aqueous, sorbed, and precipitated species) is mole/liter of fluid (Molar); the corresponding unit for the sorption distribution coefficient is dm^3/kg (= ml/g). Any units of time may be used as long as the same unit is used throughout the input file.

1.5 Limitations, Warnings and Future Plans

There are some limitations in LEHGC1.1. These include:

- The assumption of local equilibrium in geochemical reactions.
- 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 are limited to two-dimensional problems.
- Applications are limited to single-fluid phase flows with constant fluid density.
- Capture and exclusion of colloids from fractures are not explicitly represented by the current model.
- Reactions involving changes to solid solutions (solids of varying composition) cannot be represented in LEHGC1.1 simulations.
- Neither radioactive decay/production nor chemical kinetics are simulated by the current model.
- The code has limited capabilities to calculate reaction progress involving metastable assemblages. No provisions are made for changes in chemical equilibria due to

changes in temperature or pressure. No effects of chemical reactions on fluid flow can be represented.

LEHGC has limited capabilities to simulate transport in saline solutions. The code can accurately calculate chemical speciation in fluids in which the Davies activity coefficient equation is valid (I <0.5 M) (Davies, 1962). For solutions at constant but higher ionic strengths, apparent equilibrium constants must be entered into the input data sets. Note that the HYDROFLOW code used to provide flow fields for LEHGC cannot simulate the flow of concentrated brines for which variable fluid density is important.

Several other simplifying assumptions are made in LEHGC calculations. These include: 1) the diffusivity is the same for all chemical species; 2) mineral transformations that affect sorptive or ion exchange properties (e.g. specific surface area, site density or cation exchange capacity) of the rock matrix are not simulated; and 3) all chemical reactions are assumed to proceed at the same rate and to go to completion during each time step; variable time steps that could simulate the effects of different reaction rates or serial events within a single time step are not considered. For example, the onset of precipitation cannot be simulated precisely. Several other assumptions that affect how problems involving ion exchange and surface complexation must be formulated for LEHGC1.1 calculations are described in Sections 2.2.2 and 2.2.3, and in the Data Input Guide (Appendix A).

The sample problems in Section 6 are provided solely to illustrate the use of LEHGC1.1 in a variety of applications. The authors do not claim that the suite of sample problems spans all possible applications nor do they claim that numerical convergence will be reached with similar problems using different boundary conditions or chemical species. No assurances are made that the property values used in the input (physical parameters or equilibrium constants) are accurate or representative of real systems. It is the responsibility of each user of the code to choose property values that are relevant to the system of interest.

There are several of types of processes and systems for which LEHGC1.1 has not been tested. These include 1) coprecipitation, multisite ion exchange or multisite surface complexation, 3) simultaneous transport, surface complexation and ion exchange, 4) open systems at fixed pCO_2, and 5) transport in heterogeneous systems with regions of different material properties such as diffusivity and ion exchange capacity. Because these capabilities have not been adequately tested, the user is advised to avoid attempts to simulate such processes and systems or to carefully examine the results of such calculations if attempted.

Because of these limitations, the long-term plan for modifications to LEHGC include efforts to:

- Replace the EQMOD chemical equilibrium subroutine by a mixed chemical Kinetic and Equilibrium MODel (KEMOD) to deal with species whose concentrations are controlled by chemical reaction rates.

- Replace EQMOD with a chemical speciation subroutine capable of calculating chemical speciation in saline solutions (I > 0.5 M).

- Couple FEMWATER (Yeh and Ward, 1981) or its simplified version HYDROFLOW with LEHGC to yield a single code to deal with interaction between flow and transport as well as geochemical reactions.

- Couple nonisothermal transport to create a model of 2-Dimensional Flow And Chemical and Thermal (2DFACT) transport.

- Extend the model to three-dimensional space to generate a 3-Dimensional Flow And Chemical and Thermal (3DFACT) transport model.

- Modify 2DFACT and 3DFACT, respectively, with a multifluid phase flow model such as the MUlti-Region Flow (MURF) models to have a final model of multiphase nonisothermal multicomponent/multispecies hydrogeochemical transport model.

In addition, an adaptive local grid refinement algorithm should be implemented in the development of 2DFACT and 3DFACT. This would ensure accurate and efficient simulations in field-scale problems.

2.0 MATHEMATICAL FORMULATION

The hydrologic variables, including the Darcy's velocity, moisture content, and pressure head, are necessary factors 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 problems prior to simulations of solute transport with the LEHGC1.1 code. As discussed in Appendix A, provisions exist for importing data describing either steady-state and transient flow fields calculated by hydrologic flow codes. For cases in which the moisture contents and flow velocities within the system change with time, LEHGC reads velocity and moisture content at appropriate time steps from the specified flow data file. A finite-element model has been constructed to achieve this purpose (Yeh, 1987). The basic governing equation of the saturated-unsaturated flow problems is 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

$$\frac{\partial \theta}{\partial t} = \frac{d\theta}{dh}\frac{\partial h}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla H) + Q \quad , \tag{2.1.1}$$

$$H = h + z \quad , \tag{2.1.2}$$

and

$$\mathbf{V} = -\mathbf{K} \cdot \nabla H \quad , \tag{2.1.3}$$

where

θ = moisture content (L^3/L^3).
h = pressure head (L).
t = time (T).
$\mathbf{K}$ = hydraulic conductivity tensor (L/T).
H = total head (L).
Q = source or sink representing the artificial injection or withdrawal of water [$(L^3/L^3)/T$].
$\frac{d\theta}{dh}$ = specific water capacity (1/L).

z = potential head (L).
V = Darcy's velocity (L/T) (Yeh 1987).

Equations (2.1.1) through (2.1.3) and the constitutive relationships among the pressure head, moisture content, and hydraulic conductivity tensor, together with associated and 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 (2.1.3) are provided in this report because they are needed for deriving the advective form of the hydrological transport equations provided in the next section.

2.2 Hydrological Transport Equations

Two of the most frequently mentioned terms in chemical transport modeling are components and species. Definitions of these terms 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 reaction invariant (Rubin, 1983). A 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-}. In LEHGC1.1, as in aqueous speciation codes such as HYDRAQL (Papelis et al., 1988), water is not explicitly included as a reactant or product in chemical reactions. All reactions involving water are represented by production or consumption of H^+; i.e., the consumption of water during hydrolysis is represented by production of H^+.

Let us consider a system of N chemical components. In LEHGC, the N chemical components include N_a aqueous components (mobile components), N_s adsorbent components (immobile adsorbent sites), and NSITE kinds of ion-exchange sites. Some of the N_a aqueous components may react with each other to form M_x complexed species and M_p precipitated species. Each aqueous component has one species that does not bind with other components. This species is termed the aqueous component species. The total number of aqueous species, M_a, is the sum of N_a aqueous component species and M_x complexed species. Some of the N_a aqueous components and some of the N_s adsorbent components may 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 species is termed the adsorbent component species. Additionally, the M_z ion exchanged species, consisting of some of the N_a aqueous components and some of the M_x complexed species may compete with each other for the ion-exchange site. 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_a, 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 components and species considered in LEHGC.

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:

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

where

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

c_j = concentration of the j-th aqueous component species (M/L^3).

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

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

$\mathbf{J}_j = \theta c_j(\mathbf{V}_j - \mathbf{V}_f)$ 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^a = production rate of the j-th aqueous component species per unit fluid volume due to all chemical reactions [$(M/L^3)/T$)].

ι_j^a = rate of decay of the j-th aqueous component species [$(M/L^3)/T$].

m_j^a = external source/sink rate of the j-th aqueous component species [$(M/L^3)/T$].

N_a = number of aqueous component species.

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

$\mathbf{V}_j$ = the velocity of the j-th aqueous component species [$(M/T)/L^2$].

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

Table 2.1
Components and Species Considered in LEHGC

			Components													
			Aqueous						Adsorbed						Charge	Equilibrium Constant
Concentrations			1	2	...	j	...	N_a	1	2	...	j	...	N_s	ν	K_i
Aqueous Components	N_a	c_1	1	0	...	0	...	0	0	0	...	0	...	0	ν_1^a	1
		c_2	0	1	...	0	...	0	0	0	...	0	...	0	ν_2^a	1
		.														
		c_j	0	0	...	1	...	0	0	0	...	0	...	0	ν_j^a	1
		.														
		c_{N_a}	0	0	...	0	...	1	0	0	...	0	...	0	$\nu_{N_a}^a$	1
Adsorbent Components	N_s	s_1	0	0	...	0	...	0	0	1	...	0	...	0	ν_1^s	1
		s_2	0	0	...	0	...	0	0	1	...	0	...	0	ν_2^s	1
		.														
		s_j	0	0	...	0	...	0	0	0	...	1	...	0	ν_j^s	1
		.														
		s_{N_a}	0	0	...	0	...	0	0	0	...	0	...	1	$\nu_{N_s}^s$	1
Complexed Species	M_x	x_1	a_{11}^x	a_{12}^x	...	a_{1j}^x	...	a_{1N}^x	0	0	...	0	...	0	ν_1^x	K_1^x
		x_2	a_{21}^x	a_{22}^x	...	a_{2j}^x	...	a_{2N}^x	0	0	...	0	...	0	ν_2^x	K_2^x
		.														
		x_i	a_{i1}^x	a_{i2}^x	...	a_{ij}^x	...	$a_{iN_a}^x$	0	0	...	0	...	0	ν_i^x	K_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	$\nu_{M_x}^x$	$K_{M_x}^x$

Table 2.1
Components and Species Considered in LEHGC (Concluded)

			Components													Charge	Equilibrium Constant
			Aqueous						Adsorbed								
Concentrations			1	2	...	j	...	N_a	1	2	...	j	...	N_s		ν	K_i
Adsorbed Species	M_y	y_1	a_{11}^y	a_{12}^y	...	a_{1j}^y	...	$a_{1N_a}^y$	b_{11}^y	b_{12}^y	...	b_{1j}^y	...	$b_{1N_s}^y$		ν_1^y	K_1^y
		y_2	a_{21}^y	a_{22}^y	...	a_{2j}^y	...	$a_{2N_a}^y$	b_{21}^y	b_{22}^y	...	b_{2j}^y	...	$b_{2N_s}^y$		ν_2^y	K_2^y
		.															
		y_i	a_{i1}^y	a_{i2}^y	...	a_{ij}^y	...	$a_{iN_a}^y$	b_{i1}^y	b_{i2}^y	...	b_{ij}^y	...	$b_{iN_s}^y$		ν_i^y	K_i^y
		.															
		y_{M_y}	$a_{M_y1}^y$	$a_{M_y2}^y$	...	$a_{M_yj}^y$	...	$a_{M_yN_a}^y$	$b_{M_y1}^y$	$b_{M_y2}^y$	...	$b_{M_yj}^y$	...	$b_{M_yN_s}^y$		$\nu_{M_y}^y$	$K_{M_y}^y$
Ion-Exchanged Species	M_z	z_1	a_{11}^z	a_{12}^z	...	a_{1j}^z	...	$a_{1N_z}^z$	0	0	...	0	...	0		ν_1^z	K_1^z
		z_2	a_{21}^z	a_{22}^z	...	a_{2j}^z	...	$a_{2N_z}^z$	0	0	...	0	...	0		ν_2^z	K_2^z
		.															
		z_i	a_{i1}^z	a_{i2}^z	...	a_{ij}^z	...		0	0	...	0	...	0		ν_i^z	K_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		$\nu_{M_z}^z$	$K_{M_z}^z$
Precipitated Species	M_p	p_1	a_{11}^p	a_{12}^p	...	a_{1j}^p	...	$a_{1N_p}^p$	0	0	...	0	...	0		0	K_1^p
		p_2	a_{21}^p	a_{22}^p	...	a_{2j}^p	...	$a_{2N_p}^p$	0	0	...	0	...	0		0	K_2^p
		.															
		p_i	a_{i1}^p	a_{i2}^p	...	a_{ij}^p	...	$a_{iN_p}^p$	0	0	...	0	...	0		0	K_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		0	$K_{M_p}^p$
Total Concentrations			T_1	T_2		T_j	...	T_{N_a}	W_1	W_2	...	W_j		W_{N_a}			

$$\int_v \frac{\partial \theta c_j}{\partial t}\, dv + \int_\Gamma \mathbf{n} \cdot (\theta c_j \mathbf{V}_f)\, d\Gamma + \int_\Gamma \mathbf{n} \cdot \mathbf{J}_j\, d\Gamma = \int_v \theta r_j^a\, dv \qquad (2.2.2)$$

$$- \int_v \theta \iota_j^a\, dv + \int_v m_j^a\, dv \quad , \quad j \in N_a \quad ,$$

where

$\mathbf{V}_f = \mathbf{V}_{fs} + \mathbf{V}_s$ (in which $\mathbf{V}_{fs}$ is the fluid velocity relative to the solid and $\mathbf{V}_s$ is the solid velocity) is the fluid velocity (L/T).

If the compressibility of the media is neglected, then the fluid velocity $\mathbf{V}_f$ is related to the Darcy velocity $\mathbf{V}$ by

$$\mathbf{V} = \theta \mathbf{V}_f \quad . \qquad (2.2.3)$$

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:

$$\frac{\partial \theta c_j}{\partial t} + \nabla \cdot (\theta c_j \mathbf{V}_f) + \nabla \cdot \mathbf{J}_j = \theta (r_j^a - \iota_j^a) + m_j^a \quad , \quad j \in N_a \quad . \qquad (2.2.4)$$

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

$$\mathbf{J}_j = - \theta \mathbf{D} \cdot \nabla c_j \quad , \quad j \in N_a \qquad (2.2.5a)$$

and

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

where

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

Substitution of Equations (2.2.3) and (2.2.5) into Equation (2.2.4) yields

$$\frac{\partial \theta c_j}{\partial t} + \nabla \cdot (c_j \mathbf{V}) - \nabla \cdot (\theta \mathbf{D} \cdot \nabla c_j) = \theta (r_j^a - \iota_j^a) + m_j^a \quad , \quad j \in N_a \quad . \qquad (2.2.6)$$

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 chemical reactions and radioactive decay, and the last term is source/sink term corresponding to artificial injection and/or withdrawal.

Equation (2.2.6) 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 and Tripathi, 1987). An advective form of the transport equation is derived by expanding the advection term and using the continuity equation for water flow,

$$\frac{\partial \theta}{\partial t} = -\nabla \cdot \mathbf{V} + Q \quad , \tag{2.2.7}$$

which is conservation of fluid mass. Performing the necessary manipulation, we obtain

$$\theta \frac{\partial c_j}{\partial t} + \mathbf{V} \cdot \nabla c_j - \nabla \cdot (\theta \mathbf{D} \cdot \nabla c_j) = \theta(r_j^a - \iota_j^a) + m_j^a - Q c_j \quad , \quad j \in N_a \quad . \tag{2.2.8}$$

For simplicity of notation and convenience of derivation, let us rewrite Equation (2.2.8) in the following form:

$$\theta \frac{\partial c_j}{\partial t} = L(c_j) + \theta(r_j^a - \iota_j^a) + m_j^a - Q c_j \quad , \quad j \in N_a \quad , \tag{2.2.9}$$

in which L is the advection-dispersion operator denoting

$$L(c) = -\mathbf{V} \cdot \nabla c + \nabla \cdot (\theta \mathbf{D} \cdot \nabla c) \quad . \tag{2.2.10}$$

Since any complexed 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 (2.2.9). If we let x_i denote the concentration of the i-th complexed species, we have the following transport equation:

$$\theta \frac{\partial x_i}{\partial t} = L(x_i) + \theta(r_i^x - \iota_i^x) + m_i^x - Q x_i \quad , \quad i \in M_x \quad , \tag{2.2.11}$$

where

r_i^x = production rate of i-th complexed species per unit fluid volume due to the i-th complexation reaction $[(M/L^3)/T]$.

ι_i^x = rate of decay of the i-th complexed species per unit fluid volume $[(M/L^3)/T]$.

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

Because it is assumed that adsorbent component species, adsorbed species, ion-exchanged species, and precipitated species are not subject to hydrological transport, their transport equations (or more precisely the mass balance equations for these species) can be obtained by expanding the first term and dropping the second and third terms on the left-hand side of equations for these species analogous to Equation (2.2.6):

$$\theta \frac{\partial s_j}{\partial t} + \frac{\partial \theta}{\partial t} s_j = \theta(r_j^s - \iota_j^s) + m_j^s \quad , \quad j \in N_s \quad , \tag{2.2.12}$$

$$\theta \frac{\partial y_i}{\partial t} + \frac{\partial \theta}{\partial t} y_i = \theta(r_i^y - \iota_i^y) + m_i^y \quad , \quad i \in M_y \quad , \tag{2.2.13}$$

$$\theta \frac{\partial z_i}{\partial t} + \frac{\partial \theta}{\partial t} z_i = \theta(r_i^z - \iota_i^z) + m_i^z \quad , \quad i \in M_z \quad , \tag{2.2.14}$$

and

$$\theta \frac{\partial p_i}{\partial t} + \frac{\partial \theta}{\partial t} p_i = \theta(r_i^p - \iota_i^p) + m_i^p \quad , \quad i \in M_p \quad , \tag{2.2.15}$$

where

r_j^s = production rate of the j-th adsorbent component species per unit fluid volume due to all sorption reactions $[(M/L^3)/T]$.

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 fluid volume $[(M/L^3)/T]$.

r_i^y = production rate of the i-th adsorbed species per unit fluid volume due to the i-th adsorption reaction $[(M/L^3)/T]$.

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 fluid volume $[(M/L^3)/T]$.

r_i^z = production rate of the i-th ion-exchanged species per unit fluid volume due to the i-th ion-exchange reaction $[(M/T)/L^3]$.

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 fluid volume [(M/L^3)/T].

r_i^p = production rate of the i-th precipitated species per unit fluid volume due to the i-th precipitation reaction [(M/L^3)/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 fluid volume [(M/L^3)/T].

Equations (2.2.9) and (2.2.11) through (2.2.15) constitute six sets of equations for six sets of unknowns: c_j, x_i, s_j, y_i, z_i, and p_i. These equations form a closed system if the chemical production rates r_j^a, r_i^x, r_j^s, r_i^y, r_i^z, and r_i^p are known functions of c_j, x_i, s_j, y_i, z_i, and p_i. The functional relationships can be postulated from chemical reactions. Chemical reactions considered are:

- Aqueous complexation including redox and acid-base reactions.
- Adsorption/desorption.
- Ion-exchange.
- Precipitation-dissolution.

Equations (2.2.9) and (2.2.11) through (2.2.15) 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 Components

Let a_{ij}^x, a_{ij}^y, a_{ij}^z, and a_{ij}^p be the stoichiometric constants of aqueous components for the following reactions: complexation, adsorption, ion-exchange, and precipitation, respectively. (Note that the superscripts x, y, z, and p signify complexation, adsorption, ion-exchange, and precipitation reactions.) Multiplying Equation (2.2.11) by a_{ij}^x and summing over i from 1 to M_x, multiplying Equation (2.2.13) by a_{ij}^y and summing over i from 1 to M_y, multiplying Equation (2.2.14) by a_{ij}^z and summing over i from 1 to M_z, multiplying Equation (2.2.15) by a_{ij}^p and summing over i from 1 to M_p, and adding the results to Equation (2.2.9), we obtain

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t}(S_j + P_j) = L(C_j) - \theta \Lambda_j^a + M_j^a - QC_j \quad , \quad j \in N_a \quad , \tag{2.2.16}$$

in which

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i + \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i \quad , \quad j \in N_a \quad , \tag{2.2.17}$$

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i \quad , \quad j \in N_a \quad , \tag{2.2.18}$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^{y} y_i + \sum_{i=1}^{M_z} a_{ij}^{z} z_i \quad , \quad j \in N_a \quad , \tag{2.2.19}$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^{p} p_i \quad , \quad j \in N_a \quad , \tag{2.2.20}$$

$$M_j^{a} = m_j^{a} + \sum_{i=1}^{M_x} a_{ij}^{x} m_i^{x} + \sum_{i=1}^{M_y} a_{ij}^{y} m_i^{y} + \sum_{i=1}^{M_z} a_{ij}^{z} m_i^{z} + \sum_{i=1}^{M_p} a_{ij}^{p} m_i^{p} \quad , \quad j \in N_a \quad , \tag{2.2.21}$$

and

$$\Lambda_j^{a} = \iota_j^{a} + \sum_{i=1}^{M_x} a_{ij}^{x} \iota_i^{x} + \sum_{i=1}^{M_y} a_{ij}^{y} \iota_i^{y} + \sum_{i=1}^{M_z} a_{ij}^{z} \iota_i^{z} + \sum_{i=1}^{M_p} a_{ij}^{p} \iota_i^{p} \quad , \quad j \in N_a \quad , \tag{2.2.22}$$

where

T_j = total analytical concentration of the j-th aqueous component (M/L^3).
C_j = total dissolved concentration of the j-th aqueous component (M/L^3).
S_j = total sorbed concentration of the j-th aqueous component (M/L^3).
P_j = total precipitated concentration of the j-th aqueous component (M/L^3).
M_j^a = total rate of source/sink of the j-th aqueous component ($M/L^3/T$).
Λ_j^a = total decay rate of the j-th aqueous component ($M/L^3/T$).

In deriving Equation (2.2.16), we have used the relationship

$$r_j^{a} + \sum_{i=1}^{M_x} a_{ij}^{x} r_i^{x} + \sum_{i=1}^{M_y} a_{ij}^{y} r_i^{y} + \sum_{i=1}^{M_z} a_{ij}^{z} r_i^{z} + \sum_{i=1}^{M_p} a_{ij}^{p} r_i^{p} = 0 \quad , \quad j \in N_a \quad , \tag{2.2.23}$$

which results from the requirement that a component is reaction invariant (conservation of mass). The source/sink term M_j^a and decay term Λ_j^a can be defined by

$$M_j^{a} = QC_j^{*} \quad , \quad j \in N_a \tag{2.2.24}$$

and

$$\Lambda_j^{a} = \lambda_j^{a} T_j \quad , \quad j \in N_a \quad , \tag{2.2.25}$$

where

C_j^* = input concentration of the j-th aqueous component if Q is source (injection) (M/L^3), or C_j if Q is a sink (withdrawal) (M/L^3).
λ_j^a = rate constant of the j-th aqueous component (1/T).

By the definition of C_j^*, the terms M_j^a and QC_j in Equation (2.2.16) cancel each other for the cases

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.

2.2.2 Mass Balance of Adsorbent Components and Ion-Exchange Sites

Similarly, we can derive the governing equations for the total analytical concentrations of adsorbent components and the number of equivalents occupying the ion-exchange site. The total sorbed concentration of any aqueous component is not zero but is given by Equation (2.2.19) because aqueous components are present in sorbed species either via surface complexation or ion exchange. With these brief comments, we derive the governing equations for the total analytical concentrations of all adsorbent components as follows:

Let b^y signify the stoichiometric coefficients of the adsorbent components for adsorption reaction. Multiplying Equation (2.2.13) by b^y_{ij}, summing over i from 1 to M_y, and adding the results to Equation (2.2.12), we obtain

$$\theta \frac{\partial W_j}{\partial t} + \frac{\partial \theta}{\partial t} W_j = -\theta \Lambda_j^s + M_j^s \quad , \quad j \in N_s \quad , \tag{2.2.26}$$

in which

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^y y_i \quad , \quad j \in N_s \quad , \tag{2.2.27}$$

$$M_j^s = m_j^s + \sum_{i=1}^{M_y} b_{ij}^y m_i^y \quad , \quad j \in N_s \quad , \tag{2.2.28}$$

and

$$\Lambda_j^s = \iota_j^s + \sum_{i=1}^{M_y} b_{ij}^y \iota_i^y \quad , \quad j \in N_s \quad , \tag{2.2.29}$$

where

W_j = total analytical 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 ($M/L^3/T$).

The relationship that results from the requirement that adsorption is reaction-invariant with respect to any adsorbent component,

$$r_j^s + \sum_{i=1}^{M_y} b_{ij}^y r_i^y = 0 \quad , \quad j \in N_s \quad , \tag{2.2.30}$$

has been used in deriving Equation (2.2.26). In addition, the source/sink term M_j^s is assumed to be zero:

$$M_j^s = 0 \quad , \quad j \in N_s \quad . \tag{2.2.31}$$

The decay term Λ_j^s can be defined as

$$\Lambda_j^s = \lambda_j^s W_j \quad , \quad j \in N_s \quad , \tag{2.2.32}$$

where

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

2.2.3 Mass Balance of Ion-Exchange Sites

The governing equation for the i-th ion-exchange site is 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 (2.2.14) by ν_k and summing over k from (NOMZJ(i)+1) to (NOMZJ(i)+NOMZI(i)), we obtain

$$\theta \frac{\partial N_{eqi}}{\partial t} + \frac{\partial \theta}{\partial t} N_{eqi} = -\theta \Lambda_{eqi} + M_{eqi} \quad , \quad i \in \text{NSITE} \tag{2.2.33}$$

in which

$$N_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k \quad , \quad i \in \text{NSITE} \tag{2.2.34}$$

$$M_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k m_k^z \quad , \quad i \in \text{NSITE} \tag{2.2.35}$$

and

$$\Lambda_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k \iota_k^z \quad , \quad i \in \text{NSITE} \tag{2.2.36}$$

where

N_{eqi} = number of equivalents of the ion-exchange sites per liter of solution for the i-th site (M/L^3).
M_{eqi} = total rate of source/sink of the ion-exchange site for the i-th site ($M/L^3/T$).
Λ_{eqi} = total decay rate of the ion-exchange site for the i-th site ($M/L^3/T$).
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 of an ion-exchange site (conservation of charge),

$$\sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k r_k^z = 0 \quad , \quad i \in NSITE \tag{2.2.37}$$

has been used in deriving Equation (2.2.33). In addition, the source/sink term M_{eq} is assumed to be zero; that is,

$$M_{eq} = 0 \quad . \tag{2.2.38}$$

The decay term Λ_{eq} can be defined as

$$\Lambda_{eq} = \lambda_{eq} N_{eq} \quad , \tag{2.2.39}$$

where

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

Equations (2.2.16) through (2.2.20), (2.2.26), (2.2.27), and (2.2.33) along with (2.2.34) constitute eight sets of equations plus one equation in 12 sets of unknowns (T_j's, c_j's, C_j's, S_j's, P_j's, W_j's, s_j's, N_{eq}'s, x_i's, y_i's, z_i's, and p_i's); hence, the formulation is not complete. Four sets minus one constitutive relationship among those unknowns must be prescribed to complete the formulation. For hydrological transport modeling, the constitutive relationships are often posed empirically. For example, with the K_d concept the relationship is:

$$T_j = R_{dj} C_j \quad , \quad R_{dj} = 1 + \frac{\rho_b K_{dj}}{\theta} \quad , \quad j \in N_a \tag{2.2.40}$$

and

$$S_j = \frac{\rho_b K_{dj}}{\theta} C_j \quad , \quad j \in N_a \quad , \tag{2.2.41}$$

where

R_{dj} = retardation factor of the j-th component (dimensionless).
ρ_b = bulk density of the medium (M/L^3) = $\rho(1-\eta)$.
K_{dj} = distribution coefficient of the j-th aqueous component (L^3/M).
ρ = material density (M/L^3).
η = porosity (dimensionless).

For coupled hydrological transport and geochemical equilibrium modeling, a chemical equilibrium model is normally adopted to give the implicit functional relationships among T_j's, C_j's, S_j's, P_j's, c_j's, W_j's, N_{eq}'s, s_j's, x_i's, y_i's, z_i's, and p_i's, as described in Section 2.3.

2.2.4 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 analytical 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 analytical 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 analytical concentrations of all components are determined by solving the transport equation [Equation (2.2.16)] for aqueous components and the mass balance equation [Equation (2.2.26)] for adsorbent components, respectively. The number of equivalents of the ion-exchange site is obtained by solving the mass balance equation [Equation (2.2.33)]. 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^a_{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 (2.2.9) by a^a_{je} and summing over j from 1 to N_a, multiplying Equation (2.2.11) by a^x_{ie} and summing over i from 1 to M_x, multiplying Equation (2.2.12) by a^s_{je} and summing over j from 1 to N_s, multiplying Equation (2.2.13) by a^y_{ie} and summing over i from 1 to M_y, multiplying Equation (2.2.14) by a^z_{ie} and summing over i from 1 to M_z, multiplying Equation (2.2.15) 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

$$\theta \frac{\partial T_e}{\partial t} + \frac{\partial \theta}{\partial t}(S_e + P_e) = L(C_e) - \theta \Lambda^a_e + M^a_e - QC_e \quad , \tag{2.2.42}$$

which is identical in form to Equation (2.2.16) and describes the transport and reactions of operational electrons. However, the definitions of C_e, S_e, P_e, T_e, M^a_e, and Λ^a_e are slightly different from those of C_j, S_j, P_j, T_j, M^a_j, and Λ^a_j. The quantities C_e, S_e, P_e, T_e, M^a_j, and Λ^a_e are given by

$$T_e = \sum_{j=1}^{N_a} a^a_{je} c_j + \sum_{i=1}^{M_x} a^x_{ie} x_i + \sum_{i=1}^{M_z} a^z_{ie} z_i + \sum_{j=1}^{N_s} a^s_{je} s_j + + \sum_{i=1}^{M_y} a^y_{ie} y_i + \sum_{i=1}^{M_p} a^p_{ie} p_i \quad , \tag{2.2.43}$$

$$C_e = \sum_{j=1}^{N_a} a_{je}^{a} c_j + \sum_{i=1}^{M_x} a_{ie}^{x} x_i \quad , \tag{2.2.44}$$

$$S_e = \sum_{j=1}^{N_s} a_{je}^{s} s_j + \sum_{i=1}^{M_y} a_{ie}^{y} y_i + \sum_{i=1}^{M_z} a_{ie}^{z} z_i \quad , \tag{2.2.45}$$

$$P_e = \sum_{i=1}^{M_p} a_{ie}^{p} p_i \quad , \tag{2.2.46}$$

$$M_e^{a} = \sum_{j=1}^{N_a} a_{je}^{a}\, m_j^{a} + \sum_{i=1}^{M_x} a_{ie}^{x}\, m_i^{x} + \sum_{i=1}^{M_z} a_{ie}^{z}\, m_i^{z} + \sum_{j=1}^{N_s} a_{je}^{s}\, m_j^{s} + \sum_{i=1}^{M_y} a_{ie}^{y}\, m_i^{y} + \sum_{i=1}^{M_p} a_{ie}^{p}\, m_i^{p} \quad , \tag{2.2.47}$$

$$\Lambda_e^{a} = \sum_{j=1}^{N_a} a_{je}^{a}\, \iota_j^{a} + \sum_{i=1}^{M_x} a_{ie}^{x}\, \iota_i^{x} + \sum_{i=1}^{M_z} a_{ie}^{z}\, \iota_i^{z} + \sum_{j=1}^{N_s} a_{je}^{s}\, \iota_j^{s} + \sum_{i=1}^{M_y} a_{ie}^{y}\, \iota_i^{y} + \sum_{i=1}^{M_p} a_{ie}^{p}\, \iota_i^{p} \quad , \tag{2.2.48}$$

where

C_e = concentration of operational electrons in aqueous phase.
S_e = concentration of operational electrons in sorbent phase.
P_e = concentration of operational electrons in solid phase.
T_e = total concentration of operational electrons.
M_e^a = external source/sink rate of the free electron species [$(M/L^3)/T$].
ι_e^a = rate of decay of the free electron species [$(M/L^3)/T$].
Λ_e^a = total rate of decay of operational electrons [$(M/L^3)/T$].

The above stoichiometric coefficients are given by

$$a_{je}^{a} = \sum_{k=1}^{N_e} h_{jk}^{a}\left(v_{mk} - v_{jk}^{a}\right) \quad , \quad j \in N_a \quad , \tag{2.2.49}$$

$$a_{ie}^{x} = \sum_{k=1}^{N_e} h_{ik}^{x}\left(v_{mk} - v_{ik}^{x}\right) \quad , \quad i \in M_x \quad , \tag{2.2.50}$$

$$a_{je}^{s} = \sum_{k=1}^{N_e} h_{jk}^{s}\left(v_{mk} - v_{jk}^{s}\right) \quad , \quad j \in N_s \quad , \tag{2.2.51}$$

$$a_{ie}^{y} = \sum_{k=1}^{N_e} h_{ik}^{y}\left(v_{mk} - v_{ik}^{y}\right) \quad , \quad i \in M_y \quad , \tag{2.2.52}$$

$$a_{ie}^{z} = \sum_{k=1}^{N_e} h_{ik}^{z}\left(v_{mk} - v_{ik}^{z}\right) \quad , \quad i \in M_z \quad , \tag{2.2.53}$$

and

$$a_{ie}^{p} = \sum_{k=1}^{N_e} h_{ik}^{p}\left(v_{mk} - v_{ik}^{p}\right) \quad , \quad i \in M_p \quad , \tag{2.2.54}$$

where

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

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

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

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

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

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

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

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

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

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

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

v_{ik}^{p} = 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^a_{je}'s and a^s_{je}'s are equal to zero, and Equations (2.2.43) through (2.2.46) have identical formulae to Equations (2.2.17) through (2.2.20), respectively. 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.

2.2.5 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 equilibria, 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 produced a transport equation for hydroxide OH. Taking the difference of the transport equation for H and that for OH, one obtains (Miller, 1983):

$$\theta\frac{\partial T_H}{\partial t} + \frac{\partial \theta}{\partial t}(S_H + P_H) = L(C_H) - \theta\Lambda^a_H + M^a_H - QC_H \quad , \tag{2.2.55}$$

which is identical in form to Equation (2.2.16) and which describes the transport of excess protons. The algebraic equations defining T_H, C_H, S_H, P_H, M^a_H, and Λ^a_H are identical in form to Equations (2.2.17) through (2.2.22), 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 (2.2.16), 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 chemical equilibrium model.

2.3 Chemical Equilibrium 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.

In the equilibrium-constant approach, the formation of a 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.

2.3.1 Complexation Reactions

Each aqueous complex species is the product in a reaction with the aqueous components as the reactants. These reactions are written as

$$\sum_{j=1}^{N_a} a_{ij}^{x} \hat{c}_j \longleftarrow\!\!\!\!\!\!\!\!\!\!\longrightarrow \hat{x}_i \ , \quad i \in M_x \ , \tag{2.3.1}$$

where

$\hat{c}_j$ = chemical formula for the j-th aqueous component species.
$\hat{x}_i$ = chemical formula for the i-th complexed species.

The circumflex notation is used to indicate a chemical formula. Thus, $\hat{c}_j$ represents one mole of aqueous component j, whereas c_j represents molar concentration of aqueous component j.

The law of mass action for each complexation reaction given by Equation (2.3.1) is written as

$$A_i^{x} = K_i^{x} \prod_{k=1}^{N_a} X_k^{a_{ik}^{x}} \ , \quad i \in M_x \ , \tag{2.3.2}$$

where

A_i^x = activity of the i-th complexed species.
K_i^x = equilibrium constant of the i-th complexed species (M/L^3).
X_k = activity of the k-th aqueous component species.
a_{ik}^x = stoichiometric coefficient of the k-th aqueous component in the i-th complexed species.

The activities of all aqueous species are related to the species concentrations using the concept of activity coefficients. Thus,

$$A_i^{x} = \gamma_i^{x} x_i \ , \quad i \in M_x \tag{2.3.3}$$

and

$$X_j = \gamma_j^a c_j \quad , \quad j \in N_a \quad , \tag{2.3.4}$$

where

γ_i^x = activity coefficient of the i-th complexed species (L^3/M).
γ_j^a = activity coefficient of the j-th aqueous component species (L^3/M).

Substituting Equations (2.3.3) and (2.3.4) into Equation (2.3.2), we obtain

$$x_i = \alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x} \quad , \quad i \in M_x \quad , \tag{2.3.5}$$

in which

$$\alpha_i^x = K_i^x \prod_{k=1}^{N_a} \left(\gamma_k^a\right)^{a_{ik}^x} / \gamma_i^x \quad , \quad i \in M_x \tag{2.3.6}$$

is the modified stability constant of the i-th complexed species. It is noted that the thermodynamic equilibrium constant K_i^x depends on the temperature and pressure of the system, whereas the activity coefficients γ_k^a and γ_i^x are functions of the specific ion interactions, temperature, pressure and ionic strength of the system. The ionic strength of the system is a function of the concentrations of all aqueous species. Thus, the modified stability constants are functions of temperature, pressure, and concentrations of all aqueous species.

2.3.2 Adsorption Reactions

Each adsorbed species is modeled by surface complexation of aqueous component species and an adsorbent component species. Thus, an adsorbed species is the product involving both aqueous and adsorbent components as the reactants. The adsorption reactions are written as

$$\sum_{j=1}^{N_a} a_{ij}^y \hat{c}_j + \sum_{j=1}^{N_s} b_{ij}^y \hat{s}_j \longleftarrow\!\!\!\!\!\!\!\!\!\longrightarrow \hat{y}_i \quad , \quad i \in M_y \quad , \tag{2.3.7}$$

where

$\hat{c}_j$ = chemical formula for j-th aqueous component species.
$\hat{s}_j$ = chemical formula for j-th adsorbent component species.
$\hat{y}_i$ = chemical formula for i-th adsorbed species i.

The law of mass action for each adsorption reaction given by Equation (2.3.7) is written as

$$B_i^y = K_i^y \left(\prod_{k=1}^{N_a} X_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} Y_k^{b_{ik}^y} \right) \quad , \quad i \in M_y \quad , \tag{2.3.8}$$

where

B_i^y = activity of the i-th adsorbed species of surface co xation (M/L^3).

K_i^y = equilibrium constant of the i-th adsorbed species (ensionless).

Y_k = activity of the k-th adsorbent component species.

b_{ik}^y = stoichiometric coefficient of the k-th adsorbent component in the i-th adsorbed species of surface complexation.

Assuming that the activities of all adsorbent species are related to the species concentrations using the concept of activity coefficients, we obtain

$$B_i^y = \gamma_i^y y_i \quad , \quad i \in M_y \tag{2.3.9}$$

and

$$Y_j = \gamma_j^s s_j \quad , \quad j \in N_s \quad , \tag{2.3.10}$$

where

γ_i^y = activity coefficient of the i-th adsorbed species (L^3/M).
γ_j^s = activity coefficient of the j-th adsorbent component species (L^3/M).

It should be noted that there is no universally accepted way to compute activity coefficients for adsorbent species. In LEHGC,the Davies activity coefficient equation is applied to the aqueous components in surface complexation reactions but not to the adsorbed species. For the constant capacitance and the triple-layer sorption models, an additional electrostatic correction is applied to the adsorbed species as discussed in Section 3.3.5. Substitution of Equations (2.3.4), (2.3.9), and (2.3.10) into Equation (2.3.8) yields

$$y_i = \alpha_i^y \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^y} \right) \quad , \quad i \in M_y \quad , \tag{2.3.11}$$

in which

$$\alpha_i^y = K_i^y \left[\prod_{k=1}^{N_a} \left(\gamma_k^a \right)^{a_{ik}^y} \right] \left[\prod_{k=1}^{N_s} \left(\gamma_k^s \right)^{b_{ik}^y} \right] / \gamma_i^y \quad , \quad i \in M_y \tag{2.3.12}$$

is the modified stability constant of the i-th adsorbed species.

2.3.3 Ion-Exchange Reactions

Each ion-exchanged species is formed by the exchange of a corresponding aqueous species with another ion-exchanged species. The ion-exchange reactions are written with respect to a reference ion exchange species for each site as:

$$\nu_{LNI(i)}\hat{a}_k + \nu_k\hat{z}_{LNI(i)} \longleftarrow\!\!\!\!\!\!\!\!\!\!\longrightarrow \nu_{LNI(i)}\hat{z}_k + \nu_k\hat{a}_{LNI(i)} \quad , \quad k\epsilon M_z \quad , \tag{2.3.13}$$

$$NOMZJ(i)+1 \le k \le NOMZJ(i)+NOMZI(i) \ , \ i \in NSITEk \neq LNI(i) \ , \ M_z \neq 1$$

where

$\hat{a}_k$, $\hat{z}_k$ = chemical formula for the k-th aqueous and ion-exchanged species, respectively.
$\hat{a}_{LNI(i)}$, $\hat{z}_{LNI(i)}$ = chemical formula for the LNI(i)-th aqueous and ion-exchanged species, respectively.
ν_k = charge of the k-th ion-exchanged species.
$\nu_{LNI(i)}$ = charge of the LNI(i)-th reference ion-exchanged species.

The law of mass action for each ion-exchange reaction given by Equation (2.3.13) is written as

$$K_{kLNI(i)} = \left(\frac{B_k}{A_k}\right)^{\nu_{LNI(i)}}\left(\frac{A_{LNI(i)}}{B_{LNI(i)}}\right)^{\nu_k} \quad , \quad k \in M_z \quad , \quad k \neq LNI(i) \quad , \tag{2.3.14}$$

$$NOMZJ(i)+1 \le k \le NOMZJ(i)+NOMZI(i)$$

where

$K_{kLNI(i)}$ = selectivity coefficient of the k-th species with respect to the LNI(i)-th species.
A_k = activity of the k-th aqueous species.
$A_{LNI(i)}$ = activity of the LNI(i)-th aqueous species.
B_k = activity of the k-th ion-exchanged species.
$B_{LNI(i)}$ = activity of the LNI(i)-th ion-exchanged species.

In the ion-exchange model, the activities of aqueous species are related to species concentrations with activity coefficients. However, the activity of any ion-exchanged species is assumed to be equal to its mole fraction. Thus, we have

$$A_k = \gamma_k a_k \quad , \quad k \in M_z \quad , \tag{2.3.15}$$

$$B_k = z_k / s_T(i) \quad , \quad NOMZJ(i)+1 \le k \le NOMJ(i)+NOMZI(i) \quad , \tag{2.3.16}$$

and

$$s_T(i) = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} z_k \quad , \tag{2.3.17}$$

where

γ_k = activity coefficient of the k-th aqueous species denoting either γ_k^a or γ_k^x (L^3/M).
a_k = molar concentration of the k-th aqueous species denoting either c_J or x_k (M/L^3).

z_k = molar concentration of the k-th ion-exchanged species (M/L^3).
$s_T(i)$ = total concentration of all ion-exchanged species on the i-th site (M/L^3).

Substituting Equations (2.3.15) and (2.3.16) into Equation (2.3.14), we obtain

$$\kappa_{kLNI(i)} = \frac{\left(z_k/s_T(i)\right)^{\nu_{LNI(i)}}}{\left(z_{LNI(i)}/s_T(i)\right)^{\nu_k}} \frac{a_{LNI(i)}^{\nu_k}}{a_k^{\nu_{LNI(i)}}} \quad , \tag{2.3.18}$$

$$k \in M_z \quad , \quad k \neq LNI(i) \quad , \quad i \in NSITE$$

where $\kappa_{kLNI(i)}$ is the modified selectivity coefficient given by

$$\kappa_{kLNI(i)} = K_{kLNI(i)} \gamma_k^{\nu_{LNI(i)}} / \gamma_{LNI(i)}^{\nu_k} \quad . \tag{2.3.19}$$

2.3.4 Precipitation-Dissolution Reactions

Each precipitated species is a product in a reaction with the aqueous components as the reactants. These reactions are written as

$$\sum_{j=1}^{N_a} a_{ij}^p \hat{c}_j \longleftarrow\!\!\!\!\!\!\!\!\longrightarrow \hat{p}_i \quad , \quad i \in M_p \quad , \tag{2.3.20}$$

where

$\hat{c}_j$ = chemical formula for j-th aqueous component species.
$\hat{p}_i$ = chemical formula for i-th precipitated species.

The law of mass action for each precipitation-dissolution reaction as given by Equation (2.3.20) is written as

$$1 = K_i^p \prod_{k=1}^{N_a} X_k^{a_{ik}^p} \quad , \quad i \in M_p \quad , \tag{2.3.21}$$

where

K_i^p = equilibrium constant of the i-th precipitated species.
a_{ik}^p = stoichiometric coefficient of the k-th aqueous component in the i-th precipitated species.

Substituting Equations (2.3.4) into Equation (2.3.21), one obtains

$$1 = \alpha_i^p \prod_{k=1}^{N_a} c_k^{a_{ik}^p} \quad , \quad i \in M_p \quad , \tag{2.3.22}$$

in which

$$\alpha_i^p = K_i^p \prod_{k=1}^{N_a} \left(\gamma_k^a\right)^{a_{ik}^p} \quad , \quad i \in M_p \tag{2.3.23}$$

is the modified stability constant of the i-th precipitated species. Equation (2.3.22) represents a mass action expression: the solubility product equation. As in all other solubility product equations of physical chemistry, it does not contain the molar concentration of precipitated species, p_i, because it assumes that the activity of the solids is constant (Pauling, 1970). The absence of p_i's 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 the homogeneous reaction of soluble complexation. This implies that models developed specifically for dealing with complexation and sorption are not necessarily capable of handling precipitation-dissolution.

2.3.5 Redox Reactions and Electron Activity

When redox reactions occur in the system under consideration, the mass action equation for any species involving chemical elements of changing oxidation states must be modified to include the activity of electrons. For example, Equation (2.3.5) for complexation reactions is modified by multiplying its right-hand side by X_e raised to the a_{ie}^x power, and the activity coefficient for the electron component in Equation (2.3.6) is set to 1. In systems involving redox reactions, chemical components are chosen such that their chemical formulae contain elements in maximum oxidation states. Under such circumstances, the electron is considered an aqueous component, and no special computational treatment is needed for redox reactions (Reed, 1982).

For example, if Fe^{2+} and Fe^{3+} are present simultaneously in a system, we may consider Fe^{3+} a component species. Then Fe^{2+} shall be considered a complexed species, which is a product of Fe^{3+} and e^-. A mole of Fe^{2+} will contribute a mole of operational electrons to T_e and C_e. If we have not chosen the stoichiometric coefficient of electron with respect to the maximum oxidation state, a negative total analytical concentration of operational electron may result.

2.3.6 Acid-Base Reactions and Proton Activity

Acid-base reactions are defined as a class of chemical reactions involving a transfer of protons. Acid-base reactions are among the simplest types of chemical reactions (Stumm and Morgan, 1981). When acid-base reactions are considered in this system, the mass action equation for any species involving the transfer of protons or hydroxide must be modified to include the activity of protons. For example, Equation (2.3.5) for complexation reactions is modified by multiplying its right-hand side by X_{H^+} raised to the $a_{iH^+}^x$ power, and the activity coefficient for the proton component in Equation (2.3.6) is set to 1. If hydroxides appear in a species, the stoichiometric coefficient of a proton in that species is negative. If hydrogens appear in a species, the stoichiometric coefficient of a proton in that species is positive. Thus, the proton can be considered an aqueous component and no special computational treatment is needed for acid-base reactions. The only difference between a proton as an aqueous component and all other regular aqueous components is that the former can have a negative total analytical concentration (i.e., T_H may be negative), but the latter cannot have negative total analytical concentrations (i.e., T_j is always positive). Calculations in systems with constant pH and variable pH are illustrated

in Sample Problems 5 and 6, respectively.

Since the simulation of pH and/or pe uses mole balance equations that are formulaically identical to Equation (2.2.17) (in the case of mole balance equation for excess protons) or with only slight modification [i.e., Equation (2.2.43)] (in the case of mole balance equation for operational electrons), we can treat protons and/or electrons as aqueous components from here on and no special consideration to distinguish the proton and/or electron from other regular aqueous components is needed. The only things we must keep in mind are that:

- Stoichiometric coefficients of protons in a species may be negative, resulting in the possibility of negative total analytical concentration of protons.
- When a chemical element is present at several oxidation states, only one of these can be considered a component and the others must be treated as species.

Although the full complement of geochemical reactions considered here include complexation, sorption, precipitation-dissolution, redox, and acid-base reactions, the term "full complement" includes only the first three types of reactions because the latter two reactions require no special treatment, as discussed above. If only aqueous components are involved in a redox reaction, it can be treated as a complexation reaction when the resulting species is in the aqueous phase or as a precipitation reaction when the resulting species is in the solid phase. If aqueous components, adsorbent components, and the ion-exchange site are involved, it is treated as a sorption reaction. Similar treatment is given for acid-base reactions.

Equations (2.2.17), (2.2.27), (2.3.5), (2.3.11), (2.3.18) with (2.2.34) and (2.3.22) form ($N_a + N_s + M_x + M_y + M_z + M_p$) equations and contain the ($N_a + N_s + M_x + M_y + M_z + M_p$) unknowns c_i's, s_i's, x_i's, y_i's, z_i's, and p_i's; the system is closed. These equations form the basis for chemical equilibrium computation.

2.4 Initial and Boundary Conditions

To complete the description of the hydrological transport as given by Equations (2.2.16), (2.2.26), and (2.2.33), initial and boundary conditions must be specified in accordance with dynamic and physical consideration. It will be assumed initially that the total analytical concentrations for all components and the number of equivalents of the ion-exchange site are known throughout the region of interest; that is,

$$T_j = T_{jo} \quad \text{at } t = 0 \ , \ j \in N_a \ , \tag{2.4.1}$$

$$W_j = W_{jo} \quad \text{at } t = 0 \ , \ j \in N_s \ , \tag{2.4.2}$$

and

$$N_{eq} = N_{eqo} \quad \text{at } t = 0 \ , \tag{2.4.3}$$

where

T_{jo} = initial total analytical concentration of the j-th aqueous component (M/L^3).
W_{jo} = initial total analytical concentration of the j-th adsorbent component (M/L^3).
N_{eqo} = initial number of equivalents of the ion-exchange site (M/L^3).

Initial concentrations for aqueous components may be obtained from field measurements or by solving the steady-state version of Equation (2.2.16) 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 analytical concentration is prescribed; a Neumann boundary, for which the flux due to the gradient of total analytical 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 will specify the boundary conditions from the mathematical point of view in concert with dynamic and physical considerations. The boundary conditions imposed on any segment of the boundary are taken to be either Dirichlet, Neumann, Cauchy, or variable for T_j with $j = 1, 2, \ldots, N_a$ independently of each other. Thus, for any T_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

$$T_j = T_{jD} \quad \text{on} \quad B_D \ , \ j \in N_a \ , \tag{2.4.4}$$

$$-\mathbf{n} \cdot (\theta \mathbf{D} \cdot \nabla C_j) = q_{jN} \quad \text{on} \quad B_N \ , \ j \in N_a \ , \tag{2.4.5}$$

and

$$\mathbf{n} \cdot (\mathbf{V} C_j - \theta \mathbf{D} \cdot \nabla C_j) = q_{jC} \quad \text{on} \quad B_C \ , \ j \in N_a \ , \tag{2.4.6}$$

where

T_{jD} = prescribed Dirichlet total analytical concentration (M/L^3).
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

$$-\mathbf{n} \cdot (\theta \mathbf{D} \cdot \nabla C_j) = q_{cjV}$$

$$\text{if } \mathbf{V} \cdot \mathbf{n} > 0 \quad \text{on} \quad B_V \quad , \quad j \in N_a \tag{2.4.7}$$

and

$$\mathbf{n} \cdot (\mathbf{V} C_j - \theta \mathbf{D} \cdot \nabla C_j) = q_{jV}$$

$$\text{if} \quad \mathbf{V} \cdot \mathbf{n} < 0 \quad \text{on} \quad B_V \quad , \quad j \in N_a \quad . \tag{2.4.8}$$

3.0 NUMERICAL IMPLEMENTATION

3.1 Solution of Coupled Transport and Geochemical Reaction Problems

Equations (2.2.16) through (2.2.20), (2.2.26), (2.2.27), (2.2.33), (2.2.34), (2.3.5), (2.3.11), (2.3.18), and (2.3.22), respectively, constitute a system of equations describing the coupled hydrological transport and chemical equilibrium reactions for the unknowns T_j's, c_j's, C_j's, S_j's, P_j's, W_j's, s_j's, N_{eqi}'s, $z_{J's}$, x_i's, y_i's, z_i's (except for z_J), and p_i's, respectively. 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 generally divided into two subsystems: hydrologic transport and geochemical reactions. The hydrologic transport equations are Equations (2.2.16), (2.2.26), and (2.2.33), which are repeated here:

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t}(S_j + P_j) = L(C_j) - \theta \Lambda_j^a + M_j^a - QC_j \quad , \quad j \in N_a \quad , \tag{3.1.1}$$

$$\theta \frac{\partial W_j}{\partial t} + \frac{\partial \theta}{\partial t} W_j = -\theta \Lambda_j^s + M_j^s \quad , \quad j \in N_s \quad , \tag{3.1.2}$$

and

$$\theta \frac{\partial N_{eqi}}{\partial t} + \frac{\partial \theta}{\partial t} N_{eqi} = -\theta \Lambda_{eqi} + M_{eqi} \quad , \quad i \in \text{NSITE.} \tag{3.1.3}$$

The geochemical reaction equations are Equations (2.2.17) through (2.2.20), (2.2.27), (2.2.34), (2.3.5), (2.3.11), (2.3.18), and (2.3.22), which are regrouped as

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i + \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i \quad , \quad i \in N_a \quad , \tag{3.1.4}$$

$$W_j = s_j + \sum_{i=1}^{M_j} b_{ij}^y y_i \quad , \quad j \in N_s \quad , \tag{3.1.5}$$

$$\kappa_{kLNI(i)} = \frac{\left(z_k/s_T(i)\right)^{\nu_{LNI(i)}}}{\left(z_{LNI(i)}/s_T(i)\right)^{\nu_k}} \frac{a_{LNI(i)}^{\nu_k}}{a_k^{\nu_{LNI(i)}}} \quad , \quad k \in M_z \ , \ k \neq LNI(i) \ , \ i \in NSITE \tag{3.1.6}$$

and $$N_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k \quad ,$$

$$1 = \alpha_i^p \prod_{k=1}^{N_a} c_k^{a_{ik}^p} \quad , \quad i \in M_p \quad , \tag{3.1.7}$$

$$x_i = \alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x} \quad , \quad i \in M_x \quad , \tag{3.1.8}$$

$$y_i = \alpha_i^y \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^y} \right) \quad , \quad i \in M_y \quad , \tag{3.1.9}$$

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i \quad , \quad j \in N_a \quad , \tag{3.1.10}$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i \quad , \quad j \in N_a \quad , \tag{3.1.11}$$

and

$$P_j = \sum_{i=1}^{M_p} a_{ij}^p p_i \quad , \quad j \in N_a \quad . \tag{3.1.12}$$

The strategy of solving coupled hydrologic transport and geochemical equilibrium reaction problems is to solve the two subsystems of equations iteratively. The solution procedure for every time step is outlined below:

1. Solve Equation (3.1.2) and (3.1.3) for W_j's and N_{eqi}'s.

2. Solve Equation (3.1.1) for conservative aqueous components T_j's.

3. Make an initial guess for nonconservative aqueous components TW_j's.

4. With known W_j's, N_{eqi}'s, conservative T_j's, and guessed nonconservative TW_j's, solve Equations (3.1.4) through (3.1.9) for c_j's, s_j's, z_i's, p_i's, x_i's, and y_i's.

5. Compute C_j's, S_j's, and P_j's using Equations (3.1.10) through (3.1.12), respectively.

6. Solve Equation (3.1.1) for nonconservative aqueous components T_j's (and TW_j's = T_j's) using the newly computed C_j's, S_j's, and P_j's.

7. Revise the guess for nonconservative aqueous components TW_j's based on T_j's and old TW_j's.

8. With known W_j's, N_{eqi}'s, conservative T_j's, and newly guessed nonconservative T_j's, solve Equations (3.1.4) through (3.1.9) for c_j's, s_j's, z_i's, p_i's, x_i's, and y_i's.

9. Compute C_j's, S_j's, and P_j's using Equations (3.1.10) through (3.1.12), respectively.

10. Solve Equation (3.1.1) for nonconservative aqueous components T_j's using the newly computed C_j's, S_j's, and P_j's.

11. Check convergence by comparing the newly obtained T_j's and the revised TW_j's.

12. If a convergent solution is obtained, then proceed to the next time-step computation. If the solution is not convergent, repeat Steps 7 through 11.

Let us assume that there are N_c conservative aqueous components and N_r nonconservative aqueous components (i.e., $N_a = N_c + N_r$). The solution of N_s immobile adsorbent components W_j's, NSITE sites of the cation ion-exchange capacity N_{eqi}'s, and N_c conservative aqueous components among the T_j's is independent of all other components. However, the solution of N_r nonconservative aqueous components among the T_j's is not independent of all other components because the N_r nonconservative aqueous components are coupled. The N_r nonconservative aqueous components must be solved either simultaneously or iteratively. The simultaneous solution of N_r partial differential equations governing the transport of nonconservative aqueous components and the solution of the geochemical reaction equations constitute 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 (3.1.1) are finite-difference methods (FDMs) and finite-element methods (FEMs) (Forsythe and Wasow, 1960; Huebner, 1982; 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 finite differences and finite elements 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. In addition, there has been significant recent progress in using iteration 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 (Yeh, 1990) is used to solve the transport equations, Equation (3.1.1) is rearranged in the implicit Lagrangian form. Disregarding the decay term and dropping the subscript to simplify the notation, we obtain

$$\theta\left(\frac{DC}{D\tau} + \frac{\partial(S+P)}{\partial t}\right) + K(T) + \frac{\partial\theta}{\partial t}T = K(S + P) + QC_{in} \qquad (3.2.1)$$

$$\text{and} \quad \frac{\mathbf{dx}}{dt} = \frac{\mathbf{V}}{\theta} \ ,$$

where τ is the time with respect to the Lagrangian coordinate and
K is an operator denoting

$$K(!) = \left(-\nabla \cdot \theta\mathbf{D}\cdot\nabla + Q - \frac{\partial\theta}{\partial t}\right)(!) \ . \qquad (3.2.2)$$

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 (Huebner, 1982), 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 subdomains 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

$$T = \sum_{j=1}^{n} T_j N_j \quad , \quad C = \sum_{j=1}^{n} C_j N_j \quad , \quad S = \sum_{j=1}^{n} S_j N_j \quad , \quad P = \sum_{j=1}^{n} P_j N_j \quad , \tag{3.2.3}$$

where

N_j = the basis function of the spatial coordinate for j-th node.
T_j = the value of T at node j.
C_j = the value of C at node j.
S_j = the value of S at node j.
P_j = the value of P at node j.
n = number of finite-element nodes in the region.

Upon substituting Equation (3.2.3) into Equation (3.2.1) and applying the Galerkin FEM, we obtain the following matrix equation:

$$[M]\left\{\frac{DC}{D\tau} + \frac{d(S+P)}{dt}\right\} + ([K] + [E])\{T\} = [K](\{S\} + \{P\}) + \{Q\} + \{B\} \tag{3.2.4}$$

where

$\left\{\frac{DC}{DT}\right\}$ = column vector containing the values of $\frac{DC}{DT}$ at all nodes.

$\left\{\frac{d(S+P)}{dt}\right\}$ = column vector containing the value of $\frac{d(S+P)}{dt}$ at all nodes.

$\{T\}$ = column vector containing the value of T at all nodes.

$\{S\}$ = column vector containing the value of S at all nodes.

$\{P\}$ = column vector containing the value of P at all nodes.

$[M]$ = mass matrix resulting from the storage term.

$[K]$ = modified stiff matrix resulting from the combined action of dispersion, source of water, and the rate of change of moisture content.

$[E]$ = growth matrix representing the effect of the rate of change of moisture content alone.

{Q} = load vector from the internal source.

{B} = load vector from the boundary source.

The matrices [M], [K], and [E] are given by

$$M_{ij} = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e \theta N_\beta^e dR \quad , \tag{3.2.5}$$

$$K_{ij} = \sum_{e \epsilon M_e} \int_{R_e} \left[\left(\nabla N_\alpha^e \right) \cdot \theta \mathbf{D} \cdot \left(\nabla N_\beta^e \right) + N_\alpha^e \left(Q - \frac{\partial \theta}{\partial t} \right) N_\beta^e \right] dR \quad , \tag{3.2.6}$$

and

$$E_{ij} = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e \frac{\partial \theta}{\partial t} N_\beta^e dR \quad , \tag{3.2.7}$$

where

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

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

$$Q_i = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e Q C_{in} dR \tag{3.2.8}$$

and

$$B_i = - \sum_{e \epsilon N_{se}} \int_{B_e} N_\alpha^e \mathbf{n} \cdot (-\theta \mathbf{D} \cdot \nabla C) dB \quad , \tag{3.2.9}$$

where

B_e = the length of boundary segment e.
N_{se} = set of boundary segments that have 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 (3.2.4), simplifies to the evaluation of integrals on the right-hand side of Equations (3.2.5) through (3.2.9) for every element or boundary segment e. The major task that remains is the specification of base functions and the performance of 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 LEHGC1.1.

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

$$N_\alpha^e = \frac{1}{4}(1+\xi_\alpha\xi)(1+\eta_\alpha\eta) \quad \text{and} \quad \alpha = 1, 2, 3, 4 \quad , \tag{3.2.10}$$

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

$$x = \sum_{\alpha=1}^{4} x_\alpha N_\alpha^e(\xi,\eta) \quad \text{and} \quad z = \sum_{\alpha=1}^{4} z_\alpha N_\alpha^e(\xi,\eta) \quad . \tag{3.2.11}$$

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

$$N_1^e = L_1 \quad , \quad N_2^e = L_2 \quad , \quad N_3^e = L_3 \quad , \tag{3.2.12}$$

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

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

$$L_2 = \frac{1}{2A}(a_2 + b_2x + c_2z) \quad , \tag{3.2.13}$$

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

where

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

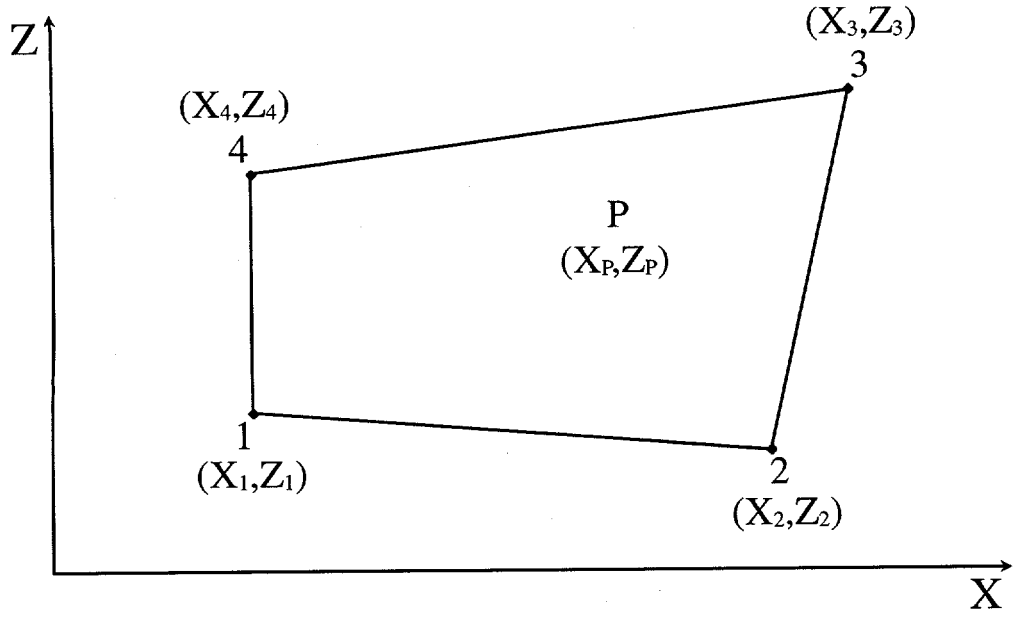
$$a_2 = x_3z_1 - x_1z_3 \quad , \quad b_2 = z_3 - z_1 \quad , \quad c_2 = x_1 - x_3 \tag{3.2.14}$$

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

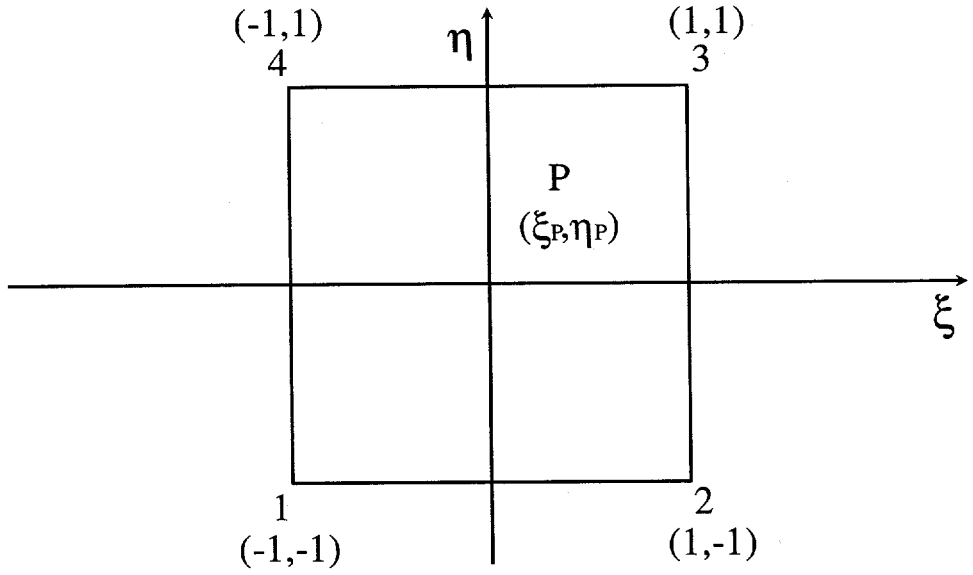
and A is the area of the triangle. It is seen from Equations (3.2.13) and (3.2.14) that

$$L_1 + L_2 + L_3 = 1 \quad . \tag{3.2.15}$$

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

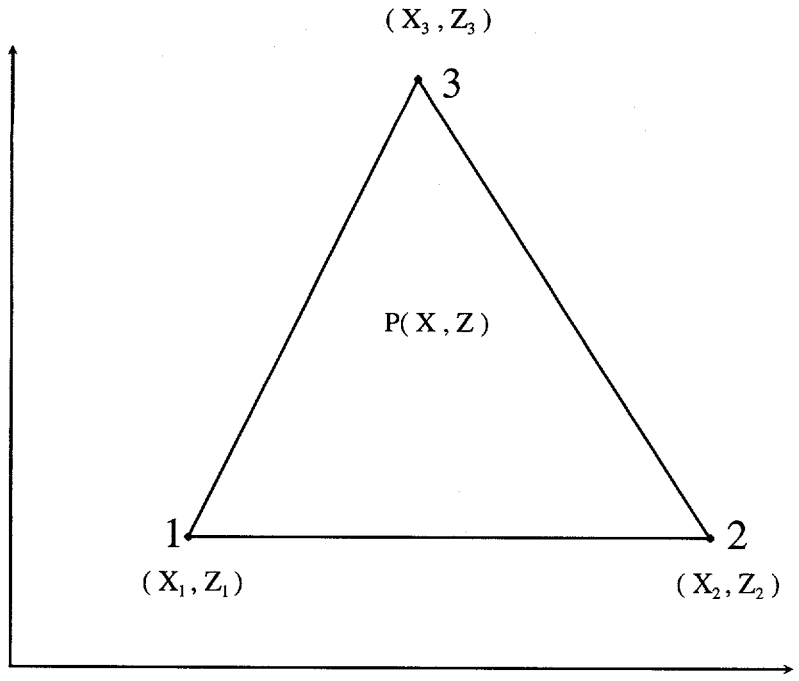


Global Coordinates

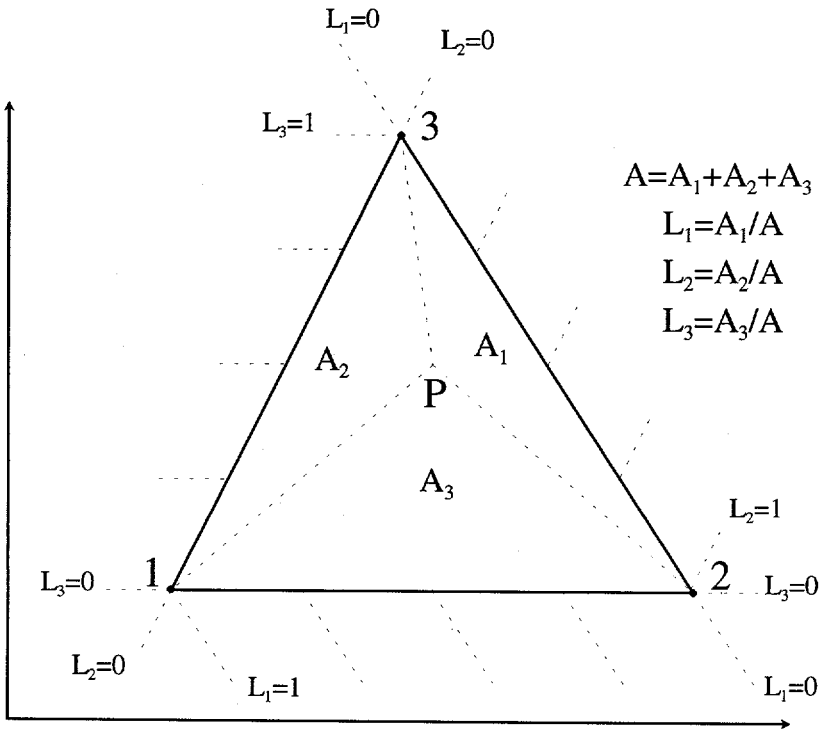


Local Coordinates

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



Global Coordinates



Local Coordinates

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

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.

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 (3.2.4)], one has to evaluate the integrals on the right-hand sides of Equations (3.2.5) through (3.2.8) for every element to yield the element mass matrix $[M^e]$, dispersion matrix $[D^e]$, fluid source matrix $[F^e]$, growth matrix $[E^e]$, and element column vector $\{Q^e\}$ as

$$M^e_{\alpha\beta} = \int_{R_e} N^e_\alpha \theta N^e_\beta dR \quad , \tag{3.2.16}$$

$$D^e_{\alpha\beta} = \int_{R_e} \left(\nabla N^e_\alpha\right) \cdot \theta \mathbf{D} \cdot \left(\nabla N^e_\beta\right) dR \quad , \tag{3.2.17}$$

$$F^e_{\alpha\beta} = \int_{R_e} N^e_\alpha Q N^e_\beta dR \quad , \tag{3.2.18}$$

$$E^e_{\alpha\beta} = \int_{R_e} N^e_\alpha \frac{\partial \theta}{\partial t} N^e_\beta dR \quad , \tag{3.2.19}$$

and

$$Q^e_\alpha = \int_{R_e} N^e_\alpha Q C_{in} dR \quad , \tag{3.2.20}$$

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

For a quadrilateral element, Equations (3.2.16) through (3.2.20) are computed by Gaussian quadrature (Conte, 1972) because it is not easy to solve Equation (3.2.11) for ξ and η in terms of x and z. For a triangular element, the transformation from the global coordinate (x,z) to the local coordinate (L_1,L_2,L_3) is already given explicitly by Equations (3.2.13) and (3.2.14). This fact and the following integration identity (Davies, 1980),

$$\int_{R_e} L_1^n L_2^m L_3^k dR = 2A \frac{n!m!k!}{(m+n+k+2)!} \quad , \tag{3.2.21}$$

make the evaluation of Equations (3.2.16) through (3.2.20) analytically possible for triangular elements. With the element matrices $[M^e]$, $[D^e]$, $[F^e]$, and $[E^e]$ and the element column vector $\{Q^e\}$ computed, the global matrices [M], [K], and [E] and the global column vector {Q} are then assembled element by element.

3.2.4 Mass Lumping Option

Mass-lumping, or diagonalization, techniques have been well-established and are widely used. The form of the element mass matrix $[M^e]$, fluid source matrix $[F^e]$, and the growth matrix $[E^e]$ lend themselves to this approach in which the consistent matrix is replaced by a diagonal matrix, greatly reducing the computational effort during the matrix solution procedure. A systematic and mathematically acceptable procedure for such lumping is described by Zienkiewicz (1977). For example, the element mass matrix can be lumped according to the following:

$$M^e_{\alpha\alpha} = \sum_{\beta=1}^{4} \int_{R_e} N^e_\alpha \theta N^e_\beta dR \qquad (3.2.22)$$

$$\text{and } M^e_{\alpha B} = 0 \quad \text{if} \quad B \neq \alpha \ .$$

where n = 4 for linear quadrilateral
and n = 3 for linear triangular

When advection and dispersion-diffusion terms are not involved in the transport equation, the lumped mass, fluid source, and growth matrices are preferred to the nonlumped, or consistent, form.

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 (3.2.4) the following matrix equation:

$$[G]\{T\}_{t+\Delta t} = [H]\left(\{S\}_{t+\Delta t} + \{P\}_{t+\Delta t}\right) + \{L\} + \{B\} \ , \qquad (3.2.23)$$

where

$\{T\}_{t+\Delta t}$ = column vector representing the value of $\{T\}$ at time $(t+\Delta t)$.
$\{S\}_{t+\Delta t}$ = column vector representing the value of $\{S\}$ at time $(t+\Delta t)$.
$\{P\}_{t+\Delta t}$ = column vector representing the values of $\{P\}$ at time $(t+\Delta t)$.
Δt = time-step size.

The matrices [G] and [H] and the load vector $\{L\}$ are given as

$$[G] = \frac{[M]}{\Delta\tau} + w([K] + [E]) \ ,$$

$$[H] = \frac{[M]}{\Delta\tau} - \frac{[M]}{\Delta t} + w[K] \qquad (3.2.24)$$

and

$$\{L\} = \frac{[M]}{\Delta t}\{C^*\} + \frac{[M]}{\Delta t}\left(\{S\}_t + \{P\}_t\right)$$
$$- (1 - w)[E]\left(\{C^*\} + \{S\}_t + \{P\}_t\right) - (1 - w)[K]\{C^*\} \qquad (3.2.25)$$

in which

$\Delta\tau$ = time step size in the Lagrangian coordinate
$\{S\}_t$ = value of $\{S\}$ at time t.
$\{P\}t$ = value of $\{P\}$ at time t.

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

$$x_i^* = x_i - \int_t^{t+\Delta t} V dt$$
$$C_i^* = \sum_j C_j(t) N_j(x_i^*) \qquad (3.2.26)$$

where

x_i^* (the Lagrangian point) = the location of the fictitious particle originating at time t, which would arrive at the node x_i at time $t+\Delta t$.

$C_j(t)$ = 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^*.

If x_i^* is located within the region of interest, we define $\Delta\tau$ in Equations (3.2.24) and (3.2.25) as

$$\Delta\tau = \Delta t \quad . \qquad (3.2.27)$$

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

$$x_i^* = x_i - \int_t^{t+\Delta\tau(x_i^*)} V dt \qquad (3.2.28)$$

will locate on the boundary. Thus, $\Delta\tau$ is less than or equal to Δt.

3.2.6 Boundary Conditions

To incorporate the boundary conditions, we have to evaluate the right-hand side of Equation (3.2.9) for every boundary segment B_e to yield the load vector $\{B^e\}$:

$$B_\alpha^e = -\int_{B_e} N_\alpha^e \mathbf{n} \cdot (-\theta \mathbf{D} \cdot \nabla C) dB \quad , \quad \alpha = 1, 2 \quad . \tag{3.2.29}$$

For the Neumann boundary condition given by Equation (2.4.5), we simply substitute Equation (2.4.5) into Equation (3.2.29) to yield a boundary-element column vector $\{B_n^e\}$ for a Neumann segment:

$$\{B_n^e\} = \{q_n^e\} \quad , \tag{3.2.30}$$

where $\{q_n^e\}$ is the Neumann boundary flux vector given by

$$q_{n\alpha}^e = -\int_{B_e} N_\alpha^e q_N dB \quad , \quad \alpha = 1, 2 \quad . \tag{3.2.31}$$

This Neumann boundary flux vector represents the normal fluxes through the two nodal points of the segment B_e on B_N.

For the Cauchy boundary condition given by Equation (2.4.6), we may rewrite Equation (3.2.29) in the following form:

$$\begin{aligned} B_\alpha^e = & -\int_{B_e} N_\alpha^e \mathbf{n} \cdot (\mathbf{V}C - \theta \mathbf{D} \cdot \nabla C) dB + \int_{B_e} N_\alpha^e \mathbf{n} \cdot \mathbf{V} T dB \\ & -\int_{B_e} N_\alpha^e \mathbf{n} \cdot \mathbf{V}(S + P) dB \quad , \quad \alpha = 1, 2 \end{aligned} \tag{3.2.32}$$

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

$$T = \sum_{\beta=1}^{2} T_\beta N_\beta^e \quad . \tag{3.2.33}$$

Similarly, the total sorbed concentration, S, and the total precipitated concentration, P, on the same boundary segment can be approximated by

$$S = \sum_{\beta=1}^{2} S_\beta N_\beta^e \quad \text{and} \quad P = \sum_{\beta=1}^{2} P_\beta N_\beta^e \quad . \tag{3.2.34}$$

Substituting Equations (2.4.6), (3.2.33), and (3.2.34) into Equation (3.2.32), we obtain the boundary-element column vector $\{B_c^e\}$ for a Cauchy segment:

$$\{B_c^e\} = \{q_c^e\} + \left[V_c^e\right]\{T\} - \left[V_c^e\right]\left(\{S\} + 1\{P\}\right) \quad , \tag{3.2.35}$$

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

$$q_{c\alpha}^e = -\int_{B_e} N_\alpha^e q_C dB \quad , \quad \alpha = 1, 2$$

and $$V_{c\alpha\beta}^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \mathbf{V} N_\beta^e dB \quad , \quad \alpha = 1, 2 \quad \text{and} \quad \beta = 1, 2 \tag{3.2.36}$$

Segments on which the variable boundary conditions are imposed are the flow-through boundaries, where the flow direction is not known a priori. When the flow is directed into the region, Cauchy boundary conditions are used. The boundary-element column vector $\{B_v^e\}$ for a variable-boundary segment can be obtained similar to $\{B_c^e\}$:

$$\{B_v^e\} = \{q_v^e\} + \left[V_v^e\right]\{T\} - \left[V_v^e\right]\left(\{S\} + \{P\}\right) \quad , \tag{3.2.37}$$

in which the variable-boundary flux vector $\{q_v^e\}$ and the variable-boundary matrix $[V_v^e]$ from the normal velocity component are given by

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

and

$$V_{v\alpha\beta}^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \mathbf{V} N_\beta^e dB \quad , \quad \alpha = 1, 2 \quad \text{and} \quad \beta = 1, 2 \quad , \tag{3.2.38}$$

where

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

When the flow is directed out from the region, both $\{q_v^e\}$ and $[V_v^e]$ are set equal to 0.

Assembling over all Neumann, Cauchy, and variable-boundary segments, we obtain the global boundary column vector $\{B\}$ as

$$\{B\} = \{q\} + [V]\{T\} - [V]\left(\{S\} + \{P\}\right) \quad , \tag{3.2.39}$$

in which

$$\{q\} = \sum_{e \epsilon N_{ne}} \{q_n^e\} + \sum_{e \epsilon N_{ce}} \{q_c^e\} + \sum_{e \epsilon N_{ve}} \{q_v^e\}$$

$$[V] = \sum_{e \epsilon N_{ce}} \left[V_c^e\right] + \sum_{e \epsilon N_{ve}} \left[V_v^e\right] \quad , \tag{3.2.40}$$

where

N_{ne} = number of Neumann segments.
N_{ce} = number of Cauchy segments.
N_{ve} = number of variable-boundary segments.

Substituting Equation (3.2.39) into Equation (3.2.23) and dropping the subscript $(t + \Delta t)$ to simplify the notation, we obtain

$$[U]\{T\} = [W](\{S\} + \{P\}) + \{R\} \tag{3.2.41}$$

where [U], [W], and {R}, after using Equations (3.2.24) through (3.2.25), are given by the following equations:

$$[U] = [G] - w_v[V], \quad [W] = [H] - w_v[V] \tag{3.2.42a}$$

and

$$\{R\} = \{L\} + \{q\} + (1 - w_v)\{C^*\}_t \quad . \tag{3.2.42b}$$

At nodes where Dirichlet boundary conditions are applied, an identity equation is generated for each node and included in the matrices of Equation (3.2.41). The detailed method of applying this type of boundary condition can be found elsewhere (Wang and Connor, 1975).

Equation (3.2.41), after being modified for the Dirichlet boundary condition, is solved iteratively and in sequence with the transport of adsorbent components, cation ion-exchange capacity and the chemical equilibrium problem specified by Equations (3.1.2) through (3.1.12) to yield {T}, {W}, N_{eq}, {c}, {s}, {z}, {p}, {x}, {y}, {C}, {S}, and {P) for all chemical components.

Boundary conditions need to be implemented in the computation of the Lagrangian concentrations $\{C^*\}$. Neumann boundary conditions normally apply to the boundary when flow is directed out from the region of interest. On the Neumann boundary, the 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. Cauchy boundary conditions normally apply to the boundary segment when the flow is directed into the region of interest. The Lagrangian concentration on the i-th Cauchy node C_{ci}^* is computed by the following formula:

$$C_{ci}^{*} = \frac{\int_{B_c} N_i q_c dB}{\int_{B_c} N_i \mathbf{n} \cdot \mathbf{V} dB} \qquad (3.2.43)$$

On the variable boundary, boundary conditions need not be implemented if the flow is directed out from the region. If the flow is directed into the region, then the Lagrangian concentration on the i-th variable boundary node C_{vi}^{*} is computed by

$$C_{vi}^{*} = \frac{\int_{B_v} N_i \mathbf{n} \cdot \mathbf{V} C_{cin} dB}{\int_{B_c} N_i \mathbf{n} \cdot \mathbf{V} dB} \quad , \qquad (3.2.44)$$

where

C_{cin} = the concentration of the incoming fluid through the variable boundary.

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

3.2.7 Solution of the Matrix Equations

Although both the matrices [U] and [W] are not functions of the unknown {T}, Equation (3.2.41) still represents a system of nonlinear algebraic equations because both {S} and {P} are functions of {T}. 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}. Using this estimate, we then compute the total sorbed concentration {S} and total precipitated concentration {P} from the chemical equilibrium reactions. Substituting the computed {S} and {P} vectors into the right-hand side of Equation (3.2.41) and combining [W]({S}+{P}) with {R} to form a new right-hand side load vector, 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 now obtained by the weighted average of the new solution and the previous estimate,

$$\{T^{k+1}\} = \omega\{T\} + (1 - \omega)\{T^{k}\} \quad , \qquad (3.2.45)$$

where

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

Two options are employed to solve the linearized matrix equation: the direct elimination method and the pointwise iteration method. 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 have been employed when the pointwise iteration method is used to solve the linearized matrix equation. These are the successive under-relaxation (SUR), Gauss-Seidel (G-S), and successive over-relaxation (SOR) iteration methods. These three 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.

3.2.8 Solution of the Total Analytical Concentrations of Adsorbent Components and N_{eq}

Equation (3.1.2) governs the mass balance of adsorbent components. It does not involve spatial derivatives and its solution can therefore be obtained by simple integration of the equation with respect to time. Furthermore, the solution of Equation (3.1.2) can be achieved independently of the solution of Equation (3.1.1). Equation (3.1.2) is solved only once during any iteration between the hydrologic transport module and chemical equilibrium module. An implicit scheme can be used to integrate Equation (3.1.2) to yield

$$\left(\theta + \Delta t\frac{\partial\theta}{\partial t}\right)(W_j)_{t+\Delta t} = \theta(W_j)_t \quad , \quad j \in N_s \quad , \tag{3.2.46}$$

where

$(W_j)_{t+\Delta t}$ = the values of W_j at time $(t+\Delta t)$.
$(W_j)_t$ = the value of W_j at time t.

Equation (3.2.46) is applicable to all nodes in the region of interest.

Similarly, the cation ion-exchange capacity N_{eq} governed by Equation (3.1.3) can be solved independent of all other components. The solution is given as

$$\left(\theta + \Delta t\frac{\partial\theta}{\partial t}\right)(N_{eqi})_{t+\Delta t} = \theta(N_{eqi})_t \quad , \quad i \in \text{NSITE} \tag{3.2.47}$$

where

$(N_{eqi})_{t+\Delta t}$ = the value of N_{eqi} at time $(t+\Delta t)$.
$(N_{eqi})_t$ = the value of N_{eqi} at time t.

Equation (3.2.47) is applicable to all nodes in the region of interest.

3.3 Solution of Geochemical Reaction Equations

Given the total analytical concentrations T_j's and W_j's of all components and the ion-exchange equivalent site, equations (3.1.4) through (3.1.9) contain six sets of unknowns (N_a c_k's, N_s s_k's, M_x x_i's, M_y y_i's, M_z z_i's, and M_p p_i's) in six sets of algebraic equations. Simultaneous solution of these values for the six sets of algebraic equations should yield six sets of unknowns. However, simplifications can be made to reduce the number of simultaneous equations to be solved.

Substitution of Equations (3.1.8) and (3.1.9) into Equations (3.1.4) and (3.1.5) yield the following mole balance equations:

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^{x} \left(\alpha_i^{x} \prod_{k=1}^{N_a} c_k^{a_{ik}^{x}} \right) + \sum_{i=1}^{M_y} a_{ij}^{y} \left[\alpha_i^{y} \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^{y}} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^{y}} \right) \right] + \sum_{i=1}^{M_z} a_{ij}^{z} z_i + \sum_{i=1}^{M_p} a_{ij}^{p} p_i \quad , \quad j \in N_a \tag{3.3.1}$$

and

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^{y} \left[\alpha_i^{y} \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^{y}} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^{y}} \right) \right] \quad , \quad j \in N_s \quad . \tag{3.3.2}$$

Let us repeat the ion-exchange site balance equation [Equation (2.2.34)] and rearrange the order of all mass action equations as follows:

$$N_{eqi} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k \quad , \quad i \in NSITE \tag{3.3.3}$$

and $$\kappa_{kLNI(i)} = \frac{\left(z_k / s_T(i)\right)^{\nu_{LNI(i)}}}{\left(z_{LNI(i)} / s_T(i)\right)^{\nu_k}} \frac{\left(a_{LNI(i)}\right)^{\nu_k}}{\left(a_k\right)^{\nu_{LNI(i)}}} \quad , \quad k \in M_z, \quad k \neq LNI(i) \quad ,$$

$$1 = \alpha_i^{p} \prod_{k=1}^{N_a} \left(c_k\right)^{a_{ik}^{p}} \quad , \quad i \in M_p \quad , \tag{3.3.4}$$

$$x_i = \alpha_i^{x} \prod_{k=1}^{N_a} \left(c_k\right)^{a_{ik}^{x}} \quad , \quad i \in M_x \quad , \tag{3.3.5}$$

and

$$y_i = \alpha_i^{y} \left[\prod_{k=1}^{N_a} \left(c_k\right)^{a_{ik}^{y}} \right] \left[\prod_{k=1}^{N_s} \left(s_k\right)^{b_{ik}^{y}} \right] \quad , \quad i \in M_y \quad . \tag{3.3.6}$$

3.3.1 Activity Coefficients and Thermodynamic Equilibrium Constants

Since the activity coefficients of all aqueous 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:

$$I = \frac{1}{2}\sum_{i=1}^{M_a} a_k v_i^2 \quad , \tag{3.3.7}$$

where

v_i = charge of the i-th aqueous species.

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

M_a = the number of aqueous species equal to the number of aqueous component species plus the number of 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):

$$\mathrm{Log}(\gamma_i) = -Av_i^2\left(\frac{\sqrt{I}}{1+a_iB\sqrt{I}}+B'I\right) + b_iI + B_iI^2 \quad , \tag{3.3.8}$$

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.

The thermodynamic equilibrium constants K_i^x, K_i^y, K_{ij}, and K_i^p 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). As discussed previously, in LEHGC1.1, the Davies activity coefficient equation is applied to the aqueous components in surface complexation reactions but not to the adsorbed species.

3.3.2 Solution of the Nonlinear Algebraic Equations

Given the T_j's, W_j's and N_{eq}, Equations (3.3.1) through (3.3.6) involve six sets of unknowns in six sets of algebraic equations: N_a c_k's, N_s s_k's, M_z z_i's, M_p p_i's, M_x x_i's, and M_y y_i's. These sets of equations can be solved by methods of nonlinear algebra. The Newton-Raphson iterative technique is used to solve these sets of equations. The 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

$$y(x) = 0 \quad . \tag{3.3.9}$$

Taylor expansion of Equation (3.3.9) about the previous iterate yields

$$y^n + \frac{dy}{dx}\left(x^{n+1} - x^n\right) = 0 \ , \tag{3.3.10}$$

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 (3.3.10) becomes

$$\mathbf{Z}^n\left(\mathbf{X}^n - \mathbf{X}^{n+1}\right) = \mathbf{Y}^n \ , \tag{3.3.11}$$

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 (3.3.9) involves the following steps:

1. Given the functions y(x) and 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 (3.3.1).
4. Compute the new iterate by

$$\mathbf{X}^{n+1} = \Delta\mathbf{X} - \mathbf{X}^n \ . \tag{3.3.12}$$

The above steps are repeated until a convergent solution is obtained. The application of the Newton-Raphson method to the chemical equilibrium model is straightforward. The residues are computed from Equations (3.3.1) through (3.3.6) (or their reduced sets). The Jacobian is computed by taking the partial differential of Equations (3.3.1) through (3.3.6) (or their reduced sets) with respect to the species concentrations (or the reduced set of species concentrations). Examination of Equations (3.3.1) through (3.3.6) reveals that while Equation (3.3.6) can be decoupled from Equations (3.3.1) through (3.3.4), Equation (3.3.5) cannot be decoupled from Equations (3.3.1) through (3.3.4) because the modified stability constants and the modified selectivities are functions of x_i's. For the Newton-Raphson method, it is advantageous to keep the number of simultaneous equations at a minimum. Therefore, Equations (3.3.1) through (3.3.4) are solved simultaneously for the c_j's, s_j's, z_i's, and p_i's during one iteration. After the c_j's, s_j's, z_i's, and p_i's are obtained, the x_i's and y_i's are computed from Equations (3.3.5) and (3.3.6), respectively, during the same iteration. The major tasks are thus the evaluation of the residuals and Jacobians for Equations (3.3.1) through (3.3.4).

3.3.3 Evaluation of the Residual and Jacobian

The computation of the residual for Equations (3.3.1) through (3.3.4) is relatively simple. All species concentrations from the most recent iterations are substituted into these equations:

$$GR_i = R_m = T_m - c_m - \sum_{k=1}^{M_x} a_{km}^{x} x_k - \sum_{k=1}^{M_y} a_{km}^{y} y_k - \sum_{k=1}^{M_z} a_{km}^{z} z_k - \sum_{k=1}^{M_p} a_{km}^{p} p_k \qquad (3.3.13)$$

$$m \in N_a \ , \ i = m \ ,$$

$$GR_i = R_m = W_m - s_m - \sum_{k=1}^{M_y} b_{km}^{y} y_k \ , \ m \in N_s \ , \ i = m+N_a \qquad (3.3.14)$$

$$GR_i = R_m = N_{eql} - \sum_{k=NOMZJ(l)+1}^{NOMZJ(l)+NOMZI(l)} \nu_k z_k \ , \ m = LNI(l), \ i = m + N_a + N_s \ ,$$

$$GR_i = R_m = z_m\left[\left(s_T(l)\right)^{\nu_m}\left(a_{LNI(l)}\right)^{\nu_m}\right]^{\frac{1}{\nu_{LNI(l)}}} - s_T(l)a_m\left[\kappa_{mLNI(l)}\left(z_{LNI(l)}\right)^{\nu_m}\right]^{\frac{1}{\nu_{LNI(l)}}} \ , \qquad (3.3.15)$$

$$m \in M_z \ , \ l \in NSITE, \ m \neq LNI(l) \ , \ i = m + N_a + N_s \ ,$$

and

$$GR_i = R_m = 1 - \alpha_m^{p} \prod_{k=1}^{N_a} \left(c_k\right)^{a_{mk}^{p}} \ , \ m \in M_p \ , \ i = m + N_a + N_s + M_z \ , \qquad (3.3.16)$$

where

GR_i = residual of the i-th equation
R_m = residual of the equation

and where the concentrations of all species appearing in Equations (3.3.13) through (3.3.16) denote the values from the previous iteration.

The computation of the Jacobian of Equations (3.3.1) through (3.3.4) is presented below:

<u>For row $m = 1, 2, \ldots, N_a$; $i = m$.</u>

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\delta_{mn} - \sum_{k=1}^{M_x} a_{km}^{x}\left(\frac{\partial x_k}{\partial c_m}\right) - \sum_{k=1}^{M_y} a_{km}^{y}\left(\frac{\partial y_k}{\partial c_n}\right)$$

$$= -\delta_{mn} - \sum_{k=1}^{M_x} a_{km}^{x}\left[a_{kn}^{x}\left(\frac{x_k}{c_n}\right)\right] - \sum_{k=1}^{M_y} a_{km}^{y}\left[a_{kn}^{y}\left(\frac{y_k}{c_n}\right)\right] \quad , \quad n \in N_a \quad , \quad j = n \quad . \tag{3.3.17}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\sum_{k=1}^{M_y} a_{km}^{y}\left(\frac{\partial y_k}{\partial s_n}\right) = -\sum_{k=1}^{M_y} a_{km}^{y}\left[b_{kn}^{y}\left(\frac{y_k}{s_n}\right)\right] \quad , \tag{3.3.18}$$

$$n \in N_s \quad , \quad j = n + N_a \quad .$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\sum_{k=1}^{M_z} a_{km}^{z}\left(\frac{\partial z_k}{\partial z_n}\right) = -\sum_{k=1}^{M_z} a_{km}^{z}\,\delta_{kn} = -a_{nm}^{z} \quad , \tag{3.3.19}$$

$$n \in M_z \quad , \quad j = n + N \quad .$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = -\sum_{k=1}^{M_p} a_{km}^{p}\left(\frac{\partial p_k}{\partial p_n}\right) = -\sum_{k=1}^{M_p} a_{km}^{p}\,\delta_{kn} = -a_{nm}^{p} \quad , \tag{3.3.20}$$

$$n \in M_p \quad , \quad j = n + M_z + N \quad .$$

<u>For row $m = 1, 2, \ldots, N_s$; $i = m + N_a$.</u>

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\sum_{k=1}^{M_y} b_{km}^{y}\left(\frac{\partial y_k}{\partial c_n}\right) = -\sum_{k=1}^{M_y} b_{km}^{y}\left[a_{kn}^{y}\left(\frac{y_k}{c_n}\right)\right] \quad , \quad n \in N_a \quad , \quad j = n \quad . \tag{3.3.21}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\delta_{mn} - \sum_{k=1}^{M_y} b_{km}^{y}\left(\frac{\partial y_k}{\partial s_n}\right)$$

$$= -\delta_{mn} - \sum_{k=1}^{M_y} b_{km}^{y}\left[b_{kn}^{y}\left(\frac{y_k}{s_n}\right)\right] \quad , \quad n \in N_s \quad ; \quad j = n + N_a \quad . \tag{3.3.22}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = 0 \quad , \quad n \in M_z \quad ; \quad j = n + N \quad . \tag{3.3.23}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0 \quad , \quad n \in M_p \quad ; \quad j = n + M_z + N \quad . \tag{3.3.24}$$

For row $m = 1, 2, \ldots, M_z$; $i = m + N$.

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \frac{R_i(\ldots, c_n + \epsilon, \ldots) - R_i(\ldots, c_n, \ldots)}{\epsilon} \quad , \quad n \in N_a \quad ; \quad j = n \quad . \tag{3.3.25}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = 0 \quad , \quad n \in N_s \quad ; \quad j = n + N_a \quad . \tag{3.3.26}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \frac{R_i(\ldots\ldots, z_n + \epsilon, \ldots) - R_i(\ldots\ldots, z_n, \ldots)}{\epsilon} \quad , \quad n \in M_z \quad ; \quad j = n + N \quad . \tag{3.3.27}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0 \quad , \quad n \in M_p \quad ; \quad j = n + M_z + N \quad . \tag{3.3.28}$$

For row $m = 1, 2, \ldots, M_z$; $i = m + N + M_z$.

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\alpha_m^p \prod_{k=1}^{N_a} a_{mn}^p \frac{(c_k)^{a_{mk}^p}}{c_n} \quad , \quad n \in N_a \quad ; \quad j = n \quad . \tag{3.3.29}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = 0 \quad , \quad n \in N_s \quad ; \quad j = n + N_a \quad . \tag{3.3.30}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = 0 \quad , \quad n \in M_z \quad ; \quad j = n + N \quad . \tag{3.3.31}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0 \quad , \quad n \in M_p \quad ; \quad j = n + M_z + N \quad . \tag{3.3.32}$$

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. Thus, the basic independent unknowns will include N_a c_k's N_s s_k's, M_z z_i's, and M_p p_i's, and the reduced sets of governing equations would be Equations (3.3.1) through (3.3.4). 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 Equation (3.3.4) into Equations (3.3.1) through (3.3.3) to eliminate M_p c_k's out of N_a c_k's and M_p p_i's from Equations (3.3.1) through (3.3.3). Thus, the basic independent unknowns will include $(N_a - M_p)$ c_k's, N_s s_k's, and M_z z_i's, and the reduced sets of governing equations would be $(N_a - M_p)$ equations out of the N_a equations in Equation (3.3.1) through (3.3.3). The detail of substituting Equation (3.3.4) into Equation (3.3.1) 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 can easily modify the code to treat mixed chemical equilibrium and chemical kinetics. This version of the code uses the simpler first approach to treat precipitation-dissolution reactions.

3.3.5 Treatment of Sorption

If simple surface complexation is used to model adsorption, no special treatment is required. However, if the constant capacitance model or the triple layer model is used to model adsorption (Gouy, 1910; Chapman, 1913; Davis and Leckie, 1978), one additional unknown (c_o in the case of the constant capacitance model) or two additional unknowns (c_o and c_b in the case of the triple layer model) are introduced in the adsorption reaction in Equation (3.1.9). These two additional unknowns are defined as

$$c_o = \exp\left(-\frac{e\psi_o}{kT} \right) \tag{3.3.33}$$

and

$$c_b = \exp\left(-\frac{e\psi_b}{kT} \right) , \tag{3.3.34}$$

where

k = the Boltzmann constant.
T = the absolute temperature.
e = the electronic charge.
ψ_o = the electric potential at the surface.
ψ_b = the electric potential at the beta layer.

In the case of the constant capacitance model, the unknown c_o defined by Equation (3.3.33) is

determined by introducing one additional equation. This additional equation assumes that the total charge, calculated by summing over the charges on the "o" plane, is equal to the total charge calculated by electrostatic theory as

$$BC\psi_o = \sum_{i=1}^{M_y} a_{io}^{y} y_i \quad , \tag{3.3.35}$$

where

C = the capacitance of the region.
B = a conversion factor from charge per unit area to moles per unit volume.

For the evaluation of the Jacobian, one needs to compute $\frac{\partial \psi}{\partial c_o}$, which can be easily computed from Equation (3.3.33) as

$$\frac{\partial \psi_o}{\partial c_o} = -\frac{kT}{e c_o} \quad . \tag{3.3.36}$$

In the case of the triple layer model, the two additional unknowns, c_o and c_b, can be determined by assuming that the total charge, calculated by summing over the charges of all surface species, is equal to the total charge calculated by electrostatic theory as given by

$$BC_1(\psi_o - \psi_b) - B\sigma_o = 0 \quad , \tag{3.3.37}$$

$$B\sigma_o = \sum_{i=1}^{M_y} a_{io}^{y} y_i \quad , \tag{3.3.38}$$

$$C_1(\psi_b - \psi_o)B + C_2(\psi_b - \psi_d)B - B\sigma_b = 0 \quad , \tag{3.3.39}$$

and

$$B\sigma_b = \sum_{i=1}^{M_y} a_{ib}^{y} y_i \quad , \tag{3.3.40}$$

where

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

Electroneutrality requires that the relationship

$$\sigma_o + \sigma_b + \sigma_d = 0 \tag{3.3.41}$$

must be satisfied. The Gouy-Chapman diffuse layer theory yields

$$\sigma_d = -\left(8\epsilon\epsilon_o RIT\right)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad , \tag{3.3.42}$$

where

σ_d = the charge density in charge per unit area in the diffusive layer "d."
R = the universal gas constant.
ϵ = the relative dielectric constant.
ϵ_o = the permitivity of the free space.
z = the ionic charge.

It should be noted that Equation (3.3.42) is valid only for the case of symmetrical monovalent electrolytes. The charge potential relationship gives

$$C_2\left(\psi_d - \psi_b\right) = \sigma_d \quad . \tag{3.3.43}$$

Combining Equations (3.3.42) and (3.3.43), we relate the unknowns ψ_d and ψ_b implicitly as follows:

$$C_2\left(\psi_d - \psi_b\right) = -\left(8\epsilon\epsilon_o RIT\right)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad . \tag{3.3.44}$$

To solve Equations (3.3.37) and (3.3.39) with the 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

$$B\sigma_o,\ B\sigma_b,\ B\frac{\partial\sigma_o}{\partial c_o},\ B\frac{\partial\sigma_o}{\partial c_b},\ B\frac{\partial\sigma_b}{\partial c_o}, \text{ and } B\frac{\partial\sigma_b}{\partial c_b}$$

is similar to the evaluation for other aqueous components. The evaluation of

$$\psi_o,\ \psi_b,\ \psi_d,\ \frac{\partial\psi_o}{\partial c_o}, \frac{\partial\psi_o}{\partial c_b}, \frac{\partial\psi_b}{\partial c_o}, \frac{\partial\psi_b}{\partial c_b}, \frac{\partial\psi_d}{\partial c_o}, \text{ and } \frac{\partial\psi_d}{\partial c_b}$$

requires further elaboration. Knowing c_o and c_b from the previous iteration, we compute ψ_o and ψ_b by inverting Equations (3.3.33) and (3.3.34) as

$$\psi_o = -\frac{kT}{e}\ln(c_o) \tag{3.3.45}$$

and

$$\psi_b = -\frac{kT}{e}\ln(c_b) \quad , \tag{3.3.46}$$

respectively. Having computed σ_o and σ_b from Equations (3.3.38) and (3.3.40), respectively, we compute σ_d from Equation (3.3.41) and then invert Equation (3.3.42) to obtain ψ_d as

$$\psi_d = \frac{2kT}{ze}\sinh^{-1}\left[-\frac{\sigma_d}{\left(8\epsilon\epsilon_o RIT\right)^{\frac{1}{2}}}\right] \quad . \tag{3.3.47}$$

Differentiating Equation (3.3.45) with respect to c_o and c_b, respectively, we obtain

$$\frac{\partial\psi_o}{\partial c_o} = \left(-\frac{kT}{e}\frac{1}{c_o}\right) \tag{3.3.48}$$

and

$$\frac{\partial\psi_o}{\partial c_b} = 0 \quad . \tag{3.3.49}$$

Similarly, differentiating Equation (3.3.46) with respect to c_o and c_b, respectively, we obtain

$$\frac{\partial\psi_b}{\partial c_o} = 0 \tag{3.3.50}$$

and

$$\frac{\partial\psi_b}{\partial c_b} = \left(-\frac{kT}{e}\frac{1}{c_b}\right) \quad . \tag{3.3.51}$$

Finally, differentiating Equation (3.3.47) with respect to c_o and c_b, respectively, and substituting Equations (3.3.50) and (3.3.51) into the resulting equation, we obtain

$$\frac{\partial\psi_d}{\partial c_o} = 0 \tag{3.3.52}$$

and

$$\frac{\partial \psi_d}{\partial c_b} = \left(-\frac{kT}{e}\frac{1}{c_b} \right) \frac{1}{1 + \frac{e}{2kT}\left(8\epsilon\epsilon_o RIT\right)^{\frac{1}{2}} \cosh\left(\frac{ze\psi_d}{2kT} \right) \frac{1}{C_2}} \quad . \tag{3.3.53}$$

3.3.6 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 of Equation (4.1.1) is set to zero and c_e (i.e., set k = e in c_k) 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.

3.3.7 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 LEHGC1.1 PROGRAM STRUCTURE

4.1 The General Solution Strategy of LEHGC1.1

LEHGC is designed to solve a system of equations describing hydrologic transport and geochemical equilibrium in a reactive multicomponent system. The transport equations are derived from the continuity of mass and the law of flux. The geochemical equilibrium equations are material balances coupled with the mass action. The transport equations, along with initial and boundary conditions and the geochemical equilibrium equations, govern the migration and chemical reactions of multispecies components 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.

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 chemical reactions, under the assumption of local equilibrium, are described by a set of nonlinear algebraic equations. The governing transport equations along with the initial boundary conditions are given by Equations (3.1.1) through (3.1.3) and Equations (2.4.1) through (2.4.8). The chemical reaction equations are Equations (3.1.4) through (3.1.12). The steps to solve the governing equations are as follows:

1. Solve Equations (3.1.2) and (3.1.3) for W_j's and N_{eqi}'s.

2. Make guesses of T_j's.

3. Solve Equations (3.1.4) through (3.1.12) to obtain all species concentrations and S_j's and P_j's.

4. Solve Equation (3.2.1) for T_j's using the S_j's and P_j's obtained from Step 3 to evaluate the right-hand terms in Equation (3.2.1).

5. Compare the newly obtained T_j's with the guessed T_j's in Step 2.

6. 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 5 until the system converges.

4.2 Description of LEHGC1.1 Subroutines

LEHGC1.1 consists of a short MAIN routine, 63 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 chemical equilibrium model is performed by the subroutine

OCSPIT. The remaining 61 subroutines and the function can be classified into four major categories:

- 19 subroutines are used to perform hydrologic transport.
- 13 subroutines and the function are used to compute the Lagrangian concentrations.
- 16 subroutines are used to simulate chemical equilibrium.
- 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 several subroutines with 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).
- 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 re-arrange LRN(J,N).
- Subroutine DATACS to read and print input data required for chemical equilibrium calculations.
- Subroutine AFABTA to compute the upstream weighting factor.
- Subroutine INTERP to obtain sources/sinks and boundary values.
- Subroutine OCSPIT to obtain total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components at all nodes given the total analytical concentrations.

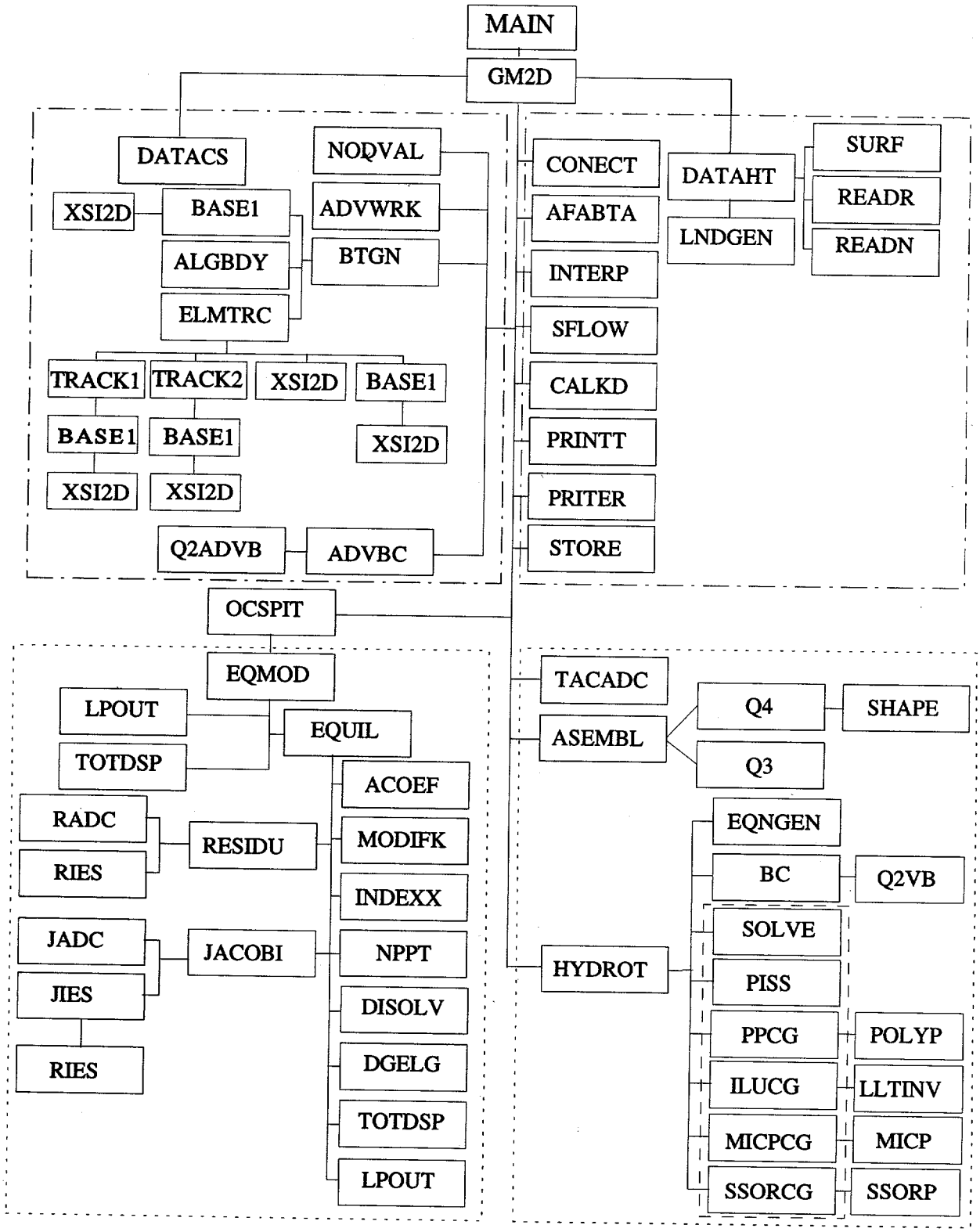


Fig. 4.1 Program Structure of LEHGC1.1

- Subroutine NODVAL to compute values of the moisture content, derivative of moisture content with respect to time, bulk density, initial cation exchange capacity, capacitances, and surface area of adsorbent sites at nodes.
- Subroutine ADVWRK to prepare working arrays for Lagrangian integration.
- Subroutine BTGN to compute the Lagrangian concentrations.
- Subroutine ADVBC to implement boundary conditions at the Lagrangian step.
- Subroutine TACADC to compute the total analytical concentrations of all adsorbent components and the number of equivalents for ion exchange.
- Subroutine ASEMBL to assemble the element matrices and load vectors over all elements to form a compressed global matrix and global load vectors.
- Subroutine HYDROT to perform hydrologic transport computations.
- Subroutine SFLOW to compute the net rate of chemicals 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 chemical equilibrium iterations.
- Subroutine STORE to store the results for plotting.

Subroutine DATAHT: Subroutine DATAHT, called by subroutine GM2D, reads Data Sets 2 through 15 as described in Appendix A. It also prints all the input information, calls subroutine SURF to identify the boundary segments and boundary nodes, and calls subroutines READR and READN to automatically generate real and integer numbers, respectively. DATAHT calls subroutine LNDGEN to generate the relationships between node number and equation number when pointwise iteration solution strategies are used.

Subroutine SURF: Subroutine SURF, called by subroutine DATAHT, identifies the boundary sides, sequences the boundary nodes, and computes the directional cosine of the surface sides. The mapping from boundary nodes to global nodes is stored in NPB(I), where NPB(I) is the global node number of the i-th boundary node. The element number associated with the boundary sides is stored in NBE. 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. The information contained in NPB, NBE, ISB, DCOSXB, and DCOSZB, 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: This subroutine is called by subroutine 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.

Subroutine READN: This subroutine is called by subroutine DATAHT to generate integers for Data Sets 5(2), 9, 13(1)(c), 13(2)(c), 14(b), 14(c), 15(b), and 15(c) in Appendix A.

Subroutine LNDGEN: This subroutine is called by subroutine DATAHT to preprocess the pointer array needed to assemble the global matrix in compressed form when pointwise solution methods are used. The pointer array generated in this subroutine is the global node connectivity (stencil) GNOJCN(J,N). Here GNOJCN(J,N) is the global node number of the J-th node connected to the global node N. This pointer array is generated based on the element connectivity IE(M,J), which is the global node number of the J-th node of element M.

Subroutine CONECT: This subroutines is called by subroutine GM2D to re-arrange LRN(J,N) such that LRN(1,N) = N.

Subroutine DATACS: This subroutine, called by subroutine GM2D, reads Data Sets 16 through 22 as described in Appendix A and prints out all input information.

Subroutine AFABTA: Subroutine AFABTA is called by subroutine 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 INTERP: This subroutine is called by subroutine GM2D to compute the functional values (such as the Dirichlet concentrations, element source/sinks, point source/sinks, and incoming concentrations of fluids through variable boundary segments) at a particular time for all profiles. It uses linear interpolation of tabular data.

Subroutine OCSPIT: This subroutine, called by subroutine GM2D, calculates the total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components and also calculates the negative logarithm of the concentrations of all component species by calling the subroutine EQMOD. The input to subroutine OCSPIT is the total analytical concentrations of all components and their identification numbers.

Subroutine EQMOD: Subroutine EQMOD is called by subroutine OCSPIT to schedule the chemical equilibrium computations. It initializes the concentrations of all product species, given the estimate of component species concentrations from subroutine OCSPIT. It then calls subroutine EQUIL to solve the set of algebraic equations for mole balances and chemical equilibrium reactions. Then EQMOD calls subroutine TOTDSP to compute the log of free species concentrations and total dissolved, total sorbed, and total precipitated concentrations of all components. Finally it calls subroutine LPOUT to print chemical species distributions.

Subroutine EQUIL: This subroutine, called by subroutine EQMOD, solves the system of

nonlinear algebraic equations specified by Equations (3.1.4) through (3.1.12) using the Newton-Raphson method for nonlinear rootfinding. For each iteration, subroutine EQUIL calls:

- Subroutine ACOEF to compute the activity coefficients for all species.
- Subroutine MODIFK to calculate the modified equilibrium constants for all product species.
- Subroutine RESIDU to evaluate the residuals of all governing equations.
- Subroutine JACOBI to compute the Jacobian of all governing equations.
- Subroutine DGELG to solve the Jacobian matrix with full pivoting.
- Subroutines DISOLV, INDEXX, NPPT, TOTDSP, and LPOUT are also called by EQUIL.

Subroutine ACOEF: This subroutine is called by subroutine EQUIL to compute the ionic strength and activity coefficients for all species.

Subroutine MODIFK: This subroutine is called by subroutine EQUIL to calculate the modified equilibrium constants for all product species.

Subroutine RESIDU: This subroutine is called by subroutine EQUIL to calculate residuals of the nonlinear algebraic equations governing chemical equilibrium. Residuals are calculated in subroutine RESIDU for

- Mole balance equations for aqueous components and adsorbent components.
- Precipitation-dissolution reaction equations.

Residuals for equations governing the balance of c_o and c_b are computed in subroutine RADC. Residuals for the ion-exchanged reactions are computed in subroutine RIES.

Subroutine RADC: This subroutine is called by subroutine RESIDU to calculate residuals for equations governing the charge balance on the "o" and "b" plane.

Subroutine RIES: This subroutine is called by subroutine RESIDU and subroutine JIES to calculate residuals for ion-exchange reactions and cation ion-exchange capacity constraint.

Subroutine JACOBI: This subroutine, called by subroutine EQUIL, evaluates the Jacobians of the nonlinear algebraic equations governing chemical equilibrium. Jacobians are evaluated in subroutine JACOBI for

- Mole balance equations for aqueous components and adsorbent components.
- Precipitation-dissolution reaction equations.

JACOBI calls:

- Subroutine JADC to obtain Jacobians for equations governing the balance of the c_o and c_b.
- Subroutine JIES to obtain Jacobians for the ion-exchanged reactions.

Subroutine JADC: This subroutine, called by subroutine JACOBI, computes the Jacobian of the equations governing the charges on the "o" and "b" planes. Detailed derivation of the Jacobian for these two equations can be found in Section 3.3.5.

Subroutine JIES: Subroutine JIES, called by subroutine JACOBI, computes the Jacobian for ion-exchange reactions and cation ion-exchange capacity constraint. Residuals for the ion-exchange reactions are computed in the subroutine RIES.

Subroutine DGELG: This subroutine is called by subroutine EQUIL to solve the Jacobian matrix equation using Gaussian elimination with full pivoting.

Subroutine DISOLV: This subroutine is called by subroutine EQUIL to determine the number of precipitated species allowed to dissolve.

Subroutine INDEXX: This subroutine is called by subroutine EQUIL to index the saturation value among all potential species that are subject to precipitation-dissolution reactions. If dissolution is to occur, the species with the lowest saturation value must dissolve first.

Subroutine NPPT: This subroutine is called by subroutine EQUIL to determine the number of precipitable species allowed to precipitate without violating the phase rule.

Subroutine TOTDSP: This subroutine, called by subroutines EQMOD and EQUIL, evaluates the log of free species concentrations, total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components.

Subroutine LPOUT: This subroutine is called by subroutines EQMOD and EQUIL to print chemical species distributions at user-specified nodes at user-specified time intervals. The information printed includes concentrations, modified equilibrium constants, and stoichiometric coefficients of all species.

Subroutine NODVAL: This subroutine is called by GM2D to convert the values of the initial cation ion exchange sites and the surface area and capacitance of adsorbing sites, the moisture content, the water capacity, and the bulk density at elements into those at nodal points.

Subroutine ADVWRK: This subroutine is called by GM2D to prepare all the working arrays to be further used in ELMTRC. This subroutine is called only when the transient simulation is required.

Subroutine BTGN: This subroutine is called by GM2D to control the process of backward particle tracking starting from global nodes. 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. During the particle tracking, this subroutine calls ELMTRC to track a particle in the element being considered. In order to make the particle tracking complete and remedy the given velocity field error on the unspecified boundaries, this subroutine calls ALGBDY to continue tracking particles along the unspecified boundaries. At the end of each particle tracking, this subroutine calls BASE1 to calculate base functions such that the Lagrangian concentration can be computed by interpolation with those base function values.

Subroutine ELMTRC: This subroutine is called by BTGN to implement particle tracking in one element. In order to increase the accuracy of particle tracking, regular refinement is considered to make the element be composed of as many subelements as wished, and the tracking is executed one subelement by one subelement. This subroutine is designed to control the process of particle tracking among the subelements. During the particle tracking, this subroutine calls (1) TRACK1 to track a particle in the subelement being considered if that particle is right standing on a node of the subelement, and (2) TRACK2 to track a particle if that particle is not on any nodes of the subelement. The tracking will not be stopped until either the tracking time is completely consumed or the particle encounters a side of the element. ELMTRC also calls subroutines XSI2D and BASE1 the local coordinate and the base function, respectively.

Subroutine TRACK1: This subroutine is called by ELMTRC to compute the particle tracking in a specified subelement when the source point coincides with a global node of the element. This subroutine determines (1) whether the particle would move backwards into the element or not, (2) which side of the element the particle would head onto if the particle does move backwards into this element, and (3) where the target point would be. After determining which side the particle is going to move onto, this subroutine computes the exact location of the target point on the side analytically. For accuracy, using the average velocity of both the source point and the target point to locate the target point is firstly considered in the subroutine. 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. Track 1 calls subroutine BASE1 to compute the base function values.

Subroutine TRACK2: This subroutine is called by ELMTRC to compute the particle tracking in a specified subelement when the source point does not coincide with a global node of the element. This subroutine determines (1) whether the particle would move backwards into the element or not, (2) which side of the element the particle would head onto if the particle does move backwards into this element, and (3) where the target point would be. After determining which side the particle is going to move onto, this subroutine computes the exact location of the target point on the side analytically. For accuracy, using the average velocity of both the source point and the target point to locate the target point is firstly considered in the subroutine. 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. Track 1 calls subroutine BASE1 to compute the base function values.

Subroutine ALGBDY: This subroutine is called by BTGN to control the process of backward

particle tracking along the unspecified boundaries. In the subroutine, the particle 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. For accuracy, using the average velocity of both the source point and the target point to locate the target point is firstly considered in the subroutine. 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.

Subroutine BASE1: This subroutine is called by BTGN, TRACK1, TRACK2, and ELMTRC to compute the base function values associated with a specified point based on the given two-dimensional global coordinates. For the cases of quadrilateral elements, it calls XSI2D to calculate the local coordinates, and computes base functions with these determined local coordinates. For the cases of triangular elements, the base functions can be analytically determined based on the given global coordinates.

Subroutine XSI2D: This subroutine, called by subroutines ELMTRC and BASE1, computes the local coordinate of an element given the global coordinate within that element. With the local coordinate, the Lagrangian concentration can then easily be interpolated from the concentrations at the nodes of the element.

Subroutine ADVBC: This subroutine, called by subroutine GM2D, implements the boundary conditions. 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. Hence the Lagrangian concentration for the boundary node has already been computed in subroutine BTGN and the implementation for such a boundary segment is bypassed. Thus, subroutine BTGN must be called before subroutine ADVBC. For variable boundaries, the concentration of incoming fluid is specified if the flow is directed into the region. The Lagrangian concentration is then calculated according to

$$C_i^* = \int_{B_v^-} N_i V_n C_{in} dB \Big/ \int_{B_v^-} N_i V_n dB \quad , \tag{4.2.1}$$

where

C_i^* = the Lagrangian concentration at the boundary node i.
V_n = the normal component of Darcy's velocity.
C_{in} = the concentration of incoming fluid.

ADVBC calls Q2ADVB to evaluate a boundary segment integration.

Subroutine Q2ADVB: This subroutine, called by subroutine ADVBC, evaluates the following integration for a boundary segment:

$$RIQ(i) = \int N_i V_n C_{in} dB \tag{4.2.2}$$

and

$$RLQ(i) = \int N_i V_n dB \quad , \tag{4.2.3}$$

where

RIQ(i) = the rate of chemical passing through node i.
RLQ(i) = the rate of water passing through node i.

Subroutine TACADC: This subroutine is called by subroutine GM2D to compute total concentrations of all adsorbent components and the number of equivalents. It basically solves Equations (3.1.2) and (3.1.3) by an implicit FDM.

Subroutine ASEMBL: This subroutine is called by subroutine GM2D and calls subroutines Q4 and Q3 to evaluate the element matrices. It then sums over all element matrices to form the compressed global matrices MMTRX, SMTRX, VMTRX, and DMTRX and the global load vector RLD.

Subroutines Q4 and Q3: These subroutines are called by subroutine ASEMBL to compute the element matrix given by

$$QA(I,J) = \int_{R_e} N_i^e \theta \, N_j^e dR \quad , \tag{4.2.4}$$

$$QB(I,J) = \int_{R_e} (\nabla N_i^e) \cdot \theta \mathbf{D} \cdot (\nabla N_j^e) dR \quad , \tag{4.2.5}$$

$$QV(I,J) = \int_{R_e} W_i^e \mathbf{V} \cdot (\nabla N_j^e) dR \quad , \tag{4.2.6}$$

$$QQ(I,J) = \int_{R_e} N_i^e Q \, N_j^e dR \quad , \tag{4.2.7}$$

and

$$QC(I,J) = \int_{R_e} N_i^e \frac{\partial \theta}{\partial t} N_j^e dR \quad . \tag{4.2.8}$$

Subroutine Q4 computes the integration in Equations (4.2.4) through (4.2.8) for quadrilateral elements, and Q3 computes those for triangular elements. Subroutines Q4 and Q3 also calculate the element load vector given by

$$QR(I,K) = \int_{R_e} N_i^e QC_k^{in} dR \quad , \quad k = 1,2,...,N_k \quad , \tag{4.2.9}$$

where C_k^{in} is the source concentration of the k-th aqueous component. Subroutine Q4 also calls subroutine SHAPE.

Subroutine SHAPE: This subroutine is called by Subroutine Q4 to evaluate the base and weighting functions and derivatives of the base functions at a Gauss point.

Subroutine HYDROT: This subroutine is called by subroutine GM2D to perform hydrologic transport computations. When subroutine HYDROT is called, it simulates the transport of conservative (i.e., nonreactive) chemical components. Subroutine HYDROT makes an initial estimate for all nonconservative chemical components by solving the transport equations and simulates the transport of nonconservative chemical components for the new iterates. Subroutine HYDROT also calls:

- Subrouting EQNGEN to produce the matrix equation from the compressed matrix and load vector for each chemical component.
- Subroutine BC to implement the boundary conditions.
- Subroutine SOLVE or subroutine PISS to solve the resulting matrix equations with direct elimination method or pointwise iteration methods.
- Subroutines PPCG, ILUCG, MICPG and SSORG.

Subroutine EQNGEN: This subroutine, called by subroutine HYDROT, generates the matrix equation for an aqueous component from the compressed global matrices and the global load vectors. It uses the array of the node connectivity produced in subroutine LNDGEN to form a banded matrix and load vector for all aqueous components.

Subroutine BC: This subroutine, called by subroutine HYDROT, controls Dirichlet and variable-boundary condition incorporation into the system of equations. 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 also implements the variable-boundary conditions, calling subroutine Q2VB to compute the contributions of a variable-boundary segment to the global matrix equation.

Subroutine Q2VB: This subroutine is called by subroutine BC to compute a two-by-two matrix, BQ, and a load vector, RQ, for each variable-boundary segment as follows:

$$BQ(I,J) = -\int_{R_e} N_i^e (\mathbf{n} \cdot \mathbf{V}) N_j^e \, dB \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) < 0 \quad , \tag{4.2.10}$$

$$BQ(I,J) = 0 \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) \geq 0 \quad , \tag{4.2.11}$$

$$RQ(I) = \int_{R_e} N_i^e (\mathbf{n} \cdot \mathbf{V}) C_{IN} \, dB \quad , \text{ if } (\mathbf{n} \cdot \mathbf{V}) < 0 \quad , \tag{4.2.12}$$

and

$$RQ(I) = 0 \quad , \text{ if } (\mathbf{n}\cdot\mathbf{V}) \geq 0 \quad . \tag{4.2.13}$$

Subroutine SOLVE: This subroutine is called by subroutine HYDROT to solve a matrix equation of the type

$$[C]\{x\} = \{y\} \quad , \tag{4.2.14}$$

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: This subroutine is called by subroutine HYDROT to solve Equation (4.2.14) with point iteration solution strategies when the user sets IPNTS = 1 in Data Set 2 (refer to Appendix A).

Subroutine PPCG: This subroutine is called by the subroutine HYDROT, if necessary, to solve the linearized matrix equation with the preconditioned conjugate gradient method using the polynomial as a preconditioner. It calls to POLYP to invert the preconditioner.

Subroutine POLYP: This subroutine is called by the subroutine PPCG to solve for a modified residual that will be used in the preconditioned conjugate gradient algorithm.

Subroutine ILUCG: This subroutine is called by the subroutine HYDROT, if necessary, to solve the linearized matrix equation with the preconditioned conjugate gradient method using the incomplete Cholesky decomposition as a preconditioner. It calls to LLTINV to invert the preconditioner.

Subroutine LLTINV: This subroutine is called by the subroutine ILUCG to solve for a modified residual that will be used in the preconditioned conjugate gradient algorithm.

Subroutine MICPCG: This subroutine is called by the subroutine HYDROT, if necessary, to solve the linearized matrix equation with the preconditioned conjugate gradient method using the modified incomplete Cholesky decomposition as a preconditioner. It calls to MICP to invert the preconditioner.

Subroutine MICP: This subroutine is called by the subroutine MICPCG to solve for a modified residual that will be used in the preconditioned conjugate gradient algorithm.

Subroutine SSORCG: This subroutine is called by the subroutine HYDROT, if necessary, to solve the linearized matrix equation with the preconditioned conjugate gradient method using the

symmetric successive over-relaxation as a preconditioner. It calls to SSORP to invert the preconditioner.

Subroutine SSORP: This subroutine is called by the subroutine SSORCG to solve for a modified residual that will be used in the preconditioned conjugate gradient algorithm.

Subroutine SFLOW: This subroutine is called by subroutine GM2D to compute mass fluxes through all open boundary nodes.

Subroutine CALKD: This subroutine is called by GM2D to calculate the equivalent K_d for all components.

Subroutine PRINTT: This subroutine, called by subroutine GM2D, is used 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.

Subroutine PRITER: This subroutine, called by subroutine GM2D, is used to print the intermediate total analytical concentrations of all components between hydrologic transport and chemical equilibrium iterations.

Subroutine STORE: This subroutine, called by subroutine GM2D, is used to store the transport variables on Logical Unit 12. This data is intended for plotting and includes region geometry and transport variables.

5.0 ADAPTATION OF LEHGC1.1 TO SITE SPECIFIC APPLICATIONS

LEHGC1.1 is available in ASCII text format and can be run on any computer with sufficient memory after compiling with a standard FORTRAN 77 compiler. Memory requirements will vary depending on the field sizes assigned to the control integers discussed below. The following describes the maximum control integers that must be defined 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, 39 maximum control integers must be assigned with the PARAMETER statements in the MAIN program to specify the size of the problem. The listing and 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.
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 DELT changes.

5.1.3 Maximum Control Integers for Source/Sinks

MXSELK = maximum number of source elements.
MXSPRK = maximum number of source profiles.
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 rainfall profiles.
MXVDPK = maximum number of data points on each rainfall 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.

5.1.7 Maximum Control Integers for Transport Components

MAXHK = maximum number of transport components
MAXH1K = maximum number of transport components plus 1 (=MAXHK+1)

5.1.8 Maximum Control Integers for Geochemical Reactions

MAXNK = maximum number of components.
MAXMK = maximum number of species.
MAXMZK = maximum number of ion-exchanging species.
MAXMPK = maximum number of species allowed for precipitation-dissolution.
MAXPDK = maximum number of product species (MAXMK - MAXNK).
MXNIXK=maximum number of ion-exchange sites.
MXNSBK=maximum number of adsorbing sites.
MAXEQK = maximum number of equations (= MAXNK + MAXMZK + MAXMPK).
MAXN1K = maximum number of components plus 1 (= MAXNK + 1).

5.1.9 Maximum Control Integers for Subelement 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 connecting number 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 element sides each on the right and left sides and 88 element sides each on the top and bottom sides of the region, for a total of 204 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 33.)

Assume that we are dealing with 12 transport components (i.e., MAXHK = 12) Let us further assume that we will deal with 12 chemical components, (i.e., MAXNK = 12). Among these 12 components, there will be chemical reactions that result in a maximum of 78 product species, 10 of which may be involved ion-exchange and eight of which are potentially precipitation-dissolution species. Thus, we have MAXPDK = 78, MAXMZK = 10, MAXMPK = 8, and MAXMK = MAXPDK + MAXNK = 90. The maximum number of equations will be MAXEQK = MAXNK + MAXMZK + MAXMPK = 30. If we have only 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 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. 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 eight data points. With these descriptions, we have MXVPRK = 3 and MXVDPK = 8.

In this version of the code, there can be up to eight material properties per material, so MXMPMK = 8. 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.

Finally, to accurately perform node 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:

```
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=8)
PARAMETER (MXMATK=3,MXMPMK=8)
PARAMETER (MAXHK=12,MAXH1K=MAXHK+1)
PARAMETER (MAXNK=12,MAXMZK=10,MAXMPK=8,MAXPDK=78)
PARAMETER(MXNIXK=3,MXNSBK=4)
PARAMETER (MAXEQK=MAXNK+MAXMZK+MAXMPK)
PARAMETER (MAXMK=MAXNK+MAXPDK,MAXN1K=MAXNK+1)
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.

5.3 Running LEHGC: Compilers, Input Devices and Output Devices

LEHGC1.1 has been successfully compiled and run on Sun workstations (SPARCstation 20) with the SPARCompiler Fortran Version 3.0.1 for Solaris. The code should compile and run on any equivalent platform.

Five logical units are needed to execute LEHGC1.1. 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 $\geq$ 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 of a restarting job. 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.

LEHGC1.1, will prompt the user five times for file names as follows:

PLEASE TYPE IN YOUR INPUT DATA FILE NAME. (Logical Unit 15).

THEN YOUR OUTPUT FILE NAME. (Logical Unit 16).

THEN YOUR BINARY FLOW-VARIABLES INPUT FILE NAME. (Logical Unit 11)

THEN YOUR BINARY STORAGE FILE NAME. (Logical Unit 12)

THEN YOUR BINARY RESTART FILE NAME. (Logical Unit 13)

A file name must be entered after each prompt. If an existing file name is chosen for the output file or binary storage file, the existing file will be overwritten.

When a problem has flow variables defined by the input file (Data Set 16), a binary flow-variable file (Logical Unit 11) will not be used by the code, but a dummy file name must be entered at the prompt. If the flow variables are not defined by the input file, a binary flow-variables file must be used. Similarly, when the restart feature is not used, a dummy file name must be entered at the prompt.

5.4 Error Messages

The following error messages are printed as stated in the source code. When an error occurs while running the code, the words in single quotes are printed. Variable names with no quotes are replaced by the value of the variable. The integer or real number format, for example I5 or D12.4, is replaced with the value for an integer or real number variable respectively. A space format, such as 5X, is replaced by spaces--in this case five. A slash indicates a new line.

5.4.1 Errors in Input File

' *** ERROR IN EXECUTING READR SINCE NODES .NE. NNP: STOP ***'

This error message is generated by subroutine READR when reading Dataset 7 or 11. The number of nodes defined in Dataset 7 or 11 does not equal the number of nodes in Dataset 2,

variable NNP. Correct Dataset 7, 11 and/or 2 so that these are equal.

' *** NNP .GT. MAXNOD IN EXECUTING READR: STOP'

This error message is generated by subroutine READR when reading Dataset 7. The number of nodes defined in Dataset 7 exceeds the maximum number of nodes defined by the code, variable MAXNPK. Correct Dataset 7, or increase the value of MAXNPK and recompile.

' ERROR IN READING',I5,' ELEMENT CARD STOP'

This error message is generated by subroutine DATAHT when reading Dataset 8. The global element number, variable MI of Dataset 8, is printed in the "I5" integer space. Check element ordering.

' ERROR IN MATERIAL TYPE CODE FOR ELEMENT ',I5

This error message is generated by subroutine DATAHT when reading Dataset 8. The global element number is printed in the "I5" integer space. There is an invalid material number for this element (variable IE(MI,5)). Correct the material number.

'***',I5,'-TH NODE HAS',I3,' NODES SURROUNDING IT WHICH IS MORE THAN MXJBD - 1 =',I3,' STOP ***'

This error message is generated by subroutine LNDGEN. The number of nodes (variable KONT, printed in the first "I3" integer space) connected to the current node (variable NP, printed in the "I5" integer space) exceeds the maximum defined in the code, variable JBND (printed in the second "I3" integer space). Correct the mesh, or increase MXJBDK and recompile.

'*** NUMBER OF ELEMENTS CONNECTING TO NODE ',I6,' IS',I3, ' WHICH IS GREATERTHAN MXKBD =',I3,' STOP'

This error message is generated by subroutine LNDGEN. The number of elements (variable NMAX, printed in the first "I3" integer space) connected to the current node (variable NOCUR, printed in the "I6" integer space) exceeds the maximum defined in the code by the code, variable MXKBD (printed in the second "I3" integer space). Correct the mesh, or increase MXJBDK and recompile.

'*** ERROR IN EXECUTING READN SINCE NTYPES .NE. NTYPE: STOP ***'

This error message is generated by subroutine READN when reading Dataset 9. The number of elements with corrected material types in Dataset 9 does not equal the number of elements with material type correction defined in Dataset 2, variable NCM. Correct Dataset 9 or 2 so that these are equal.

' *** NTYPE .GT. MXTYP IN EXECUTING READN: STOP'

This error message is generated by subroutine READN when reading Dataset 9. The number of elements with corrected material types in Dataset 9 exceeds the maximum number of elements defined by the code, variable MAXELK. Correct Dataset 9, or increase the value of MAXELK and recompile.

' ERROR IN READING RS-ELEMENT-SIDES'

This error message is generated by subroutine DATAHT when reading Dataset 14. The number of variable-boundary sides defined in Dataset 14, part d, does not equal the number of variable-boundary sides defined in Dataset 12, variable NVES. Correct Dataset 14 or 12 so that these are equal.

' *** ERROR IN READING VELOCITY SINCE NODES .NE. NNP: STOP ***'

This error message is generated by subroutine GM2D when reading Dataset 16. The number of nodes at which velocities are defined in Dataset 16 does not equal the number of nodal points defined in Dataset 2, variable NNP. Correct Dataset 26 or 2 so that these are equal.

' *** NNP .GT. MAXNP IN READING VELOCITY: STOP'

This error message is generated by subroutine GM2D when reading Dataset 16. The number of nodes at which velocities are defined in Dataset 16 exceeds the maximum number of nodes defined by the code, variable MAXNPK. Correct Dataset 16, or increase the value of MAXNPK and recompile.

' *** ERROR IN READING MOISTURE CONTENT SINCE NODES .NE. NEL: STOP ***'

This error message is generated by subroutine GM2D when reading Dataset 16. The number of elements at which moisture contents are defined in Dataset 16 does not equal the number of elements defined in Dataset 2, variable NEL. Correct Dataset 16 or 2 so that these are equal.

' *** NEL .GT. MAXEL IN READING MOISTURE CONTENT: STOP'

This error message is generated by subroutine GM2D when reading Dataset 16. The number of elements at which moisture contents are defined in Dataset 16 exceeds the maximum number of elements defined by the code, variable MAXELK. Correct Dataset 16, or increase the value of MAXELK and recompile.

'NONS.NE.NCOUNT IN DATAIO, PLEASE CHECK BOTH THE TOTAL NUMBER OF ADSORBENT SPECIES AND THE NUMBER OF ADSORBENT SPECIES IN EACH SITE ------ STOP RUNNING'

This error message is generated by subroutine DATACS while reading Dataset 20. The number of adsorbent components defined by Dataset 20 is not equal to the number of component species defined in Dataset 17, variable NONS. Correct Dataset 17 or 20 so that these are equal.

'NOMZ.NE.NCOUNT IN DATAIO, PLEASE CHECK BOTH THE TOTAL NUMBER OF ION-EXCHANGED SPECIES AND THE NUMBER OF ION-EXCHANGED SPECIES IN EACH SITE ------ STOP RUNNING'

This error message is generated by subroutine DATACS while reading Dataset 21. The number of ion-exchanged species defined by Dataset 21 is not equal to the number of ion-exchanged species defined in Dataset 17, variable NOMZ. Correct Dataset 17 or 21 so that these are equal.

'NUMBER OF ION-EXCHANGING SPECIES IS NOT CORRECT KCOUNT =',I3,' IS NOT EQUAL TO NOMZ =',I3,' STOP'

This error message is generated by subroutine DATACS while reading Dataset 25. the number of ion-exchanged species defined in Dataset 25 (printed in the first "I3" integer space) does not equal the number of ion-exchanged species defined in Dataset 17, variable NOMZ (printed in the second "I3" integer space). Correct Dataset 17 or 25 so that these are equal.

'*** ',I2,' PAIRS OF PRECIPITATED SPECIES LISTED ABOVE HAS SAME S.C.: STOP'

This error message is generated by subroutine DATACS while reading Dataset 27. The number of pairs of precipitated species printed in the "I2" integer space, have the same stoichiometric coefficients. Correct the coefficients.

5.4.2 Errors in Problem Setup

' BANDWIDTH =',I4,' EXCEEDS MAX. ALLOWABLE =',I4

This error message is generated by subroutine GM2D. The computed bandwidth of the problem, IBAND in GM2D, exceeds the maximum bandwidth defined by the code, variable MAXBWK. Check the problem bandwidth (described in Section 5.2) and increase the value of MAXBWK if needed and recompile.

'1'/5X,'*** WARNING: NONE OF THE CONNECTING NODE IN EQUATION',I3,/5X,' *** IS CORRESPONDING TO ',I5,'-TH ELEMENT-S',I2, 2'-TH NODE; STOP ****'

This error message is generated by subroutine ASEMBL. While attempting to assemble the global matrices, SMTRX and MMTRX, and the global load vector, RLD, none of the connecting nodes in equation NI (printed in the "I3" integer space) corresponds to element M (printed in the "I5" integer space) or node JQ (printed in the "I2" integer space). Check the problem mesh and connectivity.

5.4.3 Errors computing chemical equlibrium

'*** KTER =',I4,' ITER =',I4,' LTER =',I5,' IER =',I5 '*** IF IER .EQ. -1, EXACT SINGULARITY, STOP'

This error message is generated by subroutine EQUIL. While solving for the new concentrations, an exact singularity in the matrix was encountered (iteration counters and error flag are printed in the integer spaces). Correct the chemical portion of the problem definition. Possible causes include 1) phase rule violation (i.e. too many Type 3 species in Data Set 10 and 24 - 27), or 2) initial guesses for species concentrations that are too small or too large.

'*** NO CONVERGENCE: KTER =',I4,' ITER =',I4,' LTER =',I5/1X,'*** NITERC =',I4,', NFAIL =',I3,', NFAILS =',I3,', ABSOLUTE DIFMAX =',1PD12.4

This error message is generated by subroutine EQUIL. Convergence was not achieved in the KTER-th loop of the chemical equilibrium calculation after the number of iterations defined by NITERC. Check chemical portion of problem definition, or adjust the convergence criteria in Dataset 22. Initial guesses for species concentrations may be too small or too large causing the numerical solution to oscillate. If running adsorption problems, check the relationship between total SOH, surface area and interlayer capacitances to see if they are consistent. Adjust the total SOH to ensure that concentration of calculated free SOH does not become zero. If running ion exchange problems check that the CEC and concentrations of ion-exchange sites are consistent. If running redox problems make sure that the correct redox member was chosen as the component for the specified pe.

5.4.4 Errors in Computing the Mass Flow Through Out-Flow Boundaries

'** ',I3,'-TH VARIABLE BOUNDARY SIDES FIRST NODE =',I3,', WHICH IS GREATER THAN MXVNP =',I3,': STOP IN SFLOW **'

'** ',I3,'-TH VARIABLE BOUNDARY SIDES SECOND NODE =',I3,', WHICH IS GREATER THAN MXVNP =',I3,': STOP IN SFLOW **'

The 2 error messages above, generated by subroutine SFLOW, indicate a problem with variable-boundary nodes and sides defined by Dataset 12, variables NVNP and NVES, and Dataset 14. The variables printed are the number of the variable-boundary side and its node that have exceeded the limits set by the third variable. Check these node and side definitions, and increase the value of MXVNPK if needed and recompile.

'** ',I3,'-TH VARIABLE BOUNDARY SIDES FIRST NODE =',I3,', WHICH IS GREATER THAN MAXNP =',I3,': STOP IN SFLOW **'

'** ',I3,'-TH VARIABLE BOUNDARY SIDES SECOND NODE =',I3,', WHICH IS GREATER THAN MAXNP =',I3,': STOP IN SFLOW **'

The two error messages above, generated by subroutine SFLOW, indicate a problem with variable-boundary nodes and sides defined by Dataset 12, variables NVNP and NVES, and Dataset 14. The variables printed are the number of the variable-boundary side and its node that have exceeded the limits set by the third variable. Check these node and side definitions, and increase the value of MAXNPK if needed and recompile.

5.4.5 Errors in Backward Tracking

'ERROR OCCURRED AT BTGN --- THE NODE,',N,' CAN NOT BE TRACKED'

'ERROR OCCURRED AT BTGN--N1=',N1,'N2=',N2

'ERROR OCCURRED AT ALGBDY ---- NO NEXT BDY. SEG.'

'ERROR OCCURRED AT ELETRC---1'

'ERROR OCCURRED AT ELETRC---2'

'ERROR OCCURRED AT ELETRC---3'

'ERROR OCCURRED AT TRACK1 --- IBF= ',IBF

'ERROR OCCURRED AT TRACK1 --- BOTH DIRECTIONS OF VELOCITY ARE ZERO'

'ERROR OCCURRED AT TRACK1 --- IBF= ',IBF,' DT= ',DT

'ERROR OCCURRED AT TRACK2 --- IBF= ',IBF

'ERROR OCCURRED AT TRACK2 --- BOTH DIRECTIONS OF VELOCITY ARE ZERO'

'ERROR OCCURRED AT TRACK2 --- IBF= ',IBF,' DT= ',DT

'* FAIL TO CONVERGE IN COMPUTING XSI AND ETA: STOP ITER =',I3,', NITER =',I3,', M =',I4, 'DIFMAX =',D15.6,', EPS =',D15.6

The 13 error messages above, generated by subroutines BTGN, ALGBDY, ELMTRC, TRACT1, TRACK2, or XSI2D, indicate the code's inability to track one or more nodal points. Check the mesh and velocity field for irregularities.

5.4.6 Errors in Solving the Transport Equations

1H0/18X,' ::: WARNING: NO CONVERGENCE IN PISS AFTER ', I4,' ITERATIONS'

/18X,' NPITER =',I4,' ABSERR =',1PD12.4/18X, ' RELERR =',1PD12.4,'
NNCVN =',I4

This error message is generated by subroutine PISS. The pointwise iteration solution did not converge. The information printed in the three integer and two real number spaces are: the final iteration number, the number of iterations defined by the variable NPITER of Dataset 2, the computed values of an absolute and relative error that are compared to the variable TOLA of Dataset 3, and the number of nodes at which convergence was not obtained. Check the problem set up and modify the solution procedure parameters in Datasets 2 and 3 if needed.

'** WARNING: NO CONVERGENCE AT',I4,'-TH TIME STEP AFTER',I4,'
ITERATIONS'/8X 'NITER =',I4,' DIFMAX =',D12.4,' TOLB =',D12.4

This error message is generated by subroutine GM2D. The problem solution did not converge at the time step printed after the number of iterations printed. The maximum number of iterations, variable NITER is defined in Dataset 2. DIFMAX is the maximum relative error which must be less than that specified by variable TOLA of Dataset 3 (printed as TOLB). Check the problem set up and modify the solution procedure parameters in Datasets 2 and 3 if needed.

6.0 SAMPLE PROBLEMS

In this section, nine sample problems are presented to illustrate the use of LEHGC1.1 in a variety of applications. Four of these problems (Nos. 4, 5, 7 and 8) were previously presented in the user's manual for HYDROGEOCHEM (Yeh and Tripathi, 1991). In that manual, six problems test the geochemical equilibrium module only, one tests the hydrologic transport module only, and the other three test the coupled transport and geochemical equilibrium. The four problems involving transport are presented in this manual. Problems 4, 5, and 7 are used to benchmark LEHGC1.1 against HYDROGEOCHEM for one-dimensional cases. Using the upstream finite-element option in HYDROGEOCHEM (Yeh and Tripathi, 1991) and a small time-step size so that the mesh Courant number is less than 1, simulations with HYDROGEOCHEM and LEHGC should be identical (Yeh and Gwo, 1990). Problem 8 is a two-dimensional problem involving complexation and precipitation and illustrates LEHGC's ability to solve advection-dominated transport problems.

Problems 1, 2, 3, 6, and 9 are new problems for this manual. Problems 1 and 2 describe advection and diffusion, respectively and are used to benchmark LEHGC1.1 against an analytical solution (advection), a numerical solution (diffusion) and experimental data (diffusion). Problem 3 describes the effects of matrix diffusion on solute transport through fractured media under several conditions. LEHGC1.1 results are compared to those of analytical and numerical solutions. Problem 6 is based on an international benchmark problem from the CHEMVAL 2 project. It describes dissolution of a cement column by groundwater and involves one-dimensional advection, complexation, dissolution and precipitation. The problem illustrates that groundwater analyses reported in the literature are often not described in a form that can be directly used as input data for LEHGC1.1. Preliminary speciation calculations were required to prepare the LEHGC input from the CHEMVAL 2 problem description. Problem 9 describes colloid transport, advection, adsorption and complexation.

Each example includes a description of the problem, thermodynamic data for the chemical species/minerals considered, and descriptions of the results. The input data sets for the examples are presented in tabular form. Comments follow some data lines where format allows, and are not required. The output for the problems can be obtained from the first author on floppy diskettes to allow readers to compare their output from LEHGC1.1 to our results.

6.1 Problem 1: Test Problem for Advection

An analytical solution described by Martinez and Bixler (1983) was used to benchmark the use of LEHGC 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

$$C(z,0) = 0 \tag{6.1.2}$$
$$C(0,t) = 1, \qquad t>0 \tag{6.1.3}$$
$$C(l,t) = 0, \qquad l\Rightarrow\infty \tag{6.1.4}$$

is given as

$$C(z,t) = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{z-vt}{2\sqrt{Dt}}\right) + \exp\left(\frac{vz}{D}\right)\operatorname{erfc}\left(\frac{z+vt}{2\sqrt{Dt}}\right)\right] \tag{6.1.5}$$

In the application discussed 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 sample problem, 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. Figure 6.1 illustrates the column, element and node numbering, direction of flow and x/z axes. Note that the vertical axis is the z-axis and that 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. Figure 6.2 compares the concentration profile of the analytical solution to that computed using LEHGC at times of t = 5, 10 and 30 days. There is good agreement between the analytical and numerical solution over that portion of the domain (Depth < 60 cm) not influenced by the bottom boundary (treated as an infinite boundary in the analytical solution and by a finite one in the LEHGC calculation).

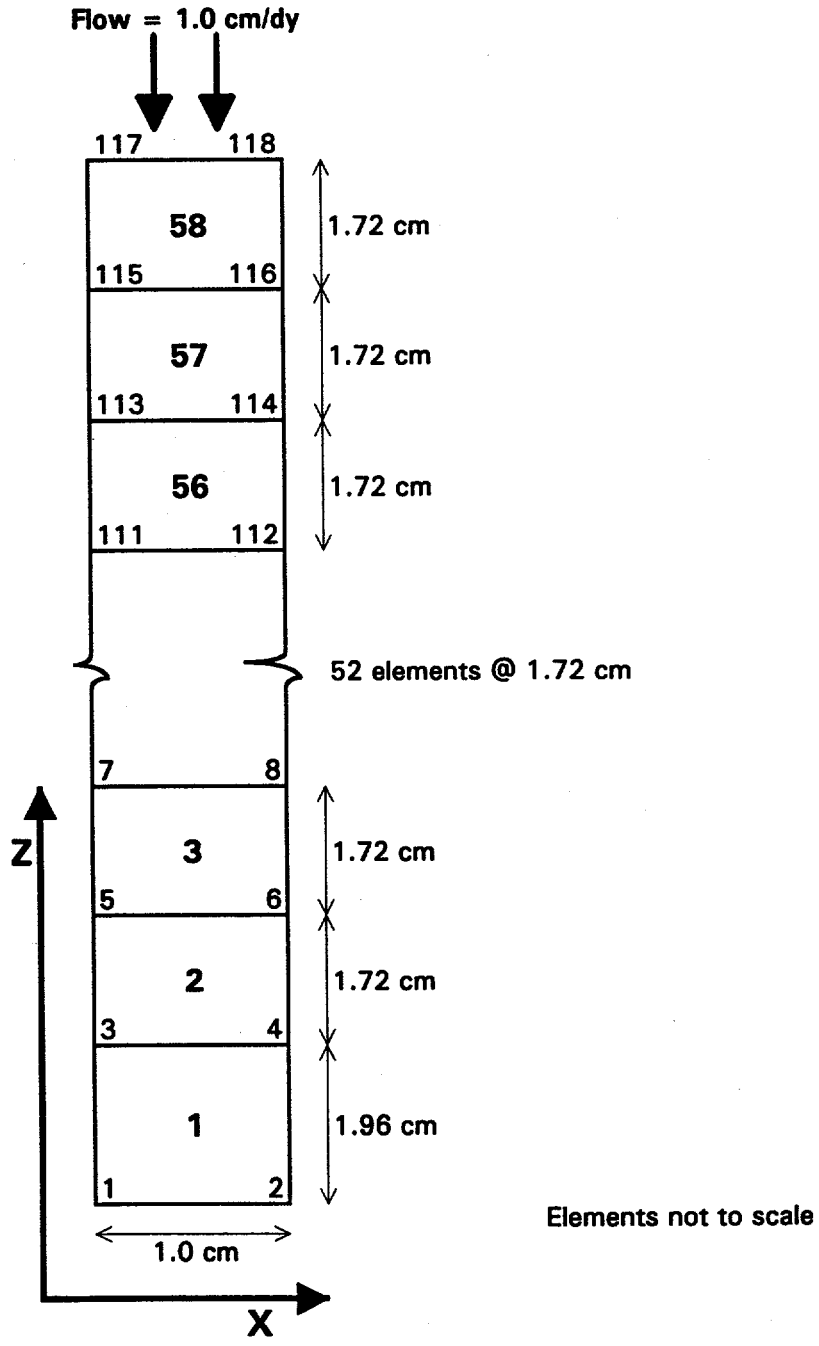


Figure 6.1
Finite Element Discretization of Problem 1

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 PARAMTERS
 118 58 1  0 121   1 4 -1 1 0 1 0 1 1 150 0 1 0 1 22 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
440000000000000000004000000000000000000040000000000000000000000000000000000000
400000000000000000040000000000000000004
110000000000000000010000000000000000001000000000000000000000000000000000000000
100000000000000000010000000000000000001
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
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
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
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 1 0 0 0 0 0 0
```

Table 6.1
Input Data Sets for Problem 1 (Concluded)

```
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 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  1.0D-6  50 50  2.0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Nickel                    1
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Nickel                    0
  0.0D0 0 0
                          END OF JOB
```

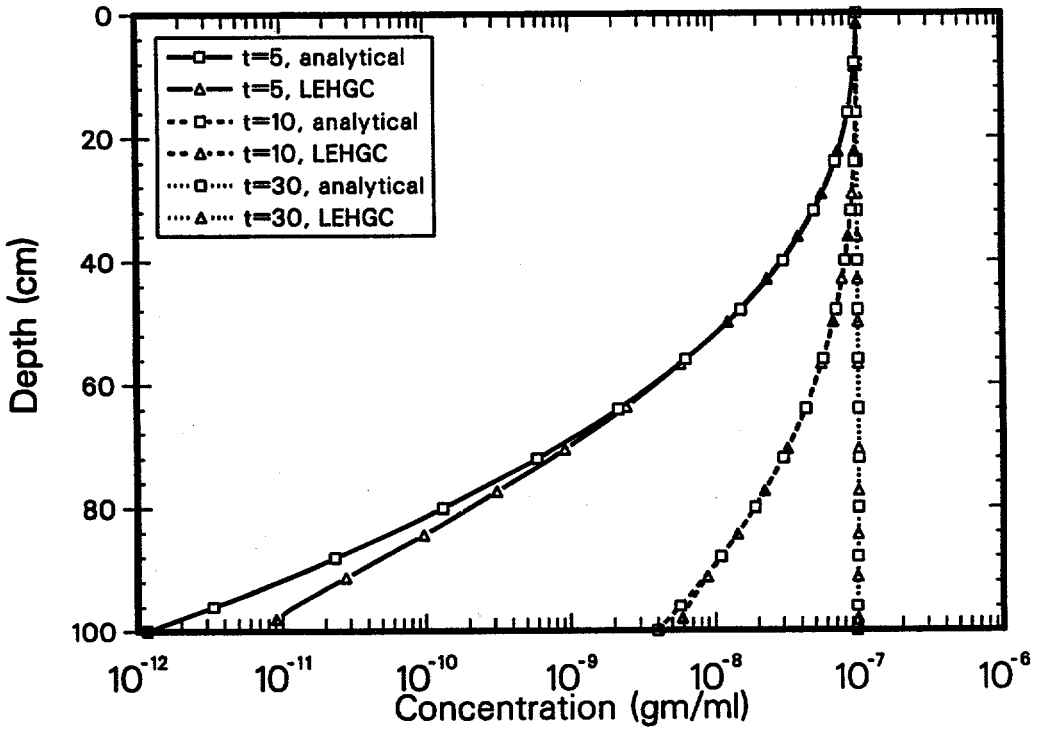


Figure 6.2
Comparison of LEHGC and Analytical Concentration Profiles.

6.2 Problem 2: Test Problem for Diffusion

To validate transport by diffusion, LEHGC was benchmarked 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 (Dykhuizen and Casey,1989). The schematic of the experimental setup is reproduced from their report in Figure 6.3. 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 cm and 6.1 cm, respectively. Given the cell volume and the 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. Figure 6.4 illustrates the column, element and node numbering and x/z axes.

Concentrations were normalized to the initial concentration in the bottom cell (C_o). Thus, the initial nondimensional concentration (C/C_o) in the bottom cell was 1.0 and in the wafer and top cell, 1.0×10^{-11}. 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 6.89×10^{-7} cm^2/s, respectively. The LEHGC simulation was carried out to 1200 hours (100 time steps of 4.32×10^4 sec each). The input data sets for LEHGC are prepared according to Appendix A and are given in Table 6.2. Note that the units in this problem are consistently in cm-gm-sec.

The same problem was solved with the COYOTE code. The equation solved by COYOTE, given simplifications of one-dimension, constant material properties and no heat source, is

$$\rho C_p \frac{DT}{Dt} = \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z}\right) \qquad (6.2.1)$$

where ρ is the material density, C_p is the heat capacity, k is the conductivity, t is time, z is the spatial coordinate, and T is temperature. The simplified equation solved by LEHGC (assuming one-dimension, constant properties, no influx/outflux of fluid, and no production, decay or reaction of species) is

$$\theta \frac{DT}{Dt} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z} \right) \tag{6.2.2}$$

where θ is the moisture content, C is concentration, and D is the ``effective" diffusion coefficient (already accounting for tortuosity). The transformation of variables is straightfoward

$$C_p = \frac{\theta}{\rho} \tag{6.2.3}$$

$$k = \frac{\theta D}{\tau} \tag{6.2.4}$$

$$T = C \tag{6.2.5}$$

A comparison of LEHGC and COYOTE results is shown in Figures 6.5 through 6.7. Figure 6.5 compares the normalized concentration in the top cell, Figure 6.6 the normalized concentration at the wafer midpoint, and Figure 6.7 the normalized concentration in the bottom cell. The scale of the plot of the bottom cell concentration presents a difference between the two codes; this difference is on the order of 0.03 percent.

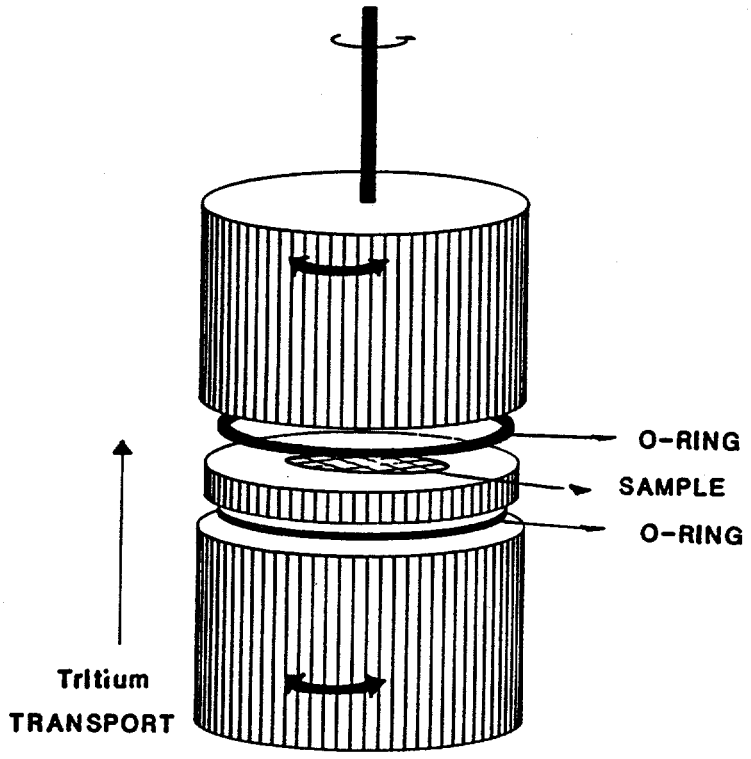


Figure 6.3
Schematic of Experimental Setup.

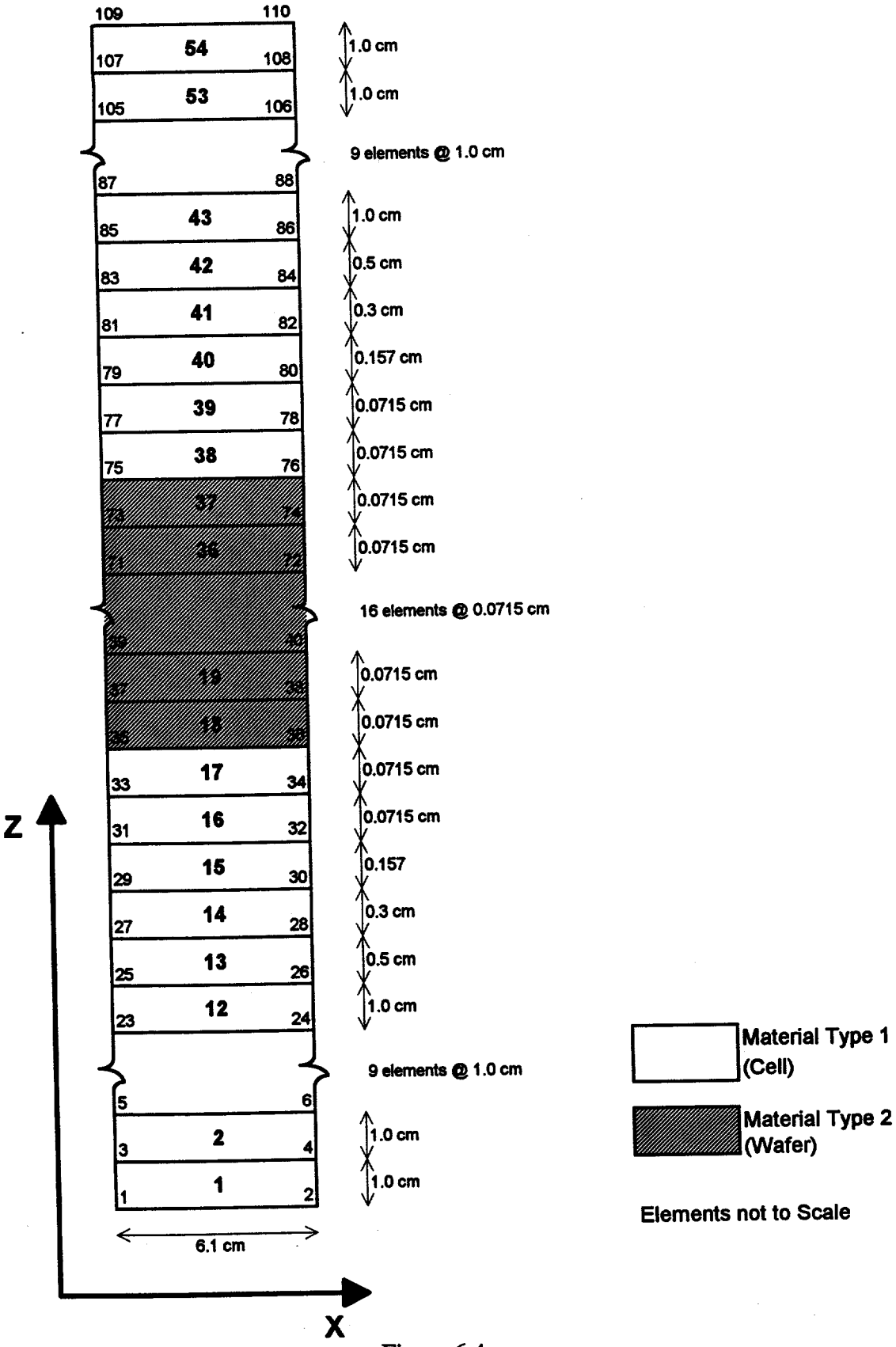


Figure 6.4
Finite Element Discretization of Problem 2

Table 6.2
Input Data Sets for Problem 2

```
    2 Caseys Diffusion Experiment: (Units in cm-gm-sec)
 0 0 0 10 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
 110 54 2 20 100 1 4 -1 1 0 1 0 1 1 150 0 1 0 1 22 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
440000000400000000040000000004000000000400000000040000000004000000004
0000000040000000004
101000100100100010010010001001001000100100100010010010001001001000100100100010001001
0010001001001000100 1
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
Tritium       1    0
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 33 1  1.0D0 0.0D0 0.0D0
 35 75 1  1.0D-11 0.0D0 0.0D0              Cannot have 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  0 0 0  4 2 1 2
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
     0.0D0   0.00D00    1.0D38   0.00D00
    1    1    1    1    0
    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
```

Table 6.2
Input Data Sets for Problem 2 (Concluded)

```
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
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 1.0D-6 50 50 2.0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Tritium                 1
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Tritium                 0
  0.0D0 0 0
                         END OF JOB
```

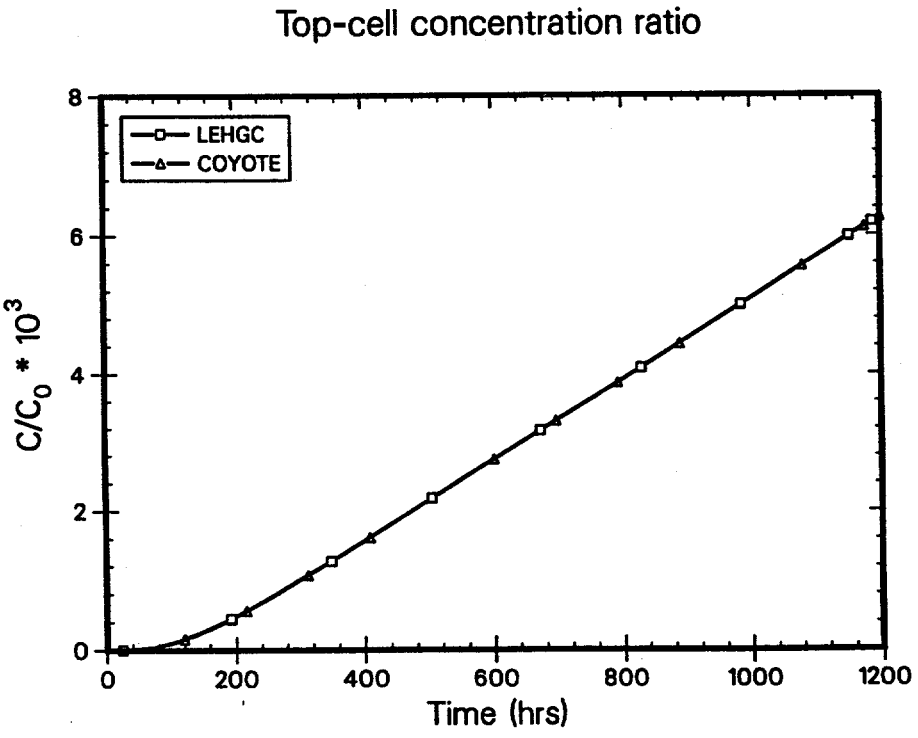


Figure 6.5
Comparison of the Normalized Concentration in the Top Cell.

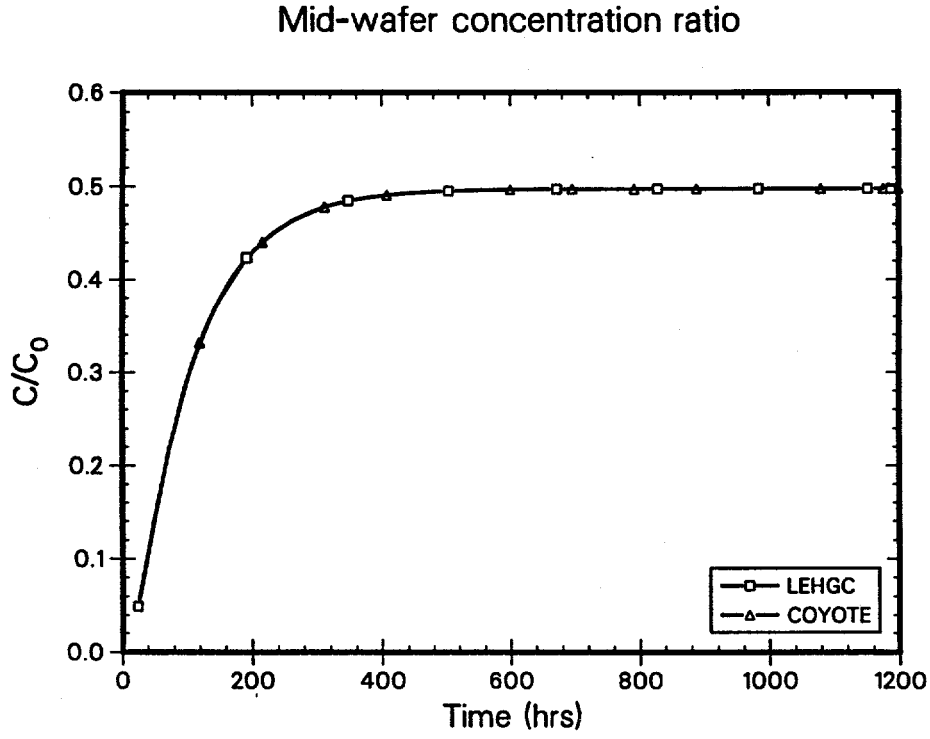


Figure 6.6
Comparison of the Normalized Concentration at the Wafer Midpoint.

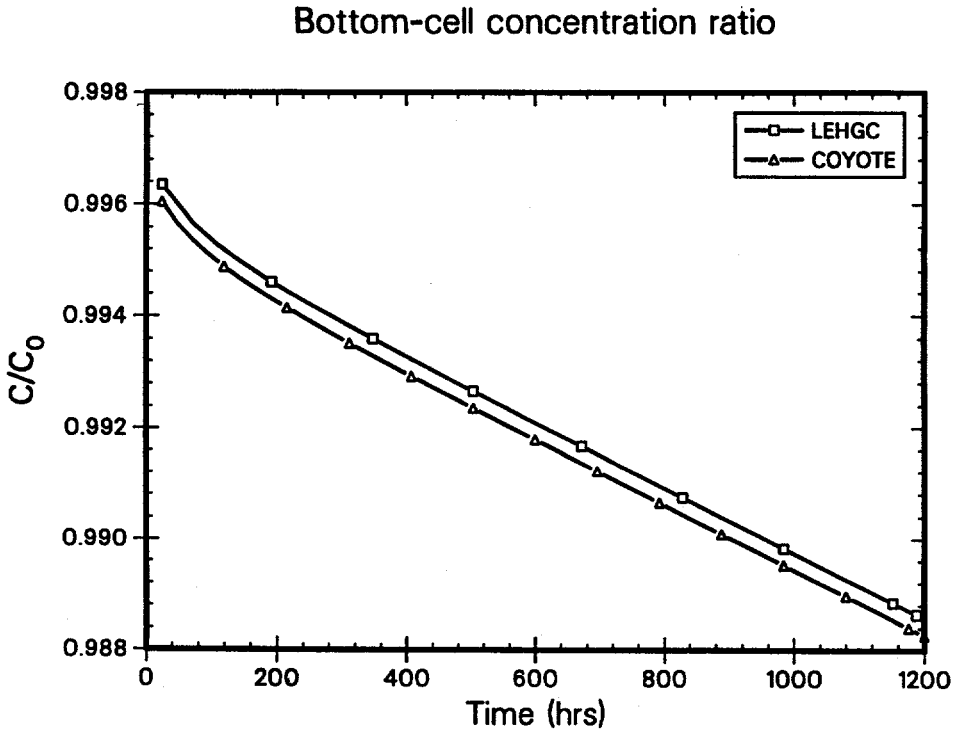


Figure 6.7
Comparison of the Normalized Concentration in the Bottom Cell.

6.3 Problem 3: Test of 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 (Figure 6.8) is 7.6 dm high by 0.325 dm wide with a $6x10^{-4}$ 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 $1.0x10^{-20}$ kg/dm^3 (a "divide-by-zero" error occurs in LEHGC 1.1 when 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 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 (Figure 6.8). The fracture element widths (x-direction) are $1.2x10^{-4}$ dm in the first column and $2.4x10^{-4}$ dm in the second and third columns. The matrix element widths gradually increased from being equal to the fracture element width, $2.4x10^{-4}$ dm, at the fracture side to 0.1 dm at the opposite side. The heights (z-direction) of rows of elements gradually increase from $6x10^{-4}$ dm to 0.2 dm, from the top to the bottom. Figure 6.9 illustrates the column, element and node numbering, and the x/z axes.

The upper boundary of the model has a constant concentration, Dirichlet boundary. Neumann boundaries are used for the other three boundaries with $\delta C/\delta x = 0$ for the two vertical boundaries and $\delta C/\delta z = 0$ for the bottom boundary. The diffusion coefficient D*, is $3.6x10^{-4}$ dm^2/hr in the fracture cells and $3.6x10^{-5}$ dm^2/hr in the matrix cells. Longitudinal dispersivity, α_L for all elements is set to 7.6 dm while lateral dispersivity, α_t, is set to 0.0 dm for all elements.

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 (Figure 6.8). 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.

$$V_f = \frac{\rho g (2b)^2 \left(dh/dx\right)}{12\mu} \qquad (6.3.1)$$

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).

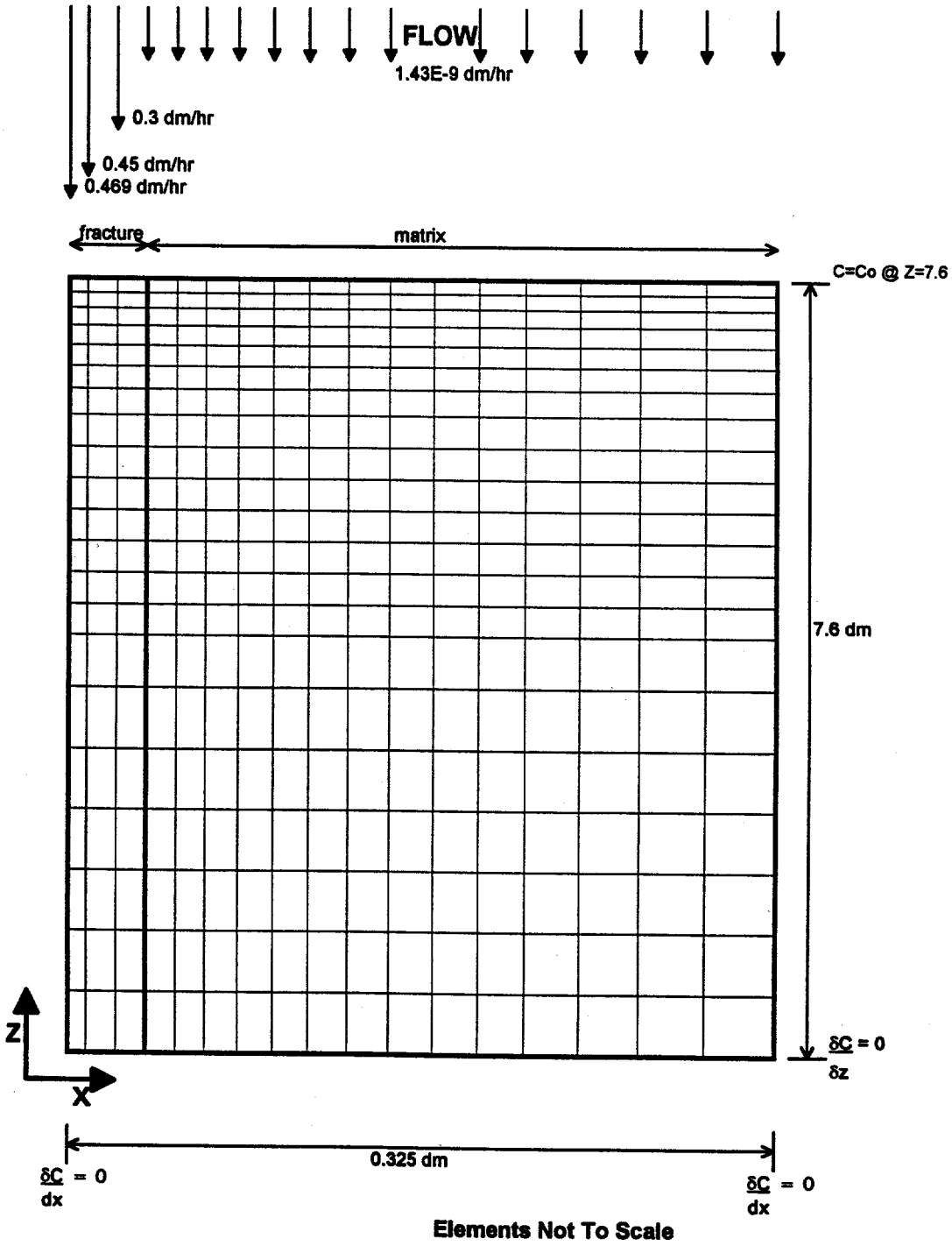


Figure 6.8
Cross Section and Flow Vectors for Problem 3

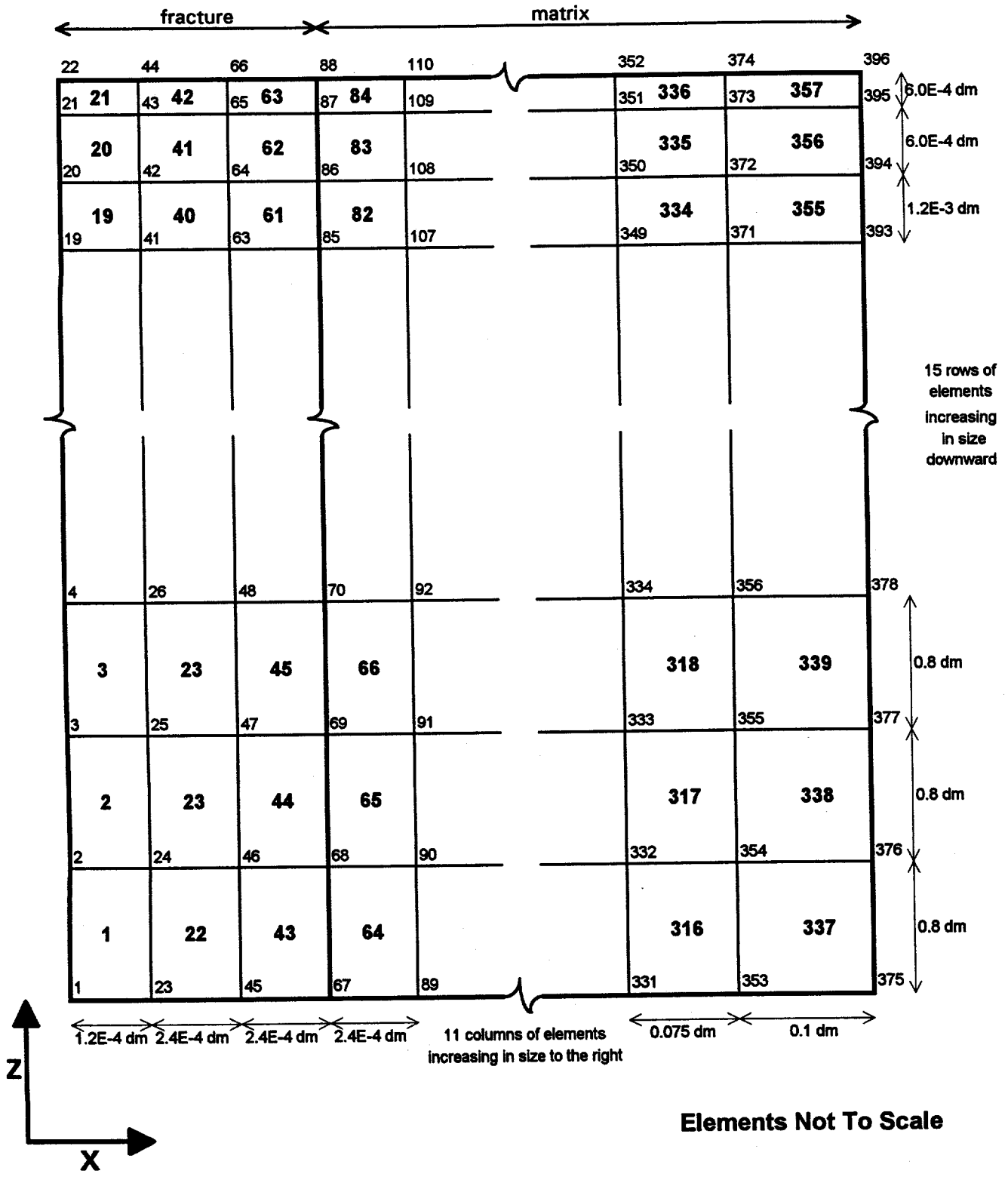


Figure 6.9
Finite Element Discretization of Problem 3

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.

$$V_m = -K\left(\frac{dh}{dx}\right) \tag{6.3.2}$$

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. Time steps of 0.024 and 2.4 hours produce identical output. The data input sets are prepared according to Appendix A and are given in Table 6.3. The resulting concentration curves produced from the LEHGC 1.1 output (Figure 6.10) are similar to concentration curves calculated by Grisak and Pickens (1980) for 144 hours (6 days). Note that some of the model parameters used by Grisak and Pickens were derived from analysis of their results. The curves labelled "Grisak & Pickens" in Figure 6.10 were obtained by interpolating curves in the graphs in their paper.

Table 6.3
Input Data Sets for Problem 3

```
 3    FRACTURE FLOW & MATRIX DIFFUSION: (Units in dm-kg-hr)
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
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
 7.6D00  0.0D00  3.6D-4  1.0D-20
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
```

Table 6.3
Input Data Sets for Problem 3 (Continued)

```
 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
  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
  TRACER   1    0
C ******* DATA SET 11: INITIAL CONDITIONS
   1   20    1    1.0D-20  0.0D0   0.0D0
  22   17   22    1.0D00   0.0D0   0.0D0
  23   20    1    1.0D-20  0.0D0   0.0D0
  45   20    1    1.0D-20  0.0D0   0.0D0
  67   20    1    1.0D-20  0.0D0   0.0D0
  89   20    1    1.0D-20  0.0D0   0.0D0
 111   20    1    1.0D-20  0.0D0   0.0D0
 133   20    1    1.0D-20  0.0D0   0.0D0
 155   20    1    1.0D-20  0.0D0   0.0D0
 177   20    1    1.0D-20  0.0D0   0.0D0
 199   20    1    1.0D-20  0.0D0   0.0D0
 221   20    1    1.0D-20  0.0D0   0.0D0
 243   20    1    1.0D-20  0.0D0   0.0D0
 265   20    1    1.0D-20  0.0D0   0.0D0
 287   20    1    1.0D-20  0.0D0   0.0D0
 309   20    1    1.0D-20  0.0D0   0.0D0
```

Table 6.3
Input Data Sets for Problem 3 (Concluded)

```
  331    20     1     1.0D-20   0.0D0     0.0D0
  353    20     1     1.0D-20   0.0D0     0.0D0
  375    20     1     1.0D-20   0.0D0     0.0D0
    0     0     0     0.0D00    0.0D0     0.0D0
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
  0  0  0     0  0  0    18 1  2      60 59  1    2
C ******* DATA SET 14: VARIABLE BOUNDARY CONDITIONS
  0.0D00      0.0D00      1.0D38      0.0D00
    1    58     1     1     0
    0     0     0     0     0                          END OF B.C. SOLUTE
    1    21     1     1     1
   23    15     1    23    22
   39    21     1   375     1
    0     0     0     0     0                          END NVNP
    1    20     1     1     2     1     1     1     1
   22     0     1     1    23     0     0     0     0
   23    15    22    23    24     1    21     1     1
   39    20   337    39    40     1     1     1     1
    0     0     0     0     0     0     0     0     0    END OF NVES
C ******* DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
  0.0D0   1.0D0    1.0D38   1.0D0
    1    17     1     1     0
    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
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
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  1.0d-6   50   1   2.0D0   1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
  TRACER                1
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
  FREE TRACER           0
    0.0D0     0.0     0
          END OF JOB
```

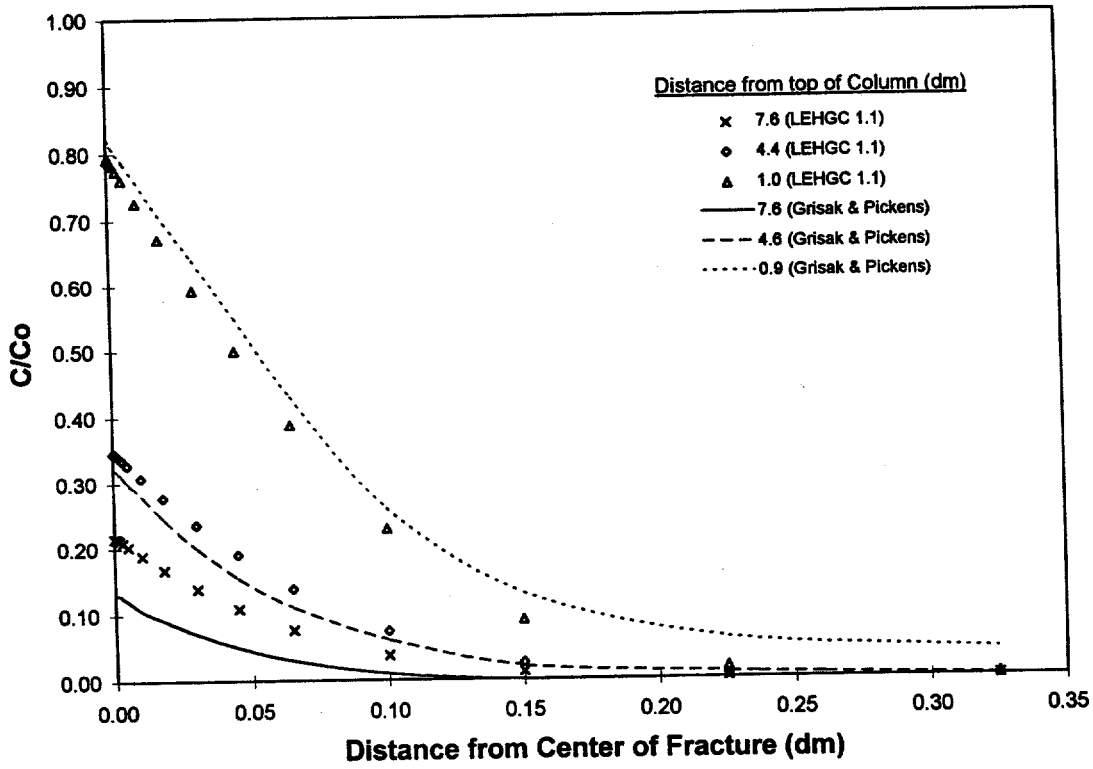


Figure 6.10
Comparison of Concentration Profiles from Fracture into Matrix at 6 Days

6.4 Problem 4: Test of Hydrologic Transport and Simple Adsorption

This problem involves transport in a 1 dm long, one-dimensional column. The flow velocity is $-1.0 \cdot 10^{-2}$ dm/h (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 $2 \cdot 10^{-3}$ dm. The transport involves four chemical components. The initial condition is a total analytical concentration of 10^{-4} M 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; at z = 0.0 dm, variable boundary conditions with zero concentration gradients are 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). In terms of geochemical equilibrium constants, the formation constants for the four adsorbed species are 0 (logK = -38), 1/9, 1, and 9, 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.

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. Figure 6.11a illustrates the column, element and node numbering, direction of flow, and x/z axes. The simulation is conducted for three time steps only because the purpose of this simulation is to verify the hydrologic module against HYDROGEOCHEM. The time-step size is 0.5 h.

The input data sets are prepared according to Appendix A and are given in Table 6.4. The results from LEHGC (figures 6.11b, 6.11c, and 6.11d) are identical to those from HYDROGEOCHEM.

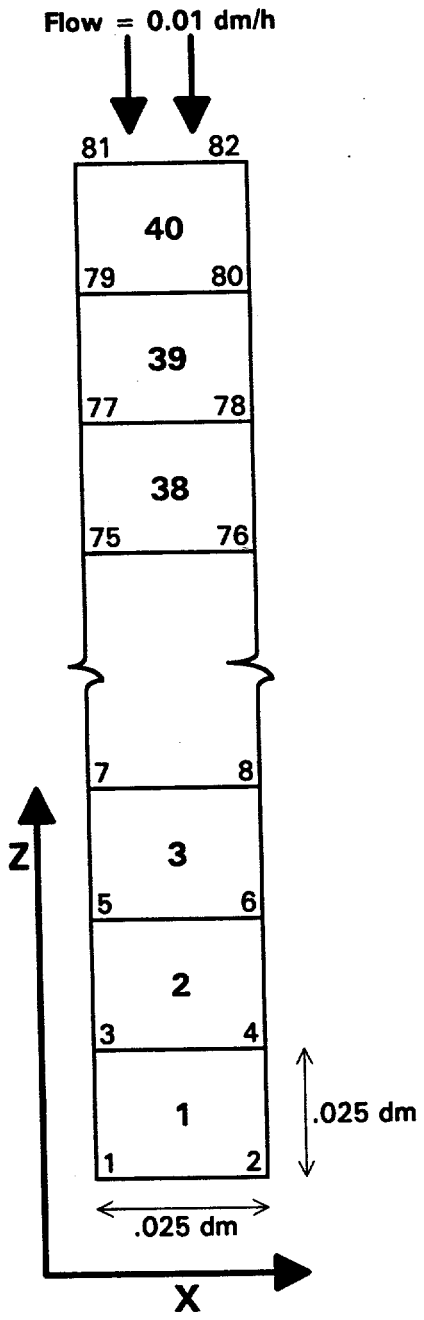


Figure 6.11a
Finite Element Discretization of Problem 4

Table 6.4
Input Data Sets for Problem 4

```
    4 TEST OF LEHGC: TRANSPORT MODULE - FOUR COMPONENTS (units in dm-kg-hr)
  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 0 0 1 12 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: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
4444
0000
1.0D38
C ******* DATA SET 5: CHEMICAL PRINTOUT
 3
 1 41 82        NODEP
C ******* DATA SET 6: MATERIAL PROPERTIES
 2.0D-3 0.0D0 0.0D0 1.2D0
C ******* DATA SET 7: NODAL POINT 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
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 4 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  1.0D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0                END OF I.C. FIRST CHEMICAL
  1 81 1  1.0D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0                END OF I.C. SECOND CHEMICAL
  1 81 1  1.0D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0                END OF I.C. THIRD CHEMICAL
  1 81 1  1.0D-4  0.0D0 0.0D0
  0  0 0  0.0     0.0   0.0                END OF I.C. FOURTH 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   0.00D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. FIRST CHEMICAL
     0.0D0   0.00D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. SECOND CHEMICAL
     0.0D0   0.00D00    1.0D38   0.00D00
    1    0    0    1    0
    0    0    0    0    0                  END OF B.C. THIRD CHEMICAL
     0.0D0   0.00D00    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 NVNP
    1    0    1    1    2    0    0    0    0
    0    0    0    0    0    0    0    0    0     END OF NVES
```

Table 6.4
Input Data Sets for Problem 4 (Concluded)

```
C *******DATA SET 15:DIRICHLET BOUNDARY CONDITIONS
   0.0D0 1.0D-3  1.0D38 1.0D-3
    1     1     1     1     0
    0     0     0     0     0                    END OF B.C.  FIRST CHEMICAL
   0.0D0 1.0D-3  1.0D38 1.0D-3
    1     1     1     1     0
    0     0     0     0     0                    END OF B. C. SECOND CHEMICAL
   0.0D0 1.0D-3  1.0D38 1.0D-3
    1     1     1     1     0
    0     0     0     0     0                    END OF B.C. THIRD CHEMICAL
   0.0D0 1.0D-3  1.0D38 1.0D-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 NDNP
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   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
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 4 0 0 4 0 0 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 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  1.0d-6 50  1  2.0d0  1.0d38
c ******* Date Set 23:  NAME OF CHEMICAL COMPONENTS AND TYPE OF COMPONENT SPECIES
  CHEM 1                1
  CHEM 2                1
  CHEM 3                1
  CHEM 4                1
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
FREE CHEMICAL 1         0
  0.0D0 0 0
FREE CHEMICAL 2         0
  0.0D0 0 0
FREE CHEMICAL 3         0
 0.0D0 0 0
FREE CHEMICAL 4         0
 0.0D0 0 0
C ******** DATA SET 26:  ADSORBED SPECIES
SORBED CHEMICAL 1       0
 0.0D0 -38.0       1 0 0 0   1 0 0 0
SORBED CHEMICAL 2       0
 0.0D0 -0.9542425  0 1 0 0   0 1 0 0
SORBED CHEMICAL 3       0
 0.0D0 0.0         0 0 1 0   0 0 1 0
SORBED CHEMICAL 4       0
 0.0D0 0.9542425   0 0 0 1   0 0 0 1
                             END OF JOB
```

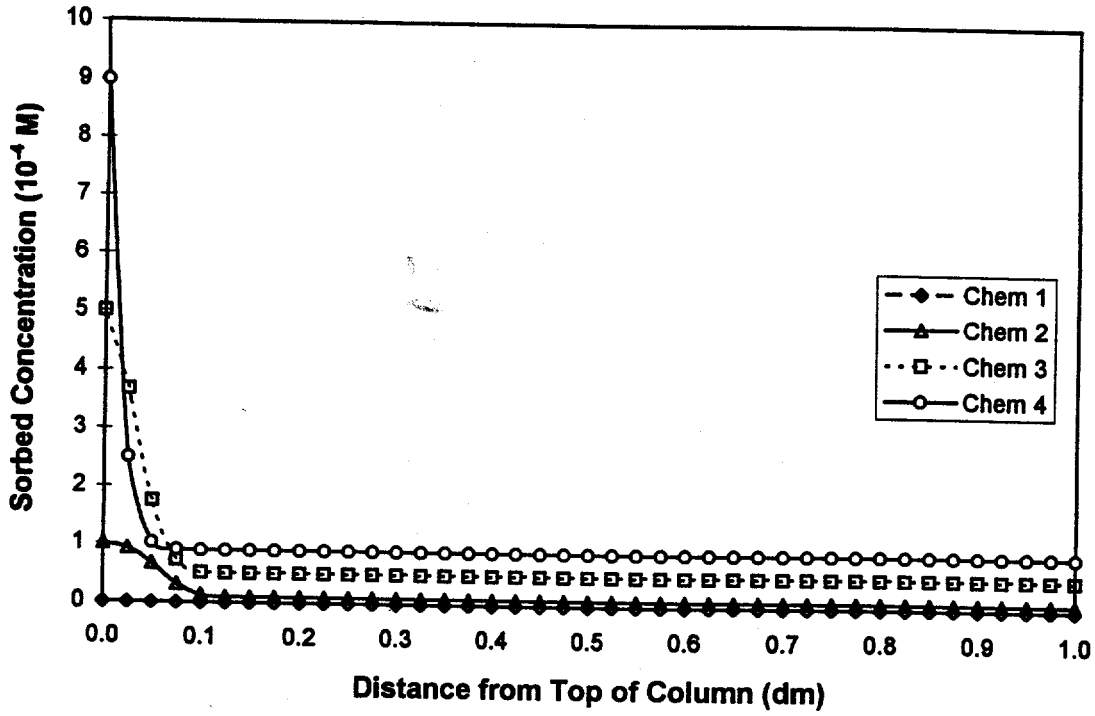


Figure 6.11b
Results from Problem 4: Sorbed concentrations at 1.5 hours

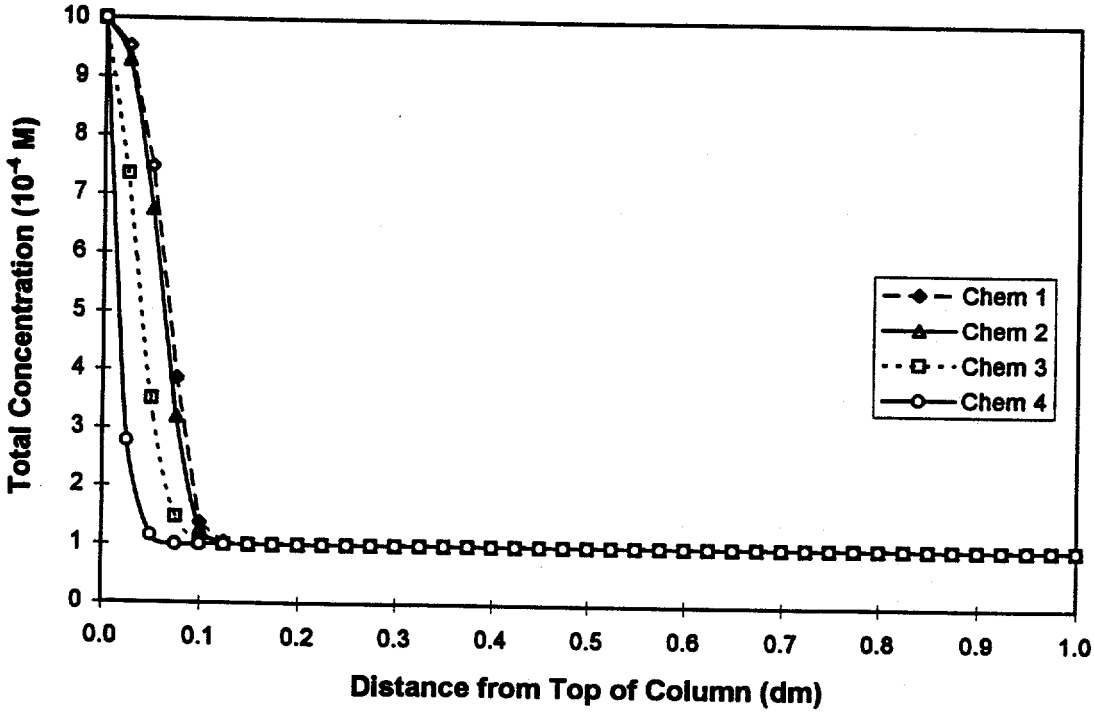


Figure 6.11c
Results from Problem 4: Total concentrations at 1.5 hours

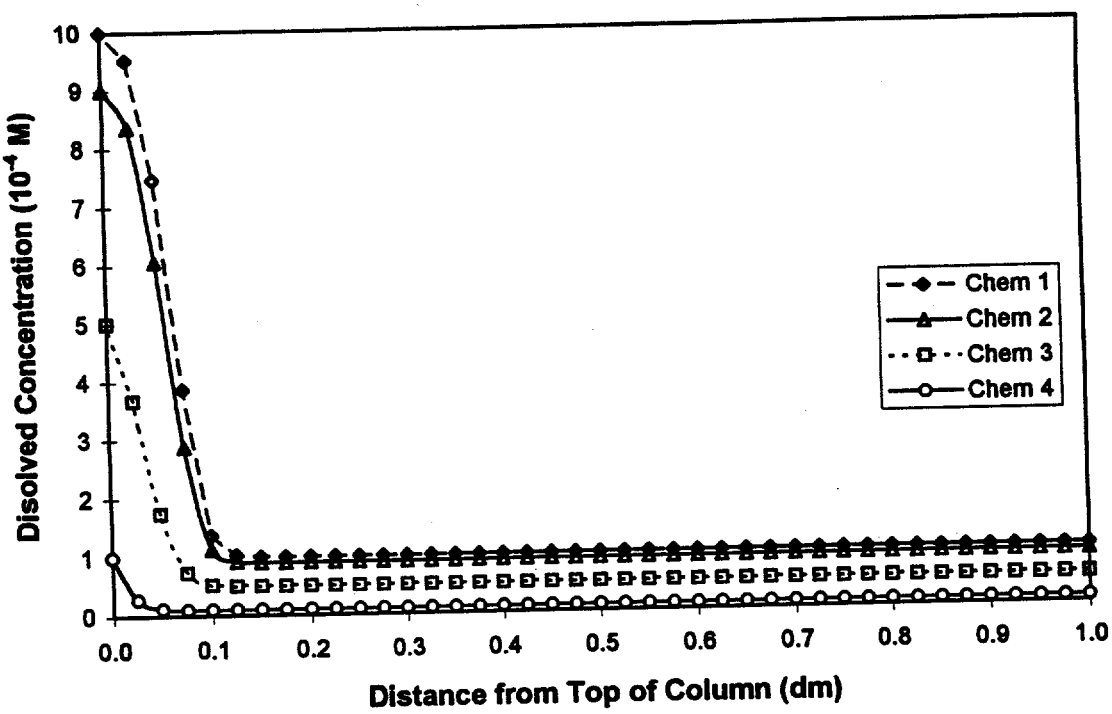


Figure 6.11.d
Results from Problem 4: Dissolved concentrations at 1.5 hours

6.5 Problem 5: Test of Coupled Transport, Complexation and Precipitation (fixed pH)

This problem considers transport with chemical reactions in a one-dimensional horizontal column; the horizontal axis is the z-axis. The flow velocity is -0.5 dm/day (flow is from right to left). The porosity is 0.3, the dispersivity is 5 dm, and the material density is 1.2 kg/dm^3. The reactions involve calcium, carbonate, magnesium, sulfate, and hydronium (H^+) in water. A total of 12 aqueous species and one mineral are considered in computations. The simulation is conducted for 150 days (300 time steps) with a time-step size of 0.5 day. The region is made up of 100 elements of 1 dm by 1 dm. Figure 6.12 illustrates the column, element and node numbering, direction of flow, and x/z axes.

Note that this problem has both ends specified as variable boundaries but only the incoming water concentration profile is used. Since the flow direction is usually unknown *a priori*, the computer code checks the direction of flow. If the flow at the boundary is incoming, the incoming water concentration is used. If the flow is outgoing, the specified incoming concentration profile is ignored and the computed concentrations are carried out of the region by advection. Thus, in this problem, the two concentration profiles specified in Data Set 14 represent potential incoming concentrations at the ends of the column. Since the flow is incoming on the right-hand side, the corresponding incoming concentration profile is used. Conversely, the flow is outgoing on the left-hand side, therefore the specified (incoming) concentration profile is ignored.

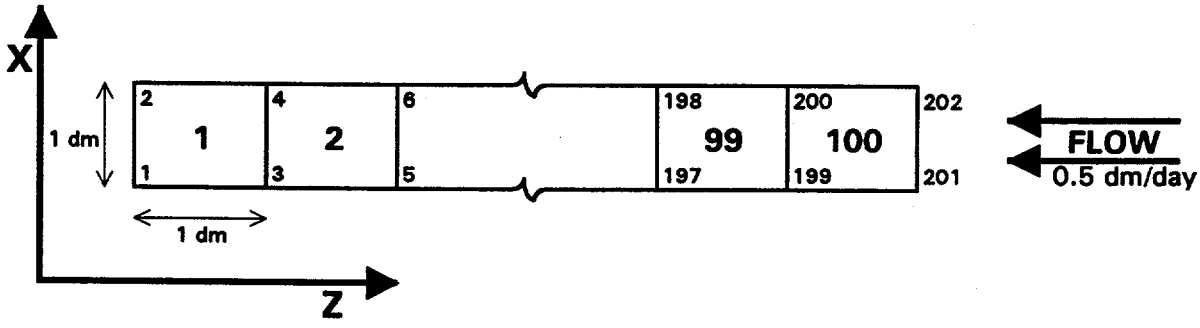


Figure 6.12
Finite Element Discretization of Problem 5

Table 6.5 shows the thermodynamic data used for this problem. Note that equilibrium constants for aqueous species correspond to formation reactions (Equation 2.3.2). Equilibrium constants for minerals are written for precipitation reactions and are the reciprocals of more the commonly tabulated solubility products (Equation 2.3.21).

Table 6.5
List of Thermodynamic Data for Problem 5

	Components Stoichiometric Coefficient					
Species	Ca^{2+}	Mg^{2+}	CO_3^{2-}	SO_4^{2-}	H^+	Log K
Ca^+	1	0	0	0	0	0.00
Mg^{2+}	0	1	0	0	0	0.00
CO_3^{2-}	0	0	1	0	0	0.00
SO_4^{2-}	0	0	0	1	0	0.00
H^+	0	0	0	0	1	0.00
$CaCO_3$	1	0	1	0	0	3.22
$CaHCO_3^+$	1	0	1	0	1	11.43
$CaSO_4$	1	0	0	1	0	2.31
$Ca(OH)^+$	1	0	0	0	-1	-12.85
$MgCO_3$	0	1	1	0	0	2.98
$MgHCO_3^+$	0	1	1	0	1	11.40
$MgSO_4$	0	1	0	1	0	2.25
$Mg(OH)^+$	0	1	0	0	-1	-11.44
HCO_3^-	0	0	1	0	1	10.32
H_2CO_3	0	0	1	0	2	16.67
H_2SO_4	0	0	0	1	2	1.99
OH^-	0	0	0	0	-1	-14.00
$CaCO_3(s)$	1	0	1	0	0	8.48

In this problem, the pH is fixed and held steady with a nonuniform distribution throughout the column. The pH is 7.7 at the left end of the column and monotonically increases at equal steps to become 8.0 at the right end of the column. The initial calcium concentration in the column is uniform at 10^{-4} M. The initial carbonate concentration increases linearly from $2 \cdot 10^{-4}$ M at the left end to $7.978 \cdot 10^{-3}$ M at 84 dm from the left. Then at 85 dm the concentration is $8 \cdot 10^{-3}$ M and increases linearly to $8.6 \cdot 10^{-3}$ M at the right end of the column. The initial magnesium concentration at the left end is $5 \cdot 10^{-3}$ M and decreases linearly to 10^{-3} M at the right end. The

initial concentration of sulfate at the left end is $2 \cdot 10^{-3}$ M and decreases linearly to 10^{-4} M at the right end.

The pH of the water entering the right end of the column is fixed at 8.0. The carbonate concentration in the incoming water is held constant at $2 \cdot 10^{-3}$ M. The concentration of calcium in incoming water is 10^{-4} M at time 0 through 0.99 days, $6 \cdot 10^{-3}$ M at time 1 through 3.5 days, and 10^{-4} M at time 3.5 days and thereafter. Concentrations of magnesium and sulfate in the incoming water are held at constant values of 10^{-3} and 10^{-4} M, respectively. The reactions in the column are driven by the increase in the initial carbonate concentration in the column and the pulse in the calcium concentration of the incoming water.

The input data sets are prepared according to the data input guide in Appendix A and are given in Table 6.6. Note that the pH is fixed at the variable boundary (Data Set 14) and in the Initial Conditions (Data Set 11) by entering the negative of the pH as the concentration and specifying hydronium as a Type 3 species (Data Sets 10 and 24). Note that although the activity of Hydronium is specified in this way, the code converts the activity to concentration for ionic strength and mass balance calculations. Similarly, Figure 6.13 illustrates selected results from the problem (recall that transport is from right to left). Figure 6.13a shows precipitation of calcite due to the early peak of incoming calcium concentration. At later times, the zone of precipitated calcite decreases due to the subsequent lower influent Ca concentration. Figures 6.13b and 6.13c show the time-dependent profiles of total (dissolved plus precipitated) and dissolved calcium, respectively. Results of simulations using both LEHGC and HYDROGEOCHEM (both the MINEQL version (Yeh and Tripathi, 1989) and the EQMOD versions (Yeh and Tripathi, 1991)) are identical, providing further code verification.

Table 6.6
Input Data Sets for Problem 5

```
    5 LEHGC: TEST OF COUPLING - COMPLEXATION AND PRECIPITATION (units in dm-kg-hr)
 0 0 0 1 0
C ******* DATA SET 2:  BASIC INTEGER PARAMETERS
 202 100 1 0 300 1 4 -1 1 0 1 0 15 1 300 0 1 0 1 11 1
C ******* DATA SET 3:  BASIC REAL PARAMETERS
 0.5 0.0 0.5 1.0D4  1.0 1.0 1.0 1.0  1.0D-2  1.0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
4444000000000000000020000000000000000002000000000000000000200000000000000000
2000000000000000000020000000000000000002000000000000000000200000000000000000
2000000000000000000020000000000000000002000000000000000000200000000000000000
2000000000000000000020000000000000000002000000000000000002
1000000000000000000010000000000000000001000000000000000001000000000000000000
1000000000000000000010000000000000000001000000000000000001000000000000000000
1000000000000000000010000000000000000001000000000000000001000000000000000000
1000000000000000000010000000000000000001000000000000000001
    1.0D38
C ******* DATA SET 5:  CHEMICAL PRINTOUT
 2
 1 201
C ******* DATA SET 6:  MATERIAL PROPERTIES
 5.0 0.0 0.0 1.2  AL AT DM ROHB
```

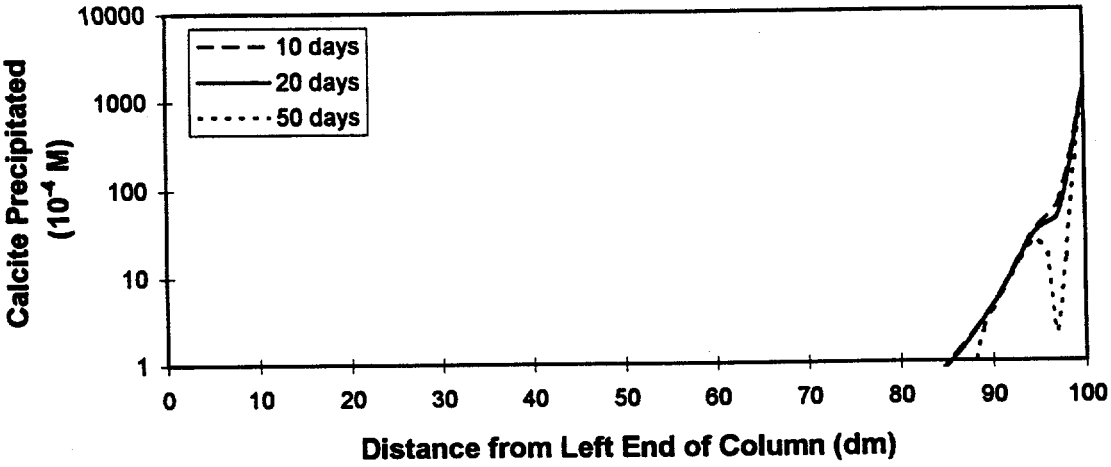
Table 6.6
Input Data Sets for Problem 5 (Continued)

```
C ******* DATA SET 7:  NODAL POINT COORDINATES
    1  100    2          0.0D0      0.0D0      0.0
    2  100    2          1.000D0    0.0D0      0.0D0
    0    0    0          0.0        0.0        0.0     END OF X
    1  100    2          0.0D0      1.000D0    0.0D0
    2  100    2          0.0D0      1.000D0    0.0
    0    0    0          0.0        0.0        0.0   END OF Z
C ******* DATA SET 8:  ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1  100
C ******* DATA SET 10:  TRANSPORT COMPONENT INFORMATION
 5 0
 CALCIUM       1    1
 CARBONATE     2    1
 MAGNESIUM     3    1
 SULFATE       4    1
 HYDROGEN      5    3
C ******* DATA SET 11:  INITIAL CONDITIONS
    1  201    1        1.00D-4     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0          END OF I.C. CA
    1   84    2        2.00D-4     9.26D-5    0.0D0
    2   84    2        2.00D-4     9.26D-5    0.000
  171   15    2        8.00D-3     0.4D-4     0.0D0
  172   15    2        8.00D-3     0.4D-4     0.0D0
    0    0    0        0.0         0.0        0.0          END OF I.C. CO3
    1  100    2        5.0D-03    -4.0D-5     0.0D0
    2  100    2        5.0D-03    -4.0D-5     0.0D0
    0    0    0        0.0         0.0        0.0          END OF I.C. MG
    1  100    2        2.00D-3    -1.9D-5     0.0D0
    2  100    2        2.00D-3    -1.9D-5     0.0D0
    0    0    0        0.0         0.0        0.0          END OF I.C. SO4
    1  100    2       -7.70D00    -0.003D0    0.0D0
    2  100    2       -7.70D0     -0.003D0    0.0D0
    0    0    0        0.0         0.0        0.0          END OF I.C. PH
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
   0 0 0   0 0 0   0 0 0   4 2 1 6
C ******* DATA SET 14:  VARIABLE BOUNDARY CONDITIONS
 0.0 1.0D-4  0.99 1.0D-4  1.0 6.0D-3  3.5 6.0D-3  3.51 1.0D-4  200.0 1.0D-4
    1    1    1    1    0
    0    0    0    0    0                                  END OF BC CA
 0.0 2.0D-3  0.99 2.0D-3  1.0 2.0D-3  3.5 2.0D-3  3.51 2.0D-3  200.0 2.0D-3
    1    1    1    1    0
    0    0    0    0    0                                  END OF BC CO3
 0.0 1.0D-3  0.99 1.0D-3  1.0 1.0D-3  3.5 1.0D-3  3.51 1.0D-3  200.0 1.0D-3
    1    1    1    1    0
    0    0    0    0    0                                  END OF BC MG
 0.0 1.0D-4  0.99 1.0D-4  1.0 1.0D-4  3.5 1.0D-4  3.51 1.0D-4  200.0 1.0D-4
    1    1    1    1    0
    0    0    0    0    0                                  END OF SO4
 0.0 -8.00   0.99 -8.0    1.0 -8.0    3.5 -8.0    3.51 -8.0    200.0 -8.0
    1    1    1    1    0
    0    0    0    0    0                                  END OF B.C. PH
    1    1    1    1    1
    3    1    1  201    1
    0    0    0    0    0                                  END OF NVNP
    1    0    1    1    2    0    0    0    0
    2    0  100    3    4    0    0    0    0
    0    0    0    0    0    0    0    0    0              END OF NVES
C ******* DATA SET 16:  VELOCITY AND MOISTURE CONTENT
    1  201    1          0.0D0    -0.500D00    0.0D0      0.0D0
    0    0    0          0.0       0.0         0.0        0.0     END OF VELOCITY
    1   99    1          0.3D0     0.0D0       0.0D0
    0    0    0          0.0       0.0         0.0       END OF MOISTURE CONTENT
C ******* DATA SET 17:  NUMBER OF COMPONENTS AND PRODUCT SPECIES
 5 0 12 0 0 1 0
```

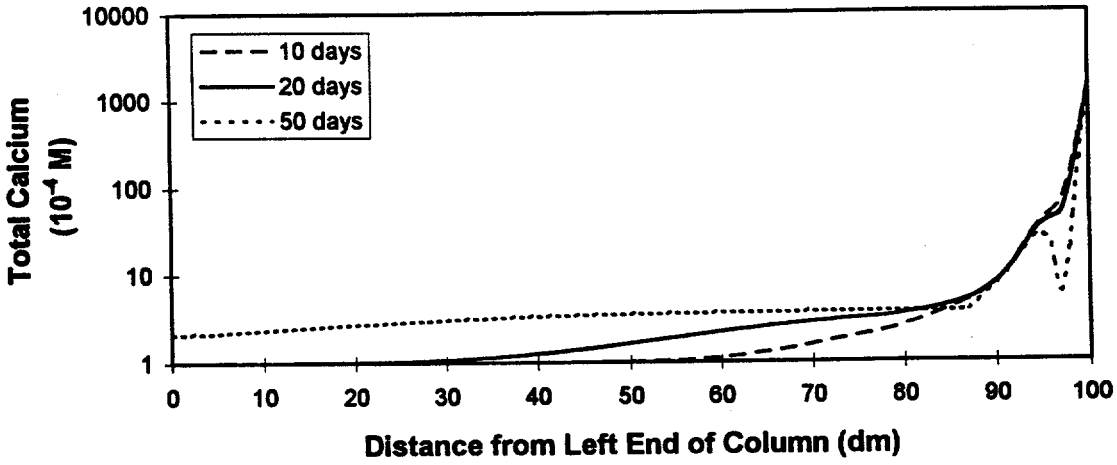
Table 6.6
Input Data Sets for Problem 5 (Concluded)

```
C ******* DATA SET 18:  H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0 5 0
c ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.3 1.0
-20.0 20.0 -20.0 20.0
c ****** DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0 1.0d-6 50 50 2.0d0 1.0d38
c ******* DATA SET 23: NAME OR CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
 CALCIUM                  1
 CARBONATE                1
 MAGNESIUM                1
 SULFATE                  1
 HYDROGEN                 1
C ******* DATA SET 24:  COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++                 0
9.8D-5  2  0
FREE CO3--                0
2.4D-7  -2 0
FREE MG++                 0
3.16D-13 2 0
FREE SO4--                0
9.80D-5  -2 0
FREE H+                   3
1.86D-8 1 0
C ******* DATA SET 25:  COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH-                       0
5.75D-7  -13.99 0 0 0 0 -1   0   0 0 0 0 -1
CACO3                     0
4.19D-8    3.22 1 1 0 0  0   0   1 1 0 0  0
HCACO3                    0
1.21D-7   11.43 1 1 0 0  1   0   1 1 0 0  1
CASO4                     0
1.96D-6    2.31 1 0 0 1  0   0   1 0 0 1  0
CAOH                      0
7.77D-10 -12.85 1 0 0 0 -1   0   1 0 0 0 -1
MGCO3                     0
1.0D-8     2.98 0 1 1 0  0   0   0 1 1 0  0
MGHCO3                    0
1.0D-8    11.40 0 1 1 0  1   0   0 1 1 0  1
MGSO4                     0
1.0D-8     2.25 0 0 1 1  0   0   0 0 1 1  0
MGOH                      0
1.0D-8   -11.44 0 0 1 0 -1   0   0 0 1 0 -1
HCO3                      0
9.58D-5   10.32 0 1 0 0  1   0   0 1 0 0  1
H2CO3                     0
3.81D-6   16.67 0 1 0 0  2   0   0 1 0 0  2
HSO4                      0
1.0D-8     1.99 0 0 0 1  1   0   0 0 0 1  1
C ******* DATA SET 27:  PRECIPITATED/DISSOLVED SPECIES
CACO3                     0
1.0D-7    8.48 1 1 0 0 0    1 1 0 0 0
                              END OF JOB
```

a)



b)



c)

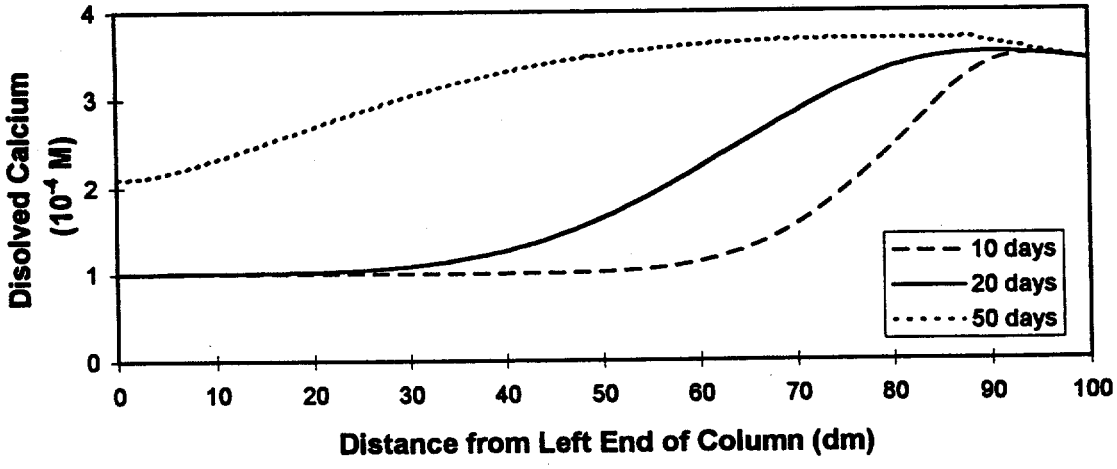


Figure 6.13
Results from Problem 5. a) Calcite Precipitation at 10, 25 and 50 Days; b) Total Calcium Concentration at 10, 25 and 50 Days; c) Dissolved Calcium at 10, 25 and 50 Days.

6.6 Problem 6: One-Dimensional Advective Transport with Coupled Dissolution, Precipitation and Complexation (variable pH)

This test problem was identified from the CHEMVAL (CHEMical VALidation) international code benchmarking exercise. It involves the dissolution of a cement by clayey water and is designated as Case 3 in CHEMVAL 2 (Made and Jamet, 1993). The problem statement specifies the intrusion of water from an aquifer into a cement solution slightly oversaturated with portlandite, $Ca(OH)_2$. The $Ca(OH)_2$ in excess of saturation represents solid portlandite that is available for dissolution as the solution composition changes. The chemical processes considered are the dissolution of portlandite, the precipitation of calcite ($CaCO_3$) and aqueous complexation. A schematic of the problem is shown in Figure 6.14. The composition of the cement pore water is greatly simplified, as is the solid phase (i.e., the cement) which consists only of portlandite. The groundwater contains Ca^{2+}, Na^+, CO_3^{2-}, and Cl^- at a pH of 7.5. The composition of the cement and clayey waters are presented in Table 6.7 as total concentrations in mol/dm^3. The thermodynamic data for the chemical species are given in Table 6.8.

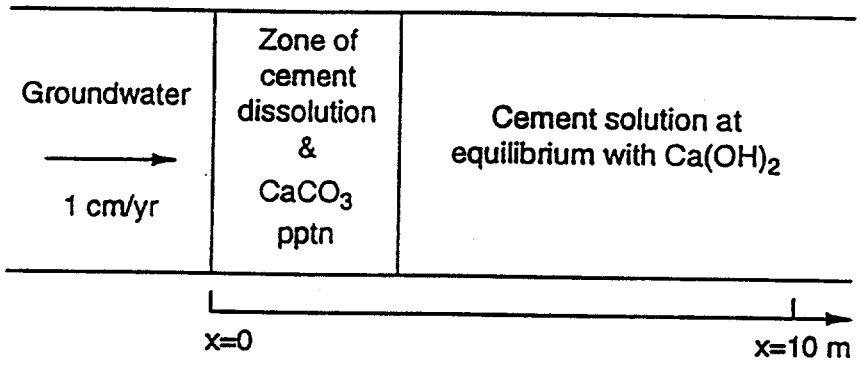


Figure 6.14.
Problem Schematic for the Dissolution of a Cement by Groundwater.

Table 6.7
Original Solution Compositions for CHEMVAL 2, Test Case 3
(Concentrations in $moles/dm^3$ (except pH))

Species	Clayey Groundwater	Cement Water
Ca^{2+}	5.5×10^{-3}	2.0×10^{-2}
Na^+	8.0×10^{-3}	8.0×10^{-3}
CO_3^{2-}	4.5×10^{-3}	1.0×10^{-10}
Cl^-	1.0×10^{-2}	4.0×10^{-2}
pH	7.5	12.5

Table 6.8
Thermodynamic Data for Problem 6

	Components Stoichiometric Coefficient					
Species	Ca^{+}	Na^{+}	CO_3^{2-}	Cl^{-}	H^{+}	Log K
Ca^{2+}	1	0	0	0	0	0.00
Na^{+}	0	1	0	0	0	0.00
CO_3^{2-}	0	0	1	0	0	0.00
Cl^{-}	0	0	0	1	0	0.00
H^{+}	0	0	0	0	1	0.00
$CaCO_3$	1	0	1	0	0	3.153
$CaHCO_3^{+}$	1	0	1	0	1	11.43
$Ca(OH)^{+}$	1	0	0	0	-1	-12.70
$NaCO_3^{-}$	0	1	1	0	0	1.27
$NaHCO_3$	0	1	1	0	1	10.08
HCO_3^{-}	0	0	1	0	1	10.33
H_2CO_3	0	0	1	0	2	16.68
OH^{-}	0	0	0	0	-1	-13.99
$CaCl^{+}$	1	0	0	1	0	0.08
NaOH	0	1	0	0	-1	-13.8
Na_2CO_3	0	2	1	0	0	0.68
NaCl	0	1	0	1	0	-0.9
$CaCO_3(s)$	1	0	1	0	0	8.35
$Ca(OH)_2(s)$	1	0	0	0	-2	-22.65

Transport is by 1-D advection through an isotropic porous medium. The pore water velocity is 0.1 dm/yr and the dispersivity, a_L, is 10 dm. The left-hand (influent) boundary is a Dirichlet boundary. Changes in porosity due to precipitation and dissolution are not considered. The problem domain is 100 dm in length (Figure 6.15). The spatial grid consists of 102 nodes (50 elements) exponentially spaced.

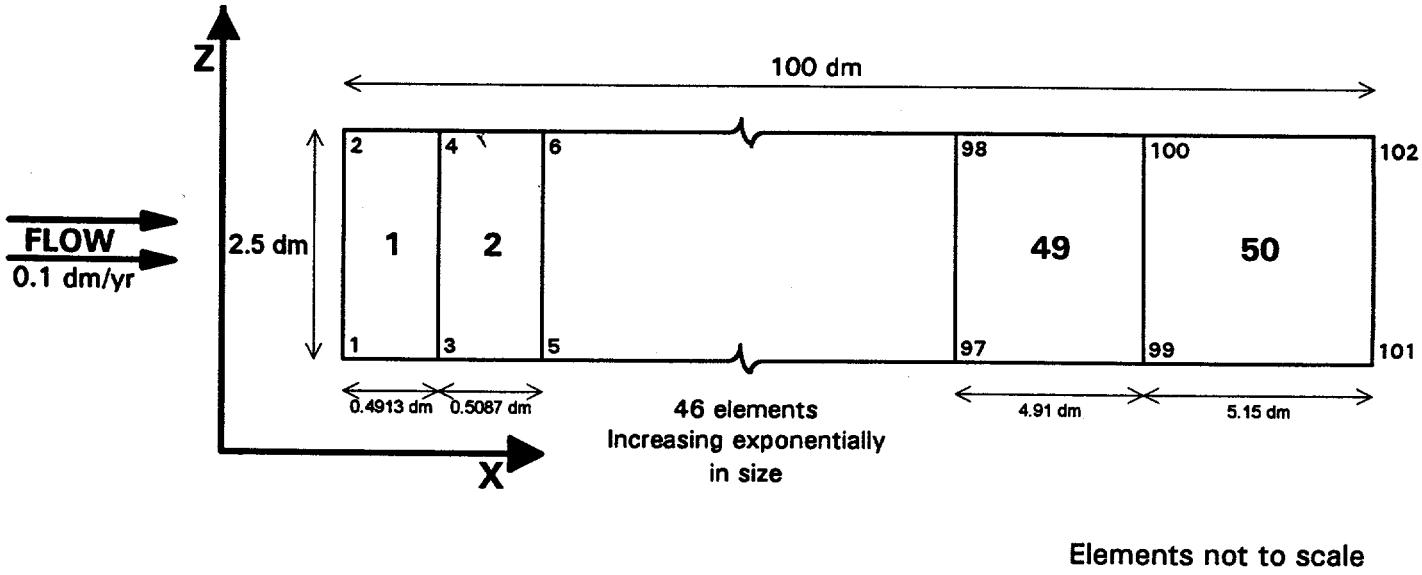


Figure 6.15.
Finite Element Discretization of Problem 6.

The results of interest as specified in the CHEMVAL 2 problem definition include the following:

- Calcium speciation in initial (cement) and boundary (groundwater) solutions, allowing portlandite or calcite to precipitate if supersaturated.

- Concentration profiles of Na^+, Ca^{2+}, and $CaOH^+$ at t=100 years.

- pH profile at t=200 years.

Both this sample problem and Sample Problem 5 described previously, involve 1-dimensional transport coupled with precipitation and complexation. The problems differ in two important ways: 1) a reactive solid ($Ca(OH)_2$) is initially present in this case but was absent in the preceding test case and 2) the pH is allowed to vary due to chemical reaction in the CHEMVAL 2 problem whereas in Sample Problem 5, the pH was fixed. The CHEMVAL 2 problem definition specifies only the initial activity of the free hydronium (pH) of the cement pore water and groundwater compositions (Table 6.7). If the pH is not fixed throughout the simulation, LEHGC1.1 requires specification of the total concentration of hydronium (proton).

In order to obtain the total concentration of hydronium for the CHEMVAL 2 problem, the chemical speciation of the cement porewater was calculated with LEHGC1.1 from the chemical compositions listed in Table 6.7 using the input data sets shown in Table 6.9. In the simulation, the pH was specified as 12.5, and both calcite and portlandite were allowed to precipitate from the solution. Note that this input deck corresponds to an LEHGC1.1 simulation in which there is no flow and the finite element grid contains only two elements; the results are summarized in the first column of Table 6.10. Note that the pH is fixed in the Initial Conditions and at the Dirichlet boundary by entering the negative of the pH (-12.5) as the concentration and specifying hydronium as a Type 3 species (Data Sets 10 and 24).

The negative value for total hydronium in Table 6.10 indicates a concentration of hydroxide in excess of hydronium. This total concentration is the sum of the concentrations of all aqueous species and precipitated species containing hydronium or hydroxide. This total concentration for hydronium was used in the initial conditions within the cement column (Data Set 11) and for the right-hand side (variable) boundary for the LEHGC runs (Data Set 14) as shown in Table 6.11. Total analytical concentration of the other components for Data Sets 11 and 14 are given in Table 6.7. Note that in Table 6.11, hydronium is specified as a Type 0 species (Data Sets 10, 24) and that the pH will be computed.

Table 6.9
Input Data Sets for Speciation Calculation for Cement Porewater

```
    6 CHEMVAL Cement Speciation batchproblem: (Units in dm-kg-yr)
  0 0 0 5 0
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
  6 2 1 0 3 1 4 -1 1 0 1 0 50 1 150 0 0 0 1 12 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.5 0 0.5 15 1.0 1.0 1.0 1.0 1.0D-5 1
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
4444
0000
1.0D38
C ******* DATA SET 5: CHEMICAL PRINTOUT
 3
 1 3 6
C ******* DATA SET 6: MATERIAL PROPERTIES
0.0 0.0 0.0 1.691
C ******* DATA SET 7: NODAL POINT COORDINATES
    1   2    2      0.0    0.0          0.0
    2   2    2      0.025  0.0          0.0
    0   0    0      0.0    0.0          0.0          END OF X-COORD
    1   2    2      0.0    0.025        0.0
    2   2    2      0.0    0.025        0.0
    0   0    0      0.0    0.0          0.0          END OF Z-COORD
C ******* DATA SET 8: ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1  2
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 5   0
Ca              1    1
Na              2    1
CO3             3    1
Cl              4    1
H               5    3
```

Table 6.9
Input Data Sets for Speciation Calculation for Cement Porewater (Continued)

```
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 5 1  2.0D-2     0.0D0 0.0D0
  0  0  0  0.0        0.0   0.0                END OF I.C. for Component 1
  1 5 1  8.0D-3     0.0D0 0.0D0
  0  0  0  0.0        0.0   0.0                END OF I.C. for Component 2
  1 5 1  1.0D-10    0.0D0 0.0D0
  0  0  0  0.0        0.0   0.0                END OF I.C. for Component 3
  1 5 1  4.0D-2     0.0D0 0.0D0
  0  0  0  0.0        0.0   0.0                END OF I.C. for Component 4
  1 5 1  -12.5 0.0D0 0.0D0
  0  0  0  0.0        0.0   0.0                END OF I.C. for Component 5
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  0.0D0    1.0D6   0.0D0             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                     END OF B.C. for Component 1
     0.0D0  0.0D0    1.0D6   0.0D0             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                     END OF B.C. for Component 2
     0.0D0  0.0D0    1.0D6   0.0D0             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                     END OF B.C. for Component 3
     0.0D0  0.0D0    1.0D6   0.0D0             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                     END OF B.C. for Component 4
     0.0D0  0.0D0    1.0D6   0.0D0              RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                     END OF B.C. for Component 5
  1  1  1  1  1
  0  0  0    0  0
  1   0   1   1   2  0   0  0   0
  0   0    0   0   0  0   0  0   0             END OF VARIABLE BC
C ******* DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
     0.0D0  2.0D-2   1.0D6  2.0D-2             LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                     END OF B.C. for Component 1
     0.0D0  8.0D-3    1.0D6  8.0D-3            LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                     END OF B.C. for Component 2
     0.0D0  1.0D-10   1.0D6 1.0D-10           LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                     END OF B.C. for Component 3
     0.0D0  4.0D-2    1.0D6  4.0D-2            LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                     END OF B.C. for Component 4
     0.0D0  -12.5  1.0D6 -12.5                LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                     END OF B.C. for Component 5
    1    1    1    5    1
    0    0    0    0    0                     END OF DIRICHET BC
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   1 5 1  0.0D0  0.0D0  0.0D0 0.0D0
   0   0 0  0.0    0.0    0.0   0.0            END OF VELOCITY
   1  1 1  1.0D0  0.0D0
   0   0 0  0.0    0.0                        END OF MOISTURE CONTENT
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 5 0 12 0 0 2 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.1 2 5 0
```

Table 6.9
Input Data Sets for Speciation Calculation for Cement Porewater (Continued)

```
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.0 1.0
-20.0 20.0 0.0 14.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0D0  1.0D-6  100  100  2.0  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Ca                          0
Na                          0
CO3                         0
Cl                          0
H                           3
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Free Ca2+                   0
 2.0D-3  2.0  0
Free Na+                    0
 8.0D-4  1.0  0
Free CO3                    0
 1.5D-3 -2.0  0
Free Cl-                    0
 2.0D-3 -1.0  0
Free H+                     3
 3.16D-13 1.0 0
C ******* DATA SET 25:  COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
CaCO3                      0
 2.0D-06  3.153 1 0 1 0 0 0 1 0 1 0  0
CaCO3H                     0
 1.0D-06  11.43 1 0 1 0 1 0 1 0 1 0  1
Ca(OH)                     0
 1.0D-04 -12.7 1 0 0 0 -1 0 1 0 0 0 -1
NaCO3                      0
 1.0D-06  1.27 0 1 1 0  0 0 0 1 1 0  0
NaCO3H                     0
 1.0D-06  10.08 0 1 1 0 1 0 0 1 1 0 1
CO3H                       0
 1.0D-06  10.33 0 0 1 0 1 0 0 0 1 0 1
CO3(H)2                    0
 1.0D-08  16.68 0 0 1 0 2 0 0 0 1 0 2
(OH)                       0
 3.0D-03 -13.99 0 0 0 0 -1 0 0 0 0 0 -1
CaCl                       0
 1.0D-07  0.08  1 0 0 1 0 0 1 0 0 1 0
Na(OH)                     0
 1.0D-04 -13.8  0 1 0 0 -1 0 0 1 0 0 -1
(Na)2CO3                   0
 1.0D-09  0.68  0 2 1 0 0 0 0 2 1 0 0
NaCl                       0
 1.0D-08 -0.9   0 1 0 1 0 0 0 1 0 1 0
C ******* DATA SET 27:  PRECIPITATED/DISSOLVED SPECIES
CaCO3                       0
 .000002  8.35  1 0 1 0 0 1 0 1 0 0
Ca(OH)2                     0
 .0002 -22.65   1 0 0 0 -2 1 0 0 0 -2
                                        END OF JOB
```

Results of speciation calculations for the same solution composition were carried out with the HYDRAQL code (Papelis et al., 1988) in order to benchmark the equilibrium chemistry subroutines of LEHGC1.1. A comparison of a portion of the calculated speciations is shown in Table 6.10. The differences in the results are not significant and are traceable, at least in part, to

differences in the the 'A' parameter in the equations used to calculate activity coefficients (HYDRAQL: A = 0.50886; EQMOD: A = 0.5). A combination of the propagation of this error and differences in numerical dispersion may lead to the differences in the concentrations shown in Table 6.10.

Table 6.10
Calculations of Speciations of Cement Pore Water and Clay Groundwater
(Concentrations in moles/dm^3)

Species	Cement Pore Water		Clay Groundwater
	LEHGC1.1	HYDRAQL	LEHGC1.1
Ca^{++}	1.149×10^{-2}	1.08×10^{-2}	3.005×10^{-3}
$CaOH^{+}$	3.570×10^{-3}	3.51×10^{-3}	1.295×10^{-8}
$CaCO_3$	6.997×10^{-11}	7.12×10^{-11}	6.353×10^{-6}
$CaHCO_3$	5.303×10^{-15}	5.31×10^{-15}	4.317×10^{-5}
$CaCl^{+}$	2.135×10^{-4}	2.14×10^{-4}	2.166×10^{-5}
Na^{+}	7.672×10^{-3}	7.67×10^{-3}	7.985×10^{-3}
H^{+} (pH)	3.162×10^{-13} (12.5)	3.16×10^{-13} (12.5)	3.162×10^{-8} (7.5)
Portlandite	4.722×10^{-3}	5.47×10^{-3}	0.0
Calcite	0.0	0.0	2.183×10^{-3}
Total proton	-5.431×10^{-2}	-5.51×10^{-2}	2.424×10^{-3}

The speciation of the clay groundwater and the influent (left-hand side) boundary was also calculated using LEHGC1.1 as a no-flow problem, as described previously for the cement groundwater. In the calculation, both calcite and portlandite were allowed to precipitate; the results are shown in Table 6.10. The total hydronium concentration listed in this table and the total concentrations of the other components listed in Table 6.7 were used to define the left-hand (influent) boundary (Data Set 15). Note that the total Ca and carbonate concentrations, specified in the left-hand boundary, include the contributions from calcite in order to match the description of the CHEMVAL 2 problem. This allows comparision of the results calculated with LEHGC1.1 to those of other CHEMVAL participants as discussed below.

The input data sets for the full transport simulation are given in Table 6.11. In the LEHGC calculations, both calcite and portlandite were allowed to dissolve and precipitate. Calculations were carried out to 400 years (4001 time steps of 0.1 yrs). The output is summarized and compared to the results of calculations by other CHEMVAL participants in Figures 6.16 - 6.18. The results from this simulation agree well with those of many of the other CHEMVAL

participants. The Chemval2 participants identified in the figures are as follows: WS Atkins Environmental Science, UK (Atkins), Valtion Teknillinen Tutkimuskeskus, Finland (VTT), Ecole Nationale Superieure des Mines de Paris, France (EMP), Commissariat a l'Energie Atomique, France (CEA), Bureau de Recherches Geologiques et Minieres, France (BRGM), Agence Nationale pour la Gestion des Dechets Radioactifs, France (ANDRA), Svensk Karnbranslehantering, Sweden (SKB), Delft Geotechnics, Netherlands (DELFT), AEA Technology, UK (Harwell), and Sandia National Laboratories, USA (SNL).

Table 6.11
Input Data Sets for Problem 6

```
   6 CHEMVAL Transport and Cement Dissolution : Units in dm-kg-yr
  0 0 0 100 1
C ******* DATA SET 2: BASIC INTEGER PARAMTERS
  102 50 1  0 4001   1 4 -1 1 0 1 0 5 1 150 0 1 0 1 12 1
C ******* DATA SET 3: BASIC REAL PARAMETERS
 0.1D0 0.0D0 0.1D0 400.0D0 0.0D0 0.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
44000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000400000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000004000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000004
40000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000044000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
```

Table 6.11
Input Data Sets for Problem 6 (Continued)

```
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000004
4
11111111111010010000100000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000001000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000001000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
10000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000001000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000
1
1.0D6
```

Table 6.11
Input Data Sets for Problem 6 (Continued)

```
C ******* DATA SET 5: CHEMICAL PRINTOUT
 14
 1 5 19 31 39 47 53 59 69 75 83 89 93 101
C ******* DATA SET 6: MATERIAL PROPERTIES
 10.0D0  10.0D0 0.0D0 1.0D0
C ******* DATA SET 7: NODAL POINT COORDINATES
```

1	0	0	0.0000D+00	0.0000D+00	0.0000D+00	Define x nodes of varying
2	0	0	0.0000D+00	0.0000D+00	0.0000D+00	size elements
3	0	0	0.4913D+00	0.0000D+00	0.0000D+00	
4	0	0	0.4913D+00	0.0000D+00	0.0000D+00	
5	0	0	0.1000D+01	0.0000D+00	0.0000D+00	
6	0	0	0.1000D+01	0.0000D+00	0.0000D+00	
7	0	0	0.1547D+01	0.0000D+00	0.0000D+00	
8	0	0	0.1547D+01	0.0000D+00	0.0000D+00	
9	0	0	0.2115D+01	0.0000D+00	0.0000D+00	
10	0	0	0.2115D+01	0.0000D+00	0.0000D+00	
11	0	0	0.2710D+01	0.0000D+00	0.0000D+00	
12	0	0	0.2710D+01	0.0000D+00	0.0000D+00	
13	0	0	0.3334D+01	0.0000D+00	0.0000D+00	
14	0	0	0.3334D+01	0.0000D+00	0.0000D+00	
15	0	0	0.3989D+01	0.0000D+00	0.0000D+00	
16	0	0	0.3989D+01	0.0000D+00	0.0000D+00	
17	0	0	0.4677D+01	0.0000D+00	0.0000D+00	
18	0	0	0.4677D+01	0.0000D+00	0.0000D+00	
19	0	0	0.5398D+01	0.0000D+00	0.0000D+00	
20	0	0	0.5398D+01	0.0000D+00	0.0000D+00	
21	0	0	0.6154D+01	0.0000D+00	0.0000D+00	
22	0	0	0.6154D+01	0.0000D+00	0.0000D+00	
23	0	0	0.6948D+01	0.0000D+00	0.0000D+00	
24	0	0	0.6948D+01	0.0000D+00	0.0000D+00	
25	0	0	0.7780D+01	0.0000D+00	0.0000D+00	
26	0	0	0.7780D+01	0.0000D+00	0.0000D+00	
27	0	0	0.8654D+01	0.0000D+00	0.0000D+00	
28	0	0	0.8654D+01	0.0000D+00	0.0000D+00	
29	0	0	0.9570D+01	0.0000D+00	0.0000D+00	
30	0	0	0.9570D+01	0.0000D+00	0.0000D+00	
31	0	0	0.1053D+02	0.0000D+00	0.0000D+00	
32	0	0	0.1053D+02	0.0000D+00	0.0000D+00	
33	0	0	0.1154D+02	0.0000D+00	0.0000D+00	
34	0	0	0.1154D+02	0.0000D+00	0.0000D+00	
35	0	0	0.1260D+02	0.0000D+00	0.0000D+00	
36	0	0	0.1260D+02	0.0000D+00	0.0000D+00	
37	0	0	0.1371D+02	0.0000D+00	0.0000D+00	
38	0	0	0.1371D+02	0.0000D+00	0.0000D+00	
39	0	0	0.1487D+02	0.0000D+00	0.0000D+00	
40	0	0	0.1487D+02	0.0000D+00	0.0000D+00	
41	0	0	0.1609D+02	0.0000D+00	0.0000D+00	
42	0	0	0.1609D+02	0.0000D+00	0.0000D+00	
43	0	0	0.1738D+02	0.0000D+00	0.0000D+00	
44	0	0	0.1738D+02	0.0000D+00	0.0000D+00	
45	0	0	0.1872D+02	0.0000D+00	0.0000D+00	
46	0	0	0.1872D+02	0.0000D+00	0.0000D+00	
47	0	0	0.2013D+02	0.0000D+00	0.0000D+00	
48	0	0	0.2013D+02	0.0000D+00	0.0000D+00	
49	0	0	0.2161D+02	0.0000D+00	0.0000D+00	
50	0	0	0.2161D+02	0.0000D+00	0.0000D+00	
51	0	0	0.2317D+02	0.0000D+00	0.0000D+00	
52	0	0	0.2317D+02	0.0000D+00	0.0000D+00	
53	0	0	0.2480D+02	0.0000D+00	0.0000D+00	
54	0	0	0.2480D+02	0.0000D+00	0.0000D+00	
55	0	0	0.2650D+02	0.0000D+00	0.0000D+00	
56	0	0	0.2650D+02	0.0000D+00	0.0000D+00	
57	0	0	0.2830D+02	0.0000D+00	0.0000D+00	

Table 6.11
Input Data Sets for Problem 6 (Continued)

```
    58     0     0  0.2830D+02  0.0000D+00  0.0000D+00
    59     0     0  0.3018D+02  0.0000D+00  0.0000D+00
    60     0     0  0.3018D+02  0.0000D+00  0.0000D+00
    61     0     0  0.3215D+02  0.0000D+00  0.0000D+00
    62     0     0  0.3215D+02  0.0000D+00  0.0000D+00
    63     0     0  0.3422D+02  0.0000D+00  0.0000D+00
    64     0     0  0.3422D+02  0.0000D+00  0.0000D+00
    65     0     0  0.3640D+02  0.0000D+00  0.0000D+00
    66     0     0  0.3640D+02  0.0000D+00  0.0000D+00
    67     0     0  0.3868D+02  0.0000D+00  0.0000D+00
    68     0     0  0.3868D+02  0.0000D+00  0.0000D+00
    69     0     0  0.4107D+02  0.0000D+00  0.0000D+00
    70     0     0  0.4107D+02  0.0000D+00  0.0000D+00
    71     0     0  0.4358D+02  0.0000D+00  0.0000D+00
    72     0     0  0.4358D+02  0.0000D+00  0.0000D+00
    73     0     0  0.4621D+02  0.0000D+00  0.0000D+00
    74     0     0  0.4621D+02  0.0000D+00  0.0000D+00
    75     0     0  0.4897D+02  0.0000D+00  0.0000D+00
    76     0     0  0.4897D+02  0.0000D+00  0.0000D+00
    77     0     0  0.5187D+02  0.0000D+00  0.0000D+00
    78     0     0  0.5187D+02  0.0000D+00  0.0000D+00
    79     0     0  0.5491D+02  0.0000D+00  0.0000D+00
    80     0     0  0.5491D+02  0.0000D+00  0.0000D+00
    81     0     0  0.5809D+02  0.0000D+00  0.0000D+00
    82     0     0  0.5809D+02  0.0000D+00  0.0000D+00
    83     0     0  0.6144D+02  0.0000D+00  0.0000D+00
    84     0     0  0.6144D+02  0.0000D+00  0.0000D+00
    85     0     0  0.6495D+02  0.0000D+00  0.0000D+00
    86     0     0  0.6495D+02  0.0000D+00  0.0000D+00
    87     0     0  0.6863D+02  0.0000D+00  0.0000D+00
    88     0     0  0.6863D+02  0.0000D+00  0.0000D+00
    89     0     0  0.7249D+02  0.0000D+00  0.0000D+00
    90     0     0  0.7249D+02  0.0000D+00  0.0000D+00
    91     0     0  0.7655D+02  0.0000D+00  0.0000D+00
    92     0     0  0.7655D+02  0.0000D+00  0.0000D+00
    93     0     0  0.8080D+02  0.0000D+00  0.0000D+00
    94     0     0  0.8080D+02  0.0000D+00  0.0000D+00
    95     0     0  0.8526D+02  0.0000D+00  0.0000D+00
    96     0     0  0.8526D+02  0.0000D+00  0.0000D+00
    97     0     0  0.8994D+02  0.0000D+00  0.0000D+00
    98     0     0  0.8994D+02  0.0000D+00  0.0000D+00
    99     0     0  0.9485D+02  0.0000D+00  0.0000D+00
   100     0     0  0.9485D+02  0.0000D+00  0.0000D+00
   101     0     0  0.1000D+03  0.0000D+00  0.0000D+00
   102     0     0  0.1000D+03  0.0000D+00  0.0000D+00
     0     0     0       0.0         0.0     0.0              END OF X-COORD
     1    50     2       0.0D0     0.0D0     0.0D0            DEFINE Z FOR ODD NODES
     2    50     2       2.5D0     0.0D0     0.0D0            DEFINE Z FOR EVEN NODES
     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  50
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 5    0
Ca              1     1
Na              2     1
CO3             3     1
Cl              4     1
H               5     1
C ******* DATA SET 11:  INITIAL CONDITIONS
  1 101 1  2.0D-2      0.0D0 0.0D0
  0   0  0  0.0         0.0   0.0                 END OF I.C. for Component 1
 -1 101 1  8.0D-3      0.0D0 0.0D0
  0   0  0  0.0         0.0   0.0                 END OF I.C. for Component 2
```

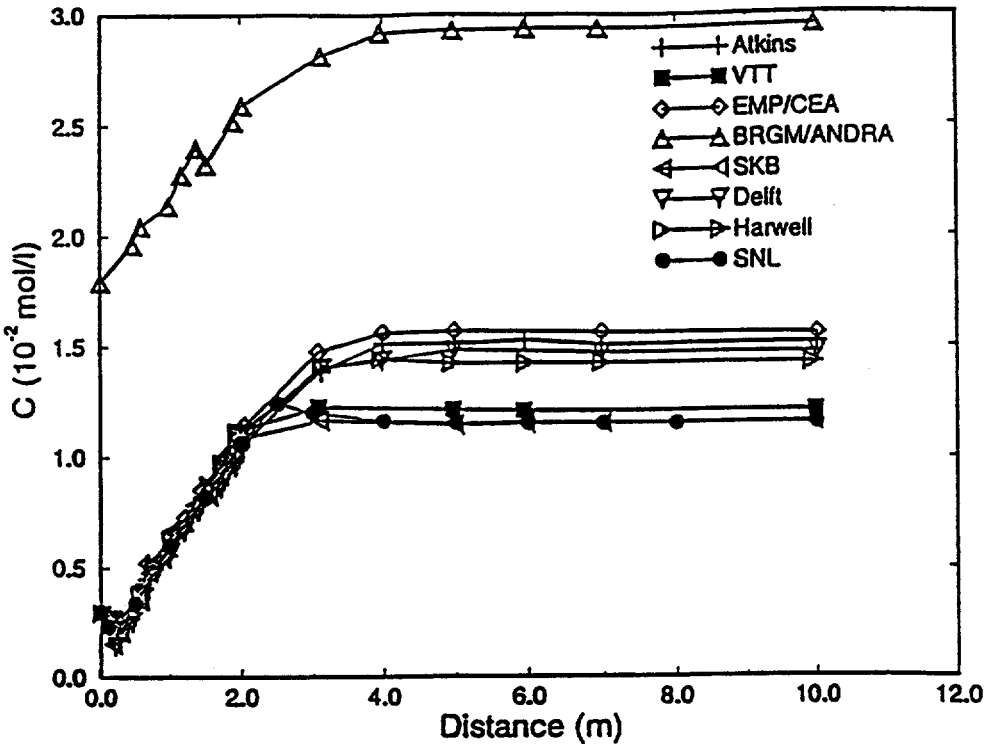
Table 6.11
Input Data Sets for Problem 6 (Continued)

```
  1 101 1  1.0D-10     0.0D0 0.0D0
  0  0  0  0.0         0.0   0.0                 END OF I.C. for Component 3
  1 101 1  4.0D-2      0.0D0 0.0D0
  0  0  0  0.0         0.0   0.0                 END OF I.C. for Component 4
  1 101 1  -5.4308D-2  0.0D0 0.0D0
  0  0  0  0.0         0.0   0.0                 END OF I.C. for Component 5
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  2.0D-2    1.0D6   2.0D-2             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                       END OF B.C. for Component 1
     0.0D0  8.0D-3    1.0D6   8.0D-3             RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                       END OF B.C. for Component 2
     0.0D0  1.0D-10    1.0D6  1.0D-10           RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                       END OF B.C. for Component 3
     0.0D0  2.0D-16    1.0D6  2.0D-16           RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                       END OF B.C. for Component 4
     0.0D0  -5.4308D-2 1.0D6 -5.4308D-2         RIGHT BOUNDARY
    1    0    0    1    0
    0    0    0    0    0                       END OF B.C. for Component 5
  1  1  1  101  1
  0  0  0    0  0
  1   0   50   1   2  0   0  0   0
  0   0    0   0   0  0   0  0   0               END OF VARIABLE BC
C ******* DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
     0.0D0  5.5D-3    1.0D6  5.5D-3             LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                       END OF B.C. for Component 1
     0.0D0  8.0D-3    1.0D6  8.0D-3             LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                       END OF B.C. for Component 2
     0.0D0  4.5D-3    1.0D6  4.5D-3             LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                       END OF B.C. for Component 3
     0.0D0  1.0D-2    1.0D6  1.0D-2             LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                       END OF B.C. for Component 4
     0.0D0  2.424D-3  1.0D6 2.1835D-3           LEFT BOUNDARY
    1    1    1    1    0
    0    0    0    0    0                       END OF B.C. for Component 5
    1    1    1    1    1
    0    0    0    0    0                       END OF DIRICHET BC
C ******* DATA SET 16: VELOCITY AND MOISTURE CONTENT
   1 101 1  0.1D0  0.0D0  0.0D0 0.0D0
   0   0 0  0.0    0.0    0.0   0.0             END OF VELOCITY
   1  49 1  1.0D0  0.0D0
   0   0 0  0.0    0.0                         END OF MOISTURE CONTENT
C ******* DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
 5 0 12 0 0 2 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.1 2 5 0
C ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.0 1.0
-20.0 20.0 0.0 14.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0D0  5.0D-9  100  100  2.0  1.0D38
```

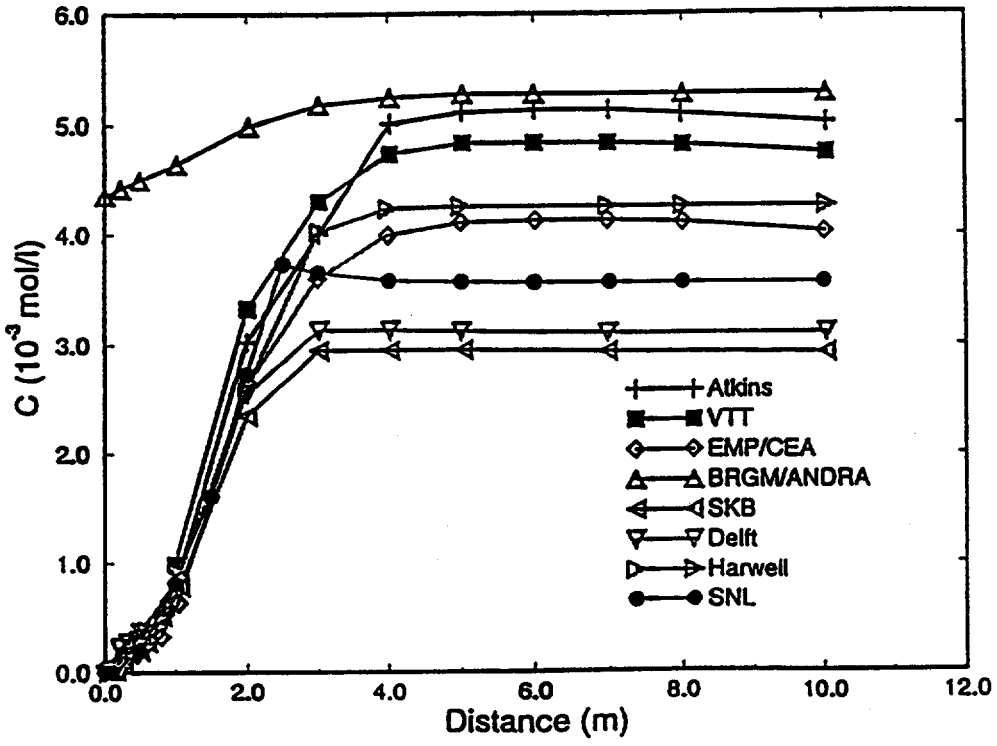
Table 6.11

Input Data Sets for Problem 6 (Concluded)

```
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
Ca                          1
Na                          1
CO3                         1
Cl                          1
H                           1
C ******* DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
Free Ca2+                   0
 2.0D-3  2.0  0
Free Na+                    0
 8.0D-4  1.0  0
Free CO3                    0
 1.5D-3 -2.0  0
Free Cl-                    0
 2.0D-3 -1.0  0
Free H+                     0
 3.16D-13 1.0 0
C ******* DATA SET 25:  COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
CaCO3                      0
 2.0D-06  3.153 1 0 1 0 0 0 1 0 1 0  0
CaCO3H                     0
 1.0D-06  11.43 1 0 1 0 1 0 1 0 1 0  1
Ca(OH)                     0
 1.0D-04 -12.7 1 0 0 0 -1 0 1 0 0 0 -1
NaCO3                      0
 1.0D-06  1.27 0 1 1 0  0 0 0 1 1 0  0
NaCO3H                     0
 1.0D-06  10.08 0 1 1 0 1 0 0 1 1 0 1
CO3H                       0
 1.0D-06  10.33 0 0 1 0 1 0 0 0 1 0 1
CO3(H)2                    0
 1.0D-08  16.68 0 0 1 0 2 0 0 0 1 0 2
(OH)                       0
 3.0D-03 -13.99 0 0 0 0 -1 0 0 0 0 0 -1
CaCl                       1
 1.0D-07  0.08  1 0 0 1 0 0 1 0 0 1 0
Na(OH)                     1
 1.0D-04 -13.8  0 1 0 0 -1 0 0 1 0 0 -1
(Na)2CO3                   1
 1.0D-09  0.68  0 2 1 0 0 0 0 2 1 0 0
NaCl                       1
 1.0D-08 -0.9   0 1 0 1 0 0 0 1 0 1 0
C ******* DATA SET 27:  PRECIPITATED/DISSOLVED SPECIES
CaCO3                      0
 .000002  8.35  1 0 1 0 0 1 0 1 0 0
Ca(OH)2                    0
 .0002 -22.65   1 0 0 0 -2 1 0 0 0 -2
                                        END OF JOB
```



a) Ca^{2+}



b) $CaOH^{+}$

Figure 6.16
Comparison of Aqueous Calcium Speciation Profiles at t=100 Yrs. a) Ca^{2+} b) $CaOH^{+}$

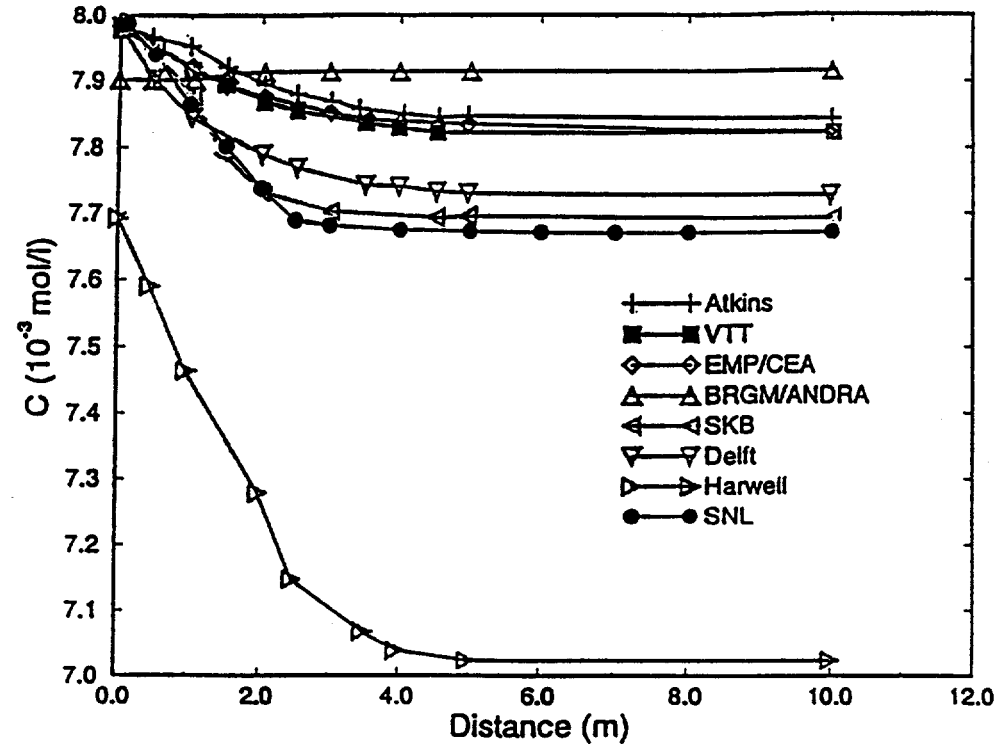


Figure 6.17
Comparison of Na^+ Concentration at t=100 yrs.

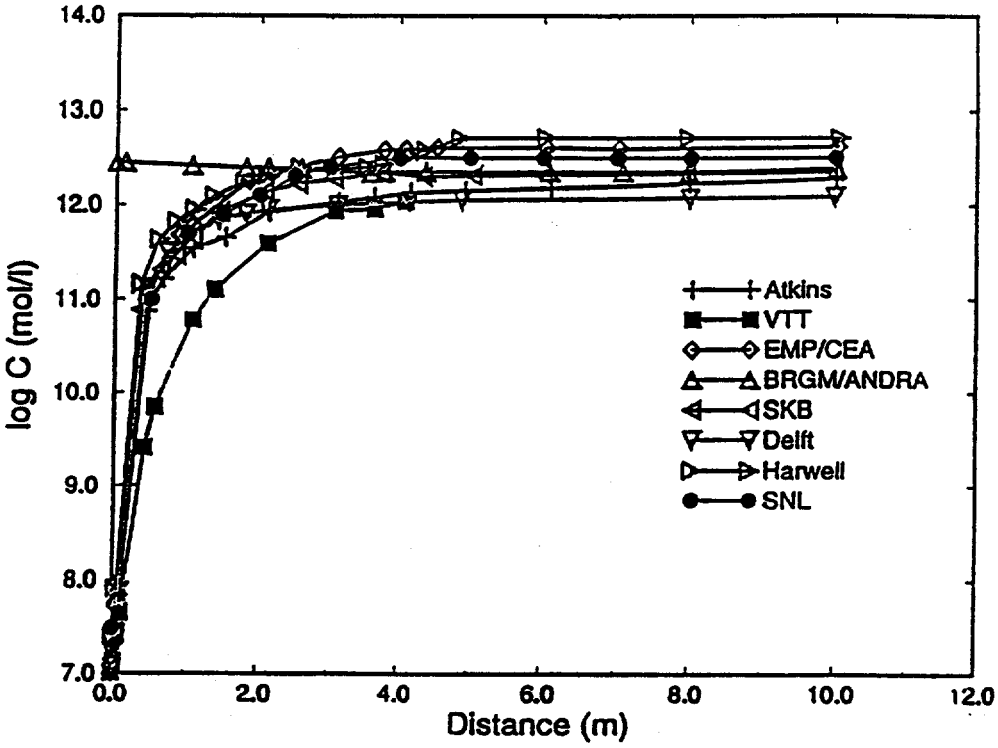


Figure 6.18
Comparison of pH at t=200 Yrs.

6.7 Problem 7: Test of Transport, Complexation, and Adsorption

This example considers the transport and interaction of eight chemical components: calcium, carbonate, uranium(VI), sulfate, neptunium(V), plutonium(IV), hydronium, and SOH (adsorbing site). Twenty-three aqueous complexes and five surface species are considered. The thermodynamic data for this problem are given in Table 6.12. The adsorbing site has properties similar to goethite or amorphous iron oxyhydroxide (Kent et al., 1988).

Table 6.12
List of Thermodynamic Data for Problem 7

	Components Stoichiometric Coefficient								
Species	Ca^{2+}	CO_3^{2-}	UO_2^{2+}	SO_4^{2-}	NpO_2^+	Pu^{4+}	H^+	SOH	Log K
Ca^{2+}	1	0	0	0	0	0	0	0	0.00
CO_3^{2-}	0	1	0	0	0	0	0	0	0.00
UO_2^{2+}	0	0	1	0	0	0	0	0	0.00
SO_4^{2-}	0	0	0	1	0	0	0	0	0.00
NpO_2^+	0	0	0	0	1	0	0	0	0.00
Pu^{4+}	0	0	0	0	0	1	0	0	0.00
H^+	0	0	0	0	0	0	1	0	0.00
SOH	0	0	0	0	0	0	0	1	0.00
OH^-	0	0	0	0	0	0	-1	0	-14.00
$CaCO_3$	1	1	0	0	0	0	0	0	3.22
$CaHCO_3^+$	1	1	0	0	0	0	1	0	11.43
$CaSO_4$	1	0	0	1	0	0	0	0	11.43
$Ca(OH)^+$	1	0	0	0	0	0	-1	0	-12.85
UO_2OH^+	0	0	1	0	0	0	-1	0	-5.30
$(UO_2)_2(OH)_2^{2+}$	0	0	2	0	0	0	-2	0	-5.68
$(UO_2)_3(OH)_4^{2+}$	0	0	3	0	0	0	-4	0	-11.88
$(UO_2)_3(OH)_5^+$	0	0	3	0	0	0	-5	0	-15.82
$(UO_2)_4(OH)_7^+$	0	0	4	0	0	0	-7	0	-21.90
$(UO_2)_3(OH)_7^-$	0	0	3	0	0	0	-7	0	-28.34
UO_2CO_3	0	1	1	0	0	0	0	0	9.65
$UO_2(CO_3)_2^{2-}$	0	2	1	0	0	0	0	0	17.08
$UO_2(CO_3)_3^{4-}$	0	3	1	0	0	0	0	0	21.70

Table 6.12
List of Thermodynamic Data for Problem 7 (concluded)

Species	Components Stoichiometric Coefficient								Log K
	Ca^{+}	CO_3^{2-}	UO_2^{2+}	SO_4^{2-}	NpO_2^{+}	Pu^{4+}	H^{+}	SOH	
$(UO_2)_2CO_3(OH)_3^-$	0	1	2	0	0	0	-3	0	-1.18
$(UO_2)(SO_4)$	0	0	1	1	0	0	0	0	2.95
$(UO_2)(SO_4)_2^{2-}$	0	0	1	2	0	0	0	0	4.00
HCO_3^-	0	1	0	0	0	0	1	0	10.32
H_2CO_3	0	1	0	0	0	0	2	0	16.67
$H(SO_4)^-$	0	0	0	1	0	0	1	0	1.99
$(NpO_2)(OH)$	0	0	0	0	1	0	-1	0	-8.85
$(NpO_2)(CO_3)^-$	0	1	0	0	1	0	0	0	5.60
$(NpO_2)(CO_3)_2^{3-}$	0	2	0	0	1	0	0	0	7.75
SO^-	0	0	0	0	0	0	-1	1	-10.30
SOH_2^+	0	0	0	0	0	0	1	1	5.40
$(UO_2)(OH)_2(SOH)$	0	0	1	0	0	0	-2	1	-7.10
$(UO_2)_3(OH)_8(SOH)^{2-}$	0	0	3	0	0	0	-8	1	-31.00
$(NpO_2)(OH)(SOH)$	0	0	0	0	1	0	-1	1	-3.50

The flow velocity (from left to right) is 3 dm/day, the porosity is 0.3, and the dispersivity is 1 dm. A total of 500 days (500 time steps of size 1 day) were simulated. The region is made up of 50 elements of 20 dm x 20 dm. Figure 6.19 illustrates the column, element and node numbering, direction of flow and x/z axes; note that the horizontal axis is the z-axis.

The initial pH is fixed within a narrow range between 7.6 and 7.9. The initial concentration of total calcium, carbonate and sulfate in the column is 10^{-4} M. The iron oxyhydroxide surface area is specified for each node so that the site concentration of surface sites (available to 1 L of the solution) is 10^{-4} M everywhere except for the region 220 to 600 dm from the left end of the column; in this region the site concentration is $2.5 \cdot 10^{-2}$ M, or 250 times the background value. The higher concentration of the adsorbent was chosen to facilitate adsorption of uranium and neptunium in the region. The initial (background) concentrations of uranium(VI), neptunium(V) and plutonium(IV) in the column are 10^{-8}, 10^{-16}, and 10^{-16} M, respectively.

The boundary condition is defined such that the composition of the groundwater entering the column at the left end is constant for all components except carbonate. The calcium

concentration is held constant at 10^{-3} M throughout the period. The sulfate concentration is set to 10^{-4} M to represent the near absence of sulfate. The boundary concentrations of uranium, neptunium and plutonium are 10^{-6}, $2.5 \cdot 10^{-10}$, and 10^{-9} M respectively. The pH value of the incoming water is held constant at 3.0. The boundary concentration of carbonate varies with time; for the first 198 days of the simulation, the total concentration of incoming carbonate is 10^{-4} M; at 202 days, it increases to 10^{-2} M; and at 498 days, it drops to 10^{-3} M.

The time-dependent carbonate boundary concentration is imposed to permit a buildup of uranium and neptunium during the first 198 days of simulation due to adsorption and to facilitate desorption of the adsorbed elements after 200 days. Uranium forms strong carbonate complexes and also adsorbs strongly onto goethite, the model adsorbent used in this simulation. Neptunium forms weaker carbonate complexes and adsorbs less strongly than uranium onto goethite. The adsorption of plutonium onto goethite and the complex formation between plutonium and carbonate is deliberately ignored; thus, plutonium is forced to behave as a totally conservative element.

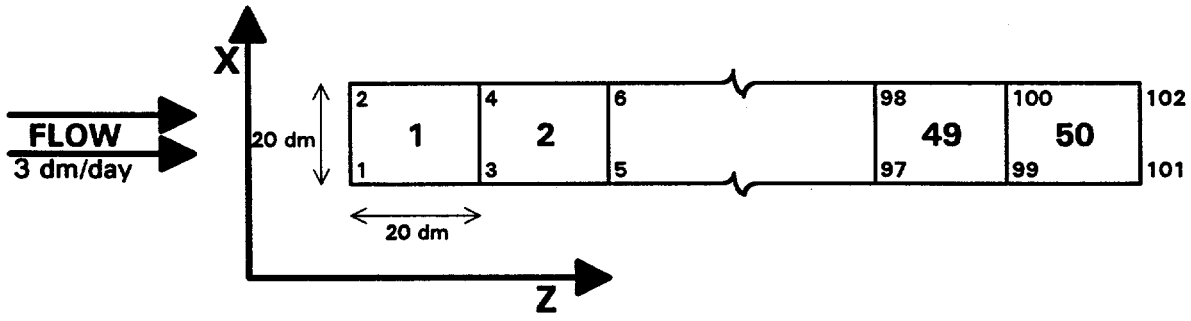


Figure 6.19
Finite Element Discretization of Problem 7

The input data sets for the problem are prepared according the data input guide in Appendix A and are given in Table 6.13. Results are illustrated in Figure 6.20, where the time-dependent profiles of dissolved uranium concentrations are shown. The region rich in iron oxyhydroxide is indicated as the "Gt-rich" region. Note that nearly quantitative adsorption of uranium occurs in this zone during the first 200 days of the simulation. When the incoming carbonate concentration increases after 200 days, desorption of this uranium is facilitated and the concentration of dissolved uranium exceeds that of the influent. The simulation results are identical to those obtained with HYDROGEOCHEM (with both the MINEQL version and the EQMOD version); thus, coupled transport and geochemical equilibrium of complexation and adsorption are verified.

Note: Both ends are specified as variable boundaries. (See note in problem 5 discussing variable boundaries.)

Table 6.13
Input Data Sets for Problem 7

```
    7 LEHGC: TEST OF COUPLING - COMPLEXATION AND ADSORPTION (units are dm-kg-day)
 0 0 0 1 0
C ******* DATA SET 2:  BASIC INTEGER PARAMETERS
 102 50 1 0 500 1 4 -1 1 0 1 0 15 1 300 0 1 0 1 12 1
C ******* DATA SET 3:  BASIC REAL PARAMETERS
 1.0 0.0 1.0 5.0D2  1.0 0.0 1.0 1.0  1.0D-2  1.0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
4444000000000000000020000000000000000000200000000000000000020000000000000000
0000000000000000000020000000000000000000200000000000000000020000000000000000
0000000000000000000020000000000000000000200000000000000000020000000000000000
0000000000000000000020000000000000000000200000000000000000020000000000000000
0000000000000000000020000000000000000000200000000000000000020000000000000000
0000000000000000000020000000000000000000200000000000000000020000000000000000
00000000000000000002
1100000000000000000010000000000000000000100000000000000000010000000000000000
1000000000000000000010000000000000000000100000000000000000010000000000000000
1000000000000000000010000000000000000000100000000000000000010000000000000000
1000000000000000000010000000000000000000100000000000000000010000000000000000
1000000000000000000010000000000000000000100000000000000000010000000000000000
1000000000000000000010000000000000000000100000000000000000010000000000000000
10000000000000000001
    1.0D38C ******* DATA SET 5:  CHEMICAL PRINTOUT
 2
 1 101
C ******* DATA SET 6:  MATERIAL PROPERTIES
 1.0 0.0 0.0 1.2
C ******* DATA SET 7:  NODAL POINT COORDINATES
    1   50    2          0.0D0      0.0D0      0.0
    2   50    2         20.000D0    0.0D0      0.0D0
    0    0    0          0.0        0.0        0.0      END OF X
    1   50    2          0.0D0     20.000D0    0.0D0
    2   50    2          0.0D0     20.000D0    0.0
    0    0    0          0.0        0.0        0.0      END OF Z
C ******* DATA SET 8:  ELEMENT CONNECTIVITY
    1    1    2    4    3    1    1   50
C ******* DATA SET 10:  TRANSPORT COMPONENT INFORMATION
 7 1
 CALCIUM      1    1
 CARBONATE    2    1
 URANIUM      3    1
 SULFATE      4    1
 NEPTUNIUM    5    1
 PLUTONIUM    6    1
 HYDROGEN     7    3
 SOH          8    2
C ******* DATA SET 11:  INITIAL CONDITIONS
    1  101    1        1.00D-4     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. CA
    1  101    1        1.00D-4     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. CO3
    1  101    1        1.0D-08     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. UO2
    1  101    1        1.00D-4     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. SO4
    1  101    1        1.0D-16     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. NPV
    1  101    1        1.0D-16     0.0D0      0.0D0
    0    0    0        0.0         0.0        0.0        END OF I.C. PUIV
    1   10    2       -7.60D00    -0.03D0     0.0D0
    2   10    2       -7.60D0     -0.03D0     0.0D0      END 1ST BLK
   23    9    2       -7.90D00     0.00D0     0.0D0
   24    9    2       -7.90D00     0.00D0     0.0D0      END 2ND BLK
   43    9    2       -7.90D00     0.0D0      0.0D0
   44    9    2       -7.90D00     0.0D0      0.0D0      END 3RD BLK
```

Table 6.13
Input Data Sets for Problem 7 (Continued)

```
   63     9     2          -7.90D00       0.0D0       0.0D0
   64     9     2          -7.90D00       0.0D0       0.0D0          END 4TH BLK
   83     9     2          -7.90D00       0.03D0      0.0D0
   84     9     2          -7.90D00       0.03D0      0.0D0          END 5TH BLK
    0     0     0           0.0           0.0         0.0            END OF I.C. PH
    1    21     1           1.00D-4       0.0D0       0.0D0
   23    19     1           2.50D-2       0.0D0       0.0D0
   43    19     1           2.50D-2       0.0D0       0.0D0
   63    19     1           1.00D-4       0.0D0       0.0D0
   83    19     1           1.00D-4       0.0D0       0.0D0
    0     0     0           0.0           0.0         0.0            END OF I.C. SOH
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
   0 0 0   0 0 0   0 0 0   4 2 2 5
C ******* DATA SET 14:  VARIABLE BOUNDARY CONDITIONS
     0.0D0     1.0D-3     1.98D2    1.0D-3     2.02D02     1.0D-3    4.98D2     1.0D-3
     1.0D38    1.0D-3
     0.0D0     1.0D-3     1.98D2    1.0D-3     2.02D02     1.0D-3    4.98D2     1.0D-3
     1.0D38    1.0D-3
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF BC CA
     0.0D0     1.0D-4    1.98D2    1.0D-4     2.02D02     1.0D-2    4.98D2     1.0D-3
     1.0D38    1.0D-3
     0.0D0     1.0D-4     1.98D2    1.0D-4     2.02D02     1.0D-2    4.98D2     1.0D-3
     1.0D38    1.0D-3
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF BC CO3
     0.0D0     1.0D-6     1.98D2    1.0D-6     2.02D02     1.0D-6    4.98D2     1.0D-6
     1.0D38    1.0D-6
     0.0D0     1.0D-6     1.98D2    1.0D-6     2.02D02     1.0D-6    4.98D2     1.0D-6
     1.0D38    1.0D-6
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF BC UO2
     0.0D0     1.0D-4     1.98D2    1.0D-4     2.02D02     1.0D-4    4.98D2     1.0D-4
     1.0D38    1.0D-4
     0.0D0     1.0D-4     1.98D2    1.0D-4     2.02D02     1.0D-4    4.98D2     1.0D-4
     1.0D38    1.0D-4
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF SO4
     0.0D0    2.5D-10    1.98D2   2.5D-10     2.02D02    2.5D-10    4.98D2    2.5D-10
     1.0D38   2.5D-10
     0.0D0    2.5D-10    1.98D2   2.5D-10     2.02D02    2.5D-10    4.98D2    2.5D-10
     1.0D38   2.5D-10
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF BC NP
     0.0D0     1.D-09     1.98D2    1.D-09     2.02D02     1.D-09    4.98D2     1.D-09
     1.0D38    1.D-09
     0.0D0     1.D-09     1.98D2    1.D-09     2.02D02     1.D-09    4.98D2     1.D-09
     1.0D38    1.D-09
    1     0     0     1     0
    2     0     0     2     0
    0     0     0     0     0                              END OF BC PU4
```

Table 6.13
Input Data Sets for Problem 7 (Continued)

```
     0.0D0     -7.6D0     1.98D2    -7.6D0     2.02D02    -7.6D00    4.98D2     -7.6D0
     1.0D38    -7.6D0
     0.0D0     -7.6D0     1.98D2    -7.6D0     2.02D02    -7.6D00    4.98D2     -7.6D0
     1.0D38    -7.6D0
    1    0     0    1     0
    2    0     0    2     0
    0    0     0    0     0                          END OF B.C. PH
     0.0D0     1.0D-3     1.98D2    1.0D-3     2.02D02     1.0D-3    4.98D2     1.0D-3
     1.0D38    1.0D-3
     0.0D0     1.0D-3     1.98D2    1.0D-3     2.02D02     1.0D-3    4.98D2     1.0D-3
     1.0D38    1.0D-3
    1    0     0    1     0
    2    0     0    2     0
    0    0     0    0     0                              END OF BC SOH (NOT USED)
    1    1     1    1     1
    3    1     1  101     1
    0    0     0    0     0                              END OF NVNP
    1    0     1    1     2    0    0    0    0
    2    0    50    3     4    0    0    0    0
    0    0     0    0     0    0    0    0    0    END OF NVES
C ******* DATA SET 16:  VELOCITY AND MOISTURE CONTENT
    1  101     1          0.0D0      3.000D00   0.0D0      0.0D0
    0    0     0          0.0        0.0        0.0        0.0     END OF VELOCITY
    1   49     1          0.3D0      0.0D0
    0    0     0          0.0        0.0                   END OF MOISTURE CONTENT
C ******* DATA SET 17:  NUMBER OF COMPONENTS AND PRODUCT SPECIES
 7 1 23 5 0 0 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0 7 0
c ******* DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.3  1.0
 -20.0 20.0 -20.0 20.0
c ******* DATA SET 20: ADSORPTION INFORMATION
 1 0
 0 0
 0.0 0.0 0.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0 1.0d-6 50 1 2.0d0 1.0d38
c ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
 CALCIUM                 1
 CARBONATE               1
 URANIUM                 1
 SULFATE                 1
 NEPTUNIUM               1
 PLUTONIUM               1
 HYDROGEN                1
 SOH                     2
C ******* DATA SET 24:  COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++                0
9.8D-5  2  0
FREE CO3--               0
2.4D-7  -2  0
FREE UO2++               0
3.16D-13 2 0
FREE SO4--               0
9.80D-5  -2 0
FREE NPO2                0
3.55D-17 1 0
FREE PU4+                0
1.0D-16 4 0
FREE H+                  3
1.78D-8 1 0
FREE SOH                 0
9.93D-5 0 0
```

Table 6.13
Input Data Sets for Problem 7 (Concluded)

```
C ******* DATA SET 25:  COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH-                              0
5.75D-7  -13.99 0 0 0 0 0 0 -1 0   0   0 0 0 0 0 0 -1 0
CACO3                            0
4.19D-8    3.22 1 1 0 0 0 0  0 0   0   1 1 0 0 0 0  0 0
HCACO3                           0
1.21D-7   11.43 1 1 0 0 0 0  1 0   0   1 1 0 0 0 0  1 0
CASO4                            0
1.96D-6    2.31 1 0 0 1 0 0  0 0   0   1 0 0 1 0 0  0 0
CAOH                             0
7.77D-10 -12.85 1 0 0 0 0 0 -1 0   0   1 0 0 0 0 0 -1 0
UO2OH                            0
7.75D-11 -5.3   0 0 1 0 0 0 -1 0   0   0 0 1 0 0 0 -1 0
(UO2)2(OH)2                      0
5.0D-16   -5.68 0 0 2 0 0 0 -2 0   0   0 0 2 0 0 0 -2 0
(UO2)3(OH)4
2.74D-19 -11.88 0 0 3 0 0 0 -4 0   0   0 0 3 0 0 0 -4 0
(UO2)3(OH)5                      0
1.77D-15 -15.82 0 0 3 0 0 0 -5 0   0   0 0 3 0 0 0 -5 0
(UO2)4(OH)7                      0
1.28D-18 -21.90 0 0 4 0 0 0 -7 0   0   0 0 4 0 0 0 -7 0
(UO2)3(OH)7                      0
1.69D-12 -28.34 0 0 3 0 0 0 -7 0   0   0 0 3 0 0 0 -7 0
(UO2)(CO3)                       0
3.17D-10   9.65  0 1 1 0 0 0  0 0   0   0 1 1 0 0 0  0 0
(UO2)(CO3)2                      0
2.20D-9   17.08  0 2 1 0 0 0  0 0   0   0 2 1 0 0 0  0 0
(UO2)(CO3)3                      0
2.36D-11  21.70 0 3 1 0 0 0  0 0   0   0 3 1 0 0 0  0 0
(UO2)2(CO3)(OH)3                 0
2.29D-10  -1.18 0 1 2 0 0 0 -3 0   0   0 1 2 0 0 0 -3 0
(UO2)(SO4)                       0
2.40D-14   2.95 0 0 1 1 0 0  0 0   0   0 0 1 1 0 0  0 0
(UO2)(SO4)2
2.64D-17   4.00 0 0 1 2 0 0  0 0   0   0 0 1 2 0 0  0 0
HCO3                             0
9.58D-5   10.32 0 1 0 0 0 0  1 0   0   0 1 0 0 0 0  1 0
H2CO3                            0
3.81D-6   16.67 0 1 0 0 0 0  2 0   0   0 1 0 0 0 0  2 0
HSO4                             0
1.70D-10   1.99 0 0 0 1 0 0  1 0   0   0 0 0 1 0 0  1 0
(NPO2)(OH)                       0
2.70D-18  -8.85 0 0 0 0 1 0 -1 0   0   0 0 0 0 1 0 -1 0
(NPO2)(CO3)                      0
3.48D-18   5.60 0 1 0 0 1 0  0 0   0   0 1 0 0 1 0  0 0
(NPO2)(CO3)2                     0
1.27D-22   7.75 0 2 0 0 1 0  0 0   0   0 2 0 0 1 0  0 0
C ******* DATA SET 26:  ADSORBED SPECIES
SO                               0
2.80D-7  -10.30 0 0 0 0 0 0 -1 1   0 0 0 0 0 0 -1 1
SOH2                             0
4.43D-7    5.40 0 0 0 0 0 0  1 1   0 0 0 0 0 0  1 1
(UO2)(OH)2(SOH)                  0
6.86D-9   -7.10 0 0 1 0 0 0 -2 1   0 0 1 0 0 0 -2 1
(UO2)3(OH)8(SOH)                 0
2.07D-11 -31.00 0 0 3 0 0 0 -8 1   0 0 3 0 0 0 -8 1
(NPO2)(OH)(SOH)                  0
5.99D-17  -3.50 0 0 0 0 1 0 -1 1   0 0 0 0 1 0 -1 1
                                 END OF JOB
```

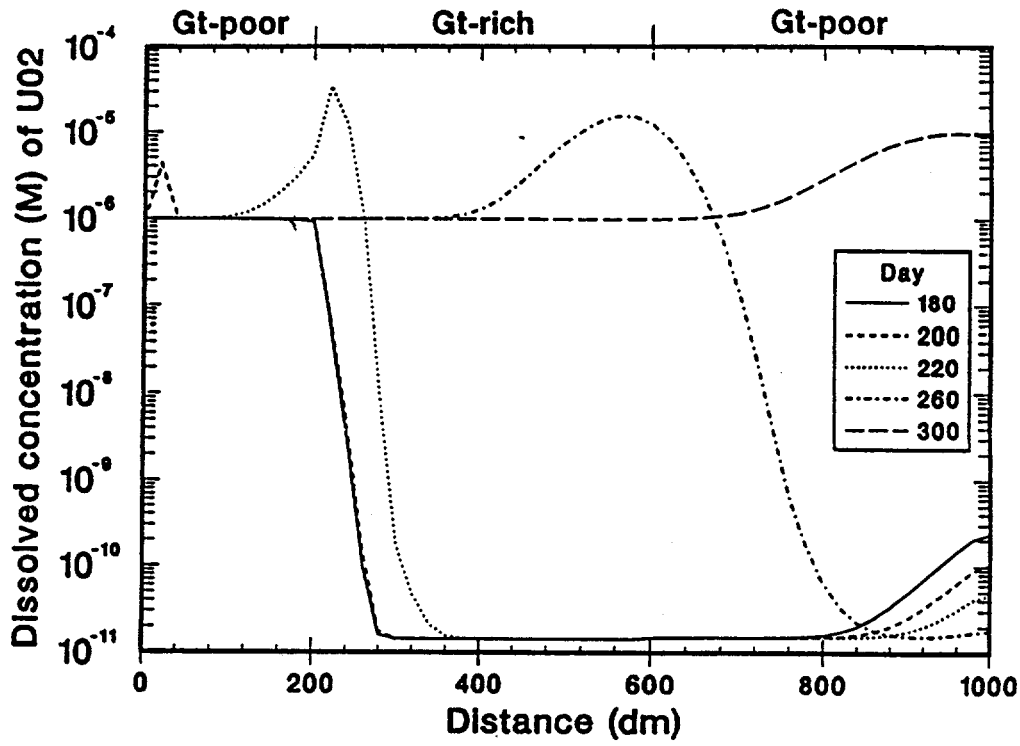


Figure 6.20
Results of Problem 7. Profiles of Dissolved Uranium Concentrations at Various Times.

6.8 Problem 8: Test of Advective Transport and Chemical Equilibrium

This problem considers the release and migration of uranium from a simplified uranium mill tailings pile. A schematic two-dimensional vertical cross section of the hypothetical site is shown in Figure 6.21. The mill tailings pile is located adjacent to a surface that slopes down to a river. The region is discretized with 158 elements and 192 nodes (Figure 6.22). The vertical left edge and horizontal bottom of the region are impermeable no-flow boundaries. The sloping region on the top right is a variable flow boundary with either zero ponding depth or a net rainfall rate of 0.0139 dm/day. The horizontal region on the top of the mill tailings pile is a Cauchy flow boundary with an infiltration rate of 0.139 dm/day. The five nodes on the vertical line on the right side and the two nodes on the river bottom are specified as known-head conditions (Dirichlet flow-boundary conditions). Total head at the five vertical nodes is 39 dm. The total head on the left and right nodes of the river bottom are 45 dm and 40 dm, respectively. Only advective transport is considered in this example.

This problem differs from previous problems in the manner in which the flow field is specified. The flow field was simulated using the HYDROFLOW program and is shown in Figure 6.23. HYDROFLOW is a simplified version of FEMWATER (Yeh 1987) that can be used to write the flow field description (velocities and moisture content) to a binary file used as input to LEHGC1.1. Readers who wish to run this sample problem should obtain a copy of the HYDROFLOW program and input data sets from the first author.

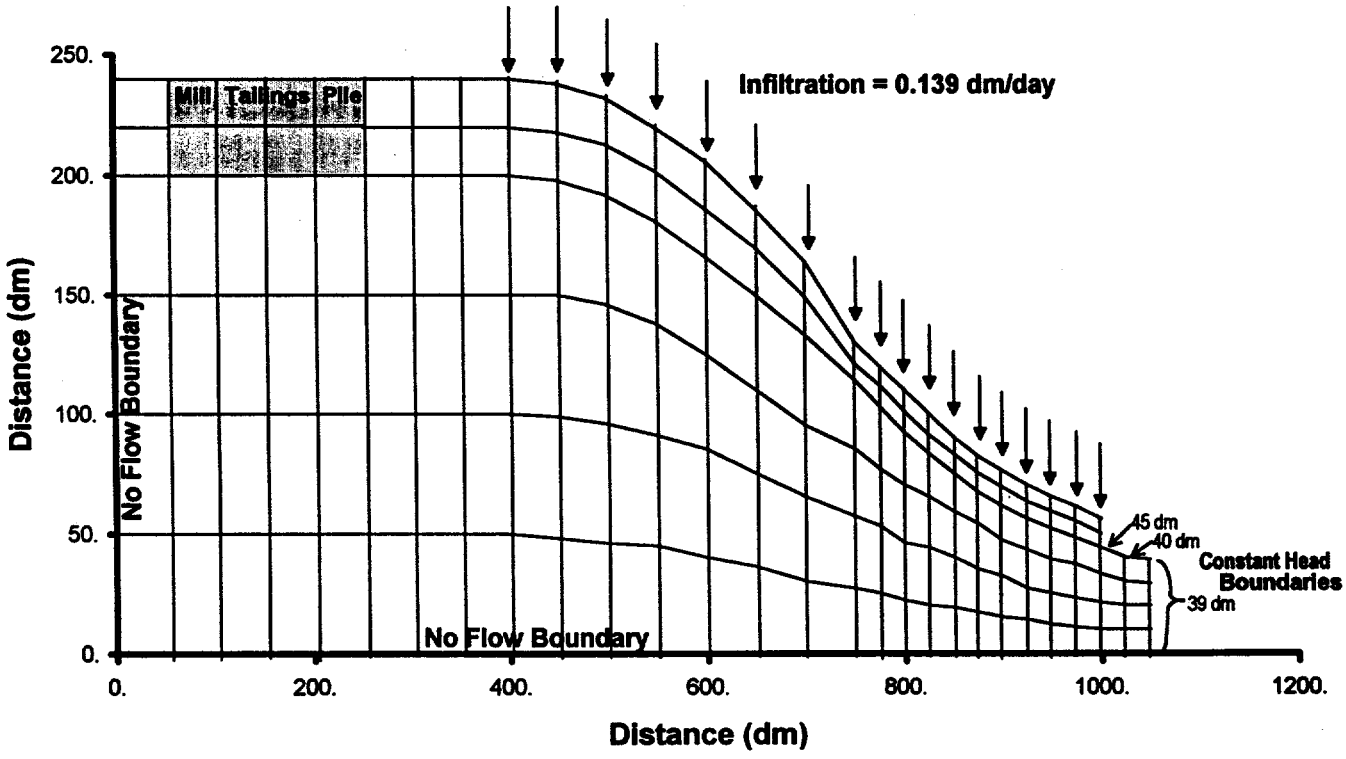


Figure 6.21
Cross Section for Problem 8. Shaded cells represent the mill tailings pile.

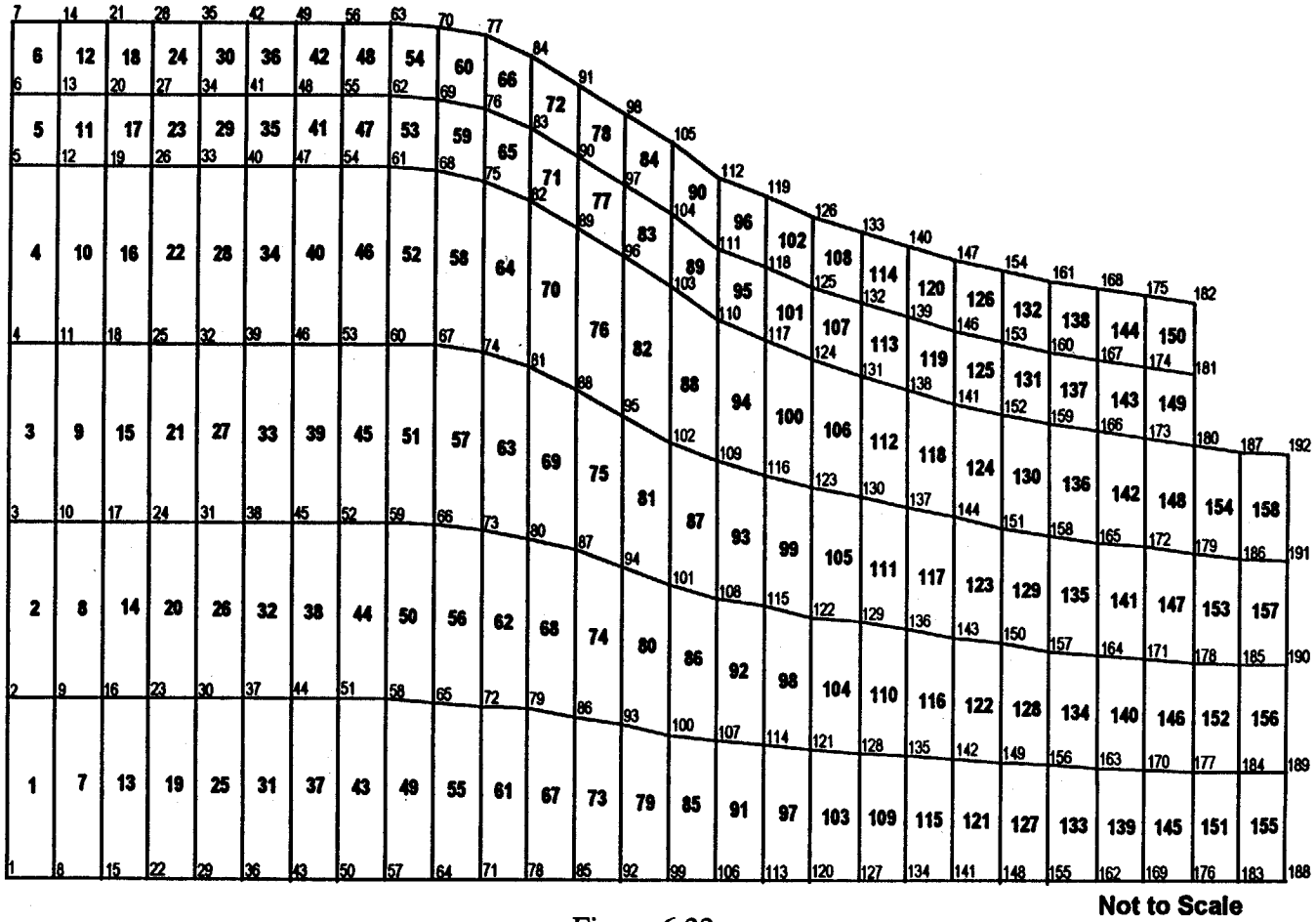


Figure 6.22

Finite Element Discretization of Problem 8. Large bold type numbers are element numbers and small numbers are node numbers.

Concentration Boundary Conditions: Nodes 63, 70, 77, 84, 91, 96, 105, 112, 119, 126, 133, 140, 147, 154, 161, 168, 175, 182, 181, 180, 187 and 192 correspond to compressed variable boundary nodes 1 - 22. Nodes 12, 13, 14, 19, 20, 21, 26, 27, 28, 33, 34, 35, 40, 41, and 42 correspond to compressed Dirichlet (specified concentration) nodes 1 - 15. (Refer to Data Sets 14 and 15.)

Flow Boundary Conditions (specified in HYDROFLOW): Nodes 63, 70, 77, 84, 91, 96, 105, 112, 119, 126, 133, 140, 147, 154, 161, 168, 175, 182, 181, 180 and 187 correspond to compressed variable boundary nodes 1 - 21. Nodes 180, 187, 192, 191, 190, 189, 188 correspond to compressed Dirichlet (specified head) nodes 1 - 7. Nodes 14, 21, 28, 35 and 42 correspond to compressed Cauchy (specified flux) nodes 1 - 5. (Refer to Data Sets 13, 14 and 15 in HYDROFLOW.)

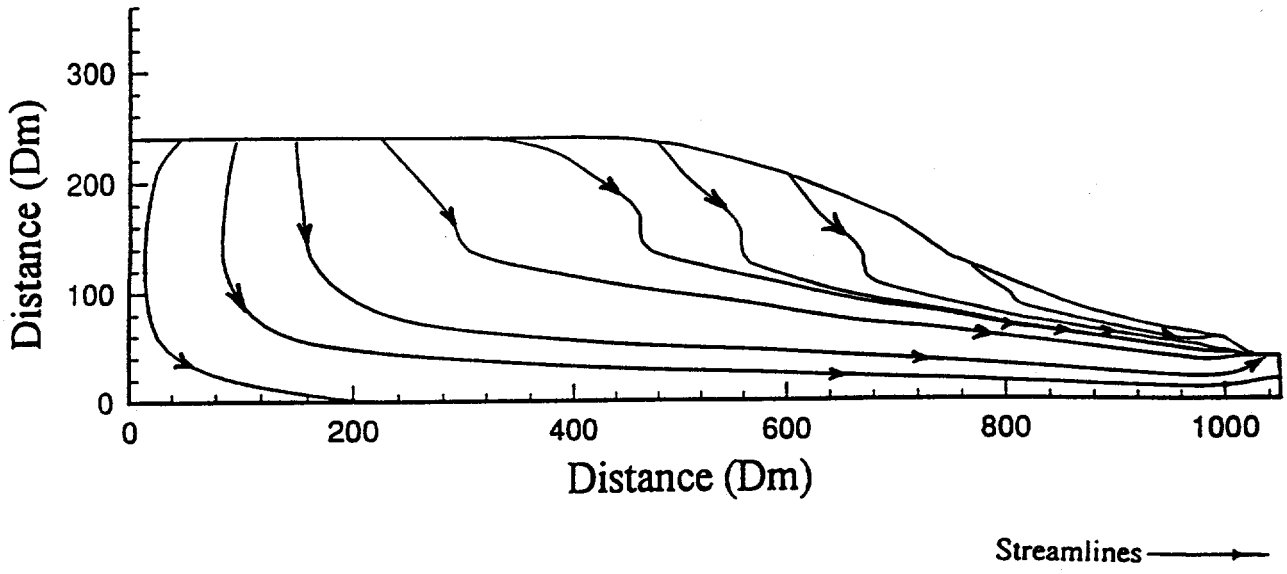


Figure 6.23
Flow Field of Infiltration from a Uranium Mill Tailing

The problem also differs from previous problems in the value chosen for the IDTI parameter (Data Set 2). For advection-dominated problems, this parameter is set to zero; the solution obtained will be similar to that obtained with LEHGC version 1.0. For dispersion or decay-dominated problems the IDTI parameter should be set to 1.0.

The problem considers the hydrogeochemical transport of seven components: calcium, carbonate, uranium(VI), sulfate, phosphate, ferrous iron, and hydronium (pH). The pH is computed for each point on the basis of the total excess hydronium designated by TOT H (total analytical excess or deficit of protons, a concept similar to the proton condition). A total of 35 species and 14 minerals are defined for the problem; redox reactions were not considered. Table 6.14 lists the thermodynamic data for the chemical system considered.

The data input sets for this problem are shown in Table 6.16. Note that the KVI parameter (Data Set 2) specifies that the binary file containing the description of the flow field is read from Logical Unit 11. A total of 300 days were simulated, 150 time steps with a constant step size of 2 days. Different initial conditions are specified for various regions of Figure 6.21. The composition of the pore water in the tailings, pore water outside of the tailing pile and the recharge water are given in Table 6.15. The mill tailings pile is represented by Dirichlet nodes in order to hold the total concentrations of the chemical components constant throughout the simulation (Data Set 15). The sloping area to the right of the tailings pile,the river bank, the

river and right-hand side of the domain below the river are variable boundary nodes (Data Set 14).

At the start of the simulation, the computed pH in the tailings pile is 1.3; the tailings pile contains high concentrations of carbonate, calcium, sulfate and uranium, and is supersaturated with gypsum. Outside of the tailings pile, both gypsum and calcite are supersaturated, and the computed pH is 7.6. Results of the simulation for several species at several times are presented as contour plots in Figures 6.24 to 6.27. They were extracted from the standard output binary file and written to text input files for use with Tecplot, a commercial data visualization tool (Amtec Engineering, Inc.; P. O. Box 3633, Bellevue, WA 98009-3633).

Figs. 6.24a - 6.24c show contour plots of computed pH at 0, 100, and 300 days, respectively. Initially, (Fig. 6.24a) the acidity is confined to the tailings pile, and the pH is greater than 7 outside. Simulations at 100 and 300 days illustrate transport of the acidity outside the tailings; however, due to reaction with $CaCO_3$ the pH is neutralized rapidly in the reaction zone as indicated by closely spaced contours.

Figs. 6.25a - 6.25c and 6.26a - 6.26c show contour plots of precipitated carbonate and sulfate, respectively. In this chemical system, these contours correspond to precipitated calcite and gypsum, respectively. The two figures show the displacement of calcite by gypsum as the simulation proceeded. $CaCO_3$, which was initially present everywhere outside of the tailings (Fig. 6.25a), disappears as acidity is transported out of the tailings. At 300 days (Fig. 6.25c), $CaCO_3$ is present only in a small zone near the right edge of the cross section. Gypsum concentration spreads from the tailings pile due to transport of sulfate and calcium. However, below the hill slope, gypsum is dissolved by incoming rainwater with low sulfate concentration. The release of calcium by dissolution of the gypsum leads to some precipitation of calcite by reaction with the carbnate transported from the tailings pile.

The distribution of uranium is significantly different from that of calcium and sulfate (Fig. 6.27a - 6.27c). Unlike calcium and sulfate that are present in high concentrations throughout the cross section, there is a difference of more than three orders of magnitude between the uranium concentration within and outside of the tailings. As a result, uranium is mobilized, and its concentration steadily increases with time in the region surrounding the tailings due to advective transport. Adsorption of uranium is not considered in this simulation; therefore, the only process that can retard uranium migration is precipitation of uranium-bearing minerals. Precipitation of uranium-bearing minerals, however, is limited due to low pH and the high carbonate concentrations. Simulations with HYDROGEOCHEM for longer time periods (Yeh and Tripathi, 1991). show that zones of uranium precipitation [$Ca(UO2)_2(PO_4)_2$] become pronouinced only at longer times (300 - 1000 days).

This hypothetical example illustrates that LEHGC1.1 is capable of simulating the complex interations between the flow, transport, and chemical reactions. The patterns in concentrations of various chemical constituents are created by the aforementioned interactions. The simulation results also indicates that an a priori selected distribution coefficient or retardation factor cannot accurately simulate the behavior patterns that arise from complex nonlinear chemical reactions and fluid flow.

Table 6.14
List of Thermodynamic Data for Problem 8

Species	Components Stoichiometric Coefficient							Log K
	Ca^{2+}	CO_3^{2-}	UO_2^{2+}	PO_4^{3-}	SO_4^{2-}	H^+	Fe^{2+}	
Ca^{2+}	1	0	0	0	0	0	0	0.00
CO_3^{2-}	0	1	0	0	0	0	0	0.00
UO_2^{2+}	0	0	1	0	0	0	0	0.00
PO_4^{3-}	0	0	0	1	0	0	0	0.00
SO_4^{2-}	0	0	0	0	1	0	0	0.00
H^+	0	0	0	0	0	1	0	0.00
Fe^{2+}	0	0	0	0	0	0	1	0.00
OH^-	0	0	0	0	0	-1	0	-13.99
$CaCO_3$	1	1	0	0	0	0	0	3.22
$CaHCO_3^+$	1	1	0	0	0	1	0	11.43
$CaSO_4$	1	0	0	0	1	0	0	2.31
$CaH_2PO_4^+$	1	0	0	1	0	2	0	20.96
$CaPO_4^-$	1	0	0	1	0	0	0	6.46
$CaHPO_4$	1	0	0	1	0	1	0	15.08
$CaOH^+$	1	0	0	0	0	-1	0	-12.85
$FeSO_4$	0	0	0	0	1	0	1	2.20
$FeOH^+$	0	0	0	0	0	-1	1	-9.50
$Fe(OH)_2$	0	0	0	0	0	-2	1	-20.57
$Fe(OH)_3^-$	0	0	0	0	0	-3	1	-31.00
$Fe(OH)_4^{2-}$	0	0	0	0	0	-4	1	-46.00
$(UO_2)(OH)^+$	0	0	1	0	0	-1	0	-5.30
$(UO_2)_2(OH)_2^{2+}$	0	0	2	0	0	-2	0	-5.68
$(UO_2)_3(OH)_4^{2+}$	0	0	3	0	0	-4	0	-11.88
$(UO_2)_3(OH)_5^+$	0	0	3	0	0	-5	0	-15.82
$(UO_2)_4(OH)_7^+$	0	0	4	0	0	-7	0	-21.90
$(UO_2)_3(OH)_7^-$	0	0	3	0	0	-7	0	-28.34
$(UO_2)(CO_3)$	0	1	1	0	0	0	0	9.65
$(UO_2)(CO_3)_2^{2-}$	0	2	1	0	0	0	0	17.08
$(UO_2)(CO_3)_3^{4-}$	0	3	1	0	0	0	0	21.70

Table 6.14
List of Thermodynamic Data for Problem 8 (Concluded)

Species	Components Stoichiometric Coefficient							Log K
	Ca^{2+}	CO_3^{2-}	UO_2^{2+}	PO_4^{3-}	SO_4^{2-}	H^+	Fe^{2+}	
$(UO_2)_2(CO_3)(OH)_3^-$	0	1	2	0	0	-3	0	-1.18
$(UO_2)(SO_4)$	0	0	1	0	1	0	0	2.95
$(UO_2)(SO_4)_2^{2-}$	0	0	1	0	2	0	0	4.00
$H_2(UO_2)(PO_4)^+$	0	0	1	1	0	2	0	23.20
$H_3(UO_2)(PO_4)^{2+}$	0	0	1	1	0	3	0	22.90
$CaH_4(UO_2)(PO_4)_2^{2+}$	1	0	1	2	0	4	0	45.24
$CaH_5(UO_2)(PO_4)_2^{3+}$	1	0	1	2	0	5	0	46.00
HCO_3^-	0	1	0	0	0	1	0	10.32
H_2CO_3	0	1	0	0	0	2	0	16.67
HSO_4^-	0	0	0	0	1	1	0	1.99
HPO_4^{2-}	0	0	0	1	0	1	0	12.35
$H_2PO_4^-$	0	0	0	1	0	2	0	19.55
H_3PO_4	0	0	0	1	0	3	0	21.75
$CaSO_4$	1	0	0	0	1	0	0	4.62
$CaCO_3$	1	1	0	0	0	0	0	8.48
$Ca_5(OH)(PO_4)_3$	5	0	0	3	0	-1	0	40.47
$FeCO_3$	0	1	0	0	0	0	1	10.50
$Ca(UO_2)_2(PO_4)_2$	1	0	2	2	0	0	0	48.61
$Ca_4H(PO_4)_3$	4	0	0	3	0	1	0	48.20
$CaH(PO_4)$	1	0	0	1	0	1	0	19.30
$Ca(OH)_2$	1	0	0	0	0	-2	0	-21.90
$Fe_3(PO_4)_2$	0	0	0	2	0	0	3	33.30
$Fe(OH)_2$	0	0	0	0	0	-2	1	-12.10
$(UO_2)(OH)_2$	0	0	1	0	0	-2	0	-5.40
$(UO_2)(CO_3)$	0	1	1	0	0	0	0	14.11
$Fe(UO_2)_2(PO_4)_2$	0	0	2	2	0	0	1	46.00
$H(UO_2)(PO_4)$	0	0	1	1	0	1	0	25.00

Table 6.15
Initial and Boundary Compositions of Recharge Water and Pore Water in the Tailings and Regions Outside of the Tailings Pile

Component	Concentration (M)		
	Outside Tailings Pile	Inside Tailings Pile	Recharge Water
Ca	10^{-2}	10^{-2}	10^{-3}
CO_3	1.5×10^{-3}	10^{-2}	1.5×10^{-3}
U(VI)	10^{-7}	5.0×10^{-4}	10^{-8}
PO_4	10^{-6}	10^{-6}	10^{-6}
SO_4	2.0×10^{-2}	2.0×10^{-1}	10^{-4}
Fe	10^{-7}	3.5×10^{-2}	10^{-7}
H^+	10^{-3}	2.0×10^{-1}	10^{-3}

Table 6.16
Input Data Sets for Problem 8

```
   8  LEHGC: TEST OF COUPLING - MILL TAILING PROBLEM (units are dm-kg-day)
 0 0 0 9 0
C ******* DATA SET 2:  BASIC INTEGER PARAMETERS
 192 158 1 0 151 1 4 1 1 0 1 0 20 1 300 0 1 0 1 12 0
C ******* DATA SET 3:  BASIC REAL PARAMETERS
 2.0 0.0 4.0 301.0  1.0 1.0 1.0 1.0 1.0D-2 1.0
C ******* DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
22000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000
00000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000022
10000000001000000000100000000010000000001000000000100000000010000000001000000000100000000010000001
11110000001000000000100000000010000000001000000000100000000010000000011
    1.0D38
C ******* DATA SET 5: CHEMICAL PRINTOUT
 4
 1 26 88 180
C ******* DATA SET 6:  MATERIAL PROPERTIES
 0.0D1 0.0D1 0.0D0 1.2D0
C ******* DATA SET 10: TRANSPORT COMPONENT INFORMATION
 7  0
CALCIUM        1    1
CARBONATE      2    1
URANIUM        3    1
PHOSPHATE      4    1 SURFATE       5    1
HYDROGEN       6    1
FERROUS        7    1
C ******* DATA SET 11:  INITIAL CONDITIONS
    1  191    1         1.00D-2      0.0D0      0.0D0
    0    0    0         0.0          0.0        0.0             END OF IC CA
    1   10    1         1.50D-3      0.0D0      0.0D0
   12    2    1         1.00D-2      0.0D0      0.0D0
   15    3    1         1.50D-3      0.0D0      0.0D0
   19    2    1         1.00D-2      0.0D0      0.0D0
   22    3    1         1.50D-3      0.0D0      0.0D0
   26    2    1         1.00D-2      0.0D0      0.0D0
   29    3    1         1.50D-3      0.0D0      0.0D0
   33    2    1         1.00D-2      0.0D0      0.0D0
   36    3    1         1.50D-3      0.0D0      0.0D0
   40    2    1         1.00D-2      0.0D0      0.0D0
   43  149    1         1.5D-03      0.0D0      0.0D0
    0    0    0         0.0          0.0        0.0           END OF IC CO3
    1   10    1         1.00D-7      0.0D0      0.0D0
   12    2    1         5.00D-4      0.0D0      0.0D0
   15    3    1         1.00D-7      0.0D0      0.0D0
   19    2    1         5.00D-4      0.0D0      0.0D0
   22    3    1         1.00D-7      0.0D0      0.0D0
   26    2    1         5.00D-4      0.0D0      0.0D0
   29    3    1         1.00D-7      0.0D0      0.0D0
   33    2    1         5.00D-4      0.0D0      0.0D0
   36    3    1         1.00D-7      0.0D0      0.0D0
   40    2    1         5.00D-4      0.0D0      0.0D0
   43  149    1         1.00D-7      0.0D0      0.0D0
    0    0    0         0.0          0.0        0.0          END OF IC UO2
    1   10    1         1.00D-6      0.0D0      0.0D0
   12    2    1         1.00D-6      0.0D0      0.0D0
   15    3    1         1.00D-6      0.0D0      0.0D0
   19    2    1         1.00D-6      0.0D0      0.0D0
   22    3    1         1.00D-6      0.0D0      0.0D0
   26    2    1         1.00D-6      0.0D0      0.0D0
   29    3    1         1.00D-6      0.0D0      0.0D0
   33    2    1         1.00D-6      0.0D0      0.0D0
   36    3    1         1.00D-6      0.0D0      0.0D0
   40    2    1         1.00D-6      0.0D0      0.0D0
   43  149    1         1.00D-6      0.0D0      0.0D0
    0    0    0         0.0          0.0        0.0        END OF IC PO4
```

Table 6.16
Input Data Sets for Problem 8 (continued)

```
    1   10    1        2.00D-2     0.0D0     0.0D0
   12    2    1        2.00D-1     0.0D0     0.0D0
   15    3    1        2.00D-2     0.0D0     0.0D0
   19    2    1        2.00D-1     0.0D0     0.0D0
   22    3    1        2.00D-2     0.0D0     0.0D0
   26    2    1        2.00D-1     0.0D0     0.0D0
   29    3    1        2.00D-2     0.0D0     0.0D0
   33    2    1        2.00D-1     0.0D0     0.0D0
   36    3    1        2.00D-2     0.0D0     0.0D0
   40    2    1        2.00D-1     0.0D0     0.0D0
   43  149    1        2.00D-2     0.0D0     0.0D0
    0    0    0        0.0         0.0       0.0       END OF IC SO4
    1   10    1        1.00D-3     0.0D0     0.0D0
   12    2    1        2.00D-1     0.0D0     0.0D0
   15    3    1        1.00D-3     0.0D0     0.0D0
   19    2    1        2.00D-1     0.0D0     0.0D0
   22    3    1        1.00D-3     0.0D0     0.0D0
   26    2    1        2.00D-1     0.0D0     0.0D0
   29    3    1        1.00D-3     0.0D0     0.0D0
   33    2    1        2.00D-1     0.0D0     0.0D0
   36    3    1        1.00D-3     0.0D0     0.0D0
   40    2    1        2.00D-1     0.0D0     0.0D0
   43  149    1        1.00D-3     0.0D0     0.0D0
    0    0    0        0.0         0.0       0.0       END OF IC H
    1   10    1        1.00D-7     0.0D0     0.0D0
   12    2    1        3.50D-2     0.0D0     0.0D0
   15    3    1        1.00D-7     0.0D0     0.0D0
   19    2    1        3.50D-2     0.0D0     0.0D0
   22    3    1        1.00D-7     0.0D0     0.0D0
   26    2    1        3.50D-2     0.0D0     0.0D0
   29    3    1        1.00D-7     0.0D0     0.0D0
   33    2    1        3.50D-2     0.0D0     0.0D0
   36    3    1        1.00D-7     0.0D0     0.0D0
   40    2    1        3.50D-2     0.0D0     0.0D0
   43  149    1        1.00D-7     0.0D0     0.0D0
    0    0    0        0.0         0.0       0.0       END OF IC  FE2
C ******* DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
    0 0 0  0 0 0  15 1 2  22 21 2 2
C ******* DATA SET 14:  VARIABLE BOUNDARY CONDITIONS
     0.0D0   1.00D-3    1.0D38   1.00D-3
     0.0D0   1.00D-3    1.0D38   1.00D-3
   1   16    1    1    0
  18    3    1    2    0
   0    0    0    0    0                    END OF BC CA
     0.0D0   1.50D-3    1.0D38   1.50D-3
     0.0D0   1.50D-3    1.0D38   1.50D-3
   1   16    1    1    0
  18    3    1    2    0
   0    0    0    0    0                    END OF BC CO3
     0.0D0   1.0D-08    1.0D38   1.0D-08
     0.0D0   1.00D-8    1.0D38   1.00D-8
   1   16    1    1    0
  18    3    1    2    0
   0    0    0    0    0                    END OF BC U02
     0.0D0   1.00D-6    1.0D38   1.00D-6
     0.0D0   1.00D-6    1.0D38   1.00D-6
   1   16    1    1    0
  18    3    1    2    0
   0    0    0    0    0                     END OF BC PO4
     0.0D0   1.00D-4    1.0D38   1.00D-4
     0.0D0   1.00D-4    1.0D38   1.00D-4
   1   16    1    1    0
  18    3    1    2    0
   0    0    0    0    0                     END OF BC SO4
```

Table 6.16
Input Data Sets for Problem 8 (continued)

```
     0.0D0    1.00D-3     1.0D38    1.00D-3
     0.0D0    1.00D-3     1.0D38    1.00D-3
    1   16     1    1     0
   18    3     1    2     0
    0    0     0    0     0                          END OF BC H
     0.0D0    1.00D-7     1.0D38    1.00D-7
     0.0D0    1.00D-7     1.0D38    1.00D-7
    1   16     1    1     0
   18    3     1    2     0
    0    0     0    0     0                          END OF BC FE2
    1   17     1   63     7
   19    1     1  181    -1
   21    1     1  187     5
    0    0     0    0     0                          END OF NPVB
    1   16    54    1     2    1     6    1     1
   18    1   150   18    19    1    -1    1     1
   20    1   154   20    21    1     4    1     1
    0    0     0    0     0    0     0    0     0  END OF MVES
C ******* DATA SET 15:  DIRICHLET BOUNDARY CONDITIONS
     0.0D0    1.00D-2     1.0D38    1.00D-2
    1   14     1    1     0
    0    0     0    0     0                     END OF BC CA
     0.0D0    1.00D-2     1.0D38    1.00D-2
    1   14     1    1     0
    0    0     0    0     0                     END OF BC CO3
     0.0D0    5.00D-4     1.0D38    5.00D-4
    1   14     1    1     0
    0    0     0    0     0                     END OF BC UO2
     0.0D0    1.00D-6     1.0D38    1.00D-6
    1   14     1    1     0
    0    0     0    0     0                     END OF BC PO4
     0.0D0    2.00D-1     1.0D38    2.00D-1
    1   14     1    1     0
    0    0     0    0     0                     END OF BC SO4
     0.0D0    2.00D-1     1.0D38    2.00D-1
    1   14     1    1     0
    0    0     0    0     0                     END OF BC H
     0.0D0    3.50D-2     1.0D38    3.50D-2
    1   14     1    1     0
    0    0     0    0     0                     END OF BC FE2
    1    2     1   12     1
    4    2     1   19     1
    7    2     1   26     1
   10    2     1   33     1
   13    2     1   40     1
    0    0     0    0     0          END OF NDNP
C ******* DATA SET 17:  NUMBER OF COMPONENTS AND PRODUCT SPECIES
 7 0 35 0 0 14 0
C ******* DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
 0.0 0 6 0
C ******* DATA SET 19:  TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
 298.3 1.0
-20.0 20.0 -20.0 20.0
C ******* DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
 1.0 1.0D-6 250 250 1.0D10  1.0D38
C ******* DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
CALCIUM                  1
CARBONATE                1
URANIUM                  1
PHOSPHATE                1
SULFATE                  1
HYDROGEN                 1
FERROUS                  1
```

Table 6.16
Input Data Sets for Problem 8 (continued)

```
C ******* DATA SET 24:  COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++                0
1.92D-3  2  0
FREE CO3--               0
1.72D-6  -2  0
FREE UO2++               0
2.53D-13 2 0
FREE PO4---              0
3.17D-12 -3 0
FREE SO4--               0
1.25D-2  -2 0
FREE H+                  0
2.45D-8  1 0
FREE FE++                0
3.34D-8  2 0
C ******* DATA SET 25:  COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH-                      0
5.75D-7  -13.99 0 0 0 0 0 -1 0   0  0 0 0 0 0 -1 0
CACO3                    0
4.19D-8    3.22 1 1 0 0 0  0 0   0  1 1 0 0 0  0 0
HCACO3                   0
1.21D-7   11.43 1 1 0 0 0  1 0   0  1 1 0 0 0  1 0
CASO4                    0
1.96D-6    2.31 1 0 0 0 1  0 0   0  1 0 0 0 1  0 0
CAH2(PO4)                0
1.0D-6    20.96 1 0 0 1 0  2 0   0  1 0 0 1 0  2 0
CA(PO4)                  0
1.0D-6     6.46 1 0 0 1 0  0 0   0  1 0 0 1 0  0 0
CAH(PO4)                 0
1.0D-6    15.08 1 0 0 1 0  1 0   0  1 0 0 1 0  1 0
CAOH                     0
7.77D-10 -12.85 1 0 0 0 0 -1 0   0  1 0 0 0 0 -1 0
FE(SO4)                  0
1.0D-6     2.20 0 0 0 0 1  0 1   0  0 0 0 0 1  0 1
FE(OH)                   0
1.0D-6    -9.50 0 0 0 0 0 -1 1   0  0 0 0 0 0 -1 1
FE(OH)2                  0
1.0D-6   -20.57 0 0 0 0 0 -2 1   0  0 0 0 0 0 -2 1
FE(OH)3                  0
1.0D-6   -31.00 0 0 0 0 0 -3 1   0  0 0 0 0 0 -3 1
FE(OH)4                  0
1.0D-6   -46.00 0 0 0 0 0 -4 1   0  0 0 0 0 0 -4 1
UO2OH                    0
7.75D-11 -5.3   0 0 1 0 0 -1 0   0  0 0 1 0 0 -1 0
(UO2)2(OH)2              0
5.0D-16   -5.68 0 0 2 0 0 -2 0   0  0 0 2 0 0 -2 0
(UO2)3(OH)4              0
2.74D-19 -11.88 0 0 3 0 0 -4 0   0  0 0 3 0 0 -4 0
(UO2)3(OH)5              0
1.77D-15 -15.82 0 0 3 0 0 -5 0   0  0 0 3 0 0 -5 0
(UO2)4(OH)7              0
1.28D-18 -21.90 0 0 4 0 0 -7 0   0  0 0 4 0 0 -7 0
(UO2)3(OH)7              0
1.69D-12 -28.34 0 0 3 0 0 -7 0   0  0 0 3 0 0 -7 0
(UO2)(CO3)               0
3.17D-10  9.65  0 1 1 0 0  0 0   0  0 1 1 0 0  0 0
(UO2)(CO3)2              0
2.20D-9  17.08  0 2 1 0 0  0 0   0  0 2 1 0 0  0 0
(UO2)(CO3)3              0
2.36D-11  21.70 0 3 1 0 0  0 0   0  0 3 1 0 0  0 0
(UO2)2(CO3)(OH)3         0
2.29D-10  -1.18 0 1 2 0 0 -3 0   0  0 1 2 0 0 -3 0
(UO2)(SO4)               0
2.40D-14   2.95 0 0 1 0 1  0 0   0  0 0 1 0 1  0 0
```

Table 6.16
Input Data Sets for Problem 8 (concluded)

```
(UO2)(SO4)2                    0
 2.64D-17   4.00 0 0 1 0 2  0 0   0  0 0 1 0 2  0 0
H2(UO2)(PO4)                   0
1.0D-6     23.20 0 0 1 1 0  2 0   0  0 0 1 1 0  2 0
H3(UO2)(PO4)                   0
1.0D-6     22.90 0 0 1 1 0  3 0   0  0 0 1 1 0  3 0
CAH4(UO2)(PO4)2                0
1.0D-6     45.24 1 0 1 2 0  4 0   0  1 0 1 2 0  4 0
CAH5(UO2)(PO4)2                0
1.0D-6     46.00 1 0 1 2 0  5 0   0  1 0 1 2 0  5 0
HCO3                           0
9.58D-5    10.32 0 1 0 0 0  1 0   0  0 1 0 0 0  1 0
H2CO3                          0
3.81D-6    16.67 0 1 0 0 0  2 0   0  0 1 0 0 0  2 0
HSO4                           0
1.70D-10    1.99 0 0 0 0 1  1 0   0  0 0 0 0 1  1 0
HPO4                           0
2.70D-10   12.35 0 0 0 1 0  1 0   0  0 0 0 1 0  1 0
H2PO4                          0
3.48D-18   19.55 0 0 0 1 0  2 0   0  0 0 0 1 0  2 0
H3PO4                          0
1.27D-22   21.75 0 0 0 1 0  3 0   0  0 0 0 1 0  3 0
C ******* DATA SET 27:  PRECIPITATED/DISSOLVED SPECIES
CA(SO4)                        0
0.0      4.62 1 0 0 0 1  0 0   1 0 0 0 1  0 0
CA(CO3)                        0
0.0      8.48 1 1 0 0 0  0 0   1 1 0 0 0  0 0
CA5(OH)(PO4)3                  0
0.0     40.47 5 0 0 3 0 -1 0   5 0 0 3 0 -1 0
FECO3                          0
0.0     10.50 0 1 0 0 0  0 1   0 1 0 0 0  0 1
CA(UO2)2(PO4)2                 0
0.0     48.61 1 0 2 2 0  0 0   1 0 2 2 0  0 0
CA4H(PO4)3                     0
0.0     48.20 4 0 0 3 0  1 0   4 0 0 3 0  1 0
CAH(PO4)                       0
0.0     19.30 1 0 0 1 0  1 0   1 0 0 1 0  1 0
CA(OH)2                        0
0.0    -21.90 1 0 0 0 0 -2 0   1 0 0 0 0 -2 0
FE3(PO4)2                      0
0.0     33.30 0 0 0 2 0  0 3   0 0 0 2 0  0 3
FE(OH)2                        0
0.0    -12.10 0 0 0 0 0 -2 1   0 0 0 0 0 -2 1
(UO2)(OH)2                     0
0.0     -5.40 0 0 1 0 0 -2 0   0 0 1 0 0 -2 0
(UO2)(CO3)                     0
0.0     14.11 0 1 1 0 0  0 0   0 1 1 0 0  0 0
FE(UO2)2(PO4)2                 0
0.0     46.00 0 0 2 2 0  0 1   0 0 2 2 0  0 1
H(UO2)(PO4)                    0
0.0     25.00 0 0 1 1 0  1 0   0 0 1 1 0  1 0
                          END OF JOB
```

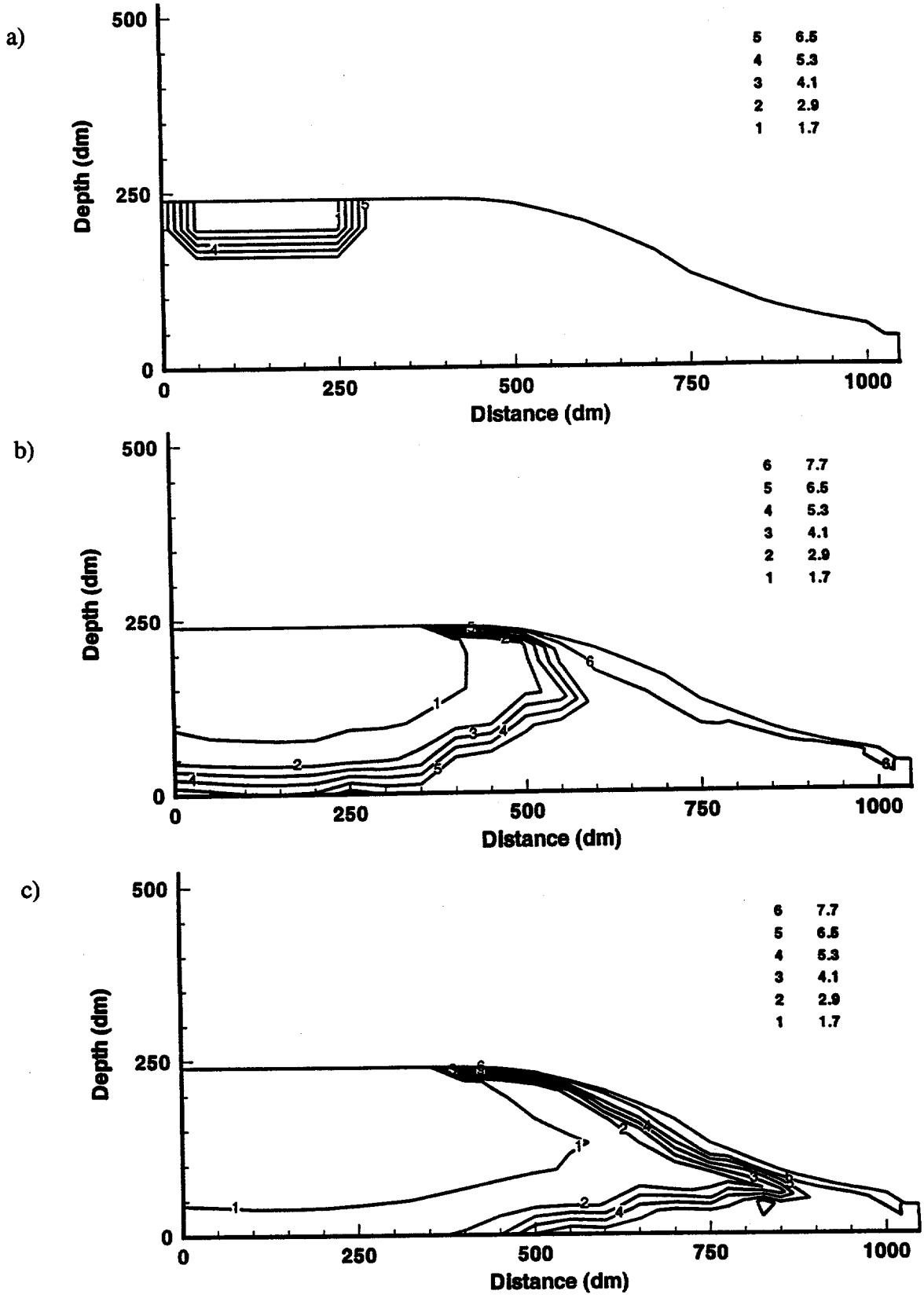


Figure 6.24
Distribution of Ph at Various Times: a) t = 0 Days; b) t = 100 Days; c) t = 300 Days

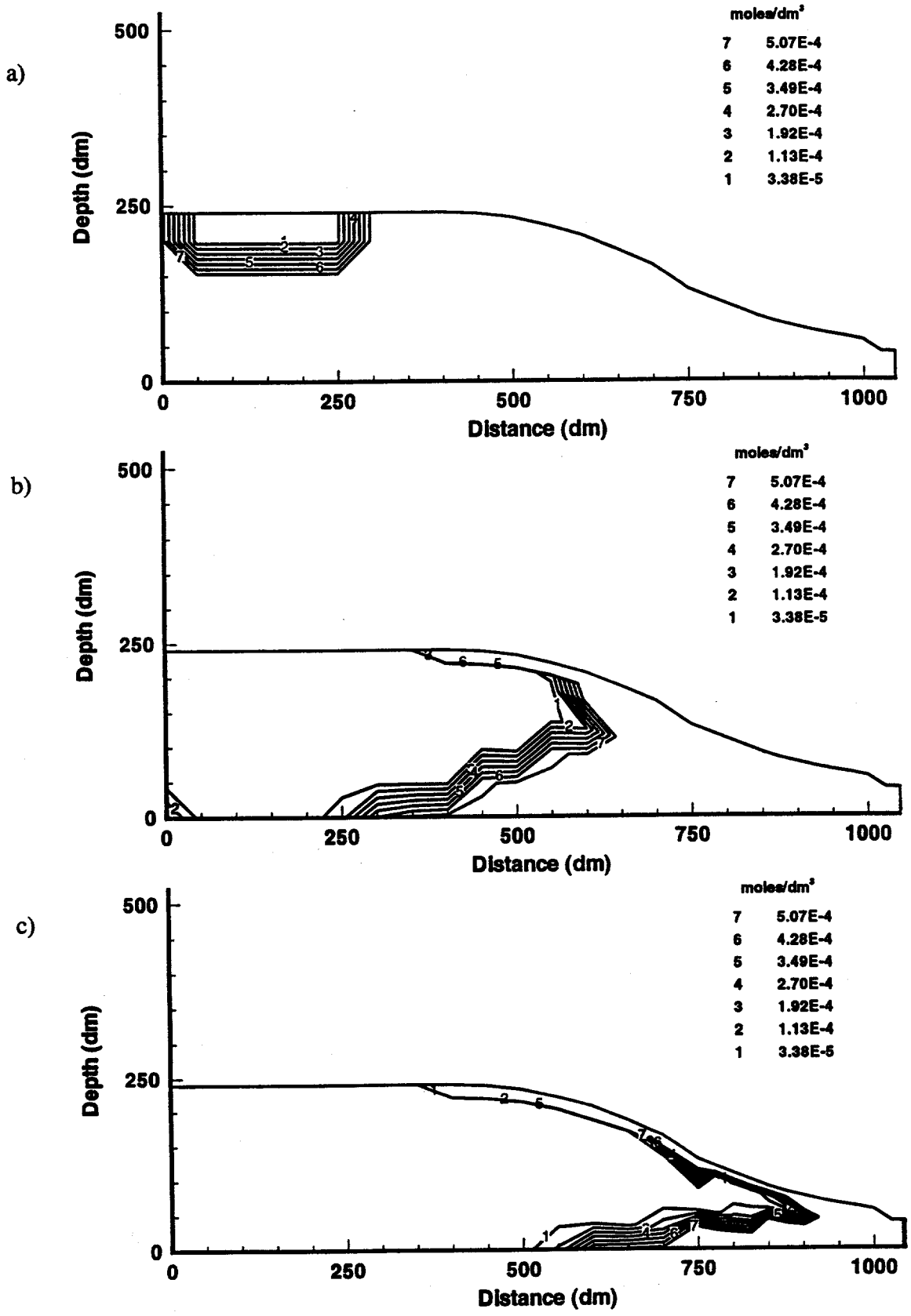


Figure 6.25

Distribution of Precipitated Carbonate (Calcite) at Various Times: a) t = 0 Days; b) t = 100 Days; c) t = 300 Days

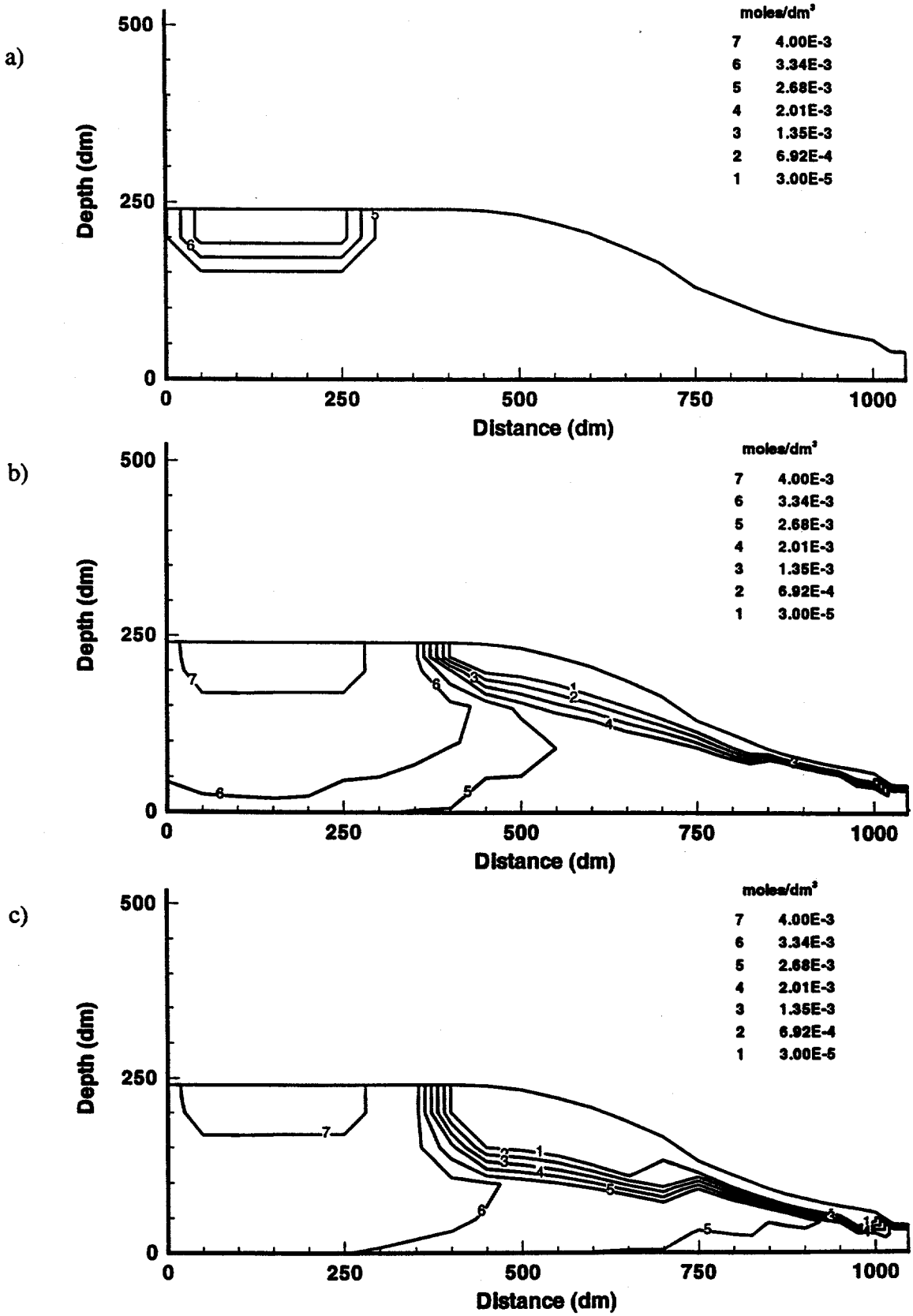


Figure 6.26

Distribution of Precipitated Sulfate (Gypsum) at Various Times: a) t = 0 Days; b) t = 100 Days; c) t = 300 Days

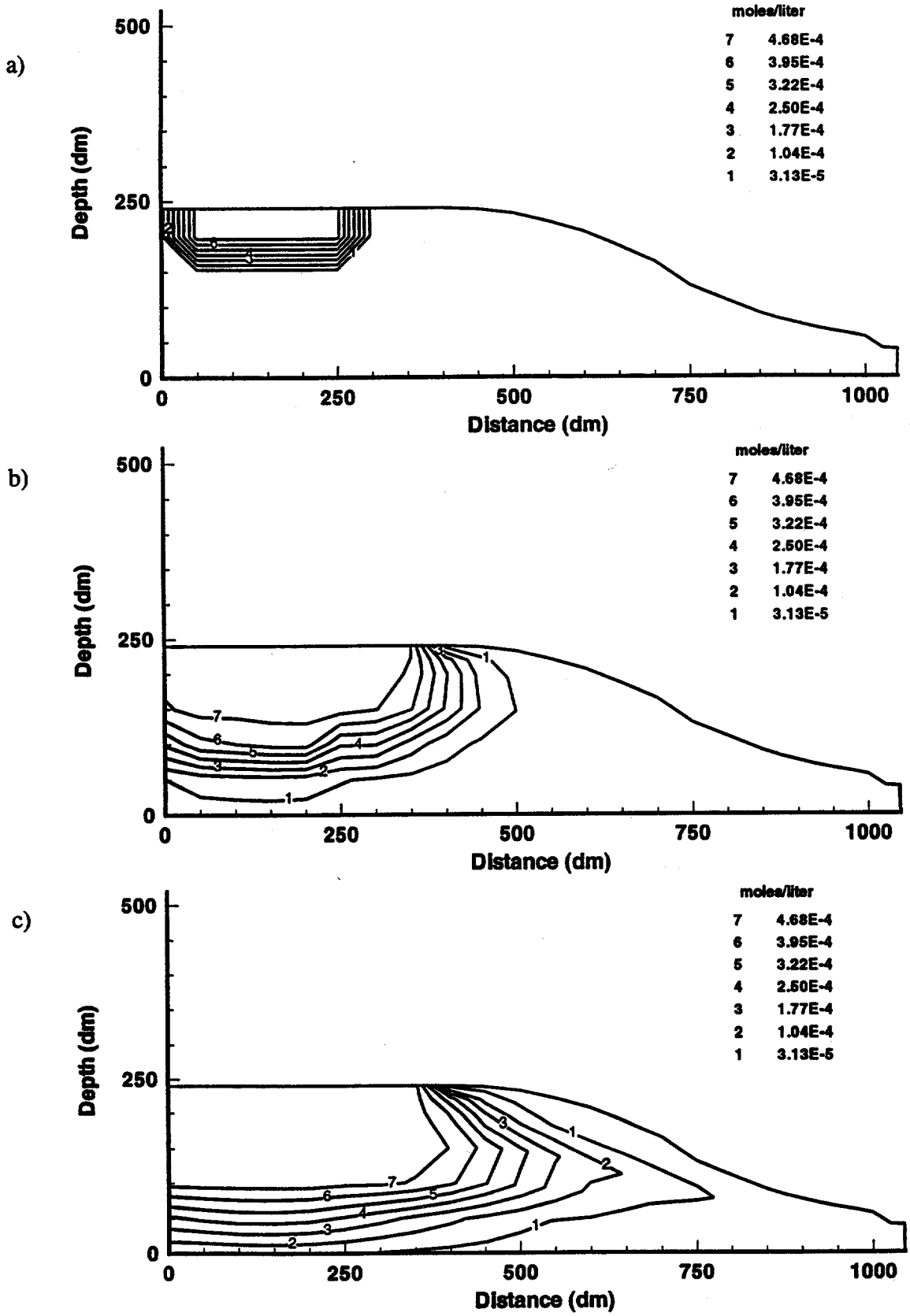


Figure 6.27

Distribution of Dissolved Uranium at Various Times: a) t = 0 Days; b) t = 100 Days; c) t = 300 Days

6.9 Problem 9: Test of Advective Transport, Colloid Transport and Chemical Equilibrium

This problem describes transport of thorium by silica colloids in a 1-D horizontal column filled with a porous silica matrix. A schematic diagram of the finite-element grid is shown in Figure 6.28. The region is made up of 40 elements of 0.0245 dm x 0.0245 dm; the horizontal axis is the z-axis. The flow velocity (from left to right) is 0.01 dm/hour, the porosity is 0.463, and the dispersivity is 0.09 dm. The bulk density of the porous matrix is 2.2 kg/dm^3.

The chemical components are: thorium (Th^{4+}), sodium (Na^+), chloride (Cl^-), hydronium (H^+), *silica* colloids (SiOH), and SOH (immobile silica adsorbing site). Thorium forms aqueous complexes with chlorine, and hydronium (as hydroxides), and is adsorbed by both immobile silica surface sites and colloidal silica. The same surface complexation constants are used for the colloidal (mobile) and immobile silica. The triple-layer model is used for adsorption calculations; each adsorption site has two electrostatic components (σ_o, σ_1) (Data Set 20). For the purposes of transport calculations and chemical speciation calculations, colloidal silica and its thorium surface complexes are treated as aqueous complexes in LEHGC1.1. Silica complexes are not included and no precipitated species are considered. The thermodynamic data are given in Table 6.17.

The pH within the column is 5.6 throughout the simulation (Type 3 species in Data Sets 24 and 10). The initial concentrations of total thorium, total sodium, chloride, and immobile silica adsorption sites in the column are 10^{-12}, 0.01, 10^{-17}, and $1.2x10^{-11}$ M, respectively.

The boundary condition is defined such that the composition of groundwater entering the left end of the column is held constant. The concentrations of thorium, chlorine and silica colloid sites in the incoming fluid are 10^{-10} M, 10^{-16} M, and $2.8x10^{-7}$ M, respectively, throughout the simulation period. The pH of the incoming water is held constant at 5.6.

The parameters for this problem have been chosen to represent a case in which transport of thorium by colloids is significant. The surface area of the porous matrix (10 dm^2/kg) specified in Data Set 20 for each node is much lower than that of the colloids ($5x10^7$ dm^2/kg). In addition, the adsorption site density consistent with immobile surface sites concentration in Data Set 11, is much lower than the site density consistent with the colloids site concentration specified in Data Set 14. Physically, this situation may arise if the matrix is composed of large cobbles, if most of the surface of the porous matrix has been passivated by nonreactive surface coatings, and/or if most of the exposed adsorption sites are already occupied by other irreversibly adsorbed species. The high colloid site density is consistent with a high concentration of very small colloids.

The relationship among site concentration (SOH or SiOH), site density, and surface area is:

SOH (M/dm^3) = Site density (M/dm^2) x surface area (dm^2/kg) x solids concentration (kg/dm^3)

Values for site densities and surface areas of geologic materials and colloids are available in the literature (e.g. Stumm and Morgan, 1981). The solids concentration for colloid suspensions can

be measured in the system of interest; the solids concentration for the matrix can be equated to the ratio of the bulk density and porosity of the matrix.

The input data sets for this problem are shown in Table 6.18. The transport of thorium for a total of 80 hours was simulated using LEHGC1.1. The breakthrough curves for dissolved and colloidal thorium are shown in Figure 6.29. After 60 hours, approximately 50% of the thorium breakthrough is associated with colloids. Profiles of total (dissolved + colloidal) thorium within the column are shown for various times in Figure 6.30.

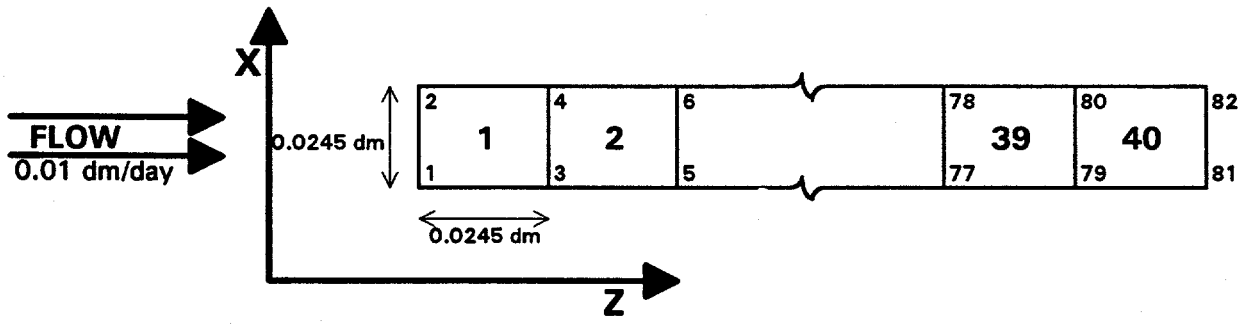


Figure 6.28
Finite Element Discretization of Problem 9

Table 6.17
List of Thermodynamic Data for Problem 9

Species	Components Stoichiometric Coefficient										LogK
	Th^{4+}	Na^+	Cl^-	H^+	SiOH	$\sigma 0_m$	$\sigma 1_m$	SOH	$\sigma 0_i$	$\sigma 1_i$	
Th^{4+}	1	0	0	0	0	0	0	0	0	0	0.00
Na^+	0	1	0	0	0	0	0	0	0	0	0.00
Cl^-	0	0	1	0	0	0	0	0	0	0	0.00
H^+	0	0	0	1	0	0	0	0	0	0	0.00
SiOH	0	0	0	0	1	0	0	0	0	0	0.00
$\sigma 0_m$	0	0	0	0	0	1	0	0	0	0	0.00
$\sigma 1_m$	0	0	0	0	0	0	1	0	0	0	0.00
SOH	0	0	0	0	0	0	0	1	0	0	0.00
$\sigma 0_i$	0	0	0	0	0	0	0	0	1	0	0.00
$\sigma 1_i$	0	0	0	0	0	0	0	0	0	1	0.00
OH-	0	0	0	-1	0	0	0	0	0	0	-13.99
$ThOH^{3+}$	1	0	0	-1	0	0	0	0	0	0	-2.34
$Th(OH)_2^{2+}$	1	0	0	-2	0	0	0	0	0	0	-6.36
$Th(OH)_3^+$	1	0	0	-3	0	0	0	0	0	0	-11.70
$Th(OH)_4$	1	0	0	-4	0	0	0	0	0	0	-15.90
$Th_2(OH)_2^{6+}$	2	0	0	-2	0	0	0	0	0	0	-5.41
$Th_2(OH)_3^{5+}$	2	0	0	-3	0	0	0	0	0	0	-8.44
$Th_4(OH)_8^{8+}$	4	0	0	-8	0	0	0	0	0	0	-20.10
$Th_6(OH)_{11}^{10+}$	6	0	0	-14	0	0	0	0	0	0	-38.80
$Th_6(OH)_{15}^{9+}$	6	0	0	-15	0	0	0	0	0	0	-43.80
$ThCl^{3+}$	1	0	1	0	0	0	0	0	0	0	1.18
$ThCl_2^{2+}$	1	0	2	0	0	0	0	0	0	0	0.92
$ThCl_3^+$	1	0	3	0	0	0	0	0	0	0	1.71
$ThCl_4$	1	0	4	0	0	0	0	0	0	0	0.94
SiO^-	0	0	0	-1	1	-1	0	0	0	0	-8.50

Table 6.17
List of Thermodynamic Data for Problem 9 (concluded)

Species	Components Stoichiometric Coefficient										LogK
	Th^{4+}	Na^+	Cl^-	H^+	SiOH	$\sigma 0_m$	$\sigma 1_m$	SOH	$\sigma 0_i$	$\sigma 1_i$	
Colloid (mobile) sites											
$SiOH_2^+$	0	0	0	1	1	1	0	0	0	0	1.50
$SiOTh^{3+}$	1	0	0	-1	1	-1	4	0	0	0	6.42
$SiOThOH^{2+}$	1	0	0	-2	1	-1	3	0	0	0	0.07
Fixed (immobile) sites											
SO^-	0	0	0	-1	0	0	0	1	-1	0	-8.50
SOH_2^+	0	0	0	1	0	0	0	1	1	0	1.50
$SOTh^{3+}$	1	0	0	-1	0	0	0	1	-1	4	6.42
$SOThOH^{2+}$	1	0	0	-1	0	0	0	1	-1	3	0.07

Table 6.18
Input Data Sets for Problem 9

```
    9   TRANSPORT OF Th BY COLLOIDS THROUGH POROUS MATRIX (units are dm-kg-hr)
0    0    0    0    0
***** DATA SET 2:  BASIC INTEGER PARAMETERS
82 40 1  0  160  1  4  -1  1  0  1  0  150  1  300  0  1  0  1  12 1
***** DATA SET 3: BASIC REAL PARAMETERS
0.5  0.0  0.5  80  1.0  1.0  1.0  1.0  1.0D-3  1.0
***** DATA SET 4: PRINTER OUTPUT, DISK STORAGE CONTROL AND TIME STEP RESET
442222000000000000004000000000000000000040000000000000000004000000000000000000
400000000000000000004000000000000000000040000000000000000004000000000000000000
4
111111000010000000010000000001000000000100000000010000000001000000000100000000
100000000010000000001000000000100000000010000000001000000000100000000010000000
1
1.0D38
***** DATA SET 5: CHEMICAL PRINTOUT
2
1  81
***** DATA SET 6: MATERIAL PROPERTIES
0.09 0.0  0.0  2.2
***** DATA SET 7: NODAL POINT COORDINATES
1    40   2    0.0D0     0.0D0     0.0
2    40   2    24.5D-3   0.0D0     0.0
0    0    0    0.0D0     0.0D0     0.0   END OF X
1    40   2    0.0D0     24.5D-3    0.0
2    40   2    0.0D0     24.5D-3    0.0
0    0    0    0.0D0     0.0D0     0.0   END OF Z
***** DATA SET 8: ELEMENT CONNECTIVITY
1    1    2    4    3    1    1    40
***** DATA SET 10: TRANSPORT COMPONENT INFORMATION
5    1
Thorium   1    1
Chlorine  2    1
Na        3    1
Hydrogen  4    3
SiOH      5    1
SOH       8    2
***** DATA SET 11:  INITIAL CONDITIONS
1    81   1    1.0D-12   0.0D0     0.0D0
0    0    0    0.0       0.0       0.0     END OF IC  Th
1    81   1    1.0D-17   0.0D0     0.0D0
0    0    0    0.0       0.0       0.0     END OF IC  Cl
1    81   1    0.01      0.0D0     0.0D0
0    0    0    0.0       0.0       0.0     END OF IC  Na
1    40   2   -5.50D0    -0.50D-2  0.0D0
2    40   2   -5.50D0    -0.50D-2  0.0D0
0    0    0    0.0       0.0       0.0     END OF IC pH
1    81   1    3.3D-11   0.0D0     0.0D0
0    0    0    0.0       0.0       0.0     END OF IC  SiOH
1    81   1    1.2D-11   0.0D0     0.0D0
0    0    0    0.0       0.0       0.0     END OF IC  SOH
***** DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
0  0  0    0  0  0    0  1  2    2  1  1  2
***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0D0     1.0D-10   1.0D38    1.0D-10
1         0         0         1         0
0         0         0         0         0     END OF BC  Th
0.0D0     1.0D-16   1.0D38    1.0D-16
1         0         0         1         0
0         0         0         0         0     END OF BC  Cl
0.0D0     0.01      1.0D38    0.01
1         0         0         1         0
0         0         0         0         0     END OF BC  Na
```

Table 6.18
Input Data Sets for Problem 9 (continued)

```
0.0D0      -5.0D0     1.0D38     -5.0D0
1          0          0          1          0
0          0          0          0          0      END OF BC  H
0.0D0      2.8D-7     1.0D38     2.8D-7
1          0          0          1          0
0          0          0          0          0      END OF BC  SiOH
0.0D0      1.2D-11    1.0D38     1.2D-11
1          0          0          1          0
0          0          0          0          0      END OF BC  SOH
1          1          1          1          1
0          0          0          0          0      END OF NVNP
1          0          1          1          2    0    0    0    0
0          0          0          0          0    0    0    0    0  END OF NVES
***** DATA SET 16: VELOCITY AND MOISTURE CONTENT
1          81         1          0.0D0      1.0D-2     0.0D0      0.0D0
0          0          0          0.0        0.0        0.0        0.0 END OF VELOCITY
1          39         1          4.63D-1    0.0D0
0          0          0          0.0        0.0        END OF MOISTURE
***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4    6     18    4     0   1   4
***** DATA SET 18: H+, e-, IONIC STRENGTH CORRECTION INFORMATION
0.01 0     4     0
***** DATA SET 19: TEMPERATURE, PRESSURE, AND EXPECTED pe AND pH
298.0      1.0
-20.0      20.0       -20.0      20.0
***** DATA SET 20: ADSORPTION INFORMATION
2          2
6          7
9          10
1.2D-2     0.2D-2     5.0D7      1.0d-2     0.2d-2     1.0d1
***** DATA SET 22: BASIC REAL AND INTEGER PARAMETERS
1.0  1.0D-6  500  1  1.0  1.0d0 1.0d38
***** DATA SET 23: NAME OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES
THORIUM              1
CHLORINE             1
Na                   1
HYDROGEN             1
COLLOIDAL SiO2       4
Colloid SIGMA 0-m    3
Colloid SIGMA 1-m    3
Immobile SOH         2
Immobile SIGMA 0-i   3
Immobile SIGMA 1-i   3
***** DATA SET 24: COMPONENT SPECIES AND THEIR ION-EXCHANGE SPECIES
FREE Th+4            0
9.7D-13  4    0
FREE Cl-             0
9.9D-17 -1    0
FREE Na+             0
9.8D-19  1    0
FREE H+              3
1.78D-8  1    0
COLLOID SiO2         0
9.8D-12  0    0
Colloid SIGMA 0-m     0
1.2d-15  0    0
Colloid SIGMA 1-m     0
9.8d-17  0    0
FREE SOH             0
9.93D-12 0    0
Immobile SIGMA 0-i   0
9.8D-15  0    0
```

Table 6.18
Input Data Sets for Problem 9 (continued)

```
FREE SIGMA 1-i        0
9.8D-18  0    0
***** Data Set 25: COMPLEXED SPECIES AND THEIR ION-EXCHANGE SPECIES
OH                    0
5.75D-7    -13.99   0 0 0  -1 0   0 0 0 0 0 0    0    0 0 0  -1 0   0 0 0 0 0
ThOH                  0
7.50D-15    -2.34   1 0 0  -1 0   0 0 0 0 0 0    0    1 0 0  -1 0   0 0 0 0 0
Th(OH)2               0
2.53D-15    -6.36   1 0 0  -2 0   0 0 0 0 0 0    0    1 0 0  -2 0   0 0 0 0 0
Th(OH)3               0
2.72D-15   -11.70   1 0 0  -3 0   0 0 0 0 0 0    0    1 0 0  -3 0   0 0 0 0 0
Th(OH)4               0
5.75D-16   -15.90   1 0 0  -4 0   0 0 0 0 0 0    0    1 0 0  -4 0   0 0 0 0 0
Th2(OH)2              0
1.79D-16    -5.41   2 0 0  -2 0   0 0 0 0 0 0    0    2 0 0  -2 0   0 0 0 0 0
Th2(OH)3              0
1.44D-17    -8.44   2 0 0  -3 0   0 0 0 0 0 0    0    2 0 0  -3 0   0 0 0 0 0
Th4(OH)8              0
0.36D-15   -20.10   4 0 0  -8 0   0 0 0 0 0 0    0    4 0 0  -8 0   0 0 0 0 0
Th6(OH)14             0
1.05D-15   -38.80   6 0 0 -14 0   0 0 0 0 0 0    0    6 0 0 -14 0   0 0 0 0 0
Th6(OH)15             0
2.17D-15   -43.80   6 0 0 -15 0   0 0 0 0 0 0    0    6 0 0 -15 0   0 0 0 0 0
ThCl                  0
4.73D-18     1.18   1 1 0   0 0   0 0 0 0 0 0    0    1 1 0   0 0   0 0 0 0 0
ThCl2                 0
5.05D-19     0.92   1 2 0   0 0   0 0 0 0 0 0    0    1 2 0   0 0   0 0 0 0 0
ThCl3                 0
7.50D-17     1.71   1 3 0   0 0   0 0 0 0 0 0    0    1 3 0   0 0   0 0 0 0 0
ThCl4                 0
2.85D-18     0.94   1 4 0   0 0   0 0 0 0 0 0    0    1 4 0   0 0   0 0 0 0 0
SiO                   0
2.25D-11    -8.50   0 0 0  -1 1  -1 0 0 0 0 0    0    0 0 0  -1 1  -1 0 0 0 0
SiOH2                 0
5.75D-13     1.50   0 0 0   1 1   1 0 0 0 0 0    0    0 0 0   1 1   1 0 0 0 0
SiOTh                 0
5.05D-14    6.420   1 0 0  -1 1  -1 4 0 0 0 0    0    1 0 0  -1 1  -1 4 0 0 0
SiOTh(OH)             0
5.01D-13    0.070   1 0 0  -2 1   1 3 0 0 0 0    0    1 0 0  -2 1   1 3 0 0 0
***** DATA SET 26: ADSORBED SPECIES
SO                    0
3.25D-12   -8.50     0 0 0 -1 0 0 0 1 -1 0      0 0 0 -1 0 0 0 1 -1 0
SOH2                  0
6.85D-17    1.50     0 0 0  1 0 0 0 1  1 0      0 0 0  1 0 0 0 1  1 0
SOTh                  0
3.25D-18    6.420    1 0 0 -1 0 0 0 1 -1 4      1 0 0 -1 0 0 0 1 -1 4
SOTh(OH)              0
5.27D-19    0.070    1 0 0 -2 0 0 0 1 -1 3      1 0 0 -2 0 0 0 1 -1 3
            END OF JOB
```

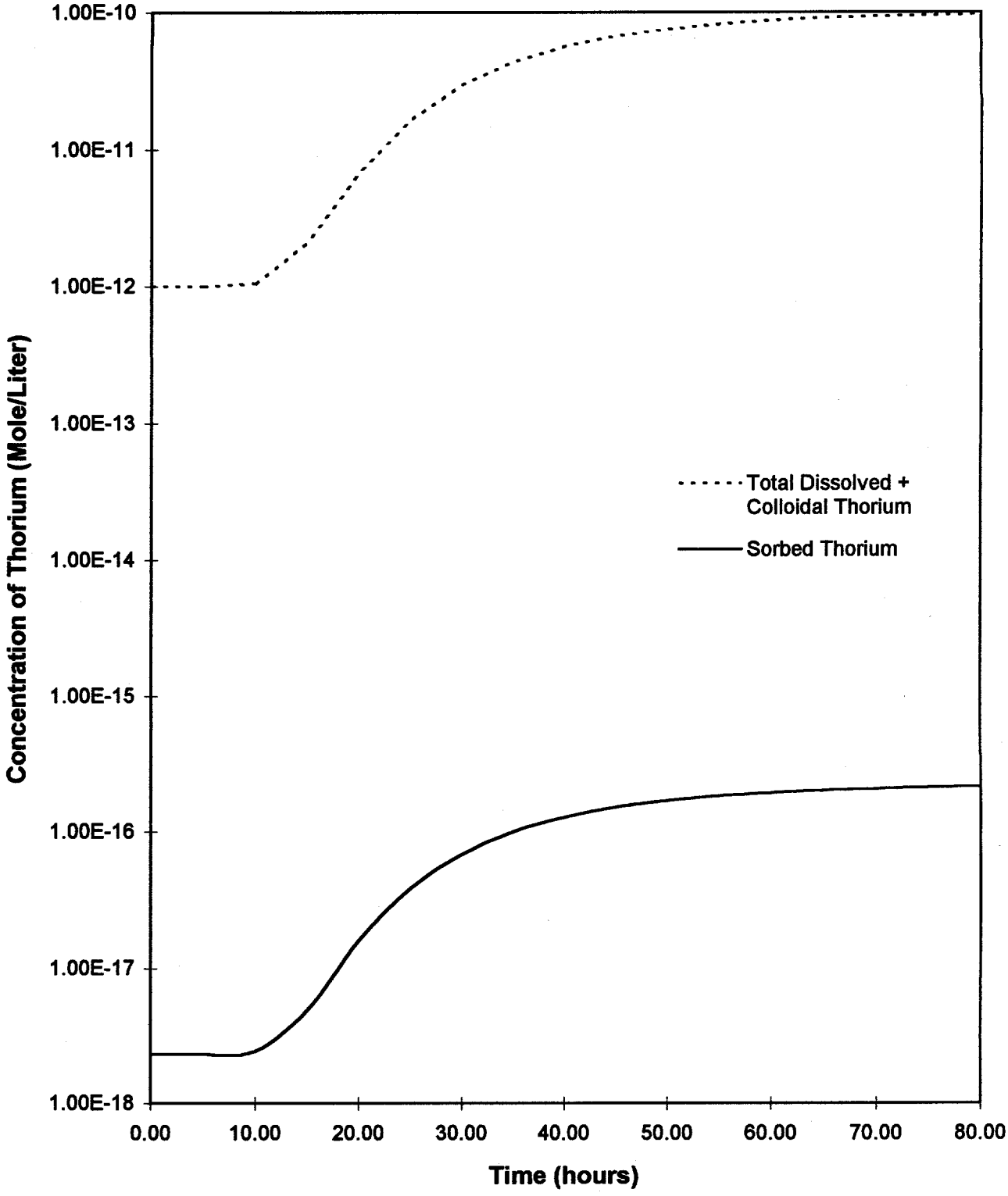


Figure 6.29
Breakthrough Curves for Sorbed and Total Dissolved + Colloidal Concentrations of Thorium

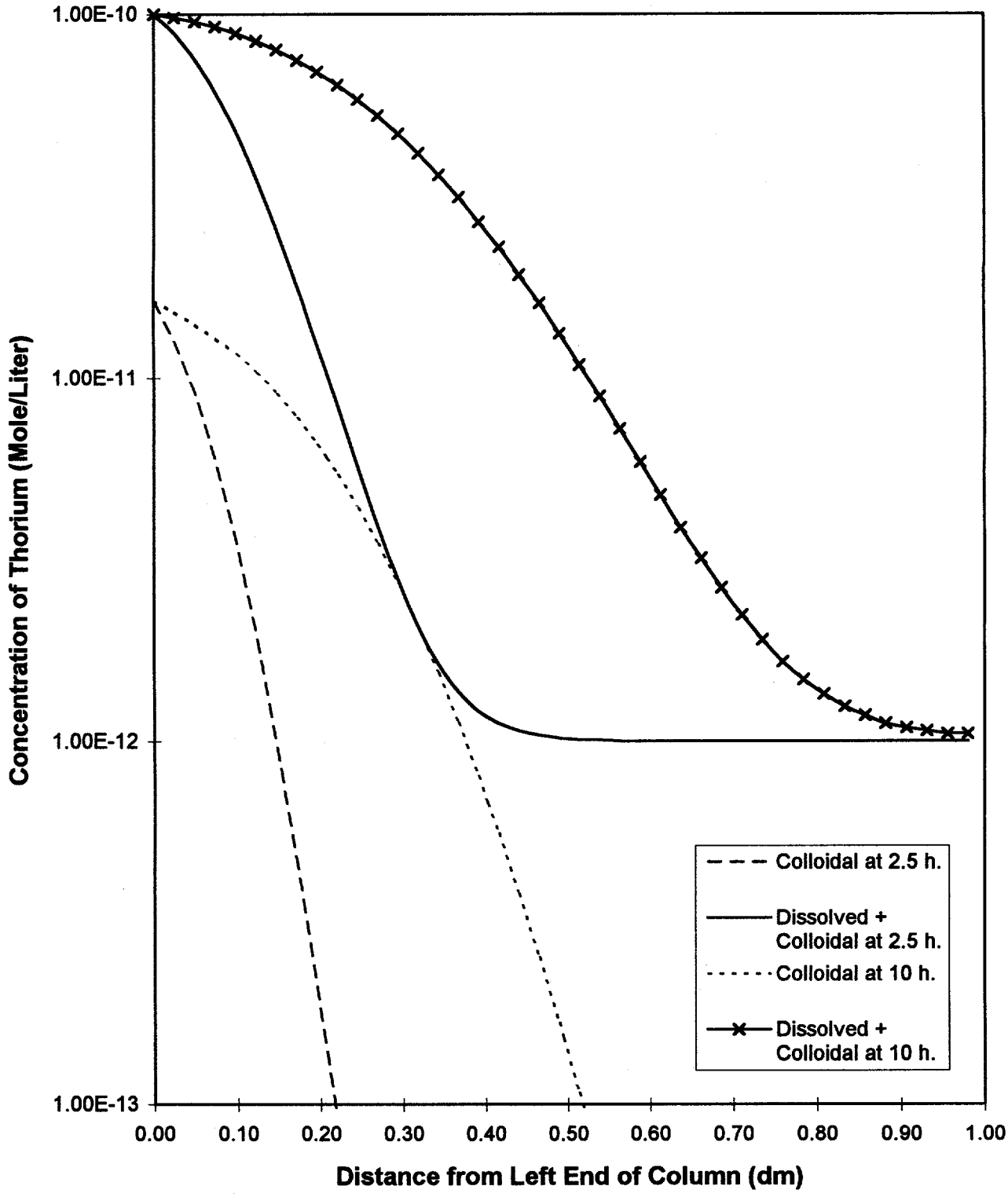


Figure 6.30
Profiles of Thorium at Various Times

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APPENDIX A

Data Input Guide for LEHGC1.1

Data Input Guide for LEHGC1.1

In LEHGC version 1.1, the unit of length should be decimeter (dm) and the unit of mass for any chemical species should be mole. The density of water and solid should be expressed in kg/dm^3 (liter). The ion-exchange capacity is in equivalents/kg of solid. The corresponding concentration unit of all species (aqueous, sorbed, and precipitated species) is mole/liter of fluid (Molar); the corresponding unit for the sorption distribution coefficient is dm^3/kg (= ml/g). Any units of time may be used as long as the same unit is used throughout the input file.

All data sets except for Data Set 1 must be preceded by a data set name or comment line.

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

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 chemical equilibrium computation to be printed:
   1 = yes.
   0 = no.

   The condition number indicates the ability to achieve a solution of the matrix equation if small perturbations are present, such as those introduced by truncation or round-off errors. A condition number close to 1 means small perturbations in the system of equations will result in small errors in the

solution, whereas, a large condition number suggests that small perturbations in the terms of the matric may cause large errors in the solution.

4. NHGCI = Integer indicating if chemical equilibrium 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-field format input contains 21 integers as follows:

1. NNP = Number of global nodal points.

2. NEL = Number of global elements.

3. NMAT = Number of material types. If the system is heterogeneous, more than one material type may exist. Different material types are characterized by different material properties as listed in Data Set 6. Examples of different material types include: different types of rock matrix that differ by their bulk density, stratigraphic layers that differ by dispersivity, etc. The material type of each element is identified in Data Sets 8 and 9.

4. NCM = Number of elements with material type correction specified in Data Set 9.

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 is wanted.

   If the steady-state solution is chosen, then the simulation will continue until concentrations at all nodes remain constant or the simulation time reaches TMAX (Data Set 3)

7. NMPPM = Number of material properties designated in Data Set 6 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.

If KSS = 0, then KVI must equal -1 or 1.

9. ILUMP = Mass matrix lumping control (Section 3.2.4):
0 = No lump.
1 = Lump.

The mass lumping formulation is often less susceptible to problems involving numerical oscillation.

10. IMID = Mid-difference control (Section 3.2.5):
0 = No mid-difference.
1 = Mid-difference, and W in Data Set 3 should be 1.

IMID indicates if the more accurate mid-difference should be used in the computations. For practical purposes, IMID = 0 should be sufficient. IMID = 1 is used only for research purposes.

11. IWET = Weighting function control:
0 = Galerkin weighting.
1 = Upstream weighting.

Use of upstream weighting may reduce oscillations or convergence problems in transport calculations involving sharp concentration fronts of chemical components.

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.

IOPTIM indicates if the upstream weighting factor is optimized. It is only used if LGRN = 0 and IWET = 1. For practical purposes IOPTIM = 0. Research purposes should use IOPTIM = 1.

13. NITER = Number of iterations allowed between hydrological-chemical iterations. Typical values range from 10 to 30 (section 3.2.7).

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. Typical values range from 150 to 300 (section 3.2.7).

16. IPNTS = Is the pointwise iteration method to be used to solve the matrix equations (section 3.2.7):
0 = No.
1 = Yes.

When the bandwidth (Section 5.2) is greater than approximately 40, then use IPNTS = 1. Otherwise, use IPNTS = 0 to activate the direct band-matrix solver.

17. KSTR = Auxiliary storage output control:
0 = No binary storage.
1 = Binary 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.

If C > 1 then LGRN should equal 1. $C = v \Delta t / \Delta l$ where C is the Courant number, v is the fluid velocity, Δt is the time step size and Δl is the node spacing. If C < 1 then LGRN should equal 0. If LGRN = 0, an Eulerian reference system is used in the transport equations. The Eulerian reference system is used in HYDROGEOCHEM.

20. IQUAD = Indicator for quadrature integration (Section 3.2.3):
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.

Normally, IQUAD = 22 should be used. If the result is an oscillating solution, then one of the other three options can be used.

21. IDTI = Tracking time parameter. The value of the tracking time may effect computations for the variable boundary nodes. Computations for interior nodes may also be affected if the tracking time is less that the time-step size (DELT; see Data Set 3). For dispersion- or decay-dominated problems, set IDTI = 1; for advection-dominated problems set IDTI = 0. In the latter mode, LEHGC1.1 will produce solutions similar to those produced by LEHGC1.0.

NOTE: The number of time steps, 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.

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). TMAX should be ≥ NTI x DELMAX.

5. W = Time-derivative weighting factor for all terms except the velocity terms (Section 3.2.5 and refer to variable IMID in Data Set 2):
   0.5 = Central difference (Crank-Nicolson) formulation.
   1.0 = Backward difference and mid-difference.

   W = 1 gives the most stable solution and should be used for practical purposes, but W = 0.5 gives the most accurate solution and should be used for research purposes.

6. WV = Time integration factor for the velocity terms (Section 3.2.7):
   0.0 = Forward difference (explicit).
   0.5 = Central difference.
   1.0 = Backward difference (completely implicit).

   WV is used only if LGRN = 0. In this case, WV has the same characteristics as W in #5 above.

7. OME = Relaxation parameter for solving the nonlinear system of algebraic equation when IPNTS = 0 in Data Set 2 (Section 3.2.7):
   0.0 - 1.0 = Under-relaxation.
   1.0 = Exact relaxation.
   1.0 - 2.0 = Over-relaxation.

   OME is used for nonlinear loop iteration. Normally OME = 1.0. If the iteration history shows that the nonlinear loop is oscillating, OME = 0.5 should be used. If convergence is non-oscillatorial but very slow, OME = approximately 1.78 should be used.

8. OMI = Relaxation parameter for pointwise solving the matrix equation by pointwise iteration when IPNTS = 1 in Data Set 2 (Section 3.2.7):
0.0 - 1.0 = Under-relaxation.
1.0 = Exact relaxation or Gauss-Seidel Method.
1.0-2.0 = Over-relaxation.

OMI is used only when IPNTS =1, for the solution of the linearized matrix equation with pointwise iteration methods. Normally OME = 1.0. If the iteration history shows that the nonlinear loop is oscillating, OME = 0.5 should be used. If convergence is non-oscillatorial but very slow, OME = approximately 1.78 should be used.

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. Typical values range from 10^{-3} to 10^{-4}.

10. APHAG = Upstream weighting factor if IOPTIM = 0 (Data Set 2, #12): 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 (Data Set 2, #5), and the number of times to reset the time step, NDTCHG (Data Set 2, #14). 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(I)	---	KPR(NTI)
1	2	3				80

KPR0 = Printer control for steady-state and initial conditions:
0 = Print nothing.
1 = Print FLOW, FRATE, and TFLOW.
2 = Print above (1) plus concentration.
3 = Print above (2) plus material flux.
4 = Print above (3) plus detailed chemical equilibrium information.

KPR(I) = Printer control for the I-th time step, the same allowable values as for KPRO.

Line [(NTI/80+1)+1] to Line [(NTI/80+1)*2]: FORMAT(80I1)

KDSK0	KDSK(1)	KDSK(2)	---	KDSK(I)	---	KDSK(NTI)
1	2	3				80

KDSK0 = Auxiliary storage control for steady-state and initial conditions:
0 = No storage.
1 = Store on Logical Unit 12.

KDSK(I) = Auxiliary storage control for the I-th time-step, the same allowable values as for KDSKO.

Line greater than line (NTI/80+1)*2: Free-field format input contains NDTCHG real number as follows:

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: CHEMICAL PRINTOUT

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 where detailed chemical equilibrium 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 equilibrium information will be printed.

2. IWRK(2) = Global node number of the second node where detailed chemical equilibrium information will be printed.

N. IWRK(N) = Global node number of the N-th node where detailed chemical equilibrium information will be printed.

NOTE: IWRK(I), for $1 \leq I \leq NCPRT$ 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. NODEP(NP) is an indicator to print detailed chemical information for the NP-th node. 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 (Data Set 2, #3) lines are required for this data set, one line for each material type.

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 described below are not needed if Logical Unit 11 is used as input (i.e., KVI>0 (Data Set 2, #6)).

DATA SET 7: NODAL POINT COORDINATES

Typically, a total of 2*NNP (Data Set 2, #1) lines are required: NNP lines for the x-coordinate and NNP lines for the z-coordinate. 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 this data set.

Line (NNP+1) to Line 2*NNP contain the same information as described above but for the z-coordinate.

DATA SET 8: ELEMENT CONNECTIVITY AND INITIAL MATERIAL TYPE

Typically, a total of NEL (Data Set 2, #2) 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. For a triangular element, IE(MI,4)=0.

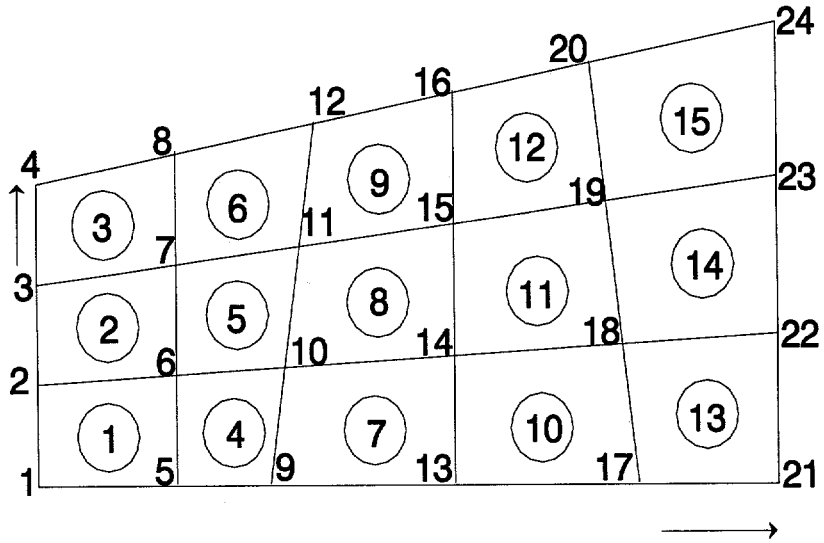
6. IE(MI,5) = Material type to be applied to element MI.

7. MODL = Number of elements in the direction with the smallest difference between adjacent node numbers.

8. NLAY = Number of elements in the direction with the largest difference between adjacent 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 facility.




```
C ******* Data Set 8:  Element Connectivity
   1    1    5    6    2    1    3    5
```

Fig. A.1
Example of Automatic Element Assignment for Data Set 8

DATA SET 9: MATERIAL TYPE CORRECTION

This data set is required only if there is more than one material type and the elements in Data Set 8 are all associated with material type 1. In this case NMAT > 1 and NCM > 0. Normally NCM (Data Set 2, #4) lines are required. However, if the elements to be corrected 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: TRANSPORT COMPONENT INFORMATION

Line 1: Free-field format input contains two integers.

1. NOHA = Number of mobile components

2. NOHS = Number of immobile components

Line 2 through Line (NOH + 1) (where NOH = NOHA + NOHS): FORMAT(A10,2I5)

Each line contains the following information:

1. CNAM(I,1) = component name of the I-th component

2. IDNTC(I,1) = Chemical component number of the I-th transport component

3. 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 (Data Set 2, #18). 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 NOH components.

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 ; will be genera utomatically.

3. NAD = Increment of the nod mber for each e NSEQ nodes.

4. RNI = Initial or pre-initial to l concentration a le NI (M/L**3). RNI must be greater than zero.

5. RAD = Increment of initial or pre-initial total concentration for each of the NSEQ nodes (M/L**3).

6. RRD = 0. (This variable is not used in this version of the code)

NOTE: A line with six zeros separated by spaces or commas must be used to signal the end of this data set for each chemical component.

NOTE: If the INDTC (Data Set 10, Line 2, #3) for any chemical component is equal to 3, then the log10 of its activity should be entered for initial or pre-initial values.

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 last 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 the 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.

NOTE ON AUXILIARY UNITS: Logical Unit 11 is used to input hydrodynamic variables to LEHGC if KVI > 0. Logical Unit 12 is used to store binary output of LEHGC if KSTR > 0 (Data Set 2, #17). Logical Unit 13 is used to input initial condition if NSTR > 0 (Data Set 2, #18). 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 (Data Set 2, #6) and NTI = 0 (Data Set 2, #5), 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 (should be ≥ 1 if NSEL ≥ 1).

3. NSDP = Number of data points in each source/sink profile (should be ≥ 2 if NSEL ≥ 1).

4. NWNP = Number of well or point source/sink nodes.

5. NWPR = Number of well or point source/sink strength profiles (should be ≥ 1 if NWNP ≥ 1).

6. NWDP = Number of data points in each of the NWPR profiles (should be ≥ 2 if NWNP ≥ 1).

7. NDNP = Number of Dirichlet nodes.

8. NDPR = Number of Dirichlet profile types (should be ≥ 1 if NDNP ≥ 1).

9. NDDP = Number of data points in each of the NDPR profiles (should be ≥ 2 if NDNP ≥ 1).

10. NVNP = Number of variable-boundary nodes.

11. NVES = Number of variable-boundary sides.

12. NVPR = Number of incoming fluid concentration profile types to be applied to variable-boundary element sides (should be ≥ 1 if NVES ≥ 1).

13. NVDP = Number of data points in each of the NVPR profiles (should be ≥ 2 if NVES ≥ 1).

Note: Not all boundary nodes will have specified boundary conditions. At unspecified nodes, the boundary conditions are unknown and will be computed by LEHGC.

DATA SET 13: ELEMENT (DISTRIBUTED) AND WELL (POINT) SOURCE/SINK

(1) Element Source/Sink: Subdata sets (a) through (c) are needed if and only if NSEL > 0. When NSEL > 0 (Data Set 12, #1), subdata sets (b) and (c) should be repeated (NOH+1) times.

(a) 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.

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NSEL. LES(NSEL) = Global element number of the NSEL-th distributed source/sink element.

(b) Element source/sink profile: Number of lines depends on NSPR (Data Set 12,#2), NSDP (Data Set 12, #3), and NOH (Data Set 10). Each line contains a number of data points = 2*NSDP numerical numbers. Each line is free-field format input.

For K =1, NOH+1 (where NOH = NOHA + NOHS)

For I = 1, NSPR (Data Set 12, #2)

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: (M/T/L**3) if K ≤ NOH (mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

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: (M/T/L**3) if K ≤ NOH (mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

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2NSDP-1. TSOSF(NSDP,I,K) = Time of NSDP-th data point in I-th profile for K-th component (T).

2NSDP. SOSF(NSDP,I,K) = Source/sink value of NSDP-th data point in I-th profile for K-th component: (M/T/L**3) if K ≤ NOH(mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

(c) 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.

(2) Point source/sink: Subdata sets (a) through (c) are needed if and only if NWNP > 0. When NWNP > 0, subdata sets (b) and (c) should be repeated for (NOH+1) times.

(a) 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.

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NWNP. NPW(NWNP) = Global node number of the NWNP-th source/sink node.

(b) Point source/sink profile: Number of lines depends on NWPR, NWDP, and NOH. Each line contains a number of data points = 2*NWDP numerical numbers. Each line is free-field format input. (This subdata set is read similarly to subdata set 14a.)

For K =1, NOH+1 (where NOH = NOHA + NOHS)

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:(M/T/L**3) if K ≤ NOH (mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

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: (M/T/L**3) if K ≤ NOH (mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

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2NWDP-1.TWSSF(NWDP,I,K) = Time of NWDP-th data point in I-th profile for K-th component (T).

2NWDP. WSSF(NWDP,I,K) = Source/sink value of NWDP-th data point in I-th profile for K-th component: (M/T/L**3) if K ≤ NOH (mass flux). (L**3/T/L**3) if K = (NOH+1) (volume flux).

(c) 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

Four groups of lines are required for this data set if and only if NVES > 0 (Data Set 12, #11). 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 (Data Set 12, #10) 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 NOH (Data Set 10) times for each one of the NOH chemical components 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.

(a) Incoming concentration profiles: A concentration profile for each component is defined by at least two data points; a data point is defined by a time and a corresponding concentration value. Include all concentration profiles for each chemical component. In some problems, only one of the chemical components might have NVPR (Data Set 12, #12) distinct concentration profiles, while the other chemical components could have only one type of concentration profile. Nevertheless, NVPR concentration profiles with NVDP (Data Set 12, #13) data points must still be entered for each chemical component in Data Set 14(a).

Note: LEHGC linearly interpolates concentrations between data points. For example if the data set specifies a concentration of 1.0 at time = 0.0, and a concentration of 2.0 at time = 2.0, then the concentration at time = 1.0 would be calculated by LEHGC as 1.0.

For I = 1, NVPR

1. TCVBF(1,I,K) = Time of first data point in I-th incoming concentration profile for K-th component (T).

2. CVBF(1,I,K) = Concentration of first data point in I-th incoming concentration profile for K-th component: (M/L**3).

3. TCVBF(2,I,K) = Time of second data point in I-th incoming concentration time profile for K-th component (T).

4. CVBF(2,I,K) = Concentration of second data point in I-th incoming concentration profile for K-th component: (M/L**3).

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2NVDP-1. TCVBF(NVDP,I,K) = Time of the NVDP-th data point in I-th incoming concentration time profile for K-th component (T).

2NVDP. CVBF(NVDP,I,K) = Concentration of the NVDP-th data point in I-th incoming concentration profile for K-thcomponent: (M/L**3).

(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 (local) 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 = Incoming concentration profile type number assigned to side MI. (MITYPE = 1.. NVPR (Data Set 12, #12).)

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 (Data Set 12, #10) 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 (Data Set 12, # 11) 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 (compressed side) for each of the NSEQ subsequent variable-boundary element sides.
7. MAD = Increment of M (global elements) for each of the NSEQ subsequent variable-boundary element sides.
8. IS1AD = Increment of IS1 (compressed node) for each of the NSEQ subsequent variable-boundary element sides.
9. IS2AD = Increment of IS2 (compressed node) 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 (Data Set 12, #7). Subdata sets (a) and (b) should be repeated NOH times, once for each of the NOH components followed by subdata set (c). 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.

(a) Dirichlet concentration profile: This subdata set is read in similarly to that in 14 (a).

Note: LEHGC linearly interpolates concentrations between data points. For example if the data set specifies a concentration of 1.0 at time = 0.0, and a concentration of 2.0 at time = 2.0, then the concentration at time = 1.0 would be calculated by LEHGC as 1.0.

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-thcomponent: (M/L**3). CDBF( ) must be greater than zero.

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: (M/L**3). CDBF( ) must be greater than zero.

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2NDDP-1. TCDBF(NDDP,I,K) = Time of the NDDP-th data point in the I-th Dirichlet concentration versus time profile for K-th component (T).

2NDDP. CDBF(NDDP,I,K) = Concentration of the NDDP-th data point in the I-th Dirichlet concentration versus time profile for K-th component: (M/L**3). CDBF( ) must be greater than zero.

(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 integers:

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 = Dirichlet concentration profile type number for node NI and the NSEQ subsequent nodes. (NITYP = 1..NDDP (Data Set 12, #9))

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 compressed 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 the global 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 AND MOISTURE CONTENT

If KVI > 0 (Data Set 2, #8), this data set is not needed because these will be read via Logical Unit 11.

(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 component of Darcy velocity at node NI (L/T).

5. VZNI = z component of Darcy velocity at node NI (L/T).

6. VXAD = Increment of x component of Darcy velocity for each of the NSEQ subsequent nodes (L/T).

7. VZAD = Increment of z component of Darcy velocity for each of the NSEQ subsequent nodes (L/T).

NOTE: A line with seven zeros separated by spaces or commas is used to signal 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 (THNI $\leq$ 1.0). THNI equals porosity in saturated systems.

5. THNIAD = Increment of moisture content for each of the NSEQ subsequent elements (THNIAD $\leq$ 1.0).

NOTE: A line with five zeros separated by spaces or commas signals the end of this subdata set.

DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES

Free-field format input contains 7 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 precipitated species.

7. NOMXC = Number of complexed species that involved the colloid components. It is a subset of NOMX. All NOMXC species should be arranged as the last species of NOMX species. For example: if NOMXC = 4 then the last four species in the NOMX list would involve one or more colloid components.

DATA SET 18: H^+, e^-, IONIC STRENGTH CORRECTION INFORMATION

Line 1: Free-field format input contains the following four variables:

1. SICOR = User's specified ionic strength for computing activity coefficient.

2. ICOR = The ionic strength is used to correct activity coefficient:
   0 = No.
   1 = Constant ionic strength is used.
   2 = Variable ionic strength is used.

3. LNH = Location of the component H^+ in the component list.

4. LNE = Location of the component e^- in the component list.

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 > 0 (Data Set 17, #2). This set reads information of NSORB adsorbing sites.

Record 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.

Record 2 to Record NSORB + 1.
Total number of records 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.

2. LNBA(I) = Location of the exp(-e*psib/kt) component in the component list for the I-th adsorbing site.

Note: In principal, all of the NSORB adsorption sites are present in all of the NMAT material types and the adsorption reactions described in Data Sets 24 and 25 will occur in all of the NMAT material types. The next set of records controls the concentration and importance of each adsorption site for each of the NMAT material types.

Record NSORB+2 to Record NSORB+1+NMAT
Total number of records in this subset is NMAT (Data Set 2, #3). Each record contains the following variables:

1. CAP1M(1,I) = Capacitance between the surface and "o" plane, (Farad/L**2) for the first adsorbing site in material I,

2. CAP2M(1,I) = Capacitance between the "o" plane and "b" plane, (Farad/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 mass), Note that this value must be consistent with the total molar concentration of the first adsorbing site (specified in data sets 11-15), bulk density, porosity and reasonable site densities. This should be set to a very low value if the adsorption site is not present in significant amounts in material I.

4. CAP1M(2,I) = Capacitance between the surface and "o" plane, (Farad/L**2) for the second adsorbing site in material I,

5. CAP2M(2,I) = Capacitance between the "o" plane and "b" plane, (Farad/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 mass).

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3J-2. CAP1M(J,I) = Capacitance between the surface and "o" plane, (Farad/L**2) for the J-th adsorbing site in material I,

3J-1. CAP2M(J,I) = Capacitance between the "o" plane and "b" plane, (Farad/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 mass).

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3NSORB-2. CAP1M(NSORB,I) = Capacitance between the surface and "o" plane, (Farad/L**2) for the NSORB-th adsorbing site in material I,

3NSORB-1. CAP2M(NSORB,I) = Capacitance between the "o" plane and "b" plane, (Farad/L**2) for the NSORB-th adsorbing site in material I,

3NSORB. SREAM(NSORB,I) = Surface area of the NSORB-th adsorbing site in material I, (L**2/M of solid mass).

DATA SET 21: ION-EXCHANGE INFORMATION

This data set is needed only if NOMZ > 0 (Data Set 17, #5). This set reads information of ion exchange information for NSITE exchange sites.

Record 1 contains the following free-field format 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 free-field format variables for the I-th site.

1. NOMZI(I) = Number of ion-exchanged species in the I-th exchanged site.

2. LNI(I) = Location of the referenced ion-exchanged species in the ion-exchanged species list for the I-th site.

Note: In principal, all of the NSITE ion exchange sites are present in all of the NMAT material types and the ion exchange reactions described in Data Sets 24 and 25 will occur in all of the NMAT material types. The next set of records controls the concentration and importance of each ion exchange site for each of the NMAT material types.

Record NSITE+2 to Record NSITE+1+NMAT
Total number of records in this subset is NMAT. Each record contains the following free-field format variables:

1. CECM(1,I) = Ion-exchange capacity (equivalents per unit mass of solids) for the first site in material I. This should be set to a very low value if the ion exchange site is not present in significant amounts in material I.

2. CECM(2,I) = Ion-exchange capacity (equivalents per unit mass of solids) for the second site in material I.

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J. CECM(J,I) = Ion-exchange capacity (equivalents per unit mss of solids) for the J-th site in material I.

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NSITE. CECM(NSITE,I) = Ion-exchange capacity (equivalents per unit mass of solids) for the NSITE-th site in material I.

DATA SET 22: BASIC REAL AND INTEGER PARAMETERS

One line of free-field format input contains the following 6 variables.

1. OMEGAC = relaxation parameters for iteration:
   0.0 to <1.0 = under-relaxation,
   1.0 = exact relaxation,
   >1.0 to 2.0 = over-relaxation.

   Always use OMEGAC = 1.0 for this version of LEHGC.

2. EPSC = error tolerance for iteration. A value of 10^{-6} should be sufficient.

3. NITERC = number of iterations allowed. A value of 50 to 200 should be sufficient for most problems.

4. NPCYL = number of cycles allowed for iterating precipitation/dissolution. A value between 10 and 50 should be sufficient for most problems.

5. CNSTRN = a factor for the constraint on complex species concentration. No complex species concentration would yield a total component concentration greater than CNSTRN times of the input total component concentration.

6. CNSTRY = used to constrain the concentration of the adsorbed species such that no adsorbed species will have concentration greater than any component making up this species. A minimum value of CNSTRY is 1.0. A large number, such as 1.0D38, would indicate that no constraint will be made.

DATA SET 23: NAMES OF CHEMICAL COMPONENTS AND TYPES OF COMPONENT SPECIES

For each component, one line is needed.

Line 1 - FORMAT(A20,I5)

1. CNAM(J,2) = Component name of the J-th component.

2. INDTC(J,2) = Types 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., sigma-o or sigma-b
   4 = mobile adsorbent species, e.g., colloid component species.

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 an ion-exchange reaction. 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.

Line 1: FORMAT(A20,I5)

1. SPECN(I) = Name of the I-th component species.

2. ISCN(I) = Indicator of the I-th species concentration:
   0 = Species concentration or activity is to be computed.
   1 = Not implemented in this version.
   2 = Not implemented in this version.
   3 = Species concentration or activity is fixed.

Line 2: Free-field format input contains three variables:

1. CW(I) = Initial guess of the I-th component species concentration (M/L**3).

2. VJ(I) = Charge of the I-the component species.

3. IONEX = Integer indicating the number of ion exchange sites with which this component species interacts:
   0 = This component species does not participate in any ion exchange reaction.
   > 0 = This component species participates in IONEX ion exchange reactions.

The following subdata set is needed only if IONEX is not equal to zero. When IONEX is not equal to 0, this subdata set is repeated IONEX times. For each IONEX, the following three lines are needed to read ion exchanged species information.

For k = 1, IONEX

Line 3 - Free Format. This line contains the following variable

1. J = This species participates in the J-th ion exchange site's reaction.

Line 4 - FORMAT(A20,I5):

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.

2. ISCN(II) = Indicator of the II-th ion-exchanged species concentration:
   0 = Species concentration is to be computed,
   1 = Not implemented in this version.
   2 = Not implemented in this version.
   3 = Species concentration is fixed.

Line 5 - Free Format. This line contains the following variables

1. CW(II) = Initial guess of the II-th ion-exchanged species concentration, (M/L**3).

2. PKIPD = Log10 of the selectivity of the II-th ion-exchanged species resulted from the I-th component species involving in the J-th ion exchange site reaction.

3. AXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

4. AXYZP(IPD,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

5. AXYZP(IPD,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

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NOH+2. AXYZP(IPD,NOH) = Stoichiometric coefficient of the NOH-th component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

NOH+3. BXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

NOH+4. BXYZP(IPD,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

NOH+5. BXYZP(IPD,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

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2*NOH+2. BXYZP(IPD,NOH) = Stoichiometric coefficient of the NOH-th component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

Note: In principal, all of the ion exchange reactions for the NSITE ion exchange sites described above will occur in all of the NMAT material types. The importance of the ion exchange reactions for solution composition in each of the material is controlled by the concentration of each ion exchange site entered in Data Set 21 for each of the NMAT material types.

DATA SET 25: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

This data set is read in similarly to Data Set 24 and is only needed if NOMX > 0.

Line 1: FORMAT(A20,I5)

1. SPECN(I) = Name of the I-th complexed species.

2. ISCN(I) = Indicator of the I-th species concentration:
   0 = Species concentration is to be computed.
   1 = Not implemented in this version.
   2 = Not implemented in this version.
   3 = Species concentration is fixed.

Line 2: Free-field format input contains the following variables:

1. CW(I) = Initial guess of the complexed species concentration (M/L**3).

2. PKIPD = Log10 of the equilibrium constant for the formation reaction of the I-th complexed species.

3. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mass action equation.

4. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mass action equation.

5. AXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mass action equation.

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NOH+2. AXYZP(I,NOH)= Stoichiometric coefficient of the NOH-th component in the I-th complexed species, for use in mass action equation.

NOH+3. IONEX = Integer indicating the number of ion exchange sites with which this complexed species interacts:
0 = This complexed species does not participate in any ion exchange reaction.
> 0 = This complexed species participates in IONEX ion exchange reactions.

NOH+4. BXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mole balance equation.

NOH+5. BXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mole balance equation.

NOH+6. BXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mole balance equation.

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2*NOH+2. BXYZP(I,NOH) = Stoichiometric coefficient of the NOH-th component in the I-th complexed species, for use in mole balance equation.

The following subdata set is needed only if IONEX is not equal to zero. When IONEX is not equal to 0, this subdata set is repeated IONEX times. For each IONEX, 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,I5):

1. SPECN(II) = Name of the II-th ion-exchanged species resulted from the I-th complexed species involving the J-th ion exchange site reaction.

Note: II is internally arranged according to the order of ion exchange site.

2. ISCN(II) = indicator of the II-th ion-exchanged species concentration:
0 = Species concentration is be computed,
1 = Not implemented in this version.
2 = Not implemented in this version.
3 = Species concentration is fixed.

Line 5 - Free Format. This line contains the following variables

1. CW(II) = Initial guess of the II-th ion-exchanged species concentration, (M/L**3).

2. PKIPD = Log10 of the selectivity of the II-th ion-exchanged species resulted from the I-th complexed species involving in the J-th ion exchange site reaction.

3. AXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

4. AXYZP(IPD,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

5. AXYZP(IPD,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

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NOH+2. AXYZP(IPD,NOH) = Stoichiometric coefficient of the NOH-th component in the II-th ion exchange species for use in mass action, where IPD=II-NOH.

NOH+3. BXYZP(IPD,1) = Stoichiometric coefficient of the first component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

NOH+4. BXYZP(IPD,2) = Stoichiometric coefficient of the second component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

NOH+5. BXYZP(IPD,3) = Stoichiometric coefficient of the third component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

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2*NOH+2. BXYZP(IPD,NOH)= Stoichiometric coefficient of the NOH-th component in the II-th ion exchange species for use in mole balance, where IPD=II-NOH.

Note: In principal, all of the ion exchange reactions for the NSITE ion exchange sites described above will occur in all of the NMAT material types. The importance of the ion exchange reactions for solution composition in each of material is controlled by the concentration of each ion exchange site entered in Data Set 21 for each of the NMAT material types.

DATA SET 26: ADSORBED SPECIES

This data set is only needed if NOMY > 0. Two lines per adsorbed species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(I) = Name of the I-th adsorbed species.

2. ISCN(I) = Indicator of the I-th species concentration:
0 = Species concentration is to be computed,
1 = Not implemented in this version.
2 = Not implemented in this version.
3 = Species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CW(I) = Initial guess of the adsorbed species concentration, (M/L**3).

2. PKIPD = Log10 of the equilibrium constant of the I-th adsorbed species.

3. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th adsorbed species, for use in the mass action equation.

4. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th adsorbed species, for use in the mass action equation.

5. AXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th adsorbed species, for use in the mass action equation.

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NOH+2. AXYZP(I,NOH) = Stoichiometric coefficient of the NOH-th component in the I-th adsorbed species, for use in the mass action equation.

NOH+3. BXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th adsorbed species, for use in the mole balance equation.

NOH+4. BXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th adsorbed species, for use in the mole balance equation.

NOH+5. BXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th adsorbed species, for use in the mole balance equation.

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2*NOH+2. BXYZP(I,NOH) = Stoichiometric coefficient of the NOH-th component in the I-th adsorbed species, for use in the mole balance equation.

Note: In principal, all of the adsorption reactions for the NOH adsorbent components described above will occur in all of the NMAT material types. The importance of a particular immobile adsorbent component for solution composition in each of the Material Types is controlled by its initial concentration at each node entered in Data Set 11 and its surface area entered in Data Set 20 for each of the NMAT material types.

DATA SET 27: PRECIPITATED/DISSOLVED SPECIES

This data set is only needed if NOMP > 0. Two lines per precipitated/dissolved species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(I) = Name of the I-th precipipated/dissolved species.

2. ISCN(I) = Indicator of the I-th species concentration:
   0 = Species concentration is to be computed,
   1 = Not implemented in this version.
   2 = Not implemented in this version.
   3 = Species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CW(I) = Initial guess of the precipitated/dissolved species concentration, (M/L**3).

2. PKIPD = Log10 of the equilibrium constant of the precipitation reaction for the I-th precipitated species. Note this value is the inverse of the more commonly given solubility product.

3. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th precipitated/dissolved species, for use in the mass action equation.

4. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th precipitated/dissolved species, for use in the mass action equation.

5. AXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th precipitated/dissolved species, for use in the mass action equation.

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NOH+2. AXYZP(I,NOH) = Stoichiometric coefficient of the NOH-th component in the I-th precipitated/dissolved species, for use in the mass action equation.

NOH+3. BXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th precipitated/dissolved species, for use in mole balance equation.

NOH+4. BXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th precipitated/dissolved species, for use in the mole balance equation.

NOH+5. BXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th precipitated/dissolved species, for use in the mole balance equation.

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2*NOH+2. BXYZP(I,NOH) = Stoichiometric coefficient of the NOH-th component in the I-th precipitated/dissolved species, for use in the mole balance equation.

DATA SET 28: END-OF-JOB LINE

A blank line must be used to signal the end of the job.

APPENDIX B

List of Symbols Used in Report

List of Symbols Used in Report

A = area of a triangular element (L^2); or constant in Debye-Huckel equation.

A_1 , A_2 , A_3 = area of a triangular element (L^2).

A_i = activity of the i-th aqueous species (dimensionless).

A_i^x = activity of the i-th complexed species (dimensionless).

A_J = activity of the i-th ion-exchanged species denoting exchanged A_J (dimensionless).

a_i = molar concentration of the i-th aqueous species denoting either c_j or x_i (M/L^3); or species dependent adjustable parameter in generalized activity coefficient equation.

$\hat{a}_i$ = chemical formula for the i-th aqueous species (dimensionless).

a_{ib}^y = stoichiometric coefficient of c_b in the i-th adsorbed species (dimensionless).

a_{ie}^p = stoichiometric coefficient of the electron in the i-th precipitated species (dimensionless).

a_{ie}^x = stoichiometric coefficient of the electron in the i-th complexed species (dimensionless).

a_{ie}^y = stoichiometric coefficient of the electron in the i-th adsorbed species (dimensionless).

a_{ie}^z = stoichiometric coefficient of the electron in the i-th ion-exchanged species (dimensionless).

a_{ij}^p , a_{ik}^p = stoichiometric coefficient of the j-th or k-th aqueous component in the i-th precipitated species (dimensionless).

a_{ij}^x , a_{ik}^x = stoichiometric coefficient of the j-th or k-th aqueous component in the i-th complexed species (dimensionless).

a_{ij}^y , a_{ik}^y = stoichiometric coefficient of the j-th or k-th aqueous component in the i-th adsorbed species (dimensionless).

a_{ij}^z , a_{ik}^z = stoichiometric coefficient of the j-th or k-th aqueous component in the i-th ion-exchanged species (dimensionless).

a_{io}^y = stoichiometric coefficient of c_o in the i-th adsorbed species.

$\hat{a}_J$ = chemical formula for the J-th ion-exchanged species (dimensionless).

a_J, a_m = molar concentration of the J-th or m-th ion exchanged species, respectively (M/L^3).

a_{je}^{a} = stoichiometric coefficient of the electron in the j-th aqueous component species (dimensionless).

a_{je}^{s} = stoichiometric coefficient of the electron in the j-th adsorbent component species (dimensionless).

a_L = longitudinal dispersivity (L).

a_m = molecular diffusion coefficient (L^2/T).

a_T = transverse dispersivity (L).

B = a conversion factor from charge per unit area to moles per unit volume; or a constant in the Debye-Huckel equation.

B' = a constant in the Debye-Huckel equation.

B_D, B_N, B_C, B_V = boundary segments for Dirichlet, Neumann, Cauchy, and Variable boundaries, respectively.

B_e = the length of boundary segment e (L).

B_i = activity of the i-th aqueous species (dimensionless); element i of vector $\{B\}$; or species dependent adjustable parameter in generalized activity coefficient equation.

B_i^y = activity of the i-th adsorbed species of surface complexation (dimensionless).

B_J = activity of the i-th ion-exchanged species denoting exchanged B_J (dimensionless).

B_α^e = element a of vector $\{B^e\}$.

$\{B^e\}$ = load vector from the boundary source.

$\{B_D^e\}, \{B_N^e\}, \{B_C^e\}, \{B_V^e\}$ = boundary element column vectors for Dirichlet, Neumann, Cauchy, and Variable boundaries, respectively.

b = half the width of a fracture (L).

b_i = species dependent adjustable parameter in generalized activity coefficient equation.

b_{ij}^y, b_{ik}^y = stoichiometric coefficient of the j-th or k-th adsorbent component in the i-th adsorbed species of surface complexation (dimensionless).

C = the capacitance term in constant capacitance model, or concentration (M/L^3).

C_1 = capacitance of the region between the "o" plane and "b" plane ($Farad/L^2$).

C_2 = capacitance of the region between "b" plane and "d" plane ($Farad/L^2$).

C_{ci}^* = Lagrangian concentration at the i-th Cauchy boundary node (M/L^3).

C_{cin} = concentration of the incoming fluid through the variable boundary (M/L^3).

C_e = concentration of operational electrons in the aqueous phase (M/L^3).

C_i = the value of C at node i (M/L^3).

C_i^* = Lagrangian concentration at the boundary node i (M/L^3).

C_{in} = total dissolved concentration of incoming fluid through variable boundaries (M/L^3).

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

C_j = total dissolved concentration of hydrogen (M/L^3).

$C_j(t)$ = the value of concentration C_j at time t (M/L^3).

C_j^* = input concentration of the j-th aqueous component if Q is a source (injection) (M/L^3); = C_j if Q is a sink (withdrawal) (M/L^3).

C_p = heat capacity ($L^2/(T^2\,°K)$).

C_{vi}^* = Lagrangian concentration at the i-th variable-boundary node (M/L^3).

$\{C^*\}$ = column vector representing the Lagrangian concentration at all nodes (M/L^3).

c_b, c_o = capacitance terms in electrostatic models (equations 3.3.33 - 3.3.53).

c_j, c_k, c_m = concentration of the j-th, k-th or m-th aqueous component species, respectively (M/L^3).

$\hat{c}_j$ = chemical formula for the j-th aqueous component species (dimensionless).

D = "effective" diffusion coefficient (L^2/T), or dispersion coefficient (L^2/T).

D = dispersion coefficient tensor (L^2/T).

$D^e_{\alpha\beta}$ = element $\alpha\beta$ of matrix $[D^e]$.

$[D^e]$ = dispersion matrix.

$\left\{\frac{DC}{D\tau}\right\}$ = column vector containing the value of $\left\{\frac{DC}{D\tau}\right\}$ at all nodes.

dh/dx = hydraulic gradient(L/L).

$\left\{\frac{d(S+P)}{dt}\right\}$ = column vector containing the value of $\frac{d(S+P)}{dt}$ at all nodes.

$\frac{d\theta}{dh}$ = specific water capacity (1/L).

$E^e_{\alpha\beta}$ = element $\alpha\beta$ of matrix $[E^e]$.

E_{ij} = element ij of matrix [E].

[E] = growth matrix (global) representing the effect of the rate of change of moisture content.

$[E^e]$ = growth matrix (element).

e = electronic charge ($1.6021892 \times 10^{-19}$ Coulomb/Electron).

$F^e_{\alpha\beta}$ = element $\alpha\beta$ of matrix $[F^e]$.

$[F^e]$ = fluid source matrix.

[G], [H] = matricies used in FDM approximation of time derivative (equations 3.2.23, 3.2.24, 3.2.42).

GRi = residual of the i-th equation.

g = gravitational acceleration (L/T^2).

H = total head (L).

h = pressure head (L).

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

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

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

h_{ik}^{z} = stoichiometric coefficient of the k-th chemical element in the i-th ion-exchanged species (dimensionless).

h_{jk}^{a} = stoichiometric coefficient of the k-th chemical element in the j-th aqueous component species (dimensionless).

h_{jk}^{s} = stoichiometric coefficient of the k-th chemical element in the j-th adsorbent component species (dimensionless).

I = ionic strength.

$\mathbf{J}_j$ = $\theta c_j(\mathbf{V}_j - \mathbf{V}_f)$ is the surface flux of the j-th aqueous component species with respect to fluid velocity $\mathbf{V}_f$ ((M/T)/L^3).

K = hydraulic conductivity (L/T).

$\mathbf{K}$ = hydraulic conductivity tensor (L/T); or an operator denoting

$$K(!)=\left(-\nabla\cdot\theta D\cdot\nabla+Q-\frac{\delta\theta}{\delta t}\right)(!).$$

K_{dj} = distribution coefficient of the j-th aqueous component (L^3/M).

K_i^{p} = equilibrium constant of the i-th precipitated species (dimensionless).

K_i^{x} = equilibrium constant of the i-th complexed species (dimensionless).

K_i^{y} = equilibrium constant of the i-th adsorbed species (dimensionless).

K_i^{z} = equilibrium constant of the i-th ion- exchanged species (dimensionless).

K_{iJ} = selectivity coefficient of the i-th species with respect to the J-th species; the effective equilibrium constant of the i-th ion-exchanged species (dimensionless); or element iJ of global matrix [K].

[K] = modified stiff matrix resulting from the action of dispersion, source of water, and the rate of change of moisture content.

k = Boltzman constant (1.380662 x 10^{-23} Joule/K), conductivity (ML/(T^3 °K)), or an indexing variable.

L_1, L_2, L_3 = three area coordinates of a triangular element (L).

{L} = the load vector.

LNI(i) = index of reference ion-exchanged species for the i-th site.

M_a = the number of aqueous species, equal to the number of aqueous component species plus the number of complexed species.

M_e = the set of elements that have a local side α-β coinciding with the global side i-j (dimensionless).

M_e^{a} = external source/sink rate of the free electron species ((M/T)/L^3).

M_{eq} = total rate of source/sink of the ion-exchange site ((M/T)/L^3).

M_{eqi} = value of M_{eq} at node i ((M/T)/L^3).

M_{ij} = element ij of global matrix M.

M_H^{a} = total rate of source/sink of hydrogen ((M/T)/L^3).

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

M_j^s = total rate of source/sink of the j-th adsorbent component ((M/T)/L^3).
M_p = number of potentially precipitated species (dimensionless).
M_s = the sum of N_s adsorbent component species, M_y adsorbed species and M_z ion-exchanged species.
M_x = number of complexed species (dimensionless).
M_y = number of adsorbed species (dimensionless).
M_z = number of ion-exchanged species (dimensionless).
$M_{\alpha\beta}^e$ = element $\alpha\beta$ of matrix [M^e].
[M] = mass matrix (global) resulting from the storage term.
[M^e] = mass matrix (element).
m = an indexing variable.
m_i^x = external source/sink rate of the i-th complexed species ((M/T)/L^3).
m_i^y = external source/sink rate of the i-th adsorbed species ((M/T)/L^3).
m_i^z = external source/sink rate of the i-th ion-exchanged species ((M/T)/L^3).
m_i^p = external source/sink rate of the i-th precipitated species ((M/T)/L^3).
m_j^a = external source/sink rate of the j-th aqueous component species ((M/T)/L^3).
m_j^s = external source/sink rate of the j-th adsorbent component species ((M/L^3)/T).
N_a = number of aqueous component species (dimensionless).
N_{ce} = number of Cauchy boundary segments (dimensionless).
N_e = number of chemical elements considered in the system (dimensionless).
N_{eq} = number of equivalents of the ion-exchange sites per liter of solution (M/L^3).
N_{eqi}, N_{eqj} = value of N_{eq} at node i or j, respectively (M/L^3).
$(N_{eqi})_t$, $(N_{eqi})_{t+\Delta t}$ = value of N_{eqj} at time t or (t+Δt), respectively (M/L^3).
N_{eqo} = initial number of equivalents of the ion exchange site (M/L^3).
N_j = the basis function of the spatial coordinate for the j-th node (dimensionless).
$N_j(x_i^*)$ = the interpolation function associated with node j, evaluated at the Lagrangian point x_i^*.
N_s = number of adsorbent component species (dimensionless).
N_{se} = set of boundary segments having a local node α coinciding with global node i (dimensionless).
N_{ne} = number of Neumann boundary segments (dimensionless).
N_{ve} = number of variable-boundary segments (dimensionless).
N_α^e = the α-th local basis function of element e (dimensionless).
n = an outward unit vector normal to the boundary (L).
n = number of nodes in the region (dimensionless); or an indexing variable.
NOMZJ(i) = number of ion exchanged species from the first site through the (i-1)th site.
NOMZI(i) = number of ion exchanged species in the i-th site.
NSITE = number of ion-exchange sites.

NSORB = number of adsorbing sites.

P = total precipitated concentration (M/L^3).

P_e = concentration of operational electrons in solid phase (M/L^3).

P_H = total precipitated concentration of hydrogen (M/L^3).

P_j = value of P at node j (M/L^3); or the total precipitated concentration of the j-th aqueous component (M/L^3).

$\{P\}$ = column vector containing the value of P at all nodes.

$\{P\}_t$ = value of $\{P\}$ at time t (M/L^3).

$\{P\}_{t+\Delta t}$ = column vector representing the value of $\{P\}$ at time $(t+\Delta t)$ (M/L^3).

p_i = concentration of the i-th precipitated species per unit fluid volume (M/L^3).

$\hat{p}_i$ = chemical formula for the i-th precipitated species (dimensionless).

Q = source or sink representing the artificial injection or withdrawal of water ($(L^3/L^3)/T$).

Q_i = the i-the element of vector $\{Q\}$.

$Q^e_{\alpha\beta}$ = element $\alpha\beta$ of matrix $[Q^e]$.

$\{Q\}$ = load vector (global) from the internal source/sink.

$\{Q^e\}$ = element column vector.

q_{jN} = normal Neumann flux ($M/L^2/T$).

q_{jC} = normal Cauchy flux ($M/L^2/T$).

$q^e_{N\alpha}$, $q^e_{C\alpha}$, $q^e_{V\alpha}$ = element α of vector $\{q^e_N\}$, $\{q^e_C\}$, $\{q^e_V\}$, respectively.

$\{q\}$ = boundary flux vector for Neumann, Cauchy and Variable boundaries, combined.

$\{q^e_N\}$, $\{q^e_C\}$, $\{q^e_V\}$ = boundary flux vector for Neumann, Cauchy or Variable boundaries, respectively.

R = universal gas constant (8.314 Joule/Mole/K).

R_{dj} = retardation factor of the j-th component (dimensionless).

R_e = the region of element e (L^2).

R_m = residual of an equation.

r_i^p = production rate of the i-th precipitated species per unit fluid volume due to the i-th precipitation reaction ($(M/T)/L^3$).

r_i^x = production rate of i-th complexed species per unit fluid volume due to the i-th complexation reaction ($(M/T)/L^3$).

r_i^y = production rate of the i-th adsorbed species per unit fluid volume due to the i-th adsorption reaction ($(M/T)/L^3$).

r_i^z = production rate of the i-th ion-exchanged species per unit fluid volume due to the i-th ion-exchange reaction ($(M/T)/L^3$).

r_j^a = production rate of the j-th aqueous component species per unit fluid volume due to all chemical reactions ($(M/T)/L^3$).

r_j^s = production rate of the j-th adsorbent component species per unit fluid volume due to all sorption reactions ($(M/T)/L^3$).

S = total sorbed concentration.

S_e = concentration of operational electrons in sorbent phase (M/L^3).

S_H = total sorbed concentration of hydrogen (M/L^3).

S_j = the value of S at node j (M/L^3); or the total sorbed concentration of the j-th aqueous component (M/L^3).

$\{S\}$ = column vector containing the value of S at all nodes (M/L^3).

$\{S\}_t$ = value of $\{S\}$ at time t (M/L^3).

$\{S\}_{t+\Delta t}$ = column vector representing the value of $\{S\}$ at time $(t+\Delta t)$ (M/L^3).

s_j, s_m = concentration of the j-th or m-th adsorbent component species, respectively (M/L^3).

$\hat{s}_j$ = chemical formula for j-th adsorbent component species (dimensionless).

s_T = total concentration of all ion-exchanged species (M/L^3).

T = total analytical concentration of any component (M/L^3); or absolute temperature (°K).

T_e = total concentration of operational electrons (M/L^3).

T_H = total analytical concentration of hydrogen (M/L^3).

T_i = the value of T (total analytical concentration) at node i (M/L^3).

T_j, T_m = total analytical concentration of the j-th or m-th aqueous component, respectively (M/L^3).

T_{jD} = prescribed Dirichlet total analytical concentration (M/L^3).

T_{jo} = initial total analytical concentration of j-th aqueous component (M/L^3).

$\{T\}$ = column vector containing the value of T (total analytical concentration) at all nodes (M/L^3).

$\{T\}_{t+\Delta t}$ = column vector representing the value of $\{T\}$ at time $(t+\Delta t)$ (M/L^3).

$\{T^{k+1}\}$ = new estimate of $\{T\}$ during the nonlinear iteration (M/L^3).

$\{T^k\}$ = previous estimate of $\{T\}$ during the nonlinear iteration (M/L^3).

t = time (T).

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

$\mathbf{V}^e_{C\alpha\beta}$, $\mathbf{V}^e_{V\alpha\beta}$ = element α of vector $[V^e_C]$, $[V^e_V]$, respectively.

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

V_f = average fluid velocity in a fracture (L/T).

$\mathbf{V}_{fs}$ = fluid velocity relative to the solid (1/L).

$\mathbf{V}_j$ = the velocity (L/T) of the j-th aqueous component species $[(M/T)/L^2]$.

V_m = Darcy velocity of fluid in a matrix (L/T).

$\mathbf{V}_n$ = the normal component of the Darcy velocity.

$\mathbf{V}_s$ = solid velocity (1/L).

$|V|$ = the magnitude of the Darcy velocity $\mathbf{V}$ (L/T).

$[V^e_C]$,$[V^e_V]$ = boundary matrix for Cauchy or Variable boundaries respectively.

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

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

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

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

v_{jk}^{a} = valence of the k-th chemical element in the j-th aqueous component species (dimensionless).

v_{jk}^{s} = valence of the k-th chemical element in the j-th adsorbent component species (dimensionless).

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

W_j, W_m = total analytical concentration of the j-th or m-th adsorbent component, respectively (M/L^3).

W_{jo} = Initial total analytical concentration of j-th adsorbent component (M/L^3).

$(W_j)_t$, $(W_j)_{t+\Delta t}$ = column vector representing the value of W_j at times t or $(t+\Delta t)$, respectively (M/L^3).

w = time weighting factor.

X_k = activity of the k-th aqueous component species (dimensionless).

x^n = value of x from previous iteration.

x^{n+1} = value of x at the new iteration.

x_i = concentration of the i-th complexed species (M/L^3); or a node used in computing the Lagrangian concentration.

x_i^* = location of a fictitious particle that would arrive at node i at time (n+1) (L), also called the Lagrangian point.

$\hat{x}_i$ = chemical formula for the i-th complexed species (dimensionless).

$\mathbf{Y}$ = residues.

Y_k = activity of the k-th adsorbent component species (dimensionless).

y^n = value of y(x) evaluated at x^n.

y_i = concentration of the i-th adsorbed species (M/L^3).

$\hat{y}_i$ = chemical formula for i-th adsorbed species i (dimensionless).

$\mathbf{Z}$ = Jacobian of $\mathbf{Y}$ with respect to $\mathbf{X}$.

z = potential head (L), spatial coordinate (L), distance (L), or the charge of the ion.

z_i = charge of the i-th aqueous species.

z_i, z_j, z_m = molar concentration of the i-th, j-th or m-th ion-exchanged species, respectively (M/L^3).

$\hat{z}_i$ = chemical formula for the i-th aqueous species (dimensionless).

z_J = molar concentration of the J-th ion-exchanged species (M/L^3).

$\hat{z}_J$ = chemical formula for the J-th ion-exchanged species (dimensionless).

α_i^p = modified stability constant for the i-th precipitated species.

α_i^x = modified stability constant for the i-th complexed species.

α_i^y = modified stability constant for the i-th adsorbed species.

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

γ_i = activity coefficient of the i-th aqueous species denoting either γ_i^a or γ_i^x (L^3/M).

γ_i^p = activity coefficient of the i-th precipitated species (L^3/M).

γ_i^x = activity coefficient of the i-th complexed species (L^3/M).

γ_i^y = activity coefficient of the i-th adsorbed species (L^3/M).

γ_i^z = activity coefficient of the i-th ion-exchanged species (L^3/M).

γ_J = activity coefficient of the J-th ion-exchanged species (L^3/M).

γ_j^a, γ_k^a = activity coefficient of the j-th or k-th aqueous component species (L^3/M).

γ_j^s = activity coefficient of the j-th adsorbent component species (L^3/M).

Δt = time-step size (T).

$\Delta\tau$ = time step size in the Lagrangian Coordinate (T).

$\delta\tau$ = time-step size, along the characteristic line (T).

δ = Kronecker delta tensor (dimensionless).

ϵ = relative dielectric constant (=78.84, dimensionless).

ϵ_o = permitivity of the free space (8.85×10^{-13} Coulomb^2/Joule/dm).

η = porosity (dimensionless); or local coordinate of a hexahedral element (dimensionless).

η_α = coordinate of the corner node of a hexahedral element (dimensionless).

θ = moisture content (L^3/L^3).

ι_e^a = rate of decay of the free electron species ($(M/L^3)/T$).

ι_i^p = rate of decay of the i-th precipitated species ($(M/L^3)/T$).

ι_i^x = rate of decay of the i-th complexed species ($(M/L^3)/T$).

ι_i^y = rate of decay of the i-th adsorbed species ($(M/L^3)/T$).

ι_i^z = rate of decay of the i-th ion-exchanged species ($(M/L^3)/T$).

ι_j^a = rate of decay of the j-th aqueous component species ($(M/L^3)/T$).

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

κ_{iJ} = modified selectivity coefficient of the i-th ion-exchanged species with respect to the J-th ion-exchanged species.

Λ_{eq} = total decay rate of the ion-exchange site ($(M/T)/L^3$).

Λ_{eqi} = value of Λ_{eq} at node i ($(M/T)/L^3$).

Λ_e^a = total rate of decay of the operational electron ($(M/T)/L^3$).

Λ_H^a = total decay rate of hydrogen ($(M/T)/L^3$).

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

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

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

λ_j^a = rate constant of the j-th aqueous component (1/T).

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

μ = dynamic fluid viscosity (M/LT).

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

ν_i = charge of the i-th aqueous species (dimensionless).

ν_J = charge of the J-th ion-exchanged species (dimensionless).

ν_k = charge of the k-th ion-exchanged species (dimensionless).

ξ = local coordinate of a hexahedral element (dimensionless).

ξ_α = corner node of the local coordinate of a hexahedral element (dimensionless).

ρ = material density (M/L^3), or fluid density (M/L^3).

ρ_b = bulk density of the medium (M/L^3).

σ_b = charge density in charge per unit area on the "b" plane (Coulomb/L^2).

σ_d = charge density in charge per unit area on the diffuse layer (Coulomb/L^2).

σ_o = charge density in charge per unit area on the "o" plane (Coulomb/L^2).

τ = tortuosity (dimensionless), or the time with respect to the Lagrangian coordinate (T).

ψ_b = electric potential at the surface "b" (Volt = Joules/Coulomb).

ψ_d = electric potential at the surface "d" (Volt = Joules/Coulomb).

ψ_o = electric potential at the surface "o" (Volt = Joules/Coulomb).

ω = iteration parameter (dimensionless).

Indices

Subscripts

J - species sorbed by ion exchange.

i - aqueous species.

j, k - used for components in reactions and equilibrium constants.

Superscripts

a - denotes aqueous species.

x - denotes adsorbent species.

x - denotes complexed species.

y - denotes adsorbed species.

z - denotes ion exchanged species.

p - denotes precipitated species.

n - denotes value at the previous iteration.

n + 1 - denotes value at the new iteration.

APPENDIX C

List of LEHGC 1.1 Code Parameters

List of LEHGC Code Parameters

The first column of the following list, alphabetically names each parameter used in the data entry sets. The second column shows where the parameter is specified: the data set number, the group or line number when applicable, and the item number. The third column lists those data sets which will be affected by the parameter in the first column. For example, the entry:

IMID DS 2, #10 DS 3, #5

shows that parameter IMID is specified in data set 2, item #10, and that data set 3, item #5 is dependent. The dependancy arises because, if IMID is specified as equal to "1", then W, which is specified by data set 3, item #5, should also equal "1".

Parameter	Data set, number	Dependent data sets
APHAG	DS 3, #10	
AXYZP(I,NOH)	DS 24, Line 5, #(NOH+2)	
"	DS25, Lines 2 & 5, #(NOH+2)	
"	DS 26, Line 2, #(NOH+2)	
"	DS 27, Line 2, #(NOH+2)	
BXYZP(I,NOH)	DS 24, Line 5, #(2*NOH+2)	
"	DS25, Lines 2 & 5, #(2*NOH+2)	
"	DS 26, Line 2, #(NOH+3)	
"	DS 27, Line 2, #(NOH+3)	
CAP1M(J,I)	DS20, Record NSORB+2, #(3J-2)	
CAP2M(J,I)	DS20, Record NSORB+2, #(3J-1)	
CDBF(J,I,K)	DS 15, Group a	
CECM(J,I)	DS21, Record NSITE+2	
CHNG	DS 3, #2	DS 2, #5
CNAM(I,1)	DS 10, Lines 2..I+1, #1	
CNAM(J,2)	DS 23, #1	
CNSTRN	DS 22, #5	
CNSTRY	DS 22, #6	
CVBF(J,I,K)	DS 14, Group a	
CW(I)	DS 24, Line 2, #1	
"	DS 25, Line2, #1	
"	DS 26, Line 2, #1	
"	DS 27, Line 2, #1	
CW(II)	DS 24, Line 5, #1	
"	DS 25, Line 5, #1	

DELMAX	DS 3, #3	DS 2, #5
DELT	DS 3, #1	DS 2, #5
ESPC	DS 22, #2	
I1	DS 2	DS 2, #5
I2	DS 2	DS 2, #5
IADS	DS 20, Record 2, #2	
ICOND	DS 1, Line 2, #3	
ICOR	DS 18, Line 1, #2	
IDNTC(I,1)	DS 10, Lines 2..I+1, #2	DS 11
IDTI	DS 2, #21	
IE(MI,1)	DS 8, #2	
IE(MI,2)	DS 8, #3	
IE(MI,3)	DS 8, #4	
IE(MI,4)	DS 8, #5	
IE(MI,5)	DS 8, #6	
IGEOM	DS 1, Line 2, #5	
IITR	DS 1, Line 2, #3	
ILUMP	DS 2, #9	
IMID	DS 2, #10	DS 3, #5
INDTC(I,1)	DS 10, Lines 2..I+1, #3	
INDTC(J,2)	DS 23, #2	
INTER	DS 1, Line 2, #4	
IONEX	DS 24, Line 2, #3	DS 24, Lines 3, 4, & 5
"	DS 25, Line 2, #(NOH+3)	DS 25, Lines 3,4, & 5
IOPTIM	DS 2, #12	DS3, #10
IPNTS	DS 2, #16	
IQUAD	DS 2, #20	
IS1	DS 14, Group d, #4	
IS1AD	DS 14, Group d, #8	
IS2	DS 14, Group d, #5	
IS2AD	DS 14, Group d, #9	
ISCN(I)	DS 24, Line 1, #2	
"	DS 25, Line 1, #2	
"	DS 26, Line 1, #2	
"	DS 27, Line 1, #2	
ISCN(II)	DS 24, Line 4, #2	
"	DS 25, Line 4, #2	
IWET	DS 2, #11	
IWRK(N)	DS 5, Line 2, #N	

J	DS 24, Line 3, #1	
"	DS 25, Line 3, #1	
KDSK0	DS 4	
KDSK(I)	DS 4	
KPR0	DS 4	
KPR(I)	DS 4	
KSS	DS 2, #6	DS 11
KSTR	DS 2, #17	DS 11
KVI	DS 2, #8	DS 7
"		DS 11
"		DS 16
LES(N)	DS 13, Group 1a, #1..N	
LGRN	DS 2, #19	
LNBA(I)	DS 20, Record 2..NSORB+1, #2	
LNE	DS 18, Line 1, #4	
LNH	DS 18, Line 1, #3	
LNI(I)	DS 21, Record 2..NSITE+1, #2	
LNOA(I)	DS 20, Record 2..NSORB+1, #1	
M	DS 14, Group d, #3	
MAD	DS 9, #3	
"	DS 13, Group 1c, #3	
"	DS 14, Group d, #7	
MI	DS 8, #1,	
"	DS 9, #1	
"	DS 13, Group 1c, #1	
"	DS 14 Groups b & d, #1	
MIAD	DS 14, Group b, #3, Group d, #6	
MITYP	DS 9, #4	
"	DS 13, Group 1c, #4	
"	DS 14, Group b, #4	
MODL	DS 8, #7	
MTYPAD	DS 9, #5	
"	DS 13, Group 1c, #5	
"	DS 14, Group b, #5	

NAD	DS 7, #3	
"	DS 11, #3	
"	DS 15, Group b, #3	
"	DS 16, Groups a & b, #3	
NCM	DS 2, #4	DS 9
NCPRT	DS 5, Line 1, #1	DS 5, Ln 2
NDDP	DS 12, #9	DS 15, Grp a
NDNP	DS 12, #7	DS 15
NDPR	DS 12, #8	DS 15, Grp a
NDTCHG	DS 2, #14	DS 4
NEL	DS 2, #2	DS 8
"		DS 16, Grp b
NHGCI	DS 1, Line 2, #4	
NI	DS 7, #1	
"	DS 11, #1	
"	DS 13, Group 2c, #1	
"	DS 14, Group c, #1	
"	DS 15, Groups b & c, #1	
"	DS 16, Groups a & b, #1	
NIAD	DS 13, Group 2c, #3	
"	DS 14, Group c, #3	
"	DS 15, Group c, #3	
NITER	DS 2, #13	
NITERC	DS 22, #3	
NITYP	DS 13, Group 2c, #4	
"	DS 15, Group b, #4	
NITYPA	DS 13, Group 2c, #5	
NLAY	DS 8, #8	
NLINE		DS 4
NMAT	DS 2, #3	DS 6
"		DS 9
"		DS 20
NMPPM	DS 2, #7	
NNP	DS 2, #1	DS 7
"		DS 11
"		DS 16, Grp a, #2
NODE	DS 14, Group c, #4	
"	DS 15 Group c, #4	
NODEAD	DS 14, Group c, #5	
"	DS 15, Group c, #5	
NODEP(NP)		DS 5

NOH	DS 10	DS 11
"		DS 13
"		DS 14
"		DS 15
"		DS 24
"		DS 25
NOHA	DS 10, Line 1, #1	
NOHS	DS 10, Line 1, #2	
NOMP	DS 17, #6	DS 27
NOMX	DS 17, #3	DS 25
NOMXC	DS 17, #7	
NOMY	DS 17, #4	DS 26
NOMZ	DS 17, #5	DS 21
NONA	DS 17, #1	
NONS	DS 17, #2	DS 20
NPCYL	DS 22, #4	
NPITER	DS 2, #15	
NPMZI(I)	DS 21, Record 2..NSITE+1, #1	
NPROB	DS 1, Line 1, #1	
NPW(N)	DS 13, Group 2a, #N	
NSDP	DS 12, #3	DS 13, Grp 1b
NSEL	DS 12, #1	DS 13, Grps 1a, 1b &1c
NSEQ	DS 7, #2	
"	DS 9, #2	
"	DS 11, #2	
"	DS 13, Groups 1c & 2c, #2	
"	DS 14, Groups b, c & d, #2	
"	DS 15, Groups b & c, #2	
"	DS 16, Groups a & b, #2	
NSITE	DS 21, Record 1, #1	
NSORB	DS 20, Line 1, #1	
NSPR	DS 12, #2	DS 13, Grp 1b
NSTR	DS 2, #18	DS 11
NTI	DS 2, #5	DS 4
"		DS 11
NTYPAD	DS 15, Group b, #5	
NVDP	DS 12, #13	DS 14, Grp a
NVES	DS 12, #11	DS 14
NVNP	DS 12, #10	DS 14, Grp c
NVPR	DS 12, #12	DS 14, Grp a
NWDP	DS 12, #6	DS 13, Grp 2b
NWNP	DS 12, #4	DS 13, Grps 2a, 2b & 2c

NWPR	DS 12, #5	DS 13, Grp 2b
OME	DS 3, #7	
OMEGAC	DS 22, #1	
OMI	DS 3, #8	
PEMN	DS 19, Line 2, #1	
PEMX	DS 19, Line 2, #2	
PHMN	DS 19, Line 2, #3	
PHMX	DS 19, Line 2, #4	
PKIPD	DS 24, Line 5, #2	
"	DS 25, Lines 2 & 5, #2	
"	DS 26, Line 2, #2	
"	DS 27, Line 2, #2	
PRESU	DS 19, Line 1, #2	
PROP(N,I)	DS 6, Lines 1..I, #N	
RAD	DS 11, #5	
RNI	DS 11, #4	
RRD	DS 11, #6	
RTIME		DS 2, #5
SICOR	DS 18, Line 1, #1	
SOSF(J,I,K)	DS 13, Group 1b	
SPECN(I)	DS 24, Line 1, #1	
"	DS 25, Line 1, #1	
"	DS 26, Line 1, #1	
"	DS 27, Line 1, #1	
SPECN(II)	DS 24, Line 4, #1	
"	DS 25, Line 4, #1	
SREAM(J,I)	DS 20, Record NSORB+2, #3J	
TCDBF(J,I,K)	DS 15, Group a	
TCVBF(J,I,K)	DS 14, Group a	
TDTCH(N)	DS 4, #N	
TEMP	DS 19, Line 1, #1	
THNI	DS 16, Group b, #4	
THNIAD	DS 16, Group b, #5	
TITLE	DS 1, Line 1, #2	
TMAX	DS 3, #4	
TOLA	DS 3, #9	

TSOSF(J,I,K)	DS 13, Group 1b
TWSSF(J,I,K)	DS 13, Group 2b
VJ(I)	DS 24, Line 2, #2
VXAD	DS 16, Group a, #6
VXNI	DS 16, Group a, #4
VZAD	DS 16, Group a, #7
VZNI	DS 16, Group a, #5
W	DS 3, #5
WSSF(J,I,K)	DS 13, Group 2b
WV	DS 3, #6
XAD	DS 7, #5
XNI	DS 7, #4
XRD	DS 7, #6

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1 D. A. Dreyfus (RW-1)
Director
OCRWM
US Department of Energy
1000 Independence Avenue SW
Washington, DC 20585

1 L. H. Barrett (RW-2)
Acting Deputy Director
OCRWM
US Department of Energy
1000 Independence Avenue SW
Washington, DC 20585

1 S. Rousso (RW-40)
Office of Storage and Transportation
OCRWM
US Department of Energy
1000 Independence Avenue SW
Washington, DC 20585

1 R. A. Milner (RW-30)
Office of Program Management
and Integration
OCRWM
US Department of Energy
1000 Independence Avenue SW
Washington, DC 20585

1 D. R. Elle, Director
Environmental Protection Division
DOE Nevada Field Office
US Department of Energy
P.O. Box 98518
Las Vegas, NV 89193-8518

1 T. Wood (RW-14)
Contract Management Division
OCRWM
US Department of Energy
1000 Independence Avenue SW
Washington, DC 20585

4 Victoria F. Reich, Librarian
Nuclear Waste Technical Review Board
1100 Wilson Blvd., Suite 910
Arlington, VA 22209

5 Wesley Barnes, Project Manager
Yucca Mountain Site Characterization
Office
US Department of Energy
P.O. Box 98608--MS 523
Las Vegas, NV 89193-8608

1 Director
Office of Public Affairs
DOE Nevada Operations Office
US Department of Energy
P.O. Box 98518
Las Vegas, NV 89193-8518

8 Technical Information Officer
DOE Nevada Operations Office
US Department of Energy
P.O. Box 98518
Las Vegas, NV 89193-8518

1 P. K. Fitzsimmons, Technical Advisor
Office of Assistant Manager for
Environmental Safety and Health
DOE Nevada Operations Office
US Department of Energy
P.O. Box 98518
Las Vegas, NV 89193-8518

1 J. A. Blink
Deputy Project Leader
Lawrence Livermore National Laboratory
101 Convention Center Drive
Suite 820, MS 527
Las Vegas, NV 89109

2 J. A. Canepa
Technical Project Officer - YMP
N-5, Mail Stop J521
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

1 Repository Licensing & Quality
Assurance
Project Directorate
Division of Waste Management
US NRC
Washington, DC 20555

1 Senior Project Manager for Yucca
Mountain
Repository Project Branch
Division of Waste Management
US NRC
Washington, DC 20555

1 NRC Document Control Desk
Division of Waste Management
US NRC
Washington, DC 20555

1 Chad Glenn
NRC Site Representative
301 E Stewart Avenue, Room 203
Las Vegas, NV 89101

1 E. P. Binnall
Field Systems Group Leader
Building 50B/4235
Lawrence Berkeley Laboratory
Berkeley, CA 94720

1 Center for Nuclear Waste
Regulatory Analyses
6220 Culebra Road
Drawer 28510
San Antonio, TX 78284

2 W. L. Clarke
Technical Project Officer - YMP
Attn: YMP/LRC
Lawrence Livermore National Laboratory
P.O. Box 5514
Livermore, CA 94551

1 V. R. Schneider
Asst. Chief Hydrologist -- MS 414
Office of Program Coordination
and Technical Support
US Geological Survey
12201 Sunrise Valley Drive
Reston, VA 22092

1 J. S. Stuckless, Chief
Geologic Studies Program
MS 425
Yucca Mountain Project Branch
US Geological Survey
P.O. Box 25046
Denver, CO 80225

1 N. Z. Elkins
Deputy Technical Project Officer
Los Alamos National Laboratory
Mail Stop 527
101 Convention Center Drive, #820
Las Vegas, NV 89109

2 Michaele C. Brady
Technical Project Officer - YMP
Sandia National Laboratories
Organization 6302, MS 1399
101 Convention Center Drive, Suite 880
Las Vegas, NV 89109

1 Ray Wallace
US Geological Survey
106 National Center
12201 Sunrise Valley Drive

1 L. R. Hayes
Technical Project Officer
Yucca Mountain Project Branch
MS 425
US Geological Survey
P.O. Box 25046
Denver, CO 80225

1 A. L. Flint
US Geological Survey
MS 721
P.O. Box 327
Mercury, NV 89023

1 R. E. Lewis
Yucca Mountain Project Branch
MS 425
US Geological Survey
P.O. Box 25046
Denver, CO 80225

1 D. Zesiger
US Geological Survey
101 Convention Center Drive
Suite 860, MS 509
Las Vegas, NV 89109

2 L. D. Foust
Nevada Site Manager
TRW Environmental Safety Systems
101 Convention Center Drive
Suite P-110, MS 423
Las Vegas, NV 89109

1 C. E. Ezra
YMP Support Office Manager
EG&G Energy Measurements Inc.
MS V-02
P.O. Box 1912
Las Vegas, NV 89125

1 E. L. Snow, Program Manager
Roy F. Weston, Inc.
955 L'Enfant Plaza SW
Washington, DC 20024

1 Technical Information Center
Roy F. Weston, Inc.
955 L'Enfant Plaza SW
Washington, DC 20024

1 Technical Project Officer - YMP
US Bureau of Reclamation
Code D-3790
P.O. Box 25007
Denver, CO 80225

1 B. T. Brady
Records Specialist
US Geological Survey
MS 421
P.O. Box 25046
Denver, CO 80225

1 M. D. Voegele
Technical Project Officer - YMP
M&O/SAIC
101 Convention Center Drive
Suite 407
Las Vegas, NV 89109

1 Paul Eslinger, Manager
PASS Program
Pacific Northwest Laboratories
P.O. Box 999
Richland, WA 99352

1 A. T. Tamura
Science and Technology Division
OSTI
US Department of Energy
P.O. Box 62
Oak Ridge, TN 37831

1 P. J. Weeden, Acting Director
Nuclear Radiation Assessment Div.
US EPA
Environmental Monitoring Sys. Lab
P.O. Box 93478
Las Vegas, NV 89193-3478

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Columbus, OH 43201

1 C. H. Johnson
Technical Program Manager
Agency for Nuclear Projects
State of Nevada
Evergreen Center, Suite 252
1802 N. Carson Street
Carson City, NV 89710

1 John Fordham, Deputy Director
Water Resources Center
Desert Research Institute
P.O. Box 60220
Reno, NV 89506

1 The Honorable Cyril Schank
Chairman
Churchill County Board of
Commissioners
190 W. First Street
Fallon, NV 89406

1 T. Hay, Executive Assistant
Office of the Governor
State of Nevada
Capitol Complex
Carson City, NV 89710

3 R. R. Loux
Executive Director
Agency for Nuclear Projects
State of Nevada
Evergreen Center, Suite 252
1802 N. Carson Street
Carson City, NV 89710

1 Brad R. Mettam
Inyo County Yucca Mountain
Repository Assessment Office
P. O. Drawer L
Independence, CA 93526

1 Lander County Board of Commissioners
315 South Humbolt Street
Battle Mountain, NV 89820

1 Vernon E. Poe
Office of Nuclear Projects
Mineral County
P.O. Box 1600
Hawthorne, NV 89415

1 Les W. Bradshaw
Program Manager
Nye County Nuclear Waste Repository
Project Office
P.O. Box 1767
Tonopah, NV 89049

1 Florindo Mariani
White Pine County Coordinator
P. O. Box 135
Ely, NV 89301

1 Judy Foremaster
City of Caliente Nuclear Waste
Project Office
P.O. Box 158
Caliente, NV 89008

1 Philip A. Niedzielski-Eichner
Nye County Nuclear Waste
Repository Project Office
P.O. Box 221274
Chantilly, VA 22022-1274

1 Dennis Bechtel, Coordinator
Nuclear Waste Division
Clark County Department of
Comprehensive Planning
301 E. Clark Avenue, Suite 570
Las Vegas, NV 89101

1 Juanita D. Hoffman
Nuclear Waste Repository
Oversight Program
Esmeralda County
P.O. Box 490
Goldfield, NV 89013

1 Eureka County Board of Commissioners
Yucca Mountain Information Office
P.O. Box 714
Eureka, NV 89316

1 Economic Development Dept.
City of Las Vegas
400 E. Stewart Avenue
Las Vegas, NV 89101

1 Community Planning & Development
City of North Las Vegas
P.O. Box 4086
North Las Vegas, NV 89030

1 Community Development & Planning
City of Boulder City
P.O. Box 61350
Boulder City, NV 89006

1 Commission of European Communities
200 Rue de la Loi
B-1049 Brussels
BELGIUM

2 Librarian
YMP Research & Study Center
MS 407
P.O. Box 98521
Las Vegas, NV 89193-8521

1 Amy Anderson
Argonne National Laboratory
Building 362
9700 S. Cass Avenue
Argonne, IL 60439

1 Glenn Van Roekel
Director of Community Development
City of Caliente
P.O. Box 158
Caliente, NV 89008

1 G. S. Bodvarsson
Head, Nuclear Waste Department
Lawrence Berkeley Laboratory
1 Cyclotron Road, MS 50E
Berkeley, CA 94720

1 Michael L. Baughman
Intertech Services Corp.
P.O. Box 93537
Las Vegas, NV 89193

1 W. Murphy
Center for Nuclear Waste
Regulatory Analyses
6220 Culebra Road
Drawer 28510
San Antonio, TX 78284

1 R. Pabalon
Center for Nuclear Waste
Regulatory Analyses
6220 Culebra Road
Drawer 28510
San Antonio, TX 78284

1 Dr. James O. Leckie
Environmental Engineering
and Science
Department of Civil Engineering
Stanford University
Stanford, CA 94305

1 Vijay Tripathi
6518 Elnido Drive
McLean, VA 22101

20 Gour-Tsyh Yeh
Professor of Civil Engineering
212 Sacket Bldg.
Penn State University
University Park, PA 16802

1 G. F. Birchard
Office of Nuclear Regulatory Research
MS NL-005
Washington, DC 20555

1 L. A. Kovach
Office of Nuclear Regulatory Research
MS NL-005
Washington, DC 20555

1 G. Jacobs
Oak Ridge National Laboratory
Box 2009
Oak Ridge, TN 37831

2 Dr. Ardyth Simmons
US Department of Energy
YMPO
101 Convention Center Drive
Las Vegas, NV 89109

3 E. Smistad
US Department of Energy
YMPO
101 Convention Center Drive
Las Vegas, NV 89109

1 Dr. Ines Triay
Los Alamos National Lab
INC 9 Mail Stop J514
Los Alamos, NM 87545

1 Dr. Everett Springer
Los Alamos National Lab
ESS 15 Mail Stop J495
Los Alamos, NM 87545

1 Dr. Paul Cloke
SAIC
101 Convention Center Drive
Las Vegas, NV 89109

1 Dr. Stephen Nelson
Woodward Clyde Federal Systems
Yucca Mountain Site
Characterization Project
101 Convention Center Drive
Las Vegas, NV 89109

1 Dr. Abraham Van Luik
INTERA
Yucca Mountain Site
Characterization Project
101 Convention Center Drive
Las Vegas, NV 89109

1 Dr. David Read
RM Consultants Ltd.
Suite 7 Hitching Court
Abingdon Business Park
Abingdon, Oxfordshire, OX14, 1RA
UNITED KINGDOM

1 Joel Chupeau
National Radioactive Waste
Management Agency
Route de Panorama Robert Schuman
B. P. 38
92286 Fontenay-aux-Roses
Cedex
FRANCE

1 Philippe Jamet
ISIGE Institute
Ecole Des Mines De Paris
35 Rue Saint Honore
77305 Fontainbleau Cedex
Paris, FRANCE

1 Benoit Made
Centre d'Informatique Geologique
Ecole Des Mines De Paris
35 Rue Saint Honore
77305 Fontainbleau Cedex
Paris, FRANCE

1 Dr. Henning von Maravic
Programme Radioactive Waste Mgmt.
Rue de la Loi
Wetstraal 200
8-104 Brussels
BELGIUM

1 Robert Fabriol
SGN/UPE/HYDR Department
BRGM
Avenue de Concyr
B. P. 6009-45060
Orleans Cedex 2
FRANCE

1 Dr. David Sevougian
INTERA
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