3.0 NUMERICAL IMPLEMENTATION

3.1 Solution of Coupled Transport and Biogeochemical Reaction Problems

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

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

For mobile chemical components:

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

$$j \in N_a \ .$$

where

$$T'_j = \frac{T_j}{\rho_\ell \theta} \quad , \ j \in N_a \ , \qquad (3.1.2)$$

$$C'_j = \frac{C_j}{\rho_\ell \theta} \quad , \ j \in N_a \ , \qquad (3.1.3)$$

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

$$j \in N_a \ .$$

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

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

$$j \in N_a \quad .$$

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

$$- \rho_\ell \theta \left(\sum_{i=1}^{K_x} a_{ij} \, r_i^x|^{chem} \right) - \rho_b \left(\sum_{i=1}^{K_y} a_{ij} \, r_i^y|^{chem} + \sum_{i=1}^{K_z} a_{ij} \, r_i^z|^{chem} + \sum_{i=1}^{K_p} a_{ij} \, r_i^p|^{chem} \right) \tag{3.1.6}$$

$$j \in N_a \quad .$$

and where

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

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

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

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

or

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

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

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

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

For the kinetic aqueous complexed chemical species:

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

where

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

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

and

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

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

$$\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k (\gamma_{Bk} B_k) \tag{3.1.13}$$

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

$$i \in K_x$$

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

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

or

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

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

For the aqueous microbial species:

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

where

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

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

and

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

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

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

or

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

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

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

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

Mass balance for the aqueous component species concentrations -

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

where

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

and

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

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

Mass balance for the adsorbent component species concentrations -

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

where

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

and

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

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

Mass action equation for equilibrium aqueous complexed species -

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

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

Mass balance equation for kinetic aqueous complexed species with the combined effects of

chemical reactions, microbial reactions, and microbial endogenous respiration -

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

where

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

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

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

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

$$i \in K_x$$

Mass action equation for equilibrium adsorbed species -

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

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

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

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

where

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

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

$$\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] \mathcal{L}_k (\gamma_{Bk} B_k) \tag{3.1.35}$$

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

$$i \in K_y$$

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

Equivalents balance for the ion exchange site constraint equations -

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

where

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

and

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

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

For equilibrium ion-exchanged species -

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

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

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

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

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

where

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

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

$$\sum_{k=1}^{NBRXNK} \frac{(\nu''_{ki} - \nu'_{ki})}{\gamma_i} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k (\gamma_{Bk} B_k) \qquad (3.1.41)$$

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

$$i \in K_z$$

For equilibrium precipitated species -

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

where K_p = number of kinetically controlled precipitated species.

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

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

where

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

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

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

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

$$i \in K_p$$

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

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

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

where

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

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

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

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

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

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

where

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

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

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

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

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

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

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

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

where

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

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

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

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

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

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

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

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

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

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

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

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

Table 3.1 Species in the Two Subsystems of HYDROBIOGEOCHEM

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3.2 Solution of Transport Equations

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

For mobile chemical components:

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

where the Lagrangian tracking velocity is

$$V_L = \frac{1}{\rho_l\theta}\left[\rho_l V\frac{C'_j}{T'_j} - \rho_l\theta\,\mathbf{D}\cdot\nabla\frac{C'_j}{T'_j}\right] \qquad \textbf{(3.2.2)}$$

and

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

and

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

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

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

where the Lagrangian velocity is

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

and

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

and

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

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

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

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

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

The kinetic aqueous complexed species and the aqueous microbial species by definition exist only in the aqueous phase. The ratio of their concentration in the aqueous phase to their total concentration is therefore unity. Equations **(3.2.5)** and **(3.2.9)** are therefore identical in form to Eq. **(3.2.1)**, with C/T = 1, ∇ (C/T) = 0, and the reaction terms defined appropriately for these

cases. The remainder of this section will discuss the solution of the transport equations in terms of Eq. **(3.2.1)**; the discussion is applicable to the solution of Equations **(3.2.5)** and **(3.2.9)** as well.

3.2.1 Spatial Discretization of Transport Equations

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

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

where

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

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

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

where

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

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

[A] = mass matrix.

[D] = stiff matrix resulting from dispersion.

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

[Q] = matrix resulting from the source term.

{R} = load vector from the biogeochemical reactions.

{S} = load vector from the external source.

{B} = load vector from the boundary source.

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

$$A_{ij} = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e \, (\rho_l \theta) \, N_\beta^e dR \quad , \tag{3.2.13}$$

$$D_{ij} = \sum_{e \epsilon M_e} \int_{R_e} \left(\nabla N_\alpha^e \right) \cdot \rho_l \theta \mathbf{D} \, \frac{C^{/}}{T^{/}} \cdot \left(\nabla N_\beta^e \right) \, dR \tag{3.2.14}$$

$$C_{ij} = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e \left[\frac{\partial \rho_l \theta}{\partial t} + \rho_l \mathbf{V} \nabla \cdot \frac{C^{/}}{T^{/}} - \frac{C^{/}}{T^{/}} \frac{\partial \rho_l \theta}{\partial t} - \nabla \cdot \left(\rho_l \theta \mathbf{D} \cdot \nabla \frac{C^{/}}{T^{/}} \right) \right] N_\beta^e dR \tag{3.2.15}$$

and

$$Q_{ij} = \sum_{e \epsilon M_e} \int_{R_e} N_\alpha^e \, Q \rho^* \, \frac{C^{/}}{T^{/}} \, N_\beta^e \, dR \tag{3.2.16}$$

where

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

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

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

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

and

$$B_i = \sum_{e \epsilon N_{se}} \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_l \theta \mathbf{D} \frac{C^{/}}{T^{/}} \cdot \nabla T^{/} \right) dB \quad , \tag{3.2.19}$$

where

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

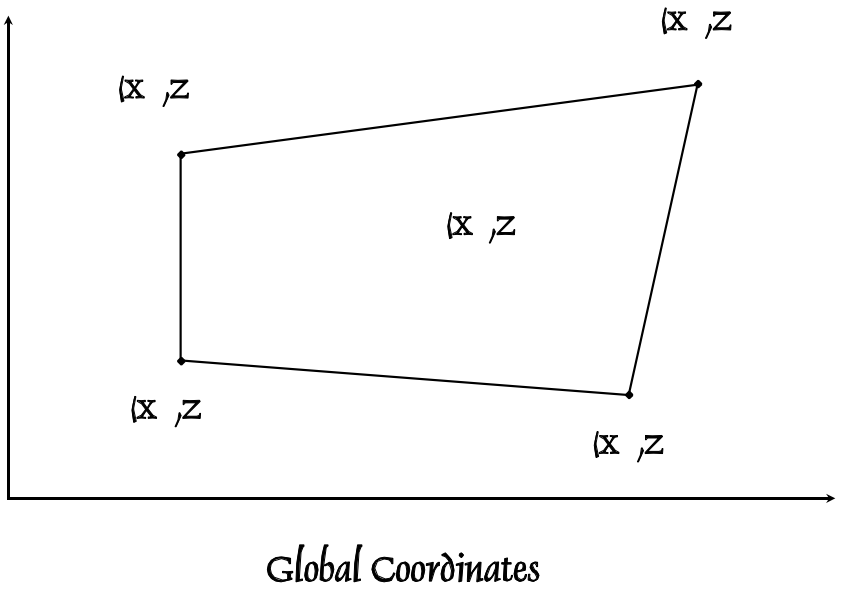
The reduction of the partial differential equation, Equation **(3.2.1)**, to the set of ordinary differential equations, Equation **(3.2.12)**, simplifies to the evaluation of integrals on the right-hand side of Equations **(3.2.13)** through **(3.2.19)** for every element or boundary segment. The major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

3.2.2 Base and Weighting Functions

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

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

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



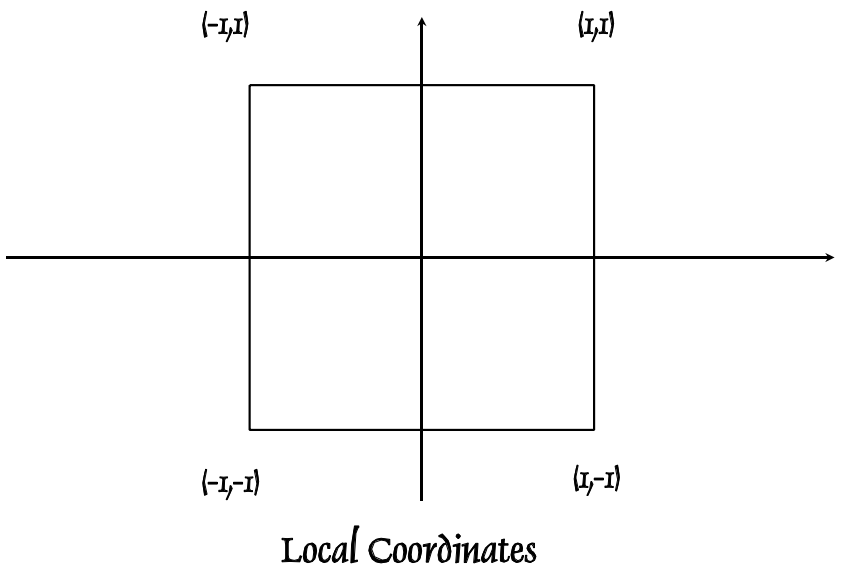


Fig. 3.1 Global Versus Local Coordinates for a Typical Quadrilateral Element

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

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

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

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

where

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

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

$$L_1 = \frac{1}{2A}\left(a_1 + b_1 x + c_1 z\right) \quad ,$$

$$L_2 = \frac{1}{2A}\left(a_2 + b_2 x + c_2 z\right) \quad , \tag{3.2.23}$$

and

$$L_3 = \frac{1}{2A}\left(a_3 + b_3 x + c_3 z\right) \quad ,$$

where

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

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

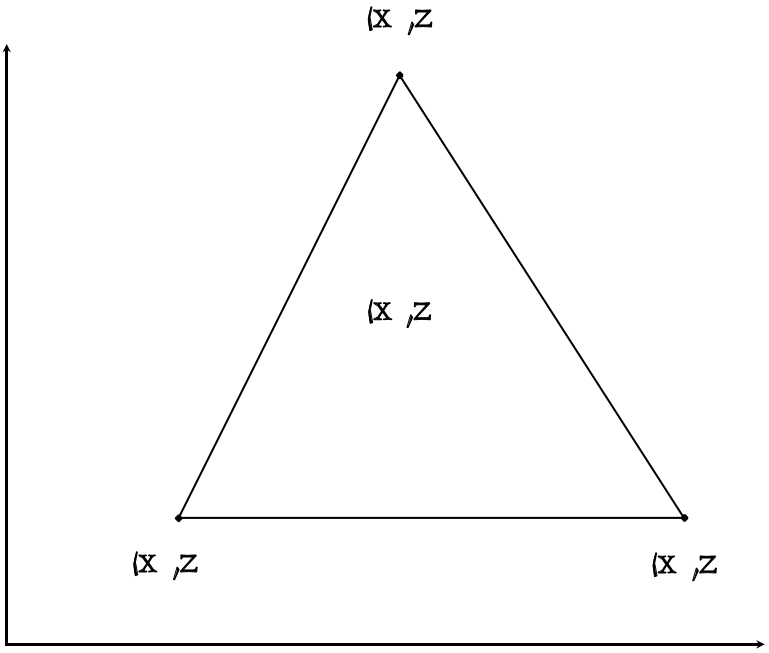
$$a_3 = x_1 z_2 - x_2 z_1 \quad , \quad b_3 = z_1 - z_2 \quad , \quad \text{and} \quad c_3 = x_2 - x_1 \quad ,$$

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

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

Thus, it is clear that only two of the area coordinates can be independent, just as in the original coordinate system, where there are only two independent coordinates, x and z. Furthermore, a little algebraic manipulation will reveal that the coordinates L_1, L_2, and L_3 are in fact the ratios

of the areas A_1, A_2, and A_3, respectively, to the triangular area A (Figure 3.2). This is why they are called area coordinates.



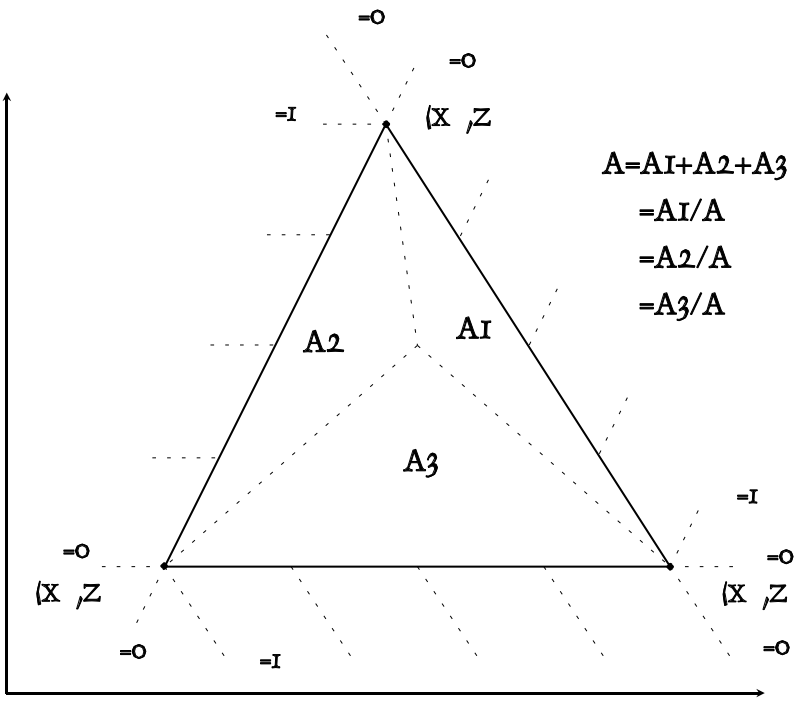


Fig. 3.2 Global Coordinates vs. Local Coordinates for a Typical Triangular Element

3.2.3 Evaluation of Element Matrices

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

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

$$D^e_{\alpha\beta} = \int_{R_e} \left(\nabla N^e_\alpha \right) \cdot \rho_\ell \theta \mathbf{D} \frac{C^l}{T^l} \cdot \left(\nabla N^e_\beta \right) dR \tag{3.2.27}$$

$$C^e_{\alpha\beta} = \int_{R_e} N^e_\alpha \left[\frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C^l}{T^l} - \frac{C^l}{T^l} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left(\rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C^l}{T^l} \right) \right] N^e_\beta dR \tag{3.2.28}$$

$$Q^e_{\alpha\beta} = \int_{R_e} N^e_\alpha Q \rho^* \frac{C^l}{T^l} N^e_\beta dR \tag{3.2.29}$$

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

and

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

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

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

3.2.4 Mass Lumping Option

Referring to the element mass matrix $[A^e]$, first order rate matrix $[C^e]$, and source matrix $[Q^e]$,

one may note that these are the unit matrices if the finite-difference formulation is adopted in the spatial discretization. Hence, by proper scaling these matrices can be reduced to the finite-difference equivalent by lumping (Clough 1971). In many cases, the lumped matrices result in a better solution. Furthermore, with these lumped element matrices, the problem can be reduced to a beaker system when advection and dispersion-diffusion terms are not involved in the transport equation. Under such circumstances, they are preferred to the nonlumped mass, fluid source, and growth matrices. Therefore, an option is provided for the lumping of these matrices. A systematic and mathematically acceptable procedure for such lumping has been well established (Zienkiewicz 1977). For example, the fluid source matrix can be lumped according to the following:

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

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

3.2.5 Time Integration

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

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

where

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

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

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

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

When w = 0, the time integration is explicit. When w = 0.5, it is the Crank-Nicolson central

difference. For the implicit (or backward) difference, w = 1.0.

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

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

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

where

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

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

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

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

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

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

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

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

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

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

3.2.6 Conventional Finite Element Method

HYDROBIOGEOCHEM allows the user to choose the conventional finite element method rather

than the hybrid Lagrangian-Eulerian method for solution of the matrix equations if desired. In this case, the matrix equation **(3.2.33)** is instead:

$$[G]\{T'\}_{t+\Delta t} = [H]\{T'\}_t + \{R\} + \{S\} + \{B\} \quad , \tag{3.2.39}$$

where

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

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

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

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

where

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

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

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

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

3.2.7 Boundary Conditions

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

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

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

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

$$\alpha = 1, 2 \quad .$$

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

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

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

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

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

where the Neuman boundary matrices are given by

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

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

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

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

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

$$\alpha = 1, 2$$

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

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

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

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

$$\text{and } V_{c\alpha\beta}^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) N_\beta^e \, dB \, , \qquad \textbf{(3.2.50)}$$

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

where

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

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

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

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

in which

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

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

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

where

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

and

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

$$V1_{v\alpha\beta}^e = \int_{B_e} N_\alpha^e \mathbf{n} \cdot \left(\rho_\ell \mathbf{V} \frac{C'}{T'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'}{T'} \right) N_\beta^e \, dB \quad , \qquad \textbf{(3.2.53)}$$

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

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

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

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

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

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

$$[U] = [G] - w\left([V1] + [V2]\right) = \frac{[A]}{\Delta\tau} + w\left([D] + [C] + [Q] - [V1] - [V2]\right) ,$$

$$[W] = [H] + (1-w)\left([V1] + [V2]\right) = \frac{[A]}{\Delta\tau} - (1-w)\left([D] + [C] + [Q] - [V1] - [V2]\right) \quad \textbf{(3.2.55)}$$

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

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

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

$$T_{vi}^* = \frac{\int_{B_v} N_i \mathbf{n} \cdot \mathbf{V} C_{in} dB}{\int_{B_v} N_i \mathbf{n} \cdot \rho_\ell \mathbf{V} \frac{C'}{T'} T' dB} \quad \textbf{(3.2.56)}$$

where

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

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

3.2.8 Solution of the Matrix Equations

Although both the matrices [U] and [W] are not functions of the unknown $\{T\}$, Equation **(3.2.54)** still represents a system of nonlinear algebraic equations because of the reaction terms, $\{R\}$. The solution of this system requires some type of iterative procedure. The approach taken here is to make an initial estimate of the unknown $\{T\}$. We compute the value of the reaction terms using the biogeochemical subsystem of equations and the working values for the concentrations of the

species involved in these reactions. Substituting the reaction term vectors into Equation **(3.2.54)**, we linearize the matrix equation, which is then solved by the method of linear algebra to obtain the new solution {T}. The new estimate is obtained by the weighted average of the new solution and the previous estimate,

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

where

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

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

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

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

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

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

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

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

Six options are employed to solve the linearized matrix equation: the direct elimination method,

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

3.3 Solution of Geochemical Reaction Equations

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

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

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

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

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

$$j \in N_a$$

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

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

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

3.3.1 Solution of the Nonlinear Algebraic Equations

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

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

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

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

where

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

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

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

where

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

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

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

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

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

For the Newton-Raphson method, it is advantageous to keep the number of simultaneous equations at a minimum. As noted above, Equations **(3.1.30)** and **(3.1.33)** for the equilibrium complexed and adsorbed species are not independent from the other equations and can be solved outside of the matrix solver. Therefore, the remaining governing equations for the biogeochemical reactions are solved simultaneously for the c_j's, s_j's, K_y kinetic y_i's, z_i's, p_i's, and a_i's during one iteration. After they are obtained, the (M_x - K_x) equlibrium x_i's and (M_y - K_y) equlibrium y_i's are computed from Equations **(3.1.30)** and **(3.1.33)**. The major tasks are thus the evaluation of the residuals and Jacobians for Equations **(3.1.24)** through **(3.1.47)**.

3.3.2 Evaluation of the Residuals

The first set of residuals that is computed are those based on the component governing equations.

The computation is relatively simple, where one just substitutes the iterates of all species concentrations into the equations below.

Residuals for the aqueous component species concentrations:

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

where

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

and

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

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

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

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

Residuals for the adsorbent component species concentrations:

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

$$GR_i = R_m = \frac{\partial W_m}{\partial t} - R_m^s + \left(\lambda_m^s + \alpha \frac{\partial p}{\partial t} \right) W_m \quad , \quad m \in N_s \quad , \quad i = m + N_a$$
$$= \frac{W_m^{(n+1)} - W_m^{(n)}}{\Delta t} - R_m^s + \left(\lambda_m^s + \alpha \frac{\partial p}{\partial t} \right) W_m \qquad \textbf{(3.3.11)}$$

where

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

and

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

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

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

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

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

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

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

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

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

$$m \in K_x , \quad i = m + N \tag{3.3.16}$$

For kinetic adsorption[3]:

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

$$m \in K_y , \quad i = m + N + K_x \tag{3.3.17}$$

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

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

$$j \in \text{NSITE} \quad m = \text{Reference species for Site } j, \quad i = m + N + K_x + K_y \tag{3.3.18}$$

where

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

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

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

and

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

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

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

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

For equilibrium ion-exchange:

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

$$k \in NRXNE \tag{3.3.22}$$

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

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

For kinetic ion-exchange:

$$GR_i = R_m = \frac{\partial z_m}{\partial t} - r_m^z + \lambda_m^z z_m + \alpha \frac{\partial p}{\partial t} z_m + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} z_m \tag{3.3.23}$$

$$m \in K_z \, , \, m \neq \text{Reference ion exchange species} \, ,$$

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

For equilibrium precipitation:

$$GR_i = R_m = 1 - K_k^{eq} \prod_{j \in M} (\gamma_j g_j)^{v'_{kj}} \quad , \quad k \in NRXNE$$
$$m \in (M_p - K_p) \; , \quad i = m + N + K_x + K_y + M_z \tag{3.3.24}$$

For kinetic precipitation:

$$GR_i = R_m = \frac{\partial p_m}{\partial t} - r_m^p + \lambda_m^p p_m + \alpha \frac{\partial p}{\partial t} p_m + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} p_m$$
$$m \in K_p \; , \quad i = m + N + K_x + K_y + M_z \tag{3.3.25}$$

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

$$GR_i = R_m = \frac{\partial b_m}{\partial t} = 0 \quad \text{if IOPTRS=0.} \qquad m \in M_b \; , \quad i = m + N + K_x + K_y + M_z + M_p \tag{3.3.26}$$

If the operator splitting scheme is used, the concentrations of the aqueous phase microbial species are adjusted in both the hydrologic transport and biogeochemical subsystem of equations. With this approach, the residuals for these species are

$$GR_i = R_m = \frac{\partial b_m}{\partial t} - r_m^b + K_m^d b_m + b_m \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta} \frac{\partial \rho_\ell \theta}{\partial t} a_m \quad \text{if IOPTRS=1}$$
$$m \in M_b \; , \quad i = m + N + K_x + K_y + M_z + M_p \tag{3.3.27}$$

For adsorbed phase microbial species:

$$GR_i = R_m = \frac{\partial a_m}{\partial t} - r^a_m + K^d_m a_m + a_m \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b}\frac{\partial \rho_b}{\partial t} a_m \qquad \textbf{(3.3.28)}$$

$$m \in M_a \,, \quad i = m + N + K_x + K_y + M_z + M_p + M_b$$

3.3.3 Evaluation of Jacobians

3.3.3.1 Rows for N_a Species

The first set of Jacobians are those involved with the component species. In the following, GJ_{ij} is the entry in the i-th row, j-th column of the Jacobian array. For a transient simulation, the Jacobians for the rows corresponding to the aqueous components, m = 1, 2, ..., N_a , i = m , are:

$$+\frac{1}{\Delta t}\rho_b\sum_{l=1}^{(M_z-K_z)}a_{lm}\left(\frac{\partial z_l}{\partial c_n}\right)+\frac{1}{\Delta t}\rho_b\sum_{l=1}^{(M_p-K_p)}a_{lm}\left(\frac{\partial p_l}{\partial c_n}\right)$$

$$-\text{IOPTRS}*\left\{\rho_\ell\theta\left(\frac{\partial r_m^{c}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_x-K_x)}a_{lm}\frac{\partial r_l^{x}\big|^{bio}}{\partial c_n}\right)\right\}$$

$$-\text{IOPTRS}*\left\{\rho_b\left(\sum_{l=1}^{(M_y-K_y)}a_{lm}\frac{\partial r_l^{y}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_z-K_z)}a_{lm}\frac{\partial r_l^{z}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_p-K_p)}a_{lm}\frac{\partial r_l^{p}\big|^{bio}}{\partial c_n}\right)\right\}+$$

$$\text{IOPTRS}*\left\{\rho_\ell\theta\sum_{l=1}^{K_x}a_{lm}\frac{\partial r_l^{x}\big|^{chem}}{\partial c_n}+\rho_b\left(\sum_{l=1}^{K_y}a_{lm}\frac{\partial r_l^{y}\big|^{chem}}{\partial c_n}+\sum_{l=1}^{K_z}a_{lm}\frac{\partial r_l^{z}\big|^{chem}}{\partial c_n}+\sum_{l=1}^{K_p}a_{lm}\frac{\partial r_l^{p}\big|^{chem}}{\partial c_n}\right)\right\}$$

(3.3.29)

$$=\frac{1}{\Delta t}\rho_\ell\theta\delta_{mn}+\frac{1}{\Delta t}\rho_\ell\theta\sum_{l=1}^{(M_x-K_x)}a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{x_l}{c_n}\right]+\frac{1}{\Delta t}\rho_b\sum_{l=1}^{(M_y-K_y)}a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{y_l}{c_n}\right]$$

$$-\text{IOPTRS}*\left\{\rho_\ell\theta\left(\frac{\partial r_m^{c}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_x-K_x)}a_{lm}\frac{\partial r_l^{x}\big|^{bio}}{\partial c_n}\right)\right\}$$

$$-\text{IOPTRS}*\left\{\rho_b\left(\sum_{l=1}^{(M_y-K_y)}a_{lm}\frac{\partial r_l^{y}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_z-K_z)}a_{lm}\frac{\partial r_l^{z}\big|^{bio}}{\partial c_n}+\sum_{l=1}^{(M_p-K_p)}a_{lm}\frac{\partial r_l^{p}\big|^{bio}}{\partial c_n}\right)\right\}+$$

$$\text{IOPTRS}*\left\{\rho_\ell\theta\sum_{l=1}^{K_x}a_{lm}\frac{\partial r_l^{x}\big|^{chem}}{\partial c_n}+\rho_b\left(\sum_{l=1}^{K_y}a_{lm}\frac{\partial r_l^{y}\big|^{chem}}{\partial c_n}+\sum_{l=1}^{K_z}a_{lm}\frac{\partial r_l^{z}\big|^{chem}}{\partial c_n}+\sum_{l=1}^{K_p}a_{lm}\frac{\partial r_l^{p}\big|^{chem}}{\partial c_n}\right)\right\},$$

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left(\frac{\partial y_l}{\partial s_n}\right)$$

$$- \text{IOPTRS} * \rho_b \left(\sum_{l=1}^{(M_y - K_y)} a_{lm} \frac{\partial r_l^{y}\big|^{bio}}{\partial s_n} - \sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^{y}\big|^{chem}}{\partial s_n} \right) \qquad \textbf{(3.3.30)}$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{y_l}{s_n}\right] - \text{IOPTRS} * \rho_b \left(\sum_{l=1}^{(M_y - K_y)} a_{lm} \frac{\partial r_l^{y}\big|^{bio}}{\partial s_n} - \sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^{y}\big|^{chem}}{\partial s_n} \right),$$

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

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

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\,\text{IOPTRS} * \rho_\ell \theta \left(-\sum_{l=1}^{K_x} a_{lm} \frac{\partial r_l^{x}\big|^{chem}}{\partial x_n} \right), \quad n \in K_x,\ j = n + N \qquad \textbf{(3.3.31)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\,\text{IOPTRS} * \rho_b \left(-\sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^{y}\big|^{chem}}{\partial y_n} \right), \quad n \in K_y,\ j = n + N + K_x \qquad \textbf{(3.3.32)}$$

$$J_{ij} = \frac{\partial R_m}{\partial z_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\left(\frac{\partial z_l}{\partial z_n}\right) - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^z|^{bio}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^z|^{chem}}{\partial z_n}\right.$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_z-K_z)} a_{lm}\delta_{ln} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^z|^{bio}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^z|^{chem}}{\partial z_n}\right) \qquad (3.3.33)$$

$$= \frac{1}{\Delta t}\,\rho_b a_{nm} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_z-K_z)} a_{lm}\frac{\partial r_l^z|^{bio}}{\partial z_n} - \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^z|^{chem}}{\partial z_n}\right),$$

$$n \in (M_z - K_z) \quad , j = n + N + K_x + K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = - IOPTRS*\rho_b\left(- \sum_{l=1}^{K_z} a_{lm}\frac{\partial r_l^z|^{chem}}{\partial z_n}\right), \quad n \in K_z \quad , j = n+N+K_x+K_y \qquad (3.3.34)$$

$$J_{ij} = \frac{\partial R_m}{\partial p_n} = \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\left(\frac{\partial p_l}{\partial p_n}\right) - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l^p|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l^p|^{chem}}{\partial p_n}\right.$$

$$= \frac{1}{\Delta t}\,\rho_b \sum_{l=1}^{(M_p-K_p)} a_{lm}\delta_{ln} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l^p|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l^p|^{chem}}{\partial p_n}\right) \qquad (3.3.35)$$

$$= \frac{1}{\Delta t}\,\rho_b a_{nm} - IOPTRS*\rho_b\left(\sum_{l=1}^{(M_p-K_p)} a_{lm}\frac{\partial r_l^p|^{bio}}{\partial p_n} - \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l^p|^{chem}}{\partial p_n}\right),$$

$$n \in (M_p - K_p) \quad , j = n + N + K_x + K_y + M_z$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = - IOPTRS*\rho_b\left(- \sum_{l=1}^{K_p} a_{lm}\frac{\partial r_l^p|^{chem}}{\partial p_n}\right), \quad n \in K_p \quad , j = n+N+K_x+K_y+M_z \qquad (3.3.36)$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\,IOPTRS * \left\{ \rho_\ell \theta \left(\frac{\partial r_m^{c}\big|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_x - K_x)} a_{lm} \frac{\partial r_l^{x}\big|^{bio}}{\partial g_n} \right) \right\}$$

$$-IOPTRS * \left\{ \rho_b \left(\sum_{l=1}^{(M_y - K_y)} a_{lm} \frac{\partial r_l^{y}\big|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_z - K_z)} a_{lm} \frac{\partial r_l^{z}\big|^{bio}}{\partial g_n} + \sum_{l=1}^{(M_p - K_p)} a_{lm} \frac{\partial r_l^{p}\big|^{bio}}{\partial g_n} \right) \right\}, \qquad \textbf{(3.3.37)}$$

$$n \in M_b + M_a \;, \; j = n + N + K_x + K_y + M_z + M_p$$

The partial derivatives of the reaction terms are evaluated as follows for any chemical species f:

$$\frac{\partial r_f\big|^{chem}}{\partial g_n} = \sum_{k=1}^{NRXNK} \frac{\partial r_f\big|_k^{chem}}{\partial g_n} = \sum_{k=1}^{NRXNK} \frac{\partial}{\partial g_n} \left[\left(\frac{\nu''_{kf} - \nu'_{kf}}{\gamma_f} \right) \left(k_k^f \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} - k_k^b \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \right] \qquad \textbf{(3.3.38)}$$

and

$$\frac{\partial r_f\big|^{bio}}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial (r_f\big|_k^{biodeg})}{\partial g_n} - \frac{\partial (r_f^{bioresp})}{\partial g_n}$$

$$= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n} \left[\left(\frac{\nu''_{kf} - \nu'_{kf}}{\gamma_f} \right) (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{G}_k (\gamma_{Bk} B_k) \right] \qquad \textbf{(3.3.39)}$$

$$- \sum_{k=1}^{M_B} \frac{\partial}{\partial g_n} \left[\alpha_{kf} K_k^d B_k \left(\frac{g_f}{\kappa_{kf} + g_f} \right) \right]$$

The derivative with respect to g_n is taken term by term for each reactant and product in each kinetic chemical and microbiological reaction and their contributions to the Jacobian matrix for row m are summed. For a given species "f" and a given reaction "k", the evaluation of the derivatives will depend only on a column "n", and not on the row "m" being considered. The evaluation of these derivatives with respect to g_n is therefore applicable for all rows and is presented in sections 3.3.3.9 through 3.3.3.11.

For a steady state simulation, the Jacobians for the rows corresponding to the aqueous

components, m = 1, 2, ..., N_a , i = m , are:

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \rho_\ell \theta \delta_{mn} + \rho_\ell \theta \sum_{l=1}^{(M_x - K_x)} a_{lm}\left(\frac{\partial x_l}{\partial c_n}\right) + \rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left(\frac{\partial y_l}{\partial c_n}\right)$$

$$+ \rho_b \sum_{l=1}^{(M_z - K_z)} a_{lm}\left(\frac{\partial z_l}{\partial c_n}\right) + \rho_b \sum_{l=1}^{(M_p - K_p)} a_{lm}\left(\frac{\partial p_l}{\partial c_n}\right)$$

$$= \rho_\ell \theta \delta_{mn} + \rho_\ell \theta \sum_{l=1}^{(M_x - K_x)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}} \frac{x_l}{c_n}\right] + \rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}} \frac{y_l}{c_n}\right] \qquad \textbf{(3.3.40)}$$

$$k \in NRXNE$$

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

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left(\frac{\partial y_l}{\partial s_n}\right) = \rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}} \frac{y_l}{s_n}\right] \qquad \textbf{(3.3.41)}$$

$$k \in NRXNE$$

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

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 , \quad n \in (K_x + K_y) , \quad j = n + N \qquad \textbf{(3.3.42)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \rho_b \sum_{l=1}^{(M_z - K_z)} a_{lm}\left(\frac{\partial z_l}{\partial z_n}\right) = \rho_b \sum_{l=1}^{(M_z - K_z)} a_{lm}\delta_{ln} = \rho_b a_{nm} , \qquad \textbf{(3.3.43)}$$

$$n \in (M_z - K_z) \quad , j = n + N + K_x + K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = 0 \;, \quad n \in K_z \;, j = n + N + K_x + K_y \tag{3.3.44}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = \rho_b \sum_{l=1}^{(M_p - K_p)} a_{lm} \left(\frac{\partial p_l}{\partial p_n} \right) = \rho_b \sum_{l=1}^{(M_p - K_p)} a_{lm} \delta_{ln} = \rho_b a_{nm} \;, \tag{3.3.45}$$

$$n \in (M_p - K_p) \;, j = n + N + K_x + K_y + M_z$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = 0 \;, \quad n \in K_p \;, j = n + N + K_x + K_y + M_z \tag{3.3.46}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \;, \quad n \in M_b + M_a \;, j = n + N + K_x + K_y + M_z + M_p \tag{3.3.47}$$

3.3.3.2 Rows for N_s Species

For a transient simulation, the Jacobians for the rows corresponding to the adsorbent component species, m = 1, 2,..., N_s, i = m + N_a are:

$$iJ_{ij} = \frac{\partial R_m}{\partial c_n} = \frac{1}{\Delta t}\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left(\frac{\partial y_l}{\partial c_n}\right) - \rho_b\left(\frac{\partial r_m^{s}|^{bio}}{\partial c_n} + \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{y}|^{bio}}{\partial c_n}\right) + \rho_b\sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{y}|^{cher}}{\partial c_n}$$

$$= \frac{1}{\Delta t}\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{y_l}{c_n}\right] - \rho_b\frac{\partial r_m^{s}|^{bio}}{\partial c_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{y}|^{bio}}{\partial c_n} + \rho_b\sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{y}|^{chem}}{\partial c_n}, \quad \textbf{(3.3.48)}$$

$$k \in NRXNE$$

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

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \frac{1}{\Delta t}\rho_b\delta_{mn} + \frac{1}{\Delta t}\rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\left[\frac{\nu'_{kn}}{\nu''_{kl}}\frac{y_l}{s_n}\right] - \rho_b\frac{\partial r_m^{s}|^{bio}}{\partial s_n}$$

$$- \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{y}|^{bio}}{\partial s_n} + \rho_b\sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{y}|^{chem}}{\partial s_n}, \quad \textbf{(3.3.49)}$$

$$k \in NRXNE$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = - \rho_b\frac{\partial r_m^{s}|^{bio}}{\partial x_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm}\frac{\partial r_l^{y}|^{bio}}{\partial x_n} + \rho_b\sum_{l=1}^{K_y} a_{lm}\frac{\partial r_l^{y}|^{chem}}{\partial x_n}, \quad \textbf{(3.3.50)}$$

$$n \in K_x,\ j = n+N$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\rho_b \frac{\partial r_m^s\big|^{bio}}{\partial y_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{bio}}{\partial y_n} + \rho_b \sum_{l=1}^{K_y} a_{lm} \frac{\partial r_l^y\big|^{chem}}{\partial y_n}, \qquad \textbf{(3.3.51)}$$

$$n \in K_y,\ j = n+N+K_x$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\rho_b \frac{\partial r_m^s\big|^{bio}}{\partial g_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{bio}}{\partial g_n} + \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{chem}}{\partial g_n}, \qquad \textbf{(3.3.52)}$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\rho_b \frac{\partial r_m^s\big|^{bio}}{\partial g_n} - \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \frac{\partial r_l^y\big|^{bio}}{\partial g_n}, \qquad \textbf{(3.3.53)}$$

$$n \in M_b+M_a, \quad j = n+N+K_x+K_y+M_z+M_p$$

The evaluation of the partial derivatives of the reaction rate terms is presented in sections 3.3.3.9 through 3.3.3.11.

For a steady state simulation, the Jacobians for the rows corresponding to the adsorbent component species, m = 1, 2,..., N_s, i = m + N_a are:

$$GJ_{ij} = \frac{\partial R_m}{\partial c_n} = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \left(\frac{\partial y_l}{\partial c_n} \right) = \rho_b \sum_{l=1}^{(M_y-K_y)} a_{lm} \left[\frac{\nu'_{kn}}{\nu''_{kl}} \frac{y_l}{c_n} \right] \qquad \textbf{(3.3.54)}$$

$$k \in NRXNE$$

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

where k ∈ NRXNE is the equilibrium reaction defining the formation of equilibrium species l.

$$GJ_{ij} = \frac{\partial R_m}{\partial s_n} = \rho_b \delta_{mn} + \rho_b \sum_{l=1}^{(M_y - K_y)} a_{lm} \left[\frac{\nu'_{kn}}{\nu''_{kl}} \frac{y_l}{s_n} \right], \qquad \textbf{(3.3.55)}$$

$$k \in NRXNE$$

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

$$GJ_{ij} = 0, \quad n \in (K_x + K_y + M_z + M_p + M_b + M_a),\ j = n + N \qquad \textbf{(3.3.56)}$$

3.3.3.3 Rows for K_x Species

The next set of Jacobians is for the rows corresponding to the K_x kinetic complexed species. If the fully implicit approach is used (IOPTRS = 0), the Jacobians for rows the m = 1, 2, ..., K_x , i = m + N and N = N_a + N_s are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in N \; , \; j = n \tag{3.3.57}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = \delta_{mn} \; , \qquad n \in K_x \; , \; j = n + N \tag{3.3.58}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in K_y + M_z + M_p + M_b + M_a \; , \; j = n + N + K_x \tag{3.3.59}$$

If the operator splitting approach is used (IOPTRS =1), the Jacobians for the rows m = 1, 2, ..., K_x, i = m + N and N = N_a + N_s are[4]:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^x}{\partial g_n} \quad , \qquad n \in N_a + N_s \; , \; j = n \tag{3.3.60}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r_m^x}{\partial x_n} + \left(\frac{1}{\Delta t} + \lambda_m^x + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta} \frac{\Delta \rho_\ell \theta}{\Delta t}\right) \delta_{mn} \; , \tag{3.3.61}$$

$$n \in K_x \; , \; j = n + N$$

[4] The change in moisture content term is included in Eq. **(3.3.61)** if $\partial \rho_\ell \theta / \partial t$ is positive, since the term is evaluated in the residual using the working concentration for this case. If $\partial \rho_\ell \theta / \partial t$ is negative, this term is included explicitly in the residual and therefore does not appear in Eq. **(3.3.61)**. See Section 3.3.2.

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r^y_m}{\partial g_n} \quad , \qquad n \in K_y + M_z + M_p + M_b + M_a \; , \; j = n + N + K_x \tag{3.3.62}$$

The evaluation of the reaction terms is detailed in sections 3.3.3.9 through 3.3.3.11.

3.3.3.4 Rows for K_y Species

The next set of Jacobians, for the kinetic adsorbed species, is similar in form to that for the kinetic aqueous complexed species. The Jacobians for the rows corresponding to the K_y kinetic adsorbed species[5], m = 1, 2, ..., K_y, i = m + N + K_x, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r^y_m}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x \; , \; j = n \tag{3.3.63}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial y_n} = - \frac{\partial r^y_m}{\partial y_n} + \left(\frac{1}{\Delta t} + \lambda^y_m + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t}\right) \delta_{mn} \; , \tag{3.3.64}$$

$$n \in K_y \; , \; j = n + N + K_x$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r^y_m}{\partial g_n} \quad , \qquad n \in M_z + M_p + M_b + M_a \; , \; j = n + N + K_x + K_y \tag{3.3.65}$$

The evaluation of the reaction terms is detailed in sections 3.3.3.9 through 3.3.3.11.

3.3.3.5 Rows for M_z Species

The Jacobians for rows corresponding to the ion-exchanged species are m = 1, 2, ..., M_z, i = m + N + K_x + K_y, depend on whether the species m is (1) a "reference" ion exchange species for one of the ion exchange sites, (2) an equilibrium controlled ion exchanged species, or (3) a

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[5] The change in bulk density term is included in Eq. **(3.3.64)** if $\partial \rho_b / \partial t$ is positive, since the term is evaluated in the residual using the working concentration for this case. If $\partial \rho_b / \partial t$ is negative, this term is included explicitly in the residual and therefore does not appear in Eq. **(3.3.64)**. See Section 3.3.2.

kinetic controlled ion exchanged species. The Jacobians for each of these three cases follow:

If species m is the "reference" species for an ion exchange site, the residual for this species for a transient simulation is given by Eq. **(3.3.18)** and the Jacobian for this row is evaluated as follows:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial R_{eqj}^{(bio)}}{\partial g_n} = -\rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^{z|bio}}{\partial g_n} \quad , \qquad \textbf{(3.3.66)}$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \frac{\rho_b \nu_n}{\Delta t} - \frac{\partial R_{eqj}^{(bio)}}{\partial z_n} = \frac{\rho_b \nu_n}{\Delta t} - \rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^{z|bio}}{\partial z_n} \quad , \qquad \textbf{(3.3.67)}$$

$$z_n \in NOMZI(\iota) \quad ,$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial R_{eqj}^{(bio)}}{\partial z_n} = -\rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^{z|bio}}{\partial z_n} \quad , \qquad \textbf{(3.3.68)}$$

$$z_n \notin NOMZI(\iota) \quad ,$$

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

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = -\frac{\partial R_{eqj}^{(bio)}}{\partial g_n} = -\rho_b \sum_{k=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} \nu_k \frac{\partial r_k^{z|bio}}{\partial g_n} \quad , \qquad \textbf{(3.3.69)}$$

$$n \in M_p + M_b + M_a \quad , \quad j = n + N + K_x + K_y + M_z$$

For a steady state simulation, the residual for the "reference" species is given by Eq. **(3.3.21)** and the Jacobian for this row is evaluated as follows:

$$GJ_{ij} = 0 \quad , \quad n \in N_a + N_s + K_x + K_y \quad , \quad j = n \qquad \textbf{(3.3.70)}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = \rho_b \nu_n \quad , \quad z_n \in NOMZI(\iota) \quad , \quad n \in M_z \, , \, j = n + N + K_x + K_y \tag{3.3.71}$$

$$GJ_{ij} = 0 \quad , \quad z_n \notin NOMZI(\iota) \quad , \quad n \in M_z \, , \, j = n + N + K_x + K_y \tag{3.3.72}$$

$$GJ_{ij} = 0 \quad , \quad n \in M_p + M_b + M_a \, , \, j = n + N + K_x + K_y + M_z \tag{3.3.73}$$

If species m is an equilibrium controlled ion exchanged species and is not the "reference" species for an ion exchange site, the residual for this species is given by Eq. **(3.3.22)** and the Jacobian for this row is evaluated as follows:

For columns $n \in N_a$, $j = n$, the contribution to the Jacobian is:

From reactant $r \in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{\nu'_{kn}}{c_n} \right) \left(\prod_{\ell \in (N_a + M_x + M_z)} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \qquad \text{if } r = n \tag{3.3.74}$$

From product $p \in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = \left(\frac{\nu''_{kn}}{c_n} \right) \left(\prod_{\ell \in (N_a + M_x + M_z)} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \qquad \text{if } p = n \tag{3.3.75}$$

From reactant $r \in (M_x - K_x)$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{\nu'_{kr}}{c_n} \right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}} \right) \left(\prod_{\ell \in N_a + M_x + M_z} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \tag{3.3.76}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species r.

From product p $\in$ (M_x-K_x) in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = \left(\frac{\nu''_{kp}}{c_n} \right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa p}} \right) \left(\prod_{\ell \in N_a+M_x+M_z} (\gamma_\ell g_\ell)^{\nu''_{kt}} \right) \qquad \textbf{(3.3.77)}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species p.

For any other reactant species r or product species p, the contribution to the Jacobian in columns $n \in N_a$ is zero.

For columns $n \in N_s, K_x, K_y$, $j = n + N_a$, the Jacobian entry is zero:

$$\frac{\partial R_m}{\partial g_n} = 0 \quad , \quad n \in N_s + K_x + K_y \quad , \quad j = n + N_a \qquad \textbf{(3.3.78)}$$

For columns $n \in M_z$, $j = n + N + K_x + K_y$, the contribution to the Jacobian is:

For reactant r $\in M_z$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial z_n} = - K_k^{eq} \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu'_{kt}} \right) \nu'_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } r = n \qquad \textbf{(3.3.79)}$$

$$= K_k^{eq} \left(\prod_{\ell \in (N_a+M_x+M_z)} (\gamma_\ell g_\ell)^{\nu'_{kt}} \right) \nu'_{kr} \gamma_r \quad \text{if } r \neq n \text{ , but } n \in \text{NOMZI}(\iota) \qquad \textbf{(3.3.80)}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } r \neq n \text{ , } \quad n \notin \text{NOMZI}(\iota) \qquad \textbf{(3.3.81)}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

For product p $\in M_z$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial z_n} = \left(\prod_{\ell \in (N_a + M_x + M_z)} (\gamma_\ell g_\ell)^{\nu''_{kl}} \right) \nu''_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } p = n \tag{3.3.82}$$

$$= - \left(\prod_{\ell \in (N_a + M_x + M_z)} (\gamma_\ell g_\ell)^{\nu''_{kl}} \right) \nu''_{kp} \gamma_p \quad \text{if } p \neq n \text{ , but } n \in \text{NOMZI}(\iota) \tag{3.3.83}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } p \neq n \text{ , } \quad n \notin \text{NOMZI}(\iota) \tag{3.3.84}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

For any other reactant or product species, the contribution to the Jacobian for columns $n \in M_z$ is zero.

For columns $n \in M_p + M_b + M_a$, $j = n + N + K_x + K_y + M_z$, the contribution to the Jacobian is zero.

$$\frac{\partial R_m}{\partial g_n} = 0 \tag{3.3.85}$$

If species m is a kinetic controlled ion exchanged species and is not a "reference" species, the residual for this row is given by Eq. **(3.3.23)** and the Jacobian for this row is evaluated as follows:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r^z_m}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x + K_y \text{ , } j = n \tag{3.3.86}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial z_n} = - \frac{\partial r^z_m}{\partial z_n} + \left(\frac{1}{\Delta t} + \lambda^z_m + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn} \quad , \tag{3.3.87}$$

$$n \in M_z \text{ , } j = n + N + K_x + K_y$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r^z_m}{\partial g_n} \quad , \qquad n \in M_p + M_b + M_a \; , \; j = n + N + K_x + K_y + M_z \tag{3.3.88}$$

As was done for the other kinetic species rows, the partial derivatives of the reaction terms are evaluated by taking the partial derivatives term by term for each species participating in each chemical and microbiological reaction. The equations in Section 3.3.3.9 through 3.3.3.11 can be used to evaluate these terms. However, because sorbent component species, adsorbed species or precipitated species do not participate in chemical reactions involving ion exchange, the contribution to the Jacobian from chemical reactions for these columns will be zeroes for the kinetic ion exchanged species rows.

3.3.3.6 Rows for M_p Species

For the rows corresponding to the precipitated species, m = 1, ..., M_p , i = m + N + K_x + K_y + M_z, the Jacobians will depend on whether the species is equilibrium or kinetic controlled. For the equilibrium case, the residual equation is **(3.3.24)** and the Jacobians for row m are:

For columns n $\in N_a$, j = n:

From reactant r $\in N_a$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{\nu'_{kn}}{c_n} \right) \left(\prod_{\ell M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \quad , \qquad \text{for } r = n \tag{3.3.89}$$

From reactant r $\in (M_x - K_x)$ in the equilibrium reaction k which defines the formation of species m:

$$\frac{\partial R_m}{\partial c_n} = - K_k^{eq} \left(\frac{\nu'_{kr}}{c_n} \right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}} \right) \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \tag{3.3.90}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species r.

For other columns, contribution to the Jacobian is zero:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \qquad n \in N_s + K_x + K_y + M_z + M_p + M_b + M_a \; , \; j = n + N_a \tag{3.3.91}$$

For the kinetic precipitated species, the residual equation is **(3.3.25)** and the Jacobians for row m are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^p}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x + K_y + M_z \; , \; j = n \tag{3.3.92}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial p_n} = - \frac{\partial r_m^p}{\partial p_n} + \left(\frac{1}{\Delta t} + \lambda_m^z + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t}\right) \delta_{mn} \quad , \tag{3.3.93}$$

$$n \in M_p \; , \; j = n + N + K_x + K_y + M_z$$

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^p}{\partial g_n} \quad , \quad n \in M_b + M_a \; , \; j = n + N + K_x + K_y + M_z + M_p \tag{3.3.94}$$

As was done for the other kinetic chemical species rows, the partial derivatives of the production/consumption rate terms are evaluated by taking the partial derivatives term by term for each species participating in each chemical and microbiological reaction. The equations in Section 3.3.3.9 through 3.3.3.11 can be used to evaluate these terms. However, because sorbent component species, adsorbed species or ion exchanged species do not participate in chemical reactions involving precipitation, the contribution to the Jacobian from chemical reactions for these columns will be zeroes for the kinetic precipitated species rows.

3.3.3.7 Rows for M_b Species

If the fully implicit scheme is used (IOPTRS = 0), the Jacobians for the rows corresponding to the aqueous phase microbial species, m = 1, ..., M_b , i = m + N + K_x + K_y + M_z + M_p, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = 0 \quad , \quad n \in N_a + N_s + K_x + K_y + M_z + M_p \; , \; j = n \tag{3.3.95}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = \delta_{mn} \quad , \quad n \in M_b \; , \; j = n + N + K_x + K_y + M_z + M_p \tag{3.3.96}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = 0 \; , \; n \in M_a \; , \; j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.97}$$

If the operator splitting approach is used (IOPTRS = 0), the Jacobians for the rows corresponding to the aqueous phase microbial species, m = 1, ..., M_b , i = m + N + K_x + K_y + M_z + M_p, are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^{bg}}{\partial g_n} \quad , \quad n \in N_a + N_s + K_x + K_y + M_z + M_p \; , \; j = n \tag{3.3.98}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = - \frac{\partial r_m^{bg}}{\partial b_n} - \frac{\partial r_m^{xfr}}{\partial b_n} + \left(\frac{1}{\Delta t} + K_m^d + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_\ell \theta} \frac{\Delta \rho_\ell \theta}{\Delta t}\right) \delta_{mn} \; , \tag{3.3.99}$$

$$n \in M_b, \; j = n + N + K_x + K_y + M_z + M_p$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = - \frac{\partial (r_m^{xfr})}{\partial a_n} \; , \; n \in M_a \; , \; j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.100}$$

The partial derivatives of the microbial growth rate terms are evaluated as follows:

$$\frac{\partial (r_m^{bg})}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial (r_m^{bg}|_k)}{\partial g_n}$$

$$= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n} \left[\frac{(\nu''_{km} - \nu'_{km})}{\gamma_m} (\Gamma_k I_{1k}) \left[\frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k (\gamma_{Bk} B_k) \right] \tag{3.3.101}$$

The derivative with respect to g_n is taken term by term for each species in each microbiological reaction and their contributions to the Jacobian for row m are summed. For a given row m, the evaluation of these derivatives is analogous to that outlined for the Jacobians for the kinetic chemical species rows. The equations in Section 3.3.3.10 can be used to evaluate the microbiological growth contributions in the Jacobian for the microbial species.

The partial derivatives of the microbial phase transfer terms are evaluated as follows:

$$\frac{\partial(r_m^{xfr})}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial(r_m^{xfr}|_k)}{\partial g_n}$$

$$= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n}\left[\frac{(\nu''_{km} - \nu'_{km})}{\gamma_m}\left(k_k^f (\gamma_m b_m)^{\nu'_{km}} - k_k^b (\gamma_j a_j)^{\nu''_{kj}}\right)\right] \quad , \; j \in M_a \qquad \textbf{(3.3.102)}$$

For columns $n \in N_a + N_s + K_x + K_y + M_z + M_p$, $j = n$, the contribution to the Jacobian from the microbial phase transfer reactions is zero.

For columns $n \in M_b$, $j = n + N_a + N_s + K_x + K_y + M_z + M_p$, the contribution to the Jacobian from the microbial phase transfer reactions is:

$$\frac{\partial(r_m^{xfr}|_k)}{\partial b_n} = \frac{(\nu''_{km} - \nu'_{km})}{\gamma_m} k_k^f \nu'_{km} (\gamma_m b_m)^{\nu'_{km}-1} \delta_{mn} \qquad \textbf{(3.3.103)}$$

For columns $n \in M_a$, $j = n + N_a + N_s + K_x + K_y + M_z + M_p + M_b$, the contribution to the Jacobian from the microbial phase transfer reactions is:

$$\frac{\partial(r_m^{xfr}|_k)}{\partial a_n} = -\frac{(\nu''_{km} - \nu'_{km})}{\gamma_m} k_k^b \nu''_{kj} (\gamma_j a_j)^{\nu''_{kj}-1} \delta_{jn} \qquad \textbf{(3.3.104)}$$

3.3.3.8 Rows for M_a Species

For the rows corresponding to the adsorbed phase microbial species, $m = 1, ..., M_a$, $i = m + N + K_x + K_y + M_z + M_p + M_b$, the residual equation is **(3.3.28)** and the Jacobians for row m are:

$$GJ_{ij} = \frac{\partial R_m}{\partial g_n} = - \frac{\partial r_m^{bg}}{\partial g_n} \quad , \qquad n \in N_a + N_s + K_x + K_y + M_z + M_p \; , \; j = n \tag{3.3.105}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial b_n} = - \frac{\partial (r_m^{xfr})}{\partial b_n} \; , \; n \in M_b \; , \; j = n + N + K_x + K_y + M_z + M_p \tag{3.3.106}$$

$$GJ_{ij} = \frac{\partial R_m}{\partial a_n} = - \frac{\partial r_m^{bg}}{\partial a_n} - \frac{\partial r_m^{xfr}}{\partial a_n} + \left(\frac{1}{\Delta t} + K_m^d + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t}\right) \delta_{mn} \; , \tag{3.3.107}$$

$$n \in M_a, \; j = n + N + K_x + K_y + M_z + M_p + M_b$$

The partial derivatives of the microbial growth rate and phase transfer terms are evaluated as for the aqueous phase microbial species rows, the derivative with respect to g_n is taken term by term for each species and their contributions to the Jacobian for row m are summed.

3.3.3.9 Contribution from chemical reactions

The contribution to the Jacobian from each term in the k-th chemical reaction (k $\in$ NRXNK) is as follows:

$$\frac{\partial r_f|_k^{chem}}{\partial g_n} = \frac{\partial}{\partial g_n} \left[\left(\frac{\nu''_{kf} - \nu'_{kf}}{\gamma_f} \right) \left(k_k^f \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} - k_k^b \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \right] \tag{3.3.108}$$

For columns n $\in$ N_a + N_s, j = n, the contribution to the Jacobian from the k-th chemical reaction is:

From reactant r $\in$ N_a or N_s:

$$\frac{\partial (r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m} \right) k_k^f \left(\frac{\nu'_{kn}}{g_n} \right) \prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \text{if } r = n \tag{3.3.109}$$

From product p $\in N_a$ or N_s:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kn}}{g_n}\right) \prod_{\ell\in M}(\gamma_\ell g_\ell)^{\nu''_{k\ell}} \qquad \text{if } p = n \qquad \textbf{(3.3.110)}$$

From reactant r $\in$ (M_x-K_x) or (M_y-K_y), i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^f \left(\frac{\nu'_{kr}}{g_n}\right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa r}}\right) \prod_{\ell\in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \textbf{(3.3.111)}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species r.

From product p $\in$ (M_x-K_x) or (M_y-K_y):

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kp}}{g_n}\right) \left(\frac{\nu'_{\kappa n}}{\nu''_{\kappa p}}\right) \prod_{\ell\in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \textbf{(3.3.112)}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species p.

For any other reactant species r or product species p, the contribution to the Jacobian in columns n $\in$ N_a + N_s is zero.

For columns n $\in$ K_x + K_y, j = n + N, the contribution to the Jacobian from the k-th chemical reaction is:

For reactant r $\in$ K_x + K_y, i.e. kinetic complexed or adsorbed species:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = \left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^f \left(\frac{\nu'_{kn}}{g_n}\right) \prod_{\ell\in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \qquad \textbf{if r = n} \qquad \textbf{(3.3.113)}$$

From product p $\in$ K_x + K_y:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = -\left(\frac{\nu''_{km}-\nu'_{km}}{\gamma_m}\right) k_k^b \left(\frac{\nu''_{kn}}{g_n}\right) \prod_{\ell\in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \qquad \textbf{if p = n} \qquad \textbf{(3.3.114)}$$

For any other reactant or product species, the contribution to the Jacobian in columns n $\in$ K_x+K_y is zero.

For columns n $\in M_z$, j = n + N + K_x + K_y, the contribution to the Jacobian from the k-th chemical reaction is:

For reactant r $\in M_z$:

$$\frac{\partial(r_m|_k^{chem})}{\partial z_n} =$$

$$= \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m} \right) k_k^f \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \nu'_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } r = n \tag{3.3.115}$$

$$= -\left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m} \right) k_k^f \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu'_{k\ell}} \right) \nu'_{kr} \gamma_r \quad \text{if } r \neq n \text{ , } n \in \text{NOMZI}(\iota) \tag{3.3.116}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } r \neq n \text{ , } \quad n \notin \text{NOMZI}(\iota) \tag{3.3.117}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

For product p $\in M_z$:

$$\frac{\partial(r_m|_k^{chem})}{\partial z_n} =$$

$$= -\left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m} \right) k_k^b \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \nu''_{kn} \left(\frac{1}{z_n} - \gamma_n \right) \qquad \text{if } p = n \tag{3.3.118}$$

$$= \left(\frac{\nu''_{km} - \nu'_{km}}{\gamma_m} \right) k_k^b \left(\prod_{\ell \in M} (\gamma_\ell g_\ell)^{\nu''_{k\ell}} \right) \nu''_{kp} \gamma_p \quad \text{if } p \neq n, \text{ but } n \in \text{NOMZI}(\iota) \tag{3.3.119}$$

where $\iota \in$ NSITE is the ion exchange site of reaction k

$$= 0 \qquad \text{if } p \neq n, \quad n \notin \text{NOMZI}(\iota)$$

$$\text{where } \iota \in \text{NSITE is the ion exchange site of reaction k} \tag{3.3.120}$$

For any other reactant or product species, the contribution to the Jacobian for columns n $\in M_z$ is zero.

For columns n $\in M_p$, $M_b + M_a$, j = n + N + K_x + K_y + M_z, the contribution to the Jacobian from the k-th chemical reaction is zero:

$$\frac{\partial(r_m|_k^{chem})}{\partial g_n} = 0 \tag{3.3.121}$$

3.3.3.10 Contribution from microbiological degradation

The contribution to the Jacobian from each term in the k-th microbial biodegradation reaction (k $\in$ NBRXNK) is:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{\partial}{\partial g_n}\left[\left(\frac{\nu''_{kf}-\nu'_{kf}}{\gamma_f}\right)(\Gamma_k I_{1k})\left[\frac{S_k}{(K_{S-k} I_{2k})+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right]\mathcal{L}_k(\gamma_{Bk} B_k)\right] \tag{3.3.122}$$

For columns n $\in$ N_a + N_s, j = n, the contribution to the Jacobian from the k-th microbial reaction is:

If substrate $S_k \in N_a$ or N_s and $S_k \neq$ I:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\Gamma_k \mathcal{L}_k I_{1k}\left[\frac{K_{S-k} I_{2k}}{(K_{S-k} I_{2k}+S_k)^2}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \tag{3.3.123}$$

$$\text{if } S_k = n$$

If electron acceptor $A_k \in N_a$ or N_s and $A_k \neq$ I:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{K_{A-k}}{(K_{A-k} + A_k)^2}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B_k) \qquad \textbf{(3.3.124)}$$

if $A_k = n$

If nutrient $N_k \in N_a$ or N_s and $N_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{G}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{K_{N-k}}{(K_{N-k} + N_k)^2}\right] (\gamma_k B_k) , \quad \text{if } N_k = n \tag{3.3.125}$$

If inhibitor $I \in N_a$ or N_s, and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$, $I \neq B_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{G}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B_k) -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{G}_k I_{1k} \frac{S_k q K_s \left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2} \left[K_s \left(1 + \frac{I}{K_{I2}}\right)^q + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B_k) \quad \text{if } I = n \tag{3.3.126}$$

If inhibitor $I \in N_a$ or N_s, and $I = S_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\,I_{1k}\frac{K_s\left(1+\frac{I}{K_{I2}}\right)^{q}-\frac{S_k q K_s}{K_{I2}}\left(1+\frac{I}{K_{I2}}\right)^{q-1}}{\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma \tag{3.3.127}$$

$$\text{if } I = S_k = n$$

If inhibitor $I \in N_a$ or N_s, and $I = A_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\,I_{1k}\frac{S_k q K_s\left(1+\frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \tag{3.3.128}$$

$$+\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{K_A}{(K_{A-k}+A_k)^2}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k)$$

$$\text{if } I = A_k = n$$

If inhibitor $I \in N_a$ or N_s, and $I = N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s\left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \frac{I}{K_{I2}}\right)^q + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.129)}$$

$$+ \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{K_N}{(K_{N-k} + N_k)^2}\right](\gamma_k B_k)$$

$$\text{if } I = N_k = n$$

If substrate $S_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $S_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{K_{S-k} I_{2k} \left(\frac{S_k}{\nu''_{\kappa S_k}} \frac{\nu'_{\kappa n}}{g_n} \right)}{(K_{S-k} I_{2k} + S_k)^2} \right] \left[\frac{A_k}{K_{A-k} + A_k} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] (\gamma_k B_k) \quad , \quad \text{if } \nu'_{\kappa n} \neq 0 \tag{3.3.130}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species S_k.

If electron acceptor $A_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $A_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k} \right] \left[\frac{K_{A-k} \left(\frac{A_k}{\nu''_{\kappa A_k}} \right) \left(\frac{\nu'_{\kappa n}}{g_n} \right)}{(K_{A-k} + A_k)^2} \right] \left[\frac{N_k}{K_{N-k} + N_k} \right] (\gamma_k B_k) \quad , \quad \text{if } \nu'_{\kappa n} \neq 0 \tag{3.3.131}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species A_k.

If nutrient $N_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species, and $N_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \wp_k I_{1k}\left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{K_{N-k}\left(\frac{N_k}{\nu''_{\kappa N_k}}\right)\left(\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{N-k} + N_k)^2}\right](\gamma_k B_k) \quad , \quad \text{if } \nu'_{\kappa n} \neq \tag{3.3.132}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species N_k.

If inhibitor $I \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n}\right) \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k I$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s \left(1 + \frac{I}{K_{I2}}\right)^{q-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n}\right)}{K_{I2} \left[K_s \left(1 + \frac{I}{K_{I2}}\right)^q + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B \quad \textbf{(3.3.133)}$$

$$\text{if } \nu'_{\kappa n} \neq 0$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species I.

If inhibitant I = substrate $S_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}} \left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n}\right) \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{\left[K_s \left(1 + \frac{I}{K_{I2}}\right)^q - \frac{K_S q I}{K_{I2}} \left(1 + \frac{I}{K_{I2}}\right)^{q-1}\right] \left(\frac{I}{\nu''_{\kappa I}} \frac{\nu'_{\kappa n}}{g_n}\right)}{\left[K_s \left(1 + \frac{I}{K_{I2}}\right)^q + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{N_k}{K_{N-k} +}\right. \quad \textbf{(3.3.134)}$$

$$\text{if } \nu'_{\kappa n} \neq 0$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species $I = S_k$.

If inhibitant I = electron acceptor $A_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left(\frac{I}{\nu''_{\kappa I}}\frac{\nu'_{\kappa n}}{g_n}\right)\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k I$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s\left(1+\frac{I}{K_{I2}}\right)^{q-1}\left(\frac{I}{\nu''_{\kappa I}}\frac{\nu'_{\kappa n}}{g_n}\right)}{K_{I2}\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \quad \textbf{(3.3.135)}$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{K_{A-k}\left(\frac{A_k}{\nu''_{\kappa A_k}}\right)\left(\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{A-k}+A_k)^2}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \quad , \text{ if } \nu'_{\kappa}$$

where $\kappa \in$ NRXNE is the equilibrium reaction defining the formation of equilibrium species I = A_k.

If inhibitant I = nutrient $N_k \in (M_x - K_x)$ or $(M_y - K_y)$, i.e. equilibrium complexed or adsorbed species:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k qK_S\left(1+\frac{I}{K_{I2}}\right)^{q-1}\left(\frac{I}{\nu''_{\kappa I}}\,\frac{\nu'_{\kappa n}}{g_n}\right)}{K_{I2}\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) + \quad \textbf{(3.3.136)}$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{K_{N-k}\left(\frac{N_k}{\nu''_{\kappa N_k}}\right)\left(\frac{\nu'_{\kappa n}}{g_n}\right)}{(K_{N-k}+N_k)^2}\right](\gamma_k B_k) \quad , \quad \text{if } \nu'_{\kappa}$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species $I = N_k$.

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian for columns $n \in N_a$ or N_s is zero.

For columns $n \in K_x + K_y + M_z + M_p$, $j = n + N$, the contribution to the Jacobian from the k-th microbial degradation reaction is:

If substrate $S_k \in K_x + K_y + M_z + M_p$ and $S_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{K_{S-k}I_{2k}}{(K_{S-k}I_{2k}+S_k)^2}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \quad , \qquad \textbf{(3.3.137)}$$

$$\text{if } S_k = n$$

If electron acceptor $A_k \in K_x + K_y + M_z + M_p$ and $A_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{G}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{K_{A-k}}{(K_{A-k} + A_k)^2}\right] \left[\frac{N_k}{K_{N-k} + N_k}\right] (\gamma_k B_k) \,, \qquad \textbf{(3.3.138)}$$

$$\textbf{if } A_k = n$$

If nutrient $N_k \in K_x + K_y + M_z + M_p$ and $N_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{G}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right] \left[\frac{A_k}{K_{A-k} + A_k}\right] \left[\frac{K_{N-k}}{(K_{N-k} + N_k)^2}\right] (\gamma_k B_k) \,, \qquad \textbf{(3.3.139)}$$

$$\textbf{if } N_k = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\,I_{1k}\frac{S_k qK_s\left(1+\frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.140)}$$

$$\textbf{if } I=n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = S_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\frac{p}{K_{I1}}\left(1+\frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf}-\nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{Y}_k\,I_{1k}\frac{K_s\left(1+\frac{I}{K_{I2}}\right)^{q}-\frac{S_k qK_s}{K_{I2}}\left(1+\frac{I}{K_{I2}}\right)^{q-1}}{\left[K_s\left(1+\frac{I}{K_{I2}}\right)^{q}+S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma \qquad \textbf{(3.3.141)}$$

$$\textbf{if } I = S_k = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = A_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s \left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \frac{I}{K_{I2}}\right)^{q} + S_k\right]^2} \left[\frac{A_k}{K_{A-k} + A_k}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.142)}$$

$$+ \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \left[\frac{S_k}{K_{S-k} I_{2k} + S_k}\right]\left[\frac{K_A}{(K_{A-k} + A_k)^2}\right]\left[\frac{N_k}{K_{N-k} + N_k}\right](\gamma_k B_k)$$

$$\text{if } I = A_k = n$$

If inhibitor $I \in K_x + K_y + M_z + M_p$, and $I = N_k$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} =$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k \frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1} [\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k) -$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} \frac{S_k q K_s\left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \frac{I}{K_{I2}}\right)^q + S_k\right]^2} [\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}](\gamma_k B_k) \qquad \textbf{(3.3.143)}$$

$$+ \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} [\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}]\left[\frac{K_N}{(K_{N-k} + N_k)^2}\right](\gamma_k B_k)$$

$$\textbf{if } I = N_k = n$$

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian for columns n $\in K_x + K_y + M_z + M_p$ is zero.

For columns n $\in M_b + M_a$, j = n + N + K_x + K_y + M_z + M_p, the contribution to the Jacobian from the k-th microbial degradation reaction is:

If $B_k \neq I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f} \Gamma_k \mathcal{L}_k I_{1k} [\frac{S_k}{K_{S-k} I_{2k} + S_k}][\frac{A_k}{K_{A-k} + A_k}][\frac{N_k}{K_{N-k} + N_k}] \delta_{mn} \qquad \textbf{(3.3.144)}$$

If $B_k = I$:

$$\frac{\partial(r_f|_k^{biodeg})}{\partial g_n} = \frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\frac{p}{K_{I1}}\left(1 + \frac{I}{K_{I1}}\right)^{p-1}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma$$

$$\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\frac{S_k q K_s\left(1 + \frac{I}{K_{I2}}\right)^{q-1}}{K_{I2}\left[K_s\left(1 + \frac{I}{K_{i2}}\right)^{q} + S_k\right]^2}\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right](\gamma_k B_k) \qquad \textbf{(3.3.145)}$$

$$+\frac{(\nu''_{kf} - \nu'_{kf})}{\gamma_f}\,\Gamma_k\,\mathcal{L}_k\,I_{1k}\left[\frac{S_k}{K_{S-k}I_{2k}+S_k}\right]\left[\frac{A_k}{K_{A-k}+A_k}\right]\left[\frac{N_k}{K_{N-k}+N_k}\right]\delta_{mn}$$

$$\text{if } I = n$$

3.3.3.11 Contribution from microbial respiration

The contribution to the Jacobian from endogenous respiration of the k-th microbial species ($k \in M_B$) is:

$$\frac{\partial r_f^{bioresp}|_k}{\partial g_n} = \frac{\partial}{\partial g_n}\left[\alpha_{kf}\,K_k^d\,B_k\left(\frac{g_f}{\kappa_{kf} + g_f}\right)\right] \qquad \textbf{(3.3.146)}$$

If the species $f \in (N_a + N_s + K_x + K_y + M_z + M_p)$, it will contribute to its own column and to the column corresponding to microbial species k. For this case, the contribution to column n in the Jacobian from maintenance/respiration of the k-th microbial species is:

$$\frac{\partial(r_f^{bioresp})}{\partial g_n} = \alpha_{kf}\,K_k^d\,B_k\left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2}\right]\delta_{fn} \quad , \quad n \in (N_a + N_s + K_x + K_y + M_z + M_p) \qquad \textbf{(3.3.147)}$$

and

$$\frac{\partial(r_f^{bioresp})}{\partial g_n} = \alpha_{kf}\,K_k^d\left[\frac{g_f}{\kappa_{jf} + g_f}\right]\delta_{kn} \quad , \quad n \in M_b + M_a \qquad \textbf{(3.3.148)}$$

If the species $f \in (M_x - K_x)$ or $(M_y - K_y)$, it will contribute to the columns for the components is contains and to the column corresponding to microbial species k. For this case, the

contribution to column n in the Jacobian from maintenance/respiration of the k-th microbial species is:

$$\frac{\partial(r_f^{bioresp})}{\partial g_n} = \alpha_{kf} K_k^d B_k \left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2}\right] \frac{\partial g_f}{\partial g_n} = \alpha_{kf} K_k^d B_k \left[\frac{\kappa_{kf}}{(\kappa_{kf} + g_f)^2}\right] \left[\frac{\nu'_{\kappa n}}{\nu''_{\kappa f}} \frac{g_f}{g_n}\right] , \quad \textbf{(3.3.149)}$$

$$f \in (M_x - K_x) \text{ or } (M_y - K_y) \quad , \quad n \in (N_a + N_s)$$

where $\kappa \in$ NRXNE is the equlibrium reaction defining the formation of equilibrium species f, and

$$\frac{\partial(r_f^{bioresp})}{\partial g_n} = \alpha_{kf} K_k^d \left[\frac{g_f}{\kappa_{jf} + g_f}\right] \delta_{kn} \quad , \quad n \in M_b + M_a \qquad \textbf{(3.3.150)}$$

3.3.4 Treatment of Precipitation/Dissolution

Precipitation/dissolution can be considered with two different approaches. The first one is to consider the concentrations of all precipitated species as independent unknowns in addition to the component species concentrations. This approach has been used in several geochemical equilibrium models such as EQ3/EQ6 (Wolery 1979), PHREEQE (Parkhurst et al. 1980), and some multispecies transport models such as THCC (Carnahan 1986). The second approach is to substitute the mass action equation for each precipitated species into the other equations to eliminate M_p c_k's out of N_a c_k's and M_p p_i's from the set of governing equations. The detail of this type of substitution and the subsequent reduction of the number of equations can be found on pages 56 through 63 in the MINEQL manual (Westall et al. 1976). For every precipitated species eliminated, the number of simultaneous equations can be reduced by two: one mass action equation describing that species and any one mole balance equation containing that species (Westall et al. 1976). However, by using the first approach, one is able to treat mixed chemical equilibrium and chemical kinetics so that precipitation/dissolution kinetics can be simulated. This version of the code uses the first approach to treat precipitation-dissolution reactions.

3.3.5 Treatment of a System Involving Oxidation-Reduction Reactions

Oxidation-reduction reactions are treated by defining electron activity as a component species and considering operational electrons as aqueous components. For multivalent elements, a species in one of the higher oxidation states of an element is chosen as the component species to represent that element. Reduction to a lower oxidation state is described by a half-cell reaction, which is analogous to complexation. The total concentration of "operational" electrons is obtained by summing over all added chemicals that contain lower oxidation state elements. The

mole balance equation for operational electrons is different from those for other aqueous components in that the first term on the right-hand side is set to zero and c_e in all other terms is interpreted as the activity of the electrons rather than the concentration of free electrons.

Mathematically, operational electrons can be treated just as other aqueous components. Numerically, however, this component requires special attention. Because the electron activity can span over at least 40 orders of magnitude, an ill-conditioned matrix often results when this equation is solved simultaneously with other mole balance equations with the Newton-Raphson method. To circumvent this difficulty, a split scheme is used in this version of the code. In this split scheme, the mole balance equation for operational electrons is solved with a modified bisection method (Forsythe et al. 1977), while all other mole balance equations are solved simultaneously with the Newton-Raphson method. This split scheme is particularly effective for reducing conditions when the solution fails to converge without the split scheme.

3.3.6 Treatment of a System Involving Acid-Base Reactions

Acid-base reactions are treated by defining hydrogen activity as a component species. The "excess" hydrogen is subject to transport as are other aqueous components. The mole balance equation for the excess hydrogen is different from those for other aqueous components. The first term on the right-hand side of Equation (3.3.1) is written as c_H/γ_H where γ_H is the activity coefficient of the free hydrogen ion. In all other terms, C_k is replaced by c_H and is interpreted as the activity of hydrogen rather than the concentration of free hydrogen. If an (OH) appears in any species, the stoichiometric coefficient of the hydrogen in that species is set to -1. If n (OH)s appear in any species, the stoichiometric coefficient of hydrogen in that species is set to -n.