KEMOD: A MIXED CHEMICAL KINETIC AND
EQUILIBRIUM MODEL OF AQUEOUS AND SOLID
PHASE GEOCHEMICAL REACTIONS

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January 1995

Prepared by Pennsylvania State University
for Pacific Northwest Laboratory
under Contract DE-AC06-76RLO 1830
with the U.S. Department of Energy
under Agreement 263646

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SUMMARY

This report presents the development of a mixed chemical Kinetic and Equilibrium MODEl (KEMOD), in which every chemical species can be treated either as a equilibrium-controlled or as a kinetically controlled reaction. The reaction processes include aqueous complexation, adsorption/desorption, ion exchange, precipitation/dissolution, oxidation/reduction, and acid/base reactions. Further development and modification of KEMOD can be made in: (1) inclusion of species switching solution algorithms, (2) incorporation of the effect of temperature and pressure on equilibrium and rate constants, and (3) extension to high ionic strength.

ACKNOWLEDGEMENT

The initial development of KEMOD was supported by Sandia National Laboratory.

Dr. Malcolm D. Siegel of Sandia initiated and encouraged this research effort. The final phase of the development, verification, and preliminary validation of KEMOD is supported by the Subsurface Science Program, Office of Health and Environmental Research, U.S. Department of Energy under Grant No. DE-FG02-91ER61197 with the Pennsylvania State University.

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1. INTRODUCTION

The attenuation of chemicals by soil matrix through sorption and precipitation has mostly been modelled with the assumption of geochemical equilibrium. While the assumption of equilibrium may be a valid one for aqueous complexation, it has been known the assumption is a poor one for chemical processes such as sorption, precipitation-dissolution, and reduction-oxidation. Thus, to adequately assess the impact of chemical transport through subsurface media, chemical kinetic study is essential. Yet, general chemical kinetic models are not available.

The earliest study of chemical transport through subsurface media was to assume chemicals as a conservative material. This, of course, oversimplified the physical and chemical systems. Later, the concept of instantaneous equilibrium was introduced to account for the attenuation of chemicals via sorption and precipitation-dissolution. However, experimental evidence has shown that many chemical processes, in particular, the sorption, precipitation-dissolution, and reduction-oxidation are, in general, very slow in comparison with physical and hydrological transport of chemicals. Thus, the assumption of instantaneous equilibrium will overestimate the attenuation of chemicals in soil solutions. Recently, there has been attempt to treat the sorption, precipitation-dissolution, and reduction-oxidation as kinetically controlled processes. These treatments are often problem-specific and are limited to a small number of chemical species. A general package that may consider any species as either kinetic or equilibrium is not available.

The objective of this report is to develop a general chemical kinetic model in which any of the chemical species can be considered in equilibrium or kinetic as desired. This chemical kinetic package

will be developed such that it can be used as a stand alone application or to couple with hydrological transport. The chemical kinetic model is formulated based on: (1) mass balance equations, one for every chemical component, (2) mass action equations, one for every equilibrium species and (3) the reaction rate equations, one for every kinetic species. Appropriate numerical schemes are used to solve the chemical kinetic model.

2. HEURISTIC DERIVATION OF GOVERNING EQUATIONS

Two of the most frequently mentioned nomenclatures in chemical equilibrium 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 such that every species can be uniquely represented as a combination of those components; and no component can be represented by other components than itself. 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).

Let us consider a system of N chemical components. The N chemical components consist of N_a aqueous components (mobile components) and N_s adsorbent components (immobile adsorbing sites) and N_{SITE} immobile ion exchange sites. The N_a aqueous components will react with each other to form M_x complexed species and M_p precipitated species. In addition, any aqueous component has a species free from chemical reactions. This species is termed the aqueous component species. Thus, the total number of aqueous species, M_a , is the sum of N_a aqueous component species and M_x complexed species. The N_a aqueous components and N_s adsorbent components will react to form M_y adsorbed species for the case of sorption via surface complexation (adsorption). Any adsorbent component has a species free from adsorption reactions. This species is termed the adsorbent component species. In the meantime, some or all of N_a aqueous component species M_x complexed species may compete with each other for the ion exchange site. Assume M_z species out of N_a aqueous component species and M_x complexed species are involved in ion exchange reactions. The total number of sorbent species, M_s , is the sum N_s adsorbent component species, M_y adsorbed species, and M_z ion-exchanged species. From the above

discussion, it is seen that the total number of chemical species, M , is equal to the sum of M_a , M_s , and M_p .

For clarity, when we speak of aqueous species, we mean aqueous component species and complexed species. Similarly, when we speak of adsorbent species, we mean to include adsorbent component species and adsorbed species whereas when we speak of sorbent species, we mean to include adsorbent component species, adsorbed species, and ion-exchanged species. When we speak of sorbed species, we mean adsorbed species and ion-exchanged species.

2.1 Mole Balance Equations

The governing equations for KEMOD can be derived based on the principle of mole balance and mass action. Detailed derivations can be found elsewhere (Yeh and Tripathi, 1989).

$$\frac{dT_j}{dt} = Q_j, \quad j \in N_a \quad (2.1)$$

$$\frac{dW_j}{dt} = R_j, \quad j \in N_s \quad (2.2)$$

$$\frac{dN_{cq_i}}{dt} = N_{ad_i}, \quad i \in \text{NSITE} \quad (2.3)$$

in which

$$T_j = c_j + \sum_{i=1}^{M_a} a_{ij}^x x_i + \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad (2.4)$$

$$j \in N_a$$

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^y y_i, \quad j \in N_s \quad (2.5)$$

$$N_{eq_i} = \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k, \quad i \in NSITE \quad (2.6)$$

and

$$M_z = \sum_{i=1}^{NSITE} NOMZI(i) \quad (2.7)$$

where

a_{ij}^p = stoichiometric coefficient of the j-th aqueous component in the i-th precipitated species.

a_{ij}^x = stoichiometric coefficient of the j-th aqueous component in the i-th complexed species.

a_{ij}^y = stoichiometric coefficient of the j-th aqueous component in the i-th adsorbed species.

a_{ij}^z = stoichiometric coefficient of the j-th aqueous component in the i-th ion-exchanged species.

b_{ij}^y = stoichiometric coefficient of the j-th adsorbent component in the i-th adsorbed species.

c_j = concentration of the j-th aqueous component species, (M/L³).

M_p = number of precipitated species.

M_x = number of complexed species.

M_y = number of adsorbed species.

M_z = number of ion-exchanged species.

N_a = number of aqueous components.

N_{ad_i} = artificial source of the i-th cation ion exchange site.

N_{eq_i}	=	number of equivalents per unit volume of solution for the i-th ion-exchange site, (M/L ³).
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 1-st through the (i-1)-th ion-exchange site.
N_s	=	number of adsorbent components.
NSITE	=	number of ion-exchanged species.
p_i	=	concentration of the i-th precipitated species, (M/L ³).
Q_j	=	artificial source of the j-th aqueous component.
R_j	=	artificial source of the j-th adsorbed component.
s_j	=	concentration of the j-th adsorbent component species, (M/L ³).
T_j	=	total analytical concentration of the j-th aqueous component, (M/L ³).
t	=	time.
W_j	=	total analytical concentration of the j-th adsorbent component, (M/L ³).
x_i	=	concentration of the i-th complexed species, (M/L ³).
y_i	=	concentration of the i-th adsorbed species, (M/L ³).
z_i	=	concentration of the i-th ion-exchanged species, (M/L ³).
v_i	=	valence of the i-th ion exchanging species.

Equations (2.1) through (2.7) constitute $2 \times (N_a + N_s + \text{NSITE})$ equations which relate chemical species to their corresponding components by laws of conservation of mass. The formulation is not yet complete however since there are $(2 \times N_a + 2 \times N_s + \text{NSITE} + M_x + M_y + M_z + M_p)$ unknowns, (N_a T_j 's, N_s W_j 's, NSITE N_{eq_i} 's, N_a c_j 's, N_s s_j 's, M_x x_i 's, M_y y_i 's, M_z z_i 's, and M_p p_i 's), which have been

created. ($M_x + M_y + M_z + M_p - \text{NSITE}$) equations are still required to close the system. Implicit functional relationships among c_j 's, s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's will be derived based on the law of mass action in the following section. Other secondary mass balance equations defining the total aqueous concentration of each component (C_j), the total sorbed concentration of each component (S_j), and the total precipitated concentration of each component (P_j) are given below

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i, \quad j \in N_a \quad (2.8)$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i, \quad j \in N_a \quad (2.9)$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad j \in N_a \quad (2.10)$$

where

- C_j = total dissolved concentration of the j -th aqueous component (M/L^3),
- S_j = total sorbed (adsorbed plus ion-exchanged) concentration of the j -th aqueous component (M/L^3),
- P_j = total precipitated concentration of the j -th aqueous component (M/L^3).

2.2 Mass Action Equations

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 by the law of mass action.

2.2.1 Complexation Reactions

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

$\hat{c}_j$ = 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 $\hat{c}_j$ means one mole of aqueous component j , whereas c_j means molar concentration of aqueous component j .

The law of mass action for the equilibrium complexation reaction is written as

$$x_i = \alpha_i^x \prod_{k=1}^{N_x} c_k^{a_k^i} \quad (2.12a)$$

in which

$$\alpha_i^x = K_i^x \prod_{k=1}^{N_x} (\gamma_k^a)^{a_k^i} / \gamma_i^x, \quad i \in M_x \quad (2.12b)$$

is the modified stability constant of the i-th complexed species. For the kinetic complexation reaction the rate reaction is given by the law of association

$$\frac{\partial x_i}{\partial t} = r_i^x = -k_i^{bx} x_i + \alpha_i^{fx} \prod_{k=1}^{N_i} c_k^{a_k} \quad (2.13a)$$

in which

$$\alpha_i^{fx} = k_i^{fx} \prod_{k=1}^{N_i} (\gamma_k^a)^{a_k}, \quad i \in M_x \quad (2.13b)$$

is the modified forward constant of the i-th complexed species. In Eqs. (2.12) and (2.13),

K_i^x = equilibrium constant of the i-th complexed species (M/L^3).

γ_k^a = activity coefficient of the k-th aqueous component species, (L^3/M).

γ_i^x = activity coefficient of the i-th complexed species, (L^3/M).

k_i^{bx} = backward rate constant of the i-th complexed species.

k_i^{fx} = forward rate constant of the i-th complexed species.

It is noted that the thermodynamic equilibrium constant K_i^x and the thermodynamic forward rate constant k_i^{fx} depends on the temperature and the pressure of the system, whereas the activity coefficients γ_k^a 's and γ_i^x 's are a function of the 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.

2.2.2 Adsorption Reactions

Each adsorbed species is a result of chemical reactions between aqueous components and adsorbent components. The adsorption reaction is generally modeled with a surface complexation formulation, and an adsorbed species is the product involving both aqueous and adsorbent components as reactants. The adsorption reaction modelled with a surface complexation is written as:

where

$\hat{c}_j$ = chemical formula for the 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.

The law of mass action for the equilibrium adsorption reaction given by Eq.(2.14) is written

as

$$Y_i = \alpha_i^y \left[\prod_{k=1}^{N_a} c_k^{a_k^y} \right] \left[\prod_{k=1}^{N_s} s_k^{b_k^y} \right] \quad (2.15a)$$

in which

$$\alpha_i^y = K_i^y \left[\prod_{k=1}^{N_a} (\gamma_k^a)^{a_k^y} \right] \left[\prod_{k=1}^{N_s} (\gamma_k^s)^{b_k^y} \right] / \gamma_i^y, \quad i \in M_y \quad (2.15b)$$

is the modified stability constant for the i-th adsorbed species. For the kinetic adsorption reaction the reaction rate is given by

$$\frac{\partial y_i}{\partial t} = r_i^y = -k_i^{by} y_i + \alpha_i^{fy} \prod_{k=1}^{N_i} c_k^{a_k^y} \prod_{k=1}^{N_i} s_k^{b_k^y} \quad (2.16a)$$

in which

$$\alpha_i^{fy} = k_i^{fy} \left[\prod_{k=1}^{N_i} (\gamma_k^a)^{a_k^y} \right] \left[\prod_{k=1}^{N_i} (\gamma_k^s)^{b_k^y} \right], \quad i \in M_y \quad (2.16b)$$

is the modified forward rate constant of the i -th adsorbed species. In Eqs. (2.15) and (2.16)

K_i^y = equilibrium constant of the i -th adsorbed species (dimensionless),

γ_k^s = activity coefficient of the k -th adsorbed component species, (L^3/M) ,

γ_i^y = activity coefficient of the i -th adsorbed species, (L^3/M) ,

k_i^{by} = backward rate constant of the i -th adsorbed species,

k_i^{fy} = forward rate constant of the i -th adsorbed species.

2.2.3 Ion Exchange Reactions

Each ion exchanged species is due to the exchange of a corresponding aqueous species with another ion-exchanged species. The ion exchange reactions are written as:

$$\begin{aligned}
 \nu_{\text{LNI}(i)} \hat{a}_k + \nu_k \hat{z}_{\text{LNI}(i)} &\overset{\text{-----}}{<} \nu_{\text{LNI}(i)} \hat{z}_k + \nu_k \hat{a}_{\text{LNI}(i)} , \\
 i &\in M_z \\
 \text{NOMZJ}(i) \leq k \leq \text{NOMZJ}(i) + \text{NOMZI}(i) \\
 k &\neq \text{LNI}(i)
 \end{aligned}
 \tag{2.17}$$

where

- $\hat{a}_i$ = chemical formula for the i-th aqueous (exchanging) species.
 $\hat{z}_i$ = chemical formula for the i-th sorbed (exchanging) species.
 ν_k = charge of the k-th aqueous species
 $\text{LNI}(i)$ = indicator of the reference species for the i-th ion-exchange site. It indicates the number of the ion-exchanged species on the ion-exchanged species list.

The law of mass action for the equilibrium ion exchange reaction is written as follows

$$\begin{aligned}
 K_{k,\text{LNI}(i)} &= \left(\frac{B_k}{A_k} \right)^{\nu_{\text{LNI}(i)}} \left(\frac{A_{\text{LNI}(i)}}{B_{\text{LNI}(i)}} \right)^{\nu_k} \\
 \text{NOMZJ}(i) \leq k \leq \text{NOMZJ}(i) + \text{NOMZI}(i) \\
 k &\neq \text{LNI}(i)
 \end{aligned}
 \tag{2.18}$$

where

- $K_{k,\text{LNI}(i)}$ = selectivity coefficient of the k-th species with respect to the $\text{LNI}(i)$ -th species, or the effective equilibrium constant of k-th ion-exchanged species,
 A_k = activity of the k-th aqueous species denoting either A_i^* or X_j ,
 B_k = activity of the k-th ion-exchanged species denoting either exchanged A_i^* or X_j .

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 proportional to its molar concentrations. Thus,

$$A_k = \gamma_k a_k \quad k \in M_z \quad (2.19)$$

where

a_k = molar concentration of the k-th aqueous species denoting either c_k or x_k
in (M/L³),

γ_k = activity coefficient of the k-th aqueous species denoting either γ_k^a or γ_k^x
in (M/L³).

$$B_k = z_k / s_T(i) \quad \begin{matrix} \text{NOMZJ}(i) \leq k \leq \text{NOMZJ}(i) + \text{NOMZI}(i) \\ k \neq \text{LNI}(i) \end{matrix} \quad (2.20)$$

$$s_T(i) = \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} z_k \quad (2.21)$$

Substituting Eqs. (2.19) and (2.20) into Eq. (2.18) will obtain

$$\kappa_{k, \text{LNI}(i)} = \frac{(z_k / s_T(i))^{v_{\text{LNI}(i)}} a_{\text{LNI}(i)}^{v_k}}{(z_{\text{LNI}(i)} / s_T(i))^{v_k} a_k^{v_{\text{LNI}(i)}}} \quad i \in \text{NSITE} \quad (2.22)$$

$$\begin{matrix} \text{NOMZJ}(i) \leq k \leq \text{NOMZJ}(i) + \text{NOMZI}(i) \\ k \neq \text{LNI}(i) \end{matrix}$$

where $\kappa_{k, \text{LNI}(i)}$ is the modified selectivity coefficient given by

$$\kappa_{k, LNI(i)} = K_{k, LNI(i)} \gamma_k^{v_{LNI(i)}} / \gamma_{LNI(i)}^{v_k} \quad (2.23)$$

For the kinetic ion exchange reaction the reaction rate is given by

$$\frac{\partial z_i}{\partial t} = r_i^z = -k_i^{bz} \left(z_i - \left[\kappa_{i, LNI(i)} z_{LNI(i)} \left(\frac{a_i^{v_{LNI(i)}}}{a_{LNI(i)}^{v_i}} \right) (S_T^{(i)})^{v_{LNI(i)} - v_i} \right]^{\frac{1}{v_{LNI(i)}}} \right) \quad (2.24)$$

In Eqs. (2.20) to (2.24)

k_i^{bz} = backward rate constant of the i-th ion-exchanging species,

$s_T(i)$ = total concentration of all ion-exchanged species in the i-th ion-exchange site, (M/L³).

γ_k = activity coefficient of the k-th aqueous species denoting either γ_i^a or γ_j^x , (L³/M).

2.2.4 Precipitation-dissolution Reactions

Precipitation species result from reactions between aqueous components. These reactions are written as:

$$\sum_{j=1}^{N_i} a_{ij}^p \hat{c}_j <-----> \hat{p}_i, \quad i \in M_p \quad (2.25)$$

The law of mass action for the equilibrium precipitation-dissolution reaction is written as

$$1 = \alpha_i^p \prod_{k=1}^{N_i} c_k^{a_k^p} \quad (2.26a)$$

in which

$$\alpha_i^p = K_i^p \prod_{k=1}^{N_i} (\gamma_k^a)^{a_k^p}, \quad i \in M_p \quad (2.26b)$$

is the modified stability constant of the i -th precipitated species. For the kinetic precipitation-dissolution reaction the reaction rate is given by

$$\frac{\partial p_i}{\partial t} = r_i^p = -A k_i^{bp} + B \alpha_i^{fp} \prod_{k=1}^{N_i} c_k^{a_k^p} \quad (2.27a)$$

in which

$$\alpha_i^{fp} = k_i^{fp} \prod_{k=1}^{N_i} (\gamma_k^a)^{a_k^p}, \quad i \in M_p \quad (2.27b)$$

is the modified forward rate constant of the i -th precipitated species. The coefficients A and B are used for the precipitation-dissolution reactions to indicate whether there is full precipitation or none at all since this reaction cannot be only partial. They are defined below.

$$A = 1 \quad \text{if } p_i > 0, \quad A = 0 \quad \text{if } p_i \leq 0 \quad (2.27c)$$

$$B = 1 \quad \text{if } \alpha_i^p \prod_{k=1}^{N_i} c_k^{a_k^p} \geq 1, \quad B = 0 \quad \text{if } \alpha_i^p \prod_{k=1}^{N_i} c_k^{a_k^p} < 1 \quad (2.27d)$$

In Eqs. (2.26) and (2.27)

K_i^p = equilibrium constant of the i-th precipitated species.

k_i^{bp} = backward rate constant of the i-th precipitated species.

k_i^{fp} = forward rate constant of the i-th precipitated species.

Equation (26a) represents the solubility product. According to convention (Sposito, 1981), it does not contain the precipitated molar concentration p_i because it assumes that the activity of the solids is constant. 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 homogeneous reactions of soluble complexation. This implies that models developed specifically for dealing with complexation and sorption are not necessarily capable of handling precipitation-dissolution.

2.2.5 Redox Reactions and Electron Activity

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 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 in this report, is used as the redox parameter. Hence in redox systems, both the total analytical concentrations of all components and 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). Because the free electron is not present in appreciable amount in solution, the mole balance equation for the "operational" electron is written as

$$\frac{dT_e}{dt} = 0 \quad (2.28)$$

in which

$$T_e = \sum_{j=1}^{N_a} a_{je}^a c_j + \sum_{i=1}^{M_c} a_{ie}^x x_i + \sum_{i=1}^{M_z} a_{ie}^z z_i + \sum_{j=1}^{N_s} a_{je}^s s_j + \sum_{i=1}^{M_y} a_{ie}^y y_i + \sum_{i=1}^{M_p} a_{ie}^p p_i \quad (2.29)$$

where

T_e = Total concentration of operational electrons,

a_{je}^a = stoichiometric coefficient of the electron in the j-th aqueous component species,

a_{ie}^x = stoichiometric coefficient of the electron in the i-th complexed species,

a_{je}^s = stoichiometric coefficient of the electron in the j-th adsorbent component species,

a_{ie}^y = stoichiometric coefficient of the electron in the i-th adsorbed species,

a_{ie}^z = stoichiometric coefficient of the electron in the i-th ion-exchanged species,

a_{ie}^p = stoichiometric coefficient of the electron in the i-th precipitated species.

The above stoichiometric coefficients are given (Walsh et al., 1984) by

$$a_{jc}^a = \sum_{k=1}^{N_e} h_{jk}^a (v_{mk} - v_{jk}^a) , \quad j \in N_a \quad (2.30a)$$

$$a_{ic}^x = \sum_{k=1}^{N_e} h_{ik}^x (v_{mk} - v_{ik}^x) , \quad i \in M_x \quad (2.30b)$$

$$a_{jc}^s = \sum_{k=1}^{N_e} h_{jk}^s (v_{mk} - v_{jk}^s) , \quad j \in N_s \quad (2.30c)$$

$$a_{ic}^y = \sum_{k=1}^{N_e} h_{ik}^y (v_{mk} - v_{ik}^y) , \quad i \in M_y \quad (2.30d)$$

$$a_{ic}^z = \sum_{k=1}^{N_e} h_{ik}^z (v_{mk} - v_{ik}^z) , \quad i \in M_z \quad (2.30e)$$

$$a_{ic}^p = \sum_{k=1}^{N_e} h_{ik}^p (v_{mk} - v_{ik}^p) , \quad i \in M_p \quad (2.30f)$$

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 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.

If component species are chosen such that they contain only chemical elements in their maximum oxidation state, then the a_{je}^a 's and a_{je}^s 's are equal to zero and Eqs. (2.29) is identical formally to Eq. (2.4). Choosing such components is very useful for describing the computation of electron activity involving redox reactions, because the operational electron can be considered computationally an aqueous component. Nevertheless, even without such a choice, operational electron can still be considered an aqueous component, but with a possibility of having a negative total concentration of operational electrons.

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, Eqs. (2.12a) and (2.13a) for complexation reactions are modified by multiplying its right-hand side by X_e raised to the a_{je}^x power and the activity coefficient for the electron component in Eqs. (2.12b) and (2.13b) is set to 1. In the meantime, chemical components are chosen such that their chemical formulae contain only elements in maximum oxidation states. Under such circumstances, the electron is considered an aqueous component, and computationally no special treatment is needed for redox reactions (Reed, 1982). Finally, the secondary mole balance equations for the electron component can be written as

$$C_e = \sum_{j=1}^{N_1} a_{je}^a c_j + \sum_{i=1}^{M_1} a_{ie}^x x_i \quad (2.31)$$

$$S_e = \sum_{j=1}^{N_1} a_{je}^s s_j + \sum_{i=1}^{M_1} a_{ie}^y y_i + \sum_{i=1}^{M_2} a_{ie}^z \bar{z}_i \quad (2.32)$$

$$P_e = \sum_{i=1}^{M_p} a_{ic}^p p_i \quad (2.33)$$

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.

2.2.6 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). In a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the activity of proton (or the pH value). The pH value may be simulated by using either the electroneutrality or proton condition. These two approaches can be shown mathematically equivalent but not computationally. In this report, it is preferable to use the proton-condition approach. In the proton-condition approach, the total concentration of the excess proton ($H^+ - OH^-$) must be known before the computation of the activity of proton can be done. A mole balance equation for excess proton is, therefore, needed to determine the total concentration of excess proton. This mole balance equation can be obtained from Eq. (2.1) by replacing with T_j with T_H and Q_j with Q_H . The secondary mole balance equations for C_H , S_H , and P_H can be obtained from Eqs. (2.8) through (2.10) by replacing j with H . However, if hydroxides appear in a species, the stoichiometric coefficient of proton in that species is negative. On the other hand, if hydrogens appear in a species, the stoichiometric coefficient of proton in that species is positive. After this slight difference is considered and the mass action equation for any species involving hydrogen and/or hydroxide is

modified to include the activity of proton, the proton can be considered an aqueous component. Thus, the computation of pH requires no special treatment; it can be simulated just as the activity of any other aqueous components. The only difference between 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_i s are always positive).

Since the simulation of pH and/or pe uses mole balance equations that are formulaically identical to Eq. (2.1), we can treat the proton and/or electron as aqueous components from here on and no special consideration to distinguish proton and/or electron from other regular aqueous components is needed anymore. The only things we must keep in mind are that (1) stoichiometric coefficient of proton in a species may be negative resulting in a possibility of negative total analytical concentration of proton and (2) 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. 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 . Of course, if we have not chosen the stoichiometric coefficient of electron with respect to maximum oxidation state, a negative total analytical concentration of operational electron may result.

Although the full complement of geochemical reactions considered here include complexation, sorption, precipitation-dissolution, redox, and acid-base reactions, the term "full complement" is meant to include only the first three types of reactions because the latter two reactions require no special treatment as discussed above. For a redox reaction, if only aqueous components are involved, it can be treated as a complexation reaction when the resulting species is in aqueous phase or as a precipitation

reaction when the resulting species is in 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.

2.2.7 Electrostatic Adsorption

In Section 2.2.2, we model the adsorption with a simple surface complexation approximation, i.e., the effect of electrostatic forces are not included. A simple surface complexation model can numerically be treated in the same manner as the aqueous complexation model. No special consideration in the numerical approach is needed. However, when the effect of electrostatic forces is to be included in modeling adsorption, we can use either the constant capacitance model or the triple layer mode (Davis, et al., 1978; Stumm and Morgan, 1981). If a constant capacitance model is used, one additional unknown (c_o) is needed for each adsorbent component. If a triple layer model is employed, two additional unknowns (c_o and c_b) are introduced for each adsorption component. These two additional unknowns are defined as

$$c_o = \exp\left[-\frac{e\psi_o}{kT}\right] \quad (2.34)$$

and

$$c_b = \exp\left[-\frac{e\psi_b}{kT}\right] \quad (2.35)$$

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

In the case of constant capacitance model, the additional unknown c_o defined by Eq. (2.34) can be obtained by setting up one additional equation. This additional equation is obtained by assuming that

the total charge calculated by summing over the charges on the 'o' plane is equal to the total charge calculated by electro-static theory as

$$BC\psi_o = \sum_{i=1}^{M_y} a_{io}^y Y_i \quad (2.36)$$

where C is the capacitance of the region, B is a conversion factor from charge per unit area to moles per unit volume. For the evaluation of Jacobian, one needs to compute $\frac{\partial \psi_o}{\partial c_o}$, which can be easily

computed from Eq. (2.34) as follows:

$$\frac{\partial \psi_o}{\partial c_o} = -\frac{kT}{e} \left(\frac{1}{c_o} \right) \quad (2.37)$$

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

$$BC_1(\psi_o - \psi_b) - B\sigma_o = 0 \quad (2.38)$$

$$B\sigma_o = \sum_{i=1}^{M_y} a_{io}^y Y_i \quad (2.39)$$

and

$$C_1(\psi_b - \psi_o)B + C_2(\psi_b - \psi_d)B - B\sigma_b = 0 \quad (2.40)$$

$$(2.41) \quad B\sigma_b = \sum_{i=1}^{M_y} a_{ib}^y Y_i \quad (2.41)$$

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

Electroneutrality requires that the following relationship must be satisfied

$$\sigma_o + \sigma_b + \sigma_d = 0 \quad (2.42)$$

and the Gouy-Chapman diffuse layer theory yields

$$\sigma_d = -(8\epsilon\epsilon_o RIT)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (2.43)$$

where σ_d is the charge density in moles per unit volume in the diffusive layer "d", R is the universal gas constant, I is ionic strength, ϵ is the relative dielectric constant, ϵ_o is the permittivity of the free space, and z is valence of the ion. It should be noted that Eq. (2.43) is valid only for the cases of symmetrical monovalent electrolyte. The charge potential relationship gives

$$C_2(\psi_d - \psi_b) = \sigma_d \quad (2.44)$$

Combining Eqs. (2.43) and (2.44), we relate the unknowns ψ_d to ψ_b implicitly as follows

$$C_2(\psi_d - \psi_b) = -(8\epsilon\epsilon_o RIT)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (2.45)$$

To solve Eqs. (2.38) and (2.45) with Newton-Raphson method, we need to evaluate σ_o , σ_b , ψ_o ,

ψ_b , and ψ_d , and their partial derivatives with respect to c_o and c_b - - $\frac{\partial \sigma_o}{\partial c_o}$, $\frac{\partial \sigma_o}{\partial c_b}$, $\frac{\partial \sigma_b}{\partial c_o}$, $\frac{\partial \sigma_b}{\partial c_b}$, $\frac{\partial \psi_o}{\partial c_o}$,

$\frac{\partial \psi_o}{\partial c_o}, \frac{\partial \psi_b}{\partial c_o}, \frac{\partial \psi_b}{\partial c_b}, \frac{\partial \psi_d}{\partial c_o}, \frac{\partial \psi_d}{\partial c_b}$. The evaluation of $B\sigma_o$ and $B\sigma_b$, and $B\frac{\partial \sigma_o}{\partial c_o}, B\frac{\partial \sigma_o}{\partial c_b}, B\frac{\partial \sigma_b}{\partial c_o}$, and $B\frac{\partial \sigma_b}{\partial c_b}$

can be performed similarly to the evaluation for other aqueous components. The evaluation of

ψ_o, ψ_b , and ψ_d , and $\frac{\partial \psi_o}{\partial c_o}, \frac{\partial \psi_o}{\partial c_b}, \frac{\partial \psi_b}{\partial c_o}, \frac{\partial \psi_b}{\partial c_b}, \frac{\partial \psi_d}{\partial c_o}$, and $\frac{\partial \psi_d}{\partial c_b}$ requires a little further

elaboration. Knowing c_o and c_b from previous iteration, we compute ψ_o and ψ_b from inverting Eqs. (2.34)

and (2.35) as

$$\psi_o = -\frac{kT}{e} \ln(c_o) \quad (2.46)$$

and

$$\psi_b = -\frac{kT}{e} \ln(c_b) \quad (2.47)$$

respectively. Having computed σ_o and σ_b from Eqs. (2.39) and (2.41), respectively, we compute σ_d from

Eq. (2.42) and then invert Eq. (2.43) to obtain ψ_d as

$$\psi_d = \frac{2kT}{ze} \sinh^{-1} \left[\frac{\sigma_d}{(\beta \epsilon \epsilon_o RIT)^{\frac{1}{2}}} \right] \quad (2.48)$$

Taking the derivative of Eq. (2.34) with respect to c_o and c_b , respectively, we obtain

$$\frac{\partial \psi_o}{\partial c_o} = \left[-\frac{kT}{e} \frac{1}{c_o} \right] \quad (2.49)$$

and

$$\frac{\partial \psi_o}{\partial c_b} = 0 \quad (2.50)$$

Similarly, taking the derivative of Eq. (2.35) with respect to c_o and c_b , respectively, we obtain

$$\frac{\partial \psi_b}{\partial c_o} = 0 \quad (2.51)$$

and

$$\frac{\partial \psi_b}{\partial c_b} = \left[-\frac{kT}{e} \frac{1}{c_b} \right] \quad (2.52)$$

Finally, taking the derivative of Eq. (2.45) with respect to c_o and c_b , respectively, and substituting Eqs. (2.51) and (2.52) into the resulting equation, we obtain

$$\frac{\partial \psi_d}{\partial c_o} = 0 \quad (2.53)$$

and

$$\frac{\partial \psi_d}{\partial c_b} = \left[-\frac{kT}{e} \frac{1}{c_b} \right] \frac{1}{1 + \frac{ze}{2kT} (8\epsilon\epsilon_o R I T)^{\frac{1}{2}} \cosh \left[\frac{ze\psi_d}{2kT} \right] \frac{1}{c_2}} \quad (2.54)$$

Equations (2.1) through (2.6) along with (2.12a), (2.13a), (2.15a), (2.16a), (2.21), (2.24), (2.26a), and (2.27a) form $(2 \times N_a + 2 \times N_s + \text{NSITE} + M_x + M_y + M_z + M_p)$ equations and contain $(2 \times N_a + 2 \times N_s + \text{NSITE} + M_x + M_y + M_z + M_p)$ unknowns (N_a T_j 's, N_s W_j 's, NSITE N_{eq_i} 's, N_a c_i 's, N_s s_i 's, M_x x_i 's, M_y y_i 's, M_z z_i 's, and M_p p_i 's); the system is closed. These equations form the bases for mixed chemical kinetic and equilibrium computations.

3. NUMERICAL APPROXIMATION

Given the total concentration of the aqueous components (T_j 's), the total concentration of the adsorbent components (W_j 's), and the total number of adsorbing sites (N_{eq_1} 's) from the mole balance equations, the remaining governing equations involve 6 sets of unknowns in 6 sets of algebraic equations after the kinetic rate equations are discretized by implicit time difference: $N_a c_k$'s, $N_s s_k$'s, $M_z z_i$'s, $M_p p_i$'s, $M_x x_i$'s, and $M_y y_i$'s. These sets of equations were solved by the Newton-Raphson iterative technique as has been described in detail elsewhere (Westall et. al., 1976). In summary considering a system of algebraic equations given by

$$y(x) = 0 \quad (3.1)$$

The Taylor expansion of Eq. (3.1) about the previous iterates yields

$$y^n + \frac{dy}{dx} (x^{n+1} - x^n) = 0 \quad (3.2)$$

where y^n is the value of $y(x)$ evaluated at x^n , x^n is the value of x from previous iteration, and x^{n+1} is the value of x at new iteration. Written in matrix notation, Eq.(3.2) becomes

$$Z^n (X^n - X^{n+1}) = Y^n \quad (3.3)$$

where Y is the residues, Z is the Jacobian of Y with respect to X , the superscript n denotes the value to be evaluated at previous iteration, and the superscript $n+1$ denotes the value to be evaluated at the new iteration. Thus, the solution of Eq. (3.1) involves the following steps. First, knowing X^n , one computes the residue Y^n via the function $y(x)$. Second, one computes the Jacobian Z^n . Third, one solves equation (3.3) to obtain the values ΔX (where ΔX denotes $X^n - X^{n+1}$). Finally, one obtains the new iterate

$$\mathbf{x}^{n+1} = \mathbf{x}^n - \Delta \mathbf{x} \quad (3.4)$$

The above four steps are repeated until a convergent solution is obtained. The application of the Newton-Raphson method to chemical equilibrium models is relatively straightforward where the residues are computed from the governing equations. The Jacobian is computed by taking the partial differential of the governing equations with respect to the species concentration. The formulation of the residuals and the Jacobians from the governing equations will be illustrated in the following sections.

For computational efficiency in the Newton-Raphson method, the number of simultaneous equations are kept to a minimum. When dealing with equilibrium reactions for both complexed and adsorbed species it is seen in equations (2.12a) and (2.15a) that the complexed species (x_i 's) and the adsorbed species (y_i 's) concentration values are functions of the aqueous and adsorbed component species. Thus the complexed species (x_i) and the adsorbed species (y_i) can be eliminated from the solution matrix by substituting for each by using these functional relations to the aqueous and adsorbed component species. This allows the program to solve the equilibrium equations for the complexed and adsorbed species outside of the matrix solver after the other species concentrations have been obtained, thereby reducing the number of simultaneous equations for the equilibrium case. The kinetic cases of the complexed and adsorbed species, however, must be solved for at the same time as the other components and species.

3.1 Evaluation of Residuals

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

$$GR_i = R_m = T_m - c_m - \sum_{k=1}^{M_x} a_{km}^x x_k - \sum_{k=1}^{M_y} a_{km}^y y_k - \sum_{k=1}^{M_z} a_{km}^z z_k - \sum_{k=1}^{M_p} a_{km}^p p_k \quad (3.5)$$

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

$$GR_i = R_m = W_m - s_m - \sum_{k=1}^{M_y} b_{km}^y y_k, \quad m \in N_s, \quad i = m + N_a \quad (3.6)$$

where GR_i is the residual of the i -th equation for the species under consideration and the concentration of all species appearing in the residual equations denote the values for the previous iteration.

The residuals for all other species are based on either the equilibrium equations or the kinetic equations for each species. Since the complexed and adsorbed equilibrium species are not computed in the matrix solver, their residuals do not need to be calculated. The remaining species residuals are shown in the forms below (in which $N = N_a + N_s$). The residual forms for the equilibrium ion-exchange and precipitated species are,

$$GR_i = R_m = N_{eq_i} - \sum_{k=NOMZJ(i)+1}^{NOMZJ(i)+NOMZI(i)} \nu_k z_k, \quad (3.7)$$

$$m \in NSITE, \quad i = m + N = NP1$$

for $i = LNI$,

$$GR_i = R_m = z_k - \left[\kappa_{k,LNI(i)} z_{LNI(i)} \left(\frac{a_k^{\nu_{LNI(i)}}}{a_{LNI(i)}^{\nu_k}} \right) (S_T)^{\nu_{LNI(i)} - \nu_k} \right]^{\frac{1}{\nu_{LNI(i)}}} \quad (3.8)$$

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

for $i \neq LNI$;

$$GR_i = R_m = 1 - \alpha_m^p \prod_{k=1}^{N_i} (c_k)^{a_{mk}^p}, \quad m \in M_p, \quad i = m + N + M_z \quad (3.9)$$

The residual forms for the kinetic species are as follows

$$GR_i = R_m = \frac{\partial x_m}{\partial t} + k_m^{bx} x_m - \alpha_m^{fx} \prod_{k=1}^{N_i} c_k^{a_{mk}^x} \quad (3.10)$$

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

$$GR_i = R_m = \frac{\partial y_m}{\partial t} + k_m^{by} y_m - \alpha_m^{fy} \left[\prod_{k=1}^{N_i} c_k^{a_{mk}^y} \right] \left[\prod_{k=1}^{N_i} s_k^{b_{mk}^y} \right] \quad (3.11)$$

$m \in M_y, \quad i = m + N + M_x$

$$GR_i = R_m = \frac{\partial z_i}{\partial t} + k_m^{bz} \left(z_m - \left[k_{m, LNI(i)} z_{LNI(i)} \left(\frac{a_m^{v_{LNI(i)}}}{a_{LNI(i)}^{v_m}} \right) (S_T)^{v_{LNI(i)} - v_m} \right]^{\frac{1}{v_{LNI(i)}}} \right) \quad (3.12)$$

$m \in M_z, \quad i = m + N + M_x + M_y$

$$GR_i = R_m = \frac{\partial p_i}{\partial t} + A k_i^{bp} - B \alpha_i^{fp} \prod_{k=1}^{N_i} c_k^{a_{ik}^p} \quad (3.13)$$

$m \in M_p, \quad i = m + N + M_x + M_y + M_z$

3.2 Evaluation of Jacobians

The first set of Jacobians are those involved with the aqueous component species.

$$\begin{aligned} GJ_{ij} &= \frac{\partial R_m}{\partial c_n} = -\delta_{mn} - \sum_{k=1}^{M_x} a_{km}^x \left[\frac{\partial x_k}{\partial c_n} \right] - \sum_{k=1}^{M_y} a_{km}^y \left[\frac{\partial y_k}{\partial c_n} \right] \\ &= -\delta_{mn} - \sum_{k=1}^{M_x} a_{km}^x \left[a_{kn}^x \left(\frac{x_k}{c_n} \right) \right] - \sum_{k=1}^{M_y} a_{km}^y \left[a_{kn}^y \left(\frac{y_k}{c_n} \right) \right], \quad n \in N_a, \quad j = n \end{aligned} \quad (3.14)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = - \sum_{k=1}^{M_y} a_{km}^y \left(\frac{\partial Y_k}{\partial s_n} \right)$$

(3.15)

$$= - \sum_{k=1}^{M_y} a_{km}^y \left[p_{kn}^y \left(\frac{Y_k}{s_n} \right) \right], \quad n \in N_s, \quad j = n + N_a$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = - \sum_{k=1}^{M_x} a_{km}^x \left(\frac{\partial x_k}{\partial x_n} \right) = - \sum_{k=1}^{M_x} a_{km}^x \delta_{kn} = -a_{nm}^x,$$

(3.16)

$$n \in M_x, \quad j = n + N$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Y_n} = - \sum_{k=1}^{M_y} a_{km}^y \left(\frac{\partial Y_k}{\partial Y_n} \right) = - \sum_{k=1}^{M_y} a_{km}^y \delta_{kn} = -a_{nm}^y,$$

(3.17)

$$n \in M_y, \quad j = n + N + M_x$$

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

(3.18)

$$n \in M_z, \quad j = n + N + M_x + M_y$$

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

(3.19)

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

The Jacobians for the adsorbent component species are,

$$\begin{aligned} GJ_{ij} &= \frac{\partial R_m}{\partial C_n} = - \sum_{k=1}^{M_y} b_{km}^y \left(\frac{\partial Y_k}{\partial C_n} \right) \\ &= - \sum_{k=1}^{M_y} b_{km}^y \left[a_{kn}^y \left(\frac{Y_k}{C_n} \right) \right], \quad n \in N_a, \quad j = n \end{aligned} \quad (3.20)$$

$$\begin{aligned} GJ_{ij} &= \frac{\partial R_m}{\partial S_n} = -\delta_{mn} - \sum_{k=1}^{M_y} b_{km}^y \left(\frac{\partial Y_k}{\partial S_n} \right) \\ &= -\delta_{mn} - \sum_{k=1}^{M_y} b_{km}^y \left[a_{kn}^y \left(\frac{Y_k}{S_n} \right) \right], \quad n \in N_s, \quad j = n + N_a \end{aligned} \quad (3.21)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial X_n} = 0, \quad n \in M_x, \quad j = n + N \quad (3.22)$$

$$\begin{aligned} GJ_{ij} &= \frac{\partial R_m}{\partial Y_n} = - \sum_{k=1}^{M_y} a_{km}^y \left(\frac{\partial Y_k}{\partial X_n} \right) = - \sum_{k=1}^{M_y} a_{km}^y \delta_{kn} = -a_{nm}^y, \\ n &\in M_y, \quad j = n + N + M_x \end{aligned} \quad (3.23)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Z_n} = 0, \quad n \in M_z, \quad j = n + N + M_x + M_y \quad (3.24)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial P_n} = 0, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.25)$$

The next set of Jacobians is for the rows of the kinetic complexed species. Since the governing

equation for these species involves less species the derivatives will be simpler.

$$GJ_{ij} = \frac{\partial R_m}{\partial C_n} = -\alpha_{fm}^x \frac{a_{mn}^x}{C_n} \prod_{k=1}^{N_i} c_k^{a_{mk}^x} \quad (3.26)$$

$$n \in N_a, \quad j = n$$

$$GJ_{ij} = \frac{\partial R_m}{\partial S_n} = 0, \quad n \in N_s, \quad j = n + N_a \quad (3.27)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial X_n} = \frac{1}{\Delta t} + k_{bm}^x, \quad n \in M_x, \quad j = n + N \quad (3.28)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Y_n} = 0, \quad n \in M_y, \quad j = n + N + M_x \quad (3.29)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Z_n} = 0, \quad n \in M_z, \quad j = n + N + M_x + M_y \quad (3.30)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial P_n} = 0, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.31)$$

The next set of Jacobians, the kinetic adsorbed species, is similar to the complexed form because the one adsorbent component is considered to act like an aqueous component making the adsorbed species act like the complexed species.

$$GJ_{ij} = \frac{\partial R_m}{\partial C_n} = -\alpha_{fm}^y \frac{a_{mn}^y}{C_n} \prod_{k=1}^{N_i} c_k^{a_{mk}^y} \quad (3.32)$$

$$n \in N_a, \quad j = n$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\alpha_{fm}^y \frac{a_{mn}^y}{s_n} \prod_{k=1}^{N_i} s_k^{a_{mk}^y} \quad (3.33)$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in M_x, \quad j = n + N \quad (3.34)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = \frac{1}{\Delta t} + k_{bm}^y, \quad n \in M_y, \quad j = n + N + M_x \quad (3.35)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = 0, \quad n \in M_z, \quad j = n + N + M_x + M_y \quad (3.36)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.37)$$

The Jacobians for the ion-exchanged species are,

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \frac{R_i(\dots, c_n + \epsilon, \dots) - R_i(\dots, c_n, \dots)}{\epsilon}, \quad (3.38)$$

$$n \in N_a, \quad j = n$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = 0, \quad n \in N_s, \quad j = n + N_a \quad (3.39)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in M_x, \quad j = n + N \quad (3.40)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Y_n} = 0, \quad n \in M_y, \quad j = n + N + M_x \quad (3.41)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Z_n} = \frac{R_i(\dots, z_n + \epsilon, \dots) - R_i(\dots, z_n, \dots)}{\epsilon}, \quad (3.42)$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.43)$$

The Jacobians for the precipitated species are,

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\alpha_m^p \prod_{k=1}^{N_i} a_{mn}^p \frac{(c_k)^{\alpha_{mk}^p}}{c_n} \quad (3.44)$$

$$n \in N_a, \quad j = n$$

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = 0, \quad n \in N_s, \quad j = n + N_a \quad (3.45)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in M_x, \quad j = n + N \quad (3.46)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Y_n} = 0, \quad n \in M_y, \quad j = n + N + M_x \quad (3.47)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial Z_n} = 0, \quad n \in M_z, \quad j = n + N + M_x + M_y \quad (3.48)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.49)$$

for the equilibrium case and

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = \frac{1}{\Delta t}, \quad n \in M_p, \quad j = n + N + M_x + M_y + M_z \quad (3.50)$$

for the kinetic case.

3.3 Treatment of Precipitated Species

In this model there is a special treatment for precipitated species in selecting which will be allowed to precipitate. For a certain example there will be an M_p number of possible precipitated species. Since a potentially precipitated species either can be precipitated or not, only a fraction of the total number will be formed. But since the user does not know which species will precipitate, a special precipitate loop was written into KEMOD to test the different combinations of actual precipitated species. This special loop incorporates the concentration solver iterative loop within it to solve for concentrations once one set of precipitated species is chosen. To avoid confusion in the following discussion, the precipitated loop will be referred to as a cycle each time it is used.

For the first cycle the program assumes that no species are allowed to be precipitated. So the program runs one set of iterations to determine concentration values for all other species involved in the system. When the convergent solution is obtained the values of the component species are then used to check if the assumption of the chosen set of precipitated species was correct. The program calculates the saturation index for each possible precipitated species and checks to see if it is greater than one, as illustrated in the following equation which was previously defined,

$$\text{Saturation Index} = \alpha_i^p \prod_{k=1}^{N_i} c_k^{a_k^p} > 1 \quad (3.51)$$

When the saturation index is greater than one for a particular species, it indicates that there is enough of its aqueous component species available in free form in the solution to form that particular precipitated species. All species whose saturation index is greater than one are thus considered candidates for precipitation. After all of the precipitated species have been tested, the candidate species are ranked in order of their saturation values and each of these candidate precipitated species is tested to insure that the phase rule is not violated. In order for each candidate species to fully precipitate, one of its component species must be variable so that the saturation index is equal to one. This component species will then become fixed for all other candidate species for testing the phase rule. Each candidate species is tested, in the order of their saturation value ranking, to find a variable component species. The highest ranked value will automatically satisfy the test because no component species have been made fixed species yet. But now one of the free aqueous species that form this candidate will be made fixed, or unavailable to the lower ranked candidate species. So the next highest ranked candidate species will be tested, and may or may not pass depending on the remaining component species. If all the component species that form this candidate species have been already fixed, then this species fails and is not considered a candidate species. If it passes, then one of its variable component species will be made unavailable to lower ranked candidate species and the process continues until all the candidate species have been tested in the order of their rankings.

The candidate species that were not eliminated will now be used to run the second cycle of the program in order to determine the concentrations for all species in the system given a new set of precipitated species. During the iterative loop to the equilibrium problem, with the chosen set of precipitated species in this cycle, if any precipitated species has a negative concentration for two

consecutive iterations it will be dissolved. This is done because consecutive negative concentrations indicates that the final precipitated species concentration will probably be zero, and it will not precipitate. When the new set of iterations is complete the remaining precipitated species will be the ones that are allowed to precipitate. However, the program will again test the dissolved precipitated species to see if their saturation values are greater than one for the new concentration values of the aqueous component species. If any of these species have acceptable saturation values, they are added to the list of precipitated species and a new saturation index ranking is made. The new set of candidate species are again tested for any violations of the phase rule, and once a new set of possible precipitated species is set, a new cycle can begin. With each new cycle the steps are repeated: running a new set of iterations to find species concentrations, testing the saturation values of the dissolved species, and then testing for phase rule violations among the candidate precipitated species. When there are no changes in the calculated concentration values or in the species allowed to be precipitated, then the program accepts these as the final values and the simulation is complete.

4. DESIGN OF COMPUTER CODE - KEMOD

To solve the set of governing equations, one can use the set of component species concentrations as the unknowns or the set of all species as the unknowns. Practically, all the major geochemical equilibrium models including MINEQL (Westall, et al., 1976), GEOCHEM (Sposito and Mittigod, 1980), and PHREEQE (Parkhurst, et. al., 1980) use the first approach. However, to allow the flexibility of treating any species as kinetic reactions, we have used the second approach, i.e., use the set of all species concentrations as unknowns. Because of this approach, we are able to design a highly modular program that can be easily modified when new information is to be incorporated in the model. For example, if ion-exchange kinetics are not governed by Eq. (2.24), one simply modifies these FORTRAN statements in Subroutine RIES, which evaluate the residues of the equation governing the ion-exchange reactions. If optional adsorption models are to be included, then one simply modifies the subroutine RADDC, which evaluates the residues of equations governing the mole balance of adsorbent components.

To solve Eqs. (2.1) through (2.6) along with (2.12a), (2.13a), (2.15a), (2.16a), (2.22), (2.24), (2.26a), and (2.27a), the computer code KEMOD is designed. KEMOD consists of a MAIN program, a DATA BLOCK, and twenty five (25) subroutines. The MAIN is utilized to specify the sizes for all arrays. The control and coordinate activity are performed by the subroutine KEQMOD. Figure 3.1 shows the structure of the program. The function of these subroutines are described in this section.

Fig. 3.1 Program Structure of KEMOD

Subroutine KEQMOD

The subroutine KEQMOD controls the entire sequence of operations, a function generally performed by the MAIN program. It is, however, preferable to keep a short MAIN and several subroutines with variable storage allocation. This makes it possible to place most of the FORTRAN deck on a permanent file and to deal with a specific problem without making changes in array dimensions throughout all subroutines.

The subroutine KEQMOD is called by the program MAIN and will perform either the steady-state computation alone ($KSS = 1$ and $NTI = 0$), or a transient state computation using the steady-state solution as the initial conditions ($KSS = 1$, $NTI > 0$), or a transient computation using user-supplied initial conditions ($KSS = 0$, $NTI > 0$).

KEQMOD calls subroutine DATAIO to read and print input data required for chemical kinetic and equilibrium computation, and calls subroutine KINEQL to solve a set of mixed ordinary differential and algebraic equations governing mole balance, and chemical kinetic and equilibrium reactions. Finally, it calls subroutine TOTDSP to compute total dissolved, total sorbed, and total precipitated concentrations of all components after concentrations of all species have been found.

Subroutine KINEQL

This subroutine solves the system of mixed ordinary differential and nonlinear algebraic equations governing chemical kinetics and equilibrium. The method of solution is done with Newton-Ralphson iteration. For each iteration, subroutine KINEQL calls subroutine ACOEF to compute the activity coefficients for all species, subroutine MODIFK to calculate the modified forward rate and

equilibrium constants for all product species, subroutine RESIDU to evaluate residuals of all governing equations, subroutine JACOBI to compute the Jacobian of all governing equations, subroutine DECOMP to decompose the Jacobian matrix with partial pivoting, and subroutine SOLVE for back substitution to obtain the differences between new iteration and previous iterations of all unknowns. New iterations are obtained by adding these differences to the old iterations.

Subroutine ACOEF

This subroutine is called by subroutine KINEQL to compute ionic strength and activity coefficients of all species.

Subroutine MODIFK

This subroutine is called by subroutine KINEQL to calculate the modified forward rate and equilibrium constants for all product species.

Subroutine RESIDU

This subroutine is called to evaluate residuals of discretized ordinary differential and nonlinear algebraic equations governing chemical kinetics and equilibrium. Residuals are evaluated in the subroutine RESIDU for the following equations: (1) mole balance equations for aqueous components, (2) aqueous complexation reaction equations, and (3) precipitation/dissolution reaction equations. Residuals for equations governing the balance of adsorbent components are obtained by calling subroutine RADC. Residuals for equations governing adsorbed species are obtained by calling subroutine RADS. Residuals for the ion-exchanged reactions are obtained by calling subroutines RIES. Residuals for the equilibrium and kinetic precipitation reactions are obtained by calling subroutines RPEQS and RPKIS respectively.

Subroutine RADC

This subroutine is called by subroutine RESIDU to evaluate residuals for equations governing the mole balance for adsorbent components.

Subroutine RADS

This subroutine is called by subroutine RESIDU to evaluate residuals for equations governing the reaction of adsorbed species.

Subroutine RIES

This subroutine is called by subroutine RESIDU to evaluate residuals for ion-exchange reactions and cation ion exchange capacity constraint.

Subroutine RPEOS

This subroutine is called by subroutine RESIDU to evaluate residuals for equations governing the equilibrium reaction of precipitated species.

Subroutine RPKIS

This subroutine is called by subroutine RESIDU to evaluate residuals for equations governing the kinetic reaction of precipitated species.

Subroutine JACOBI

This subroutine is called to evaluate Jacobians of discretized ordinary differential and nonlinear algebraic equations governing chemical kinetics and equilibrium. Jacobians are evaluated in the subroutine JACOBI for the following equations: (1) mole balance equations for aqueous

components, (2) reaction equations governing aqueous complexation, and (3) precipitation/dissolution reaction equations. Jacobians for equations governing the balance of adsorbent mole balance equations are obtained by calling subroutines JADC. Jacobians for equations governing the reactions of adsorbed species are obtained by calling JADS. Jacobians for the ion-exchanged reactions are obtained by calling subroutines JIES. Jacobians for the equilibrium and kinetic precipitation reactions are obtained by calling subroutines JPEQS and JPKIS, respectively.

Subroutine JADC

This subroutine is called by subroutine JACOBI to compute the Jacobian for mole balance equations of adsorbent components.

Subroutine JADS

This subroutine is called by subroutine JACOBI to compute the Jacobian for reaction equations of adsorbed species.

Subroutine JIES

This subroutine is called by subroutine JACOBI to compute the Jacobian for ion-exchange reactions and cation ion exchange capacity constraint.

Subroutine JPEQS

This subroutine is called by subroutine JACOBI to compute the Jacobian for equilibrium reaction equations of precipitated species.

Subroutine JPKIS

This subroutine is called by subroutine JACOBI to compute the Jacobian for kinetic reaction equations of precipitated species.

Subroutine DGELG

This subroutine is called by subroutine KINEQL to solve the Jacobian matrix equation. Gaussian elimination with full pivoting is used in the algorithm.

Subroutine TOTDSP

This subroutine is called by subroutine KEMOD to evaluate the log of free species concentrations and total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components.

Subroutine DATAIO

This subroutine reads and prints all necessary data for simulations.

Subroutine STORE

This subroutine is used to store the species variables on Logical Unit 2. It is intended for use for plotting.

Subroutine LPOUT

This subroutine is called by the subroutine KEQMOD to line print chemical species distribution at desired nodes at desired time interval. The information printed included concentrations, modified equilibrium constants, and stoichiometric coefficients of all species.

Subroutine INDEXX

This subroutine is used to index the saturation value among all potential species that are subject to precipitation/dissolution reactions.

Subroutine NPPT

This subroutine is used to determine the number of species allowed to precipitate without violating the phase rule.

Subroutine DISOLV

This subroutine is called by KINEQL to dissolve an assumed precipitated species that has shown negative concentrations during two successive iterations.

Subroutine SOSFCT

This subroutine is called by the subroutine KEMOD to compute the artificial input of all chemical species.

5. EXAMPLE PROBLEMS

Four (4) example problems are used to test and verify KEMOD. Input files (Appendix B and on disk) and output files (disk only) are included with this document. Problem No. 1 is used to verify KEMOD for a simple equilibrium problem that has been modeled by both MINEQL (Westall, et. al., 1976) and EQMOD, KEMOD's predecessor program. Problem No. 2 tests the case of kinetic precipitation/dissolution and Problems No. 3 and 4 are used to test the case of both a simple and a complex mixed system of equilibrium and kinetic reactions, respectively.

5.1 Problem No. 1 - Test of a Simple Equilibrium System

This problem deals with a simple equilibrium problem involving three components; calcium, carbonate, and hydrogen. Initially 0.001 moles of calcium carbonate are mixed with 1 liter of pure water at 1 atmosphere pressure and 25°C temperature. In determining what will be the concentrations at equilibrium, chemical analysis is used to find the possible species; Ca^{2+} , CO_3^{2-} , H^+ , OH^- , H_2O , $\text{CaCO}_3(\text{aq})$, CaHCO_3^+ , $\text{Ca}(\text{OH})^+$, HCO_3^- , H_2CO_3 , $\text{Ca}(\text{OH})_2(\text{solid})$, $\text{CaCO}_3(\text{solid})$. The problem is defined by three components, six complexed species and two precipitated species. The input data set for this simple problem is given in Appendix B, Sect. B.1, and floppy-disk output data set can be requested (Appendix C, Sect. C.1). Table 5.1 lists the geochemical data and the simulated logarithms of species concentrations (last column) at equilibrium. Simulation results are in perfect agreement with those given by EQMOD and are in agreement with those given by MINEQL (Westall, et. al., 1976) accounting for the activity corrections.

TABLE 5.1. List of geochemical data and species concentrations
at equilibrium for Problem No. 1

Species	Ca^{2+}	CO_3^{2-}	H^+	Log(K)	Log(C)
Ca^{2+}	1	0	0	0.00	-3.886
CO_3^{2-}	0	1	0	0.00	-4.332
H^+	0	0	1	0.00	-9.913
OH^-	0	0	-1	-14.00	-4.077
$\text{CaCO}_3 \text{ (aq)}$	1	1	0	3.00	-5.300
CaHCO_3^+	1	1	1	11.60	-6.602
CaOH^+	1	0	-1	-12.20	-6.204
HCO_3^-	0	1	1	10.20	-4.076
H_2CO_3	0	1	2	16.50	-7.698
$\text{Ca(OH)}_2\text{(s)}$	1	0	-2	-21.90	$-\infty$
$\text{CaCO}_3 \text{ (s)}$	1	1	0	8.30	-3.063
Given	10^{-3}	10^{-3}	0		
Total (M)					

5.2 Problem 2 - Test of Kinetic Precipitation

The second example problem tested the code's ability to solve a kinetic precipitation-dissolution problem involving silica (Rimstidt and Barnes, 1980). The total analytical concentration of silica is 0.4017 moles in 1 liter of pure water at 1 atmosphere pressure and 105°C temperature. This problem involves one aqueous silica component (H_4SiO_4) and one precipitated silica species, quartz ($\text{SiO}_2(\text{s})$). The input data for this simple problem is given in Appendix B, Sect. B.2, and floppy-disk output data set can be requested (Appendix C, Sect C.2). Table 5.2 lists the geochemical data and the simulated logarithm of species concentrations (last columns) at initial conditions and after 8.0 hrs. The results indicated that KEMOD yields agreement with the analytical solution up to the fourth digit.

Table 5.2. List of geochemical data and initial and final concentrations for Problem No. 2

	Component					
Species	H_4SiO_4	$\text{Log}(\text{K}^{\text{f}})$	$\text{Log}(\text{K}^{\text{b}})$	$\text{Log}(\text{K}^{\text{e}})$	Initial	Final
H_4SiO_4	1	—	—	—	0.0017	0.0016
$\text{SiO}_2(\text{s})$	1	-2.12	-6.36	4.24	0.4000	0.4001
Given Total (M)	0.4017					

5.3 Problem No. 3 - Test of a Simple Mixed Equilibrium and Kinetic System

To test a simple mixed equilibrium and kinetic system this third problem involves the same chemical system used in the first example problem, however the formation of calcite is now allowed to be a kinetic process. Most of the initial conditions are kept from the first example, but this latter analysis involves a reaction period of 100.0 hours. The problem involves the same eight species as in the first example, however the precipitated species, $\text{CaCO}_3(\text{s})$, will now be forming due to a kinetic reaction, with logarithm of forward and backward rate constants of 3.30 and -5.00 respectively. The input data set for this problem is given in Appendix B, Sect. B.3, and floppy-disk output data set can be requested (Appendix C, Sect. C.3). Table 5.3 lists the geochemical data and the simulated logarithm of the species concentrations at 100.0 hrs. It is seen that after 100.0 hours this mixed system reaches the same equilibrium values as were found in Problem No. 1.

Table 5.3. List of geochemical data and species concentrations
at 100.0 hrs for Problem No. 3

Species	Ca^{2+}	CO_3^{2-}	H^+	Log(K)	Log(C)
Ca^{2+}	1	0	0	0.00	-3.886
CO_3^{2-}	0	1	0	0.00	-4.332
H^+	0	0	1	0.00	-9.913
OH^-	0	0	-1	-14.00	-4.077
$\text{CaCO}_3(\text{aq})$	1	1	0	3.00	-5.300
CaHCO_3^+	1	1	1	11.60	-6.602

CaOH^+	1	0	-1	-12.20	-6.204
HCO_3^-	0	1	1	10.20	-4.076
H_2CO_3	0	1	2	16.50	-7.698
$\text{Ca(OH)}_2(\text{s})$	1	0	-2	-21.90	$-\infty$
$\text{CaCO}_3(\text{s})$	1	1	0	8.30	-3.063
Total	10^{-3}	10^{-3}	0		

5.4 Problem 4 - Test of Complexation and Adsorption in a Mixed System

To test a more complicated system of mixed kinetic and equilibrium controlled species, data for this example (Szecsody et al., 1994) came from laboratory experiments on a system containing seven chemical components: calcium, aqueous ferric, cobalt, hydrogen, EDTA, chlorate, and solid ferric oxide. The ferric component is in two forms in this problem because part of it, the aqueous component, is considered free in the solution and part of it, the solid ferric oxide, is considered as a species that acts as adsorption sites. The total analytical concentrations of calcium, aqueous ferric, cobalt, EDTA, chlorate, and solid ferric oxide are 2×10^{-3} , 2.37×10^{-5} , 8.51×10^{-6} , 8.51×10^{-6} , 1×10^{-3} , and 1.12×10^{-7} M, respectively, and the activity of hydrogen is fixed at $\text{pH} = 4.5$. In addition to these seven free species, twenty-three complexed species and seven adsorbed species are included for simulation. Thus a total of thirty-seven species resulting from chemical reactions of seven components are involved. Of the total number of species, there are three kinetic complexed species, FeEDTA^- , $\text{Fe(OH)}_3(\text{sand})$, and CoEDTA^{2-} , and four kinetic adsorbed species, $\text{FeOH}_2\text{-CoEDTA}^-$, $\text{FeOH}_2\text{-FeEDTA}$, $\text{FeOH}_2\text{-H}_2\text{EDTA}^-$ and FeO-Co^+ . Thus there is a total of seven kinetic species while

the remaining chemical species will be under equilibrium conditions. The input data set for this complex problem of mixed kinetic and equilibrium species is given in Appendix B, Sect. B.4, and floppy-disk output data set can be requested (Appendix C, Sect. C.4). Table 5.4 lists the geochemical data and the simulated logarithm of species concentration (last column) after 100.0 hours of simulation. Table 5.5 lists the logarithms of the reaction constants for the seven kinetic species.

TABLE 5.4. List of geochemical data and species concentrations
at 100 hours for Problem No. 4

Species	Ca ²⁺	Fe ³⁺	Co ²⁺	H ⁺	EDTA ⁴⁻	ClO ₄ ⁻	FeOH	Log K	Log C
Ca ²⁺	1	0	0	0	0	0	0	0.00	-2.699
Fe ³⁺	0	1	0	0	0	0	0	0.00	-8.201
Co ²⁺	0	0	1	0	0	0	0	0.00	-5.070
H ⁺	0	0	0	1	0	0	0	0.00	-4.500
EDTA ⁴⁻	0	0	0	0	1	0	0	0.00	-24.44
ClO ₄ ⁻	0	0	0	0	0	1	0	0.00	-3.000
FeOH	0	0	0	0	0	0	1	0.00	-8.173
CaEDTA ²⁻	1	0	0	0	1	0	0	12.32	-14.82
CaHEDTA ⁻	1	0	0	1	1	0	0	15.93	-15.71
CaOH ⁺	1	0	0	-1	0	0	0	-12.60	-10.80

FeEDTA ⁻	0	1	0	0	1	0	0	27.57	-5.072
FeHEDTA	0	1	0	1	1	0	0	29.08	-8.062
FeEDTA(OH) ²⁻	0	1	0	-1	1	0	0	19.65	-8.492
FeEDTA(OH) ₂ ³⁻	0	1	0	-2	1	0	0	-36.30	-59.94
FeOH ²⁺	0	1	0	-1	0	0	0	-2.19	-5.891
Fe(OH) ₂ ⁺	0	1	0	-2	0	0	0	-5.67	-4.871
Fe(OH) ₃ (aq)	0	1	0	-3	0	0	0	-13.60	-8.301
Fe(OH) ₃ (sand)	0	1	0	-3	0	0	0	-2.70	-6.353
Fe(OH) ₄ ⁻	0	1	0	-4	0	0	0	-21.60	-11.80
Fe ₂ (OH) ₂ ⁴⁺	0	2	0	-2	0	0	0	-2.95	-10.35
CoEDTA ²⁻	0	0	1	0	1	0	0	17.97	-11.54
CoHEDTA ⁻	0	0	1	1	1	0	0	21.40	-12.61
Co(OH) ⁺	0	0	1	-1	0	0	0	-9.67	-10.24
Co(OH) ₂	0	0	1	-2	0	0	0	-18.76	-14.83
Co(OH) ₃ ⁻	0	0	1	-3	0	0	0	-32.23	-23.80
HEDTA ³⁻	0	0	0	1	1	0	0	11.03	-17.91
H ₂ EDTA	0	0	0	2	1	0	0	17.78	-15.66
H ₃ EDTA	0	0	0	3	1	0	0	20.89	-17.05

H ₄ EDTA	0	0	0	4	1	0	0	23.10	-19.34
OH ⁻	0	0	0	-1	0	0	0	-14.00	-9.500
FeO ⁻	0	0	0	-1	0	0	1	-11.60	-15.27
FeOH ₂ ⁺	0	0	0	1	0	0	1	5.60	-7.073
FeO-Co ⁺	0	0	1	-1	0	0	1	-2.69	-7.684
FeOH ₂ -FeEDTA	0	1	0	1	1	0	1	37.63	-13.69
FeOH ₂ -CoEDTA ⁻	0	0	1	1	1	0	1	28.49	-11.43
FeOH ₂ -H ₂ EDTA ⁻	0	0	0	3	1	0	1	30.48	-15.63
FeOH ₂ -CaEDTA ⁻	1	0	0	1	1	0	1	23.81	-16.00
Given Total (M)	10 ^{-2.7}	10 ^{-4.6}	10 ^{-5.1}	10 ^{-4.5}	10 ^{-5.07}	10 ^{-3.0}	10 ^{-6.95}		

Table 5.5 Reaction constant data for seven kinetic species

Species	Log K ^e	Log K ^b	Log K ^f
FeEDTA ⁻	27.57	-2.57	25.00
Fe(OH) ₃ (sand)	-2.70	-1.40	-38.00
CoEDTA ²⁻	17.97	2.03	20.00
FeO-Co ⁺	-2.69	1.70	-0.99
FeOH ₂ -FeEDTA	37.63	2.37	40.00
FeOH ₂ -CoEDTA ⁻	28.49	1.51	30.00
FeOH ₂ -H ₂ EDTA ⁻	30.48	1.52	32.00

6. REFERENCES

- Davis, J. A., and D. B. Kent. 1990. Surface Complexation Modeling in Aqueous Geochemistry, Mineral-Water Interface Geochemistry Reviews in Mineralogy, Vol 23, 177-260.
- Miller, C. W., 1983. CHEMTRN USER's MANUAL, LBL-16152, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.
- Parkhurst, D. L., D. C. Thorstenson, and L. N. Plummer, 1980. PHREEQE- A Computer Program for Geochemical Calculations, U. S. Geological Survey, Water Resources Investigations 80-96, USGS, Reston, VA.
- Pauling, L., 1956. General Chemistry, 2nd Ed., W. H. Freeman and Company, San Francisco, 710 pp.
- Reed, M. H., 1982. Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases, and an aqueous phase, *Geochimica et Cosmochimica Acta* Vol. 46, 513-528.
- Rimstidt, J. D. and H. L. Barnes, 1980. The kinetics of silica-water reactions, *Geochimica et Cosmochimica Acta*, Vol. 44, 1683-1699.

- Rubin, J. 1983. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions, *Water Resour. Res.* Vol. 19, No. 5, 1231-1252.
- Sposito, G. and S. V. Mitrano, 1980. GEOCHEM: A computer Program for the Calculation of Chemical Equilibria in Soil and Other Natural Water Systems, Department of Soil and Environmental Sciences, University of California, Riverside, CA 92 pp.
- Stumm, W. and J. J. Morgan, 1981. *Aquatic Chemistry An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley & Sons, New York, 780 pp.
- Szeccsödy, J. E., J. M. Zachara, and P. Bruckhart, 1994. Adsorption-dissolution reactions affecting the distribution and stability of Co(II)-EDTA in Fe-oxide coated sand. *Environmental Science and Technology*, Vol. 28, No. 9, 1706-1716.
- Walsh, M. P., S. L. Bryant, and L. W. Lake, 1984. Precipitation and dissolution of solids attending flow through porous media, *AIChE Journal* Vol 30, No. 2, 317-328.
- Westall, J. C., Zachary, J. L., and F. M. M. Morel. 1976. MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous System, Technical Note 18, Department of Civil Engineering, MIT, Cambridge, MA, 91 pp.
- Yeh, G. T. and V. S. Tripathi, 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components, *Water Resources Research*, Vol. 25, No. 1, 93-108

APPENDIX A: Data Input Guide of EQMOD

**** NOTE: All data sets except for data set 1 must be ****
**** preceded by a data set name. ****

1. DATA SET: TITLE

One line per problem.

FORMAT(I5,7A10,3X,2I1)

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.
3. IITR = Inter indicating if iteration table of convergence information to be printed?
1 = yes, 0 = no.
4. ICOND = Integer indicating if the condition number the Jacobian matrix to be printed?
1 = yes, 0 = no.

2. DATA SET 2: NUMBER OF COMPONENTS AND SPECIES

Unformatted 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 species subject to precipitation/dissolution.
7. NOTI = Number of time steps.

3. DATA SET 3: H⁺, e⁻, AND IONIC STRENGTH CORRECTION INFORMATION

Two lines per problem are required.

Line 1 unformatted input containing the following 4 variables.

1. SICOR = User's specified ionic strength for computing activity coefficient.
2. ICOR = Is Ionic strength 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 among component list.
4. LNE = Location of the component e among component list.

Line 2 unformatted input containing the following 2 variables.

1. KSS = Steady state simulation control,
 0 = no steady state simulation
 1 = with steady state simulation
2. NSTR = Integer indicating if restart computation is desired?
 0 = no restart, > 0 = restart

4. DATA SET 4: 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.

5. DATA SET 5: ADSORPTION INFORMATION

This data set is needed if and only if NONS .GT. 0. This set reads information of NSORB adsorbing sites.

Line 1 contains the following two variables

1. NSORB = Number of adsorbing sites
2. IADS = Adsorption model index:
 - 0 = simple surface complexation,
 - 1 = constant capacitance model,
 - 2 = triple layer model.

Line 2 to Line NSORB + 1.

Each line contains the following five variables.

1. CAP1A(I) = Capacitance between the surface and "o" plane, (Farady/L**2) for the I-th adsorbing site
2. CAP2A(I) = Capacitance between the "o" plane and "b" plane, (Farady/L**2) for the I-th adsorbing site.
3. SREAA(I) = Surface area of the I-th adsorbing site, (L**2/M of liter).
4. LNOA(I) = Location of the $\exp(-e*\psi_{io}/kt)$ component in the component list for the I-th adsorbing site.
5. LNBA(I) = Location of the $\exp(-e*\psi_{ib}/kt)$ component in the component list for the I-th adsorbing site.

6. DATA SET 6: ION-EXCHANGE INFORMATION

This subdata set is needed only if NOMZ .GT. 0. This set reads information of ion exchange information for NSITE exchange sites.

Line 1 contains the following variable

1. NSITE = Number of ion-exchange sites

Line 2 to NSITE + 1

Each line contains the following three variables for the I-th site

1. NOMZI(I) = Number of ion-exchanged species in the I-th exchanged site,
2. EC(I) = Ion-exchange capacity (equivalents per unit volume of solution) for the I-th exchange site,
3. LNI(I) = Location of the referenced ion-exchanged species in the ion-exchanged species list for the I-th site.

7. DATA SET 7: BASIC REAL AND INTEGER PARAMETERS

Two lines per problem are required.

Line 1 unformatted input contains the following 6 variables.

1. DELT = time step size, (T)
2. CHNG = time step increment for each of the subsequent time steps, (decimal point)
3. DELMX = maximum time step size allowed, (T)
4. TBNG = beginning simulation time, (T)
5. TEND = ending simulation time, (T)
6. THETA = time integration parameter,
 0.0 = explicit integration
 0.5 = central difference integration
 1.0 = implicit integration

Line 2 unformatted input contains the following 5 variables.

1. OMEGA = relaxation parameters for iteration:
 0 ~ 1 = under-relaxation,
 1 = exact relaxation,
 1 ~ 2 = over-relaxation.
2. EPS = error tolerance for iteration.
3. NITER = number of iterations allowed.
4. NPCYL = number of cycles allowed for iterating precipitation-dissolution.

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.

8. DATA SET 8: PRINTER AND AUXILLIARY STORAGE CONTROL

Two groups of lines are needed for this data set. The number of lines in each group depends on NOTI. Each line contains 80 integers.

(1) Group 1 - FORMAT(80I1)

1. KPR0 = line printout control for steady state solution,
 0 = print nothing,
 1 = print component information only,
 2 = print above plus component species information,
 3 = print above plus product species information,
 4 = print above plus thermodynamic equilibrium constants and
 stoichiometric coefficients of all product species.
2. KPR(1) = similar to KPR0 but for the first time step
3. KPR(2) = similar to KPR0 but for the second time step

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KPR(NOTI) = similar to KPR0 but for the NOTI-th time step

(2) Group 2 - FORMAT(80I1)

1. KAU0 = auxiliary storage output control for steady state solution,
 0 = no output on auxiliary device,
 1 = output on auxiliary device.
2. KAU(1) = similar to KAU0 but for the first time step
3. KAU(2) = similar to KAU0 but for the second time step

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KAU(NOTI) = similar to KAU0 but for the NOTI-th time step

9. DATA SET 9: TOTAL ANALYTICAL CONCENTRATIONS OF ALL COMPONENTS

For each component, one line is needed.

Line 1 - FORMAT(A10,D10.12)

1. CNAM(J) = Component name of the J-th component.
2. TOTACP(J) = Total analytical concentration of the J-th component.

10. DATA SET 10: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES

For each component species, either two lines or four lines are needed depending on whether the species participates in 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 ion-exchanged reaction, four lines are needed.

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 is to be computed,
 3 = species concentration or activity is fixed.

Line 2 - Unformatted input containing three variables

1. CP(I) = Initial guess of the I-th component species concentration, (M/L**3).
2. VJ(I) = Charge of the I-th component species.
3. IONEX = Integer indicating the number of ion exchange sites to which this component species participates.
 0 = This component species does not participate in an ion exchange reaction.
 IONEX = 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.

Line 1 - This line contains the following variable

1. ISITE = This species participates in the ISITE-th ion exchange site's reaction.

Line 2 - FORMAT(A20,I5):

1. SPECN(II) = Name of the II-th ion-exchanged species resulted from the I-th component species involving in the ISITE-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,
 3 = species concentration is fixed.

Line 3 - Free Format. This line contains the following five variables

1. CP(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 ISITE-th ion-exchange site reaction.
3. PBIPD = Log10 of the backward rate constant of the II-th ion-exchanged species resulted from the I-th component species involving in the ISITE-th ion-exchange site reaction.
4. PFIPD = Log10 of the forward rate constant of the II-th ion-exchanged species resulted from the I-th component species involving in the ISITE-th ion-exchange site reaction.
5. KI(IPD) = Kinetic indicator of the ion-exchanged species resulted from the I-th component species,
 0 = equilibrium reaction
 1 = kinetic reaction

11. DATA SET 11: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

This data set is read in similar to DATA SET 6.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) = Name of the II-th species or the I-th complexed species.
2. ISCN(II) = Indicator of the II-th species concentration:
 0 = species concentration is be computed,
 2 = a component species included as a complexed species in a mole balance equation other than for the component.
 3 = species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CP(II) = Initial guess of the complexed species concentration, (M/L**3).
2. PKIPD = Log10 of the equilibrium constant of the I-th complexed species.
3. PBIPD = Log10 of the backward rate constant of the I-th complexed species.
4. PFIPD = Log10 of the forward constant of the I-th complexed species.

5. KI(I) = Kinetic indicator of the I-th complexed species
 0 = equilibrium reaction
 1 = kinetic reaction

6. XYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mass action equation.

7. XYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mass action equation.

8. XYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mass action equation.

NON+5. XYZP(I, NON) = Stoichiometric coefficient of the NON-th component in the I-th complexed species, for use in mass action equation.

NON+6. IONEX = Integer indicating the number of ion exchange sites to which this complexed species participates.

0 = This complexed species does not participate in any ion exchange reaction.

IONEX = This complexed species participates in IONEX ion exchange reactions.

BXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mole balance equation.

BXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mole balance equation.

BXYZP(I,3) = Stoichiometric coefficient of the third component in the I-th complexed species, for use in mole balance equation.

BXYZP(I, NON) = Stoichiometric coefficient of the NON-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.

Line 1 - This line contains the following variable

1. ISITE = This complexed species participates in the ISITE-th ion exchange site's reaction.

Line 2 - FORMAT(A20,I5):

1. SPECN(II) = Name of the II-th ion-exchanged species resulted from the I-th complexed species involving in the ISITE-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,
 3 = species concentration is fixed.

Line 3 - Free Format. This line contains the following five variables

1. CP(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 ISITE-th ion exchange site reaction.
3. PBIPD = Log10 of the backward rate constant of the II-th ion-exchanged species resulted from the I-th complexed species involving in the ISITE-th ion-exchange site reaction.
4. PFIPD = Log10 of the forward rate constant of the II-th ion-exchanged species resulted from the I-th complexed species involving in the ISITE-th ion-exchange site reaction.
5. KI(IPD) = Kinetic indicator of the ion exchanged species resulted from the I-th complexed species,
 0 = equilibrium reaction
 1 = kinetic reaction

12. DATA SET 12: ADSORBED SPECIES

Two lines per adsorbed species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) = Name of the II-th species or the I-th adsorbed species.
2. ISCN(II) = Indicator of the II-th species concentration:
 0 = species concentration is to be computed,
 3 = species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CP(II) = Initial guess of the adsorbed species concentration, (M/L**3).
2. PKIPD = Log10 of the equilibrium constant of the I-th adsorbed species.
3. PBIPD = Log10 of the backward rate constant of the I-th adsorbed species.
4. PFIPD = Log10 of the forward constant of the I-th adsorbed species.
5. KI(I) = Kinetic indicator of the I-th adsorbed species
 0 = equilibrium reaction
 1 = kinetic reaction
6. AXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th adsorbed species, for use in mass action equation.
7. AXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th adsorbed species, for use in mass action equation.
8. AXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th species or in the I-th adsorbed species, for use in mass action equation.
- ...
- NON+5. AXYZP(II, NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th adsorbed species, for use in mass action equation.
- ...
- BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.
- BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.
- BXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.
- ...
- BXYZP(II, NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.

13. DATA SET 13: PRECIPITATED/DISSOLVED SPECIES

Two lines per adsorbed species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) = Name of the II-th species or the I-th precipitated/dissolved species
2. ISCN(II) = Indicator of the II-th species concentration
 0 = species concentration is to be computed.
 3 = species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CP(II) = Initial guess of the precipitated species concentration, (M/L**3).
 2. PKIPD = Log10 of the equilibrium constant of the I-th precipitated/dissolved species.
 3. PBIPD = Log10 of the backward rate constant of the I-th precipitated/dissolved species.
 4. PFIPD = Log10 of the forward constant of the I-th precipitated/dissolved species.
 5. KI(I) = Kinetic indicator of the I-th precipitated/dissolved species
 0 = equilibrium reaction
 1 = kinetic reaction
 6. XYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation.
 7. XYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation.
 8. XYZP(II,3) = Stoichiometric coefficient of the third component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation.
- .
- .
- .
- NON+5. XYZP(II, NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation.
- BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.
- BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.

BXYZP(II,3) = Stoichiometric coefficient of the third component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.

BXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.

14. DATA SET 14: SOURCE PARAMETERS

A total of (NONA + NONS + NOMX + NOMY + NOMZ + NOMP) lines are needed, one for each species.

Unformatted Input: each line contains eight numbers, p_1 , p_2 , p_3 , p_4 , p_5 , p_6 , p_7 , and p_8 , to specify the source input given as

$$Q = p_1 + p_2 t / (p_3 + p_4 t) + p_5 \exp(-p_6 t) \quad \text{if } p_7 < t < p_8$$

$$Q = 0 \quad \text{otherwise}$$

15. DATA SET 15: END OF JOB CARD

A blank line must be used to signal the end of the job.

APPENDIX B: Input Files

B.1. Input Data Set for Problem No. 1

1 SIMULATION OF Ca, CO₃, and H 00

C ***** DATA SET 2: NUMBER OF COMPONENTS, SPECIES, AND TIME INCREMENTS

3 0 6 0 0 2 0 NONA NONS NOMX NOMY NOMZ NOMP NOTI

C ***** DATA SET 3: H⁺, E⁻, IONIC STRENGTH, AND SORPTION INFORMATION

0.0 2 3 0 SICOR ICOR LNH LNE

1 0 KSS NSTR

C ***** DATA SET 4 TEMPERATURE, PRESSURE AND EXPECTED PE AND PH

298.3 1.0 TEMP PRESU

-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX

C ***** DATA SET 7: BASIC AND INTEGER REAL PARAMETERS

1.0 0.0 101.0 0.1 1.0D39 1.0 DELT CHNG DELMX TBNG TEND THETA

1.0 1.0D-6 500 10 2.0 OMEGA EPS NITER NPCYL CNSTRN

C ***** DATA SET 7.5: PRINTER AND AUXILIARY STORAGE CONTROL

44

00

C ***** DATA SET 8: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS

CALCIUM 1.0D-3

CARBONATE 1.0D-3

HYDROGEN 0.0D00

C ***** DATA SET 9: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES

FREE CA++ 0

1.30D-5 2 0 CP(I) VJ(I) IONEX

FREE CO₃-- 0

4.652D-6 -2 0 CP(I) VJ(I) IONEX

FREE H+ 0

1.0D-7 1 0 CP(I) VJ(I) IONEX

C ***** DATA SET 10: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

OH- 0

1.00D-7 -14.0 0.0 -14.0 0 0 0 -1 0 0 0 -1 CP(II) PKIPD XYZP(I,J) IONEX

CACO₃ 0

5.012D-7 3.0 0.0 3.0 0 1 1 0 0 1 1 0

CAHCO₃+ 0

2.498D-8 11.60 0.0 11.6 0 1 1 1 0 1 1 1

CAOH+ 0

6.250D-8 -12.2 0.0 -12.2 0 1 0 -1 0 1 0 -1

HCO₃- 0

8.404D-6 10.20 0.0 10.20 0 0 1 1 0 0 1 1

H₂CO₃ 0

2.003D-9 16.5 0.0 16.5 0 0 1 2 0 0 1 2

C ***** DATA SET 12: PRECIPITATED SPECIES

CA(OH)₂ 0

0.0 -21.9 0.0 -21.9 0 1 0 -2 1 0 -2

CACO3 3
 8.642D-5 8.3 0.0 8.3 0 1 1 0 1 1 0
 C ***** DATA SET 13: SOURCE PARAMETERS
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38
 END OF JOB

B.2. Input Data Set for Problem No. 2

2 SIMULATION OF SILICA PRECIPITATION/DISSOLUTION KINETICS 00
 C ***** DATA SET 2: NUMBER OF COMPONENTS, SPECIES, AND TIME INCREMENTS
 1 0 0 0 0 1 80 NONA NONS NOMX NOMY NOMZ NPMP NOTI
 C ***** DATA SET 3: H+ E- IONIC STRENGTH SORPTION INFORMATION
 0.0 0 0 0 SICOR ICOR LNH LNE
 0 0 KSS NSTR
 C ***** DATA SET 4: TEMPERATURE, PRESSURE AND EXPECTED PE AND PH
 378.0 1.0 TEMP PRESU
 -20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
 C ***** DATA SET 7: BASIC AND INTEGER PARAMETERS
 0.1 0.0 1.0 0.0 200.0 1.0 DELT CHNG DELMAX TBNG TEND THETA
 1.0 1.0D-6 100 10 2.0 OMEGA EPS NITER NPCYL CNSTRN
 C ***** DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL
 44 4 4 4 4 4 4 4
 4
 00 0 0 0 0 0 0 0
 0
 C ***** DATA SET 9: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS
 SILICA 0.4017
 C ***** DATA SET 10: COMPOENT SPECIES AND THEIR ION-EXCHANGED SPECIES
 free SILICA 0
 1.7D-3 0 0
 C ***** DAT SET 13: PRECITIATED SPECIES
 QUARTZ 0
 0.4 4.24 -6.36 -2.12 1 1 1

C ***** DATA SET 14: SOURCE PARAMETERS

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

END OF JOB

B.3. Input Data Set for Problem No. 3

3 SIMULATION OF Ca, CO₃, and H

00

C ***** DATA SET 2: NUMBER OF COMPONENTS, SPECIES, AND TIME INCREMENTS

3 0 6 0 0 2 100 NONA NONS NOMX NOMY NOMZ NOMP NOTI

C ***** DATA SET 3: H⁺, E⁻, IONIC STRENGTH, AND SORPTION INFORMATION

0.0 2 3 0 SICOR ICOR LNH LNE

0 0 KSS NSTR

C ***** DATA SET 4 TEMPERATURE, PRESSURE AND EXPECTED PE AND PH

298.3 1.0 TEMP PRESU

-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX

C ***** DATA SET 7: BASIC AND INTEGER REAL PARAMETERS

1.0 0.0 101.0 0.1 1.0D39 1.0 DELT CHNG DELMX TBNG TEND THETA

1.0 1.0D-6 500 10 2.0 OMEGA EPS NITER NPCYL CNSTRN

C ***** DATA SET 7.5: PRINTER AND AUXILIARY STORAGE CONTROL

4444444444444 4 4 4 4 4 4

4 4 4

0000000000000 0 0 0 0 0 0

0 0 0

C ***** DATA SET 8: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS

CALCIUM 1.0D-3

CARBONATE 1.0D-3

HYDROGEN 0.0D00

C ***** DATA SET 9: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES

FREE CA++ 0

1.30D-5 2 0 CP(I) VJ(I) IONEX

FREE CO₃-- 0

4.652D-6 -2 0 CP(I) VJ(I) IONEX

FREE H+ 0

1.0D-7 1 0 CP(I) VJ(I) IONEX

C ***** DATA SET 10: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

OH- 0

1.00D-7 -14.0 0.0 -14.0 0 0 0 -1 0 0 0 -1

CACO₃ 0

5.012D-7 3.0 0.0 3.0 0 1 1 0 0 1 1 0

CAHCO₃+ 0

2.498D-8 11.60 0.0 11.6 0 1 1 1 0 1 1 1

CAOH+ 0

6.250D-8 -12.2 0.0 -12.2 0 1 0 -1 0 1 0 -1

HCO₃- 0

8.404D-6 10.20 0.0 10.20 0 0 1 1 0 0 1 1
H2CO3 0

2.003D-9 16.5 0.0 16.5 0 0 1 2 0 0 1 2

C ***** DATA SET 12: PRECIPITATED SPECIES

CA(OH)2 0

0.0 -21.9 0.0 -21.9 0 1 0 -2 1 0 -2

CACO3 0

8.642D-5 8.3 -5.0 3.3 1 1 1 0 1 1 0

C ***** DATA SET 13: SOURCE PARAMETERS

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0D38

END OF JOB

B.4. Input Data Set for Problem No. 4

4 SIMULATION OF CoEDTA - Fe(OH)3 REACTION KINETICS

00

C ***** DATA SET 2: NUMBER OF COMPONENTS, SPECIES, AND TIME INCREMENTS

6 1 23 7 0 0 2000 NONA NONS NOMX NOMY NOMZ NPMP NOTI

C ***** DATA SET 3: H+ E- IONIC STRENGTH SORPTION INFORMATION

0.0 0 4 0 SICOR ICOR LNH LNE

0 0 KSS NSTR

C ***** DATA SET 4: TEMPERATURE, PRESSURE AND EXPECTED PE AND PH

298.3 1.0 TEMP PRESU

-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX

C ***** DATA SET 5: ADSORPTION INFORMATION

1 0

0.0 0.0 0.0 0 0

C ***** DATA SET 7: BASIC AND INTEGER PARAMETERS

0.05 0.0 1.0 0.01 1000.0 1.0 DELT CHNG DELMAX TBNG TEND THETA

1.0 1.0D-6 250 50 2.0 OMEGA EPS NITER NPCYL CNSTRN

C ***** DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL

444 4 4 4 4

4

4

4

4

4

4

4

4

4

4

4
000

0

0

0

0

0

0

0

0

0

0

C ***** DATA SET 9: TOTAL ANALYTICAL CONCENTRATIONS OF ALL COMPONENTS

CALCIUM 2.00D-3
 FERRIC 2.37D-5
 COBALT 8.51D-6
 HYDROGEN 0.00D0
 EDTA 8.51D-6
 CHLORATE 1.00D-3
 FeOH 1.12D-7

C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX

Calcium 0
 2.00d-3 2 0 CW VJ IONEX
 Ferric 0
 1.00d-10 3 0 CW VJ IONEX
 Cobolt 0
 1.00d-10 2 0 CW VJ IONEX
 Hydrogen 3
 3.162d-5 1 0 CW VJ IONEX
 EDTA 0
 1.00d-10 -4 0 CW VJ IONEX
 ClO4- 0
 1.0d-3 -1 0 CW VJ IONEX
 FeOH 0
 1.12d-7 0 0 CW VJ IONEX

C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPEC.

CaEDTA 0
 1.0d-7 12.32 0 12.32 0 1 0 0 0 1 0 0 0 1 0 0 0 1 0 0
 CaHEDTA 0
 1.0d-7 15.93 0 15.93 0 1 0 0 1 1 0 0 0 1 0 0 1 1 0 0
 CaOH 0
 1.0d-7 -12.60 0 -12.60 0 1 0 0 -1 0 0 0 0 1 0 0 -1 0 0 0
 FeEDTA 0
 1.0d-7 27.57 -2.57 25.00 1 0 1 0 0 1 0 0 0 0 1 0 0 1 0 0
 FeHEDTA 0
 1.0d-7 29.08 0 29.08 0 0 1 0 1 1 0 0 0 0 1 0 1 1 0 0
 FeEDTA(OH) 0
 1.0d-7 19.65 0 19.65 0 0 1 0 -1 1 0 0 0 0 1 0 -1 1 0 0
 FeEDTA(OH)2 0
 1.0d-7 -36.30 0 -36.30 0 0 1 0 -2 1 0 0 0 0 1 0 -2 1 0 0
 FeOH 0
 1.0d-7 -2.19 0 -2.19 0 0 1 0 -1 0 0 0 0 0 1 0 -1 0 0 0
 Fe(OH)2 0
 1.0d-7 -5.67 0 -5.67 0 0 1 0 -2 0 0 0 0 0 1 0 -2 0 0 0
 Fe(OH)3(aq) 0
 1.0d-7 -13.60 0 -13.60 0 0 1 0 -3 0 0 0 0 0 1 0 -3 0 0 0
 Fe(OH)3(sand) 0
 2.37d-5 -2.70 -1.40 -38.00 1 0 1 0 -3 0 0 0 0 0 1 0 -3 0 0 0
 Fe(OH)4 0
 1.0d-7 -21.60 0 -21.60 0 0 1 0 -4 0 0 0 0 0 1 0 -4 0 0 0
 Fe2(OH)2 0

1.0d-7	-2.95	0	-2.95	0	0	2	0	-2	0	0	0	0	0	2	0	-2	0	0	0
CoEDTA2-			0																
8.51D-6	17.97	2.03	20.00	1	0	0	1	0	1	0	0	0	0	0	0	1	0	1	0
CoHEDTA			0																
1.0d-7	21.40	0	21.40	0	0	0	1	1	1	0	0	0	0	0	0	1	1	1	0
Co(OH)			0																
1.0d-7	-9.67	0	-9.67	0	0	0	1	-1	0	0	0	0	0	0	0	1	-1	0	0
Co(OH)2			0																
1.0d-7	-18.76	0	-18.76	0	0	0	1	-2	0	0	0	0	0	0	0	1	-2	0	0
Co(OH)3			0																
1.0d-7	-32.23	0	-32.23	0	0	0	1	-3	0	0	0	0	0	0	0	1	-3	0	0
HEDTA			0																
1.0d-7	11.03	0	11.03	0	0	0	0	1	1	0	0	0	0	0	0	1	1	0	0
H2EDTA			0																
1.0d-7	17.78	0	17.78	0	0	0	0	2	1	0	0	0	0	0	0	2	1	0	0
H3EDTA			0																
1.0d-7	20.89	0	20.89	0	0	0	0	3	1	0	0	0	0	0	0	3	1	0	0
H4EDTA			0																
1.0d-7	23.10	0	23.10	0	0	0	0	4	1	0	0	0	0	0	0	4	1	0	0
OH			0																
1.0d-8	-14.00	0	-14.00	0	0	0	0	-1	0	0	0	0	0	0	0	-1	0	0	0

C ***** DATA SET 21: ABSORBED SPECIES

FeO-	0																	
2.0D-18	-11.60	0	-11.60	0	0	0	0	-1	0	0	1	0	0	0	-1	0	0	1
FeOH2+	0																	
2.0D-18	5.60	0	5.60	0	0	0	0	1	0	0	1	0	0	0	1	0	0	1
FeOH2-FeEDTA	0																	
1.0d-19	37.63	-0.13	37.50	1	0	1	0	1	1	0	1	0	1	0	1	1	0	1
FeOH2-CoEDTA-	0																	
1.0d-19	28.49	1.51	30.00	1	0	0	1	1	1	0	1	0	0	1	1	1	0	1
FeO-Co+	0																	
1.0D-19	-2.69	1.70	-0.99	1	0	0	1	-1	0	0	1	0	0	1	-1	0	0	1
FeOH2-H2EDTA-	0																	
1.0d-19	30.48	1.52	32.00	1	0	0	0	3	1	0	1	0	0	0	3	1	0	1
FeOH2-CaEDTA-	0																	
1.0d-19	23.81	0	23.81	0	1	0	0	1	1	0	1	1	0	0	1	1	0	1

C ***** DATA SET 14: SOURCE PARAMETERS

[illegible]

[illegible]

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