Chemistry Implementation in PFLOTRAN: Colloids, Surface Complexation, Ion Exchange, Biogeochemistry with Monode Kinetics, Precipitation/Dissolution, Solid Solutions, Species-Dependent Diffusion, Pitzer Model, Multiple Interacting Continua...

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1   Reading the Thermodynamic Database

1.1   Database Format

The thermodynamic database stores all chemical reaction properties (equilibrium constant $\log K_r$, reaction stoichiometry ν_{ir}, species valence z_i, Debye parameter a_i, mineral molar volume $\overline{V}_m$, and formula weight w_i) used in PFLOTRAN, with the exception of ion exchange. Reactions included in the database consist of aqueous complexation, mineral precipitation and dissolution, gaseous reactions, and surface complexation. The database is divided in five sections: database primary species, aqueous complex reactions, gaseous reactions, mineral reactions, and surface complexation. The format of the database is set up as shown in Table 1. Equilibrium constants are stored at the temperatures: $\{0, 25, 60, 100, 150, 200, 250, 300\}°$C. In the standard database the equilibrium constants are interpolated using a least squares fit to the Meier-Kelly expansion

$$\log K = c_{-1} \ln T + c_0 + c_1 T + \frac{c_2}{T} + \frac{c_3}{T^2}, \tag{1.1}$$

with coefficients c_i. As a consequence the entries in the database are not exactly reproduced at the corresponding temperatures.

Table 1: Thermodynamic database format.

Primary Species:	name, a_0, z, w
Secondary Species:	name, nspec, (ν(n), name(n), n=1, nspec), $\log K$(1:8) a_0, z, w
Gaseous Species:	name, $\overline{V}$, nspec, (ν(n), name(n), n=1, nspec), $\log K$(1:8), w
Minerals:	name, $\overline{V}$, nspec, (ν(n), name(n), n=1, nspec), $\log K$(1:8), w
Surface Complexes:	>name, nspec, (ν(n), name(n), n=1, nspec), $\log K$(1:8), z, w

     Redox reactions in the standard database are usually written in terms of $O_{2(g)}$. Complexation reactions involving redox sensitive species are written in such a manner as to preserve the redox state.

1.2   Primary Species: Transforming the Database

The user must first select a set of aqueous primary species in terms of which the reactions in the database are then transformed. This is typically carried out as follows. For an arbitrary reaction corresponding to an aqueous complex that is read from the database with the form

$$\varnothing \; \rightleftharpoons \; \sum_i \nu_{ir} \mathcal{A}_i, \tag{1.2}$$

with $\varnothing$ representing the null species, the species are partitioned into primary and secondary species leading to the reaction

$$\varnothing \; \rightleftharpoons \; \sum_j \nu_{jr} \mathcal{A}_j + \sum_i \nu_{ir} \mathcal{A}_i. \tag{1.3}$$

Because, by construction, the matrix ν_{ir} is nonsingular, it can be inverted to give the canonical form

$$\sum_j \widetilde{\nu}_{ji} \mathcal{A}_j \; \rightleftharpoons \; \mathcal{A}_i, \tag{1.4}$$

where

$$\widetilde{\nu}_{ji} \; = \; - \sum_r \nu_{jr} (\nu^{-1})_{ri}. \tag{1.5}$$

These reactions are presumed to apply to both aqueous complexes and gaseous reactions. For mineral reactions, the database form

$$\sum_j \nu_{jm} \mathcal{A}_j + \sum_i \nu_{im} \mathcal{A}_i \; \rightleftharpoons \; \mathcal{M}_m, \tag{1.6}$$

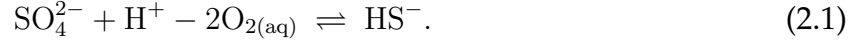is transformed by eliminating the secondary species $\mathcal{A}_i$ using Eqn.(1.4) to give

$$\sum_j \widetilde{\nu}_{jm} \mathcal{A}_j \; \rightleftharpoons \; \mathcal{M}_m, \tag{1.7}$$

where

$$\widetilde{\nu}_{jm} \; = \; \nu_{jm} + \sum_i \widetilde{\nu}_{ji} \nu_{im}. \tag{1.8}$$

2   Homogeneous Reactions

Homogeneous reactions taking place within the aqueous phase can either be governed by local equilibrium relations or by kinetics as, for example, in sulfate reduction described by the reaction

$$\mathrm{SO}_4^{2-} + \mathrm{H}^+ - 2\mathrm{O}_{2(\mathrm{aq})} \;\rightleftharpoons\; \mathrm{HS}^-. \tag{2.1}$$

In this reaction sulfur is transformed through electron transfer from S^{VI} to $\mathrm{S}^{-\mathrm{II}}$. Here it is necessary to ensure that complexes do not mix different redox states together. For example, the reactions

$$\mathrm{SO}_4^{2-} + \mathrm{H}^+ \;\rightleftharpoons\; \mathrm{HSO}_4^-, \tag{2.2}$$

and

$$\mathrm{HS}^- + \mathrm{H}^+ \;\rightleftharpoons\; \mathrm{H}_2\mathrm{S}_{(\mathrm{aq})}. \tag{2.3}$$

preserve the sulfur redox state and can be consider to be in local equilibrium.

Local equilibrium reactions can always be written in the canonical form

$$\sum_j \nu_{ji}\mathcal{A}_j \;\rightleftharpoons\; \mathcal{A}_i. \tag{2.4}$$

Kinetic reactions depend on the specific mechanism and are assumed to have the general form

$$\varnothing \;\rightleftharpoons\; \sum_i \nu_{ir}\mathcal{A}_i. \tag{2.5}$$

Breaking this reaction out into primary and secondary species gives

$$\varnothing \;\rightleftharpoons\; \sum_j \nu_{jr}\mathcal{A}_j + \sum_i \nu_{ir}\mathcal{A}_i. \tag{2.6}$$

Eliminating the secondary species $\mathcal{A}_i$ yields the reactions

$$\varnothing \;\rightleftharpoons\; \sum_j \widetilde{\nu}_{jr}\mathcal{A}_j, \tag{2.7}$$

where

$$\widetilde{\nu}_{jr} \;=\; \nu_{jr} + \sum_i \nu_{ji}\nu_{ir}. \tag{2.8}$$

The transport equations in the presence of homogeneous reactions take the form

$$\frac{\partial}{\partial t}\varphi C_j + \boldsymbol{\nabla} \cdot \boldsymbol{F}_j \;=\; -\sum_i \nu_{ji}I_i + \sum_r \widetilde{\nu}_{jr}I_r, \tag{2.9}$$

for primary species, and

$$\frac{\partial}{\partial t}\varphi C_i + \boldsymbol{\nabla} \cdot \boldsymbol{F}_i \;=\; I_i, \tag{2.10}$$

for secondary species. Noting that the rates I_i for local equilibrium reactions are determined through algebraic mass action equations providing the concentrations of secondary species, these rates can be eliminated to yield the primary species transport equations

$$\frac{\partial}{\partial t} \varphi \Psi_j + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j = \sum_r \widetilde{\nu}_{jr} I_r, \tag{2.11}$$

where the total concentration Ψ_j and flux $\boldsymbol{\Omega}_j$ are defined by

$$\Psi_j = C_j + \sum_i \nu_{ji} C_i, \tag{2.12}$$

and

$$\boldsymbol{\Omega}_j = \boldsymbol{F}_j + \sum_i \nu_{ji} \boldsymbol{F}_i. \tag{2.13}$$

The flux $\boldsymbol{F}_k$ has the usual form with contributions from advection and diffusion/dispersion given by

$$\boldsymbol{F}_k = \boldsymbol{q} C_k - \varphi D \boldsymbol{\nabla} C_k, \tag{2.14}$$

with diffusion/dispersion coefficient D assumed to be identical for all species. This condition is relaxed in the section below on species-dependent diffusion. The concentration of the ith secondary species is given by the relation

$$m_i = \gamma_i^{-1} \prod_j \left(\gamma_j m_j \right)^{\nu_{ji}}, \tag{2.15}$$

where the molality m_l is related to molarity C_l by the approximate expression

$$C_l = \rho_w m_l, \tag{2.16}$$

where ρ_w denotes the density of pure water. Activity coefficients γ_l are obtained from the Debye-Hückel algorithm

$$\log \gamma_i = -\frac{z_i^2 A \sqrt{\mathcal{I}}}{1 + B \, \mathring{a}_i \, \sqrt{I}} + \dot{b} \mathcal{I}, \tag{2.17}$$

and the Davies algorithm defined by the expression

$$\log \gamma_i = -\frac{z_i^2}{2} \left[\frac{\sqrt{\mathcal{I}}}{1 + \sqrt{\mathcal{I}}} - 0.3 \mathcal{I} \right]. \tag{2.18}$$

The ionic strength $\mathcal{I}$ is defined by

$$\mathcal{I} = \frac{1}{2} \sum_j z_j^2 m_j + \frac{1}{2} \sum_i z_i^2 m_i, \tag{2.19}$$

with molality m_l and valence z_l. In the case of the Debye-Hückel and Davies algorithms, the activity coeffients are determined by solving a nonlinear equation for the ionic strength. For high ionic strength solutions, the Pitzer model must be used which is described in a later section.

3   Mineral Precipitation/Dissolution Reactions

Mineral precipitation/dissolution reactions are assumed to have the form

$$\sum_j \nu_{jm} \mathcal{A}_j \; \rightleftharpoons \; \mathcal{M}_m. \tag{3.1}$$

The rate law based on transition state theory has the general form

$$\widehat{I}_m \;=\; -\text{sgn}_m s_m \left(\sum_l \mathcal{P}_{ml} k_{ml} \right) \left| 1 - (K_m Q_m)^{\frac{1}{\sigma_m}} \right|^{\beta_m}, \tag{3.2}$$

$$=\; -\text{sgn}_m s_m \left(\sum_l \mathcal{P}_{ml} k_{ml} \right) \left| 1 - \mathrm{e}^{-A_m/(\sigma_m RT)} \right|^{\beta_m}, \tag{3.3}$$

where the affinity A_m is defined as

$$A_m \;=\; -RT \ln K_m Q_m, \tag{3.4}$$

the quantity sgn_m denotes the sign of the affinity factor

$$\text{sgn}_m \;=\; \frac{1 - (K_m Q_m)^{1/\sigma_m}}{\left| 1 - (K_m Q_m)^{1/\sigma_m} \right|}, \tag{3.5}$$

where K_m represents the equilibrium constant, Q_m denotes the ion activity product

$$Q_m \;=\; \prod_j \left(\gamma_j C_j \right)^{\nu_{jm}}, \tag{3.6}$$

the prefactor $\mathcal{P}_{ml}$ is defined as the product of contributions from primary and secondary species:

$$\mathcal{P}_{ml} \;=\; \left[\prod_{j=1}^{N_c} \frac{a_j^{\alpha_{jl}^m}}{1 + K_{jl} a_j^{\beta_{jl}^m}} \right] \left[\prod_{i=1}^{N_{cx}} \frac{a_i^{\alpha_{il}^m}}{1 + K_{il} a_i^{\beta_{il}^m}} \right], \tag{3.7}$$

k_{ml} denotes the kinetic rate constant for the lth parallel reaction, s_m denotes the specific mineral surface area participating in the reaction, σ_m denotes Tempkin's constant, a_i represents the activity of the ith species, and α_{jl}^m, α_{il}^m are a constants. A transport-limited form of the rate law can be devised according to the expression

$$\widehat{I}_m \;=\; -s_m \sum_l \mathcal{P}_{ml} k_{ml} \left[\frac{1 - (K_m Q_m)^{1/\sigma_m}}{1 + \dfrac{k_{ml}}{r_m^{\text{lim}}} (K_m Q_m)^{1/\sigma_m}} \right], \tag{3.8}$$

with transport-limited rate r_{lim}. In the limit $K_m Q_m \to \infty$, the rate becomes

$$\lim_{K_m Q_m \to \infty} \widehat{I}_m \;=\; r_m^{\text{lim}} s_m \sum_l \mathcal{P}_{ml}. \tag{3.9}$$

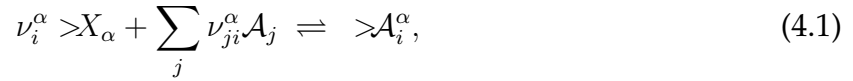Adding mineral precipitation/dissolution to the mass conservation equations yields

$$\frac{\partial}{\partial t}\varphi\Psi_j + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j = \sum_r \widetilde{\nu}_{jr}I_r - \sum_m \nu_{jm}I_m, \tag{3.10}$$

$$\frac{\partial\varphi_m}{\partial t} = \overline{V}_m I_m. \tag{3.11}$$

4 Sorption

4.1 Surface Complexation Reactions

Surface complexation reactions are assumed to have the general form

$$\nu_i^\alpha >X_\alpha + \sum_j \nu_{ji}^\alpha \mathcal{A}_j \;\rightleftharpoons\; >\mathcal{A}_i^\alpha, \tag{4.1}$$

for surface complex $>\mathcal{A}_i^\alpha$ and empty surface site $>X_\alpha$ on surface sites designated by α. Each surface site α corresponds to a particular type of site s_m associated with a particular mineral $\mathcal{M}_m$. Thus $\alpha = (m,\, s_m)$ can be represented by two indices m and s_m. Conservation of surface sorption sites is expressed as

$$\omega_\alpha = S_X^\alpha + \sum_i \nu_i^\alpha S_i^\alpha, \tag{4.2}$$

where the surface site concentration ω_α is given by

$$\omega_\alpha = \frac{N_\alpha}{V} = \frac{N_\alpha}{A_m}\frac{A_m}{M_m}\frac{M_m}{V_m}\frac{V_m}{V} = \eta_m^\alpha \mathcal{A}_m \rho_m \varphi_m. \tag{4.3}$$

The reaction rate:

$$I_i^\alpha = k_i^{\alpha f}(S_X^\alpha)^{\nu_i^\alpha}\prod_j a_j^{\nu_{ji}^\alpha} - k_i^{\alpha b}S_i^\alpha \tag{4.4}$$

The mass conservation equations in the presence of surface complexation reactions have the form

$$\frac{\partial}{\partial t}\varphi\Psi_j + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j = -\sum_{i\alpha}\nu_{ji}^\alpha I_i^\alpha, \tag{4.5}$$

$$\frac{\partial S_i^\alpha}{\partial t} = I_i^\alpha, \tag{4.6}$$

$$\frac{\partial S_X^\alpha}{\partial t} = -\sum_i \nu_i^\alpha I_i^\alpha. \tag{4.7}$$

Eliminating the reaction rates I_i^α leads to the equations

$$\frac{\partial}{\partial t}\left\{\varphi\Psi_j + \sum_{i\alpha}\nu_{ji}^\alpha S_i^\alpha\right\} + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j = 0. \tag{4.8}$$

4.1.1 Site Conservation

Note that the sorption site concentration ω_α is conserved with respect to surface complexation reactions:

$$\left(\frac{\partial \omega_\alpha}{\partial t}\right)_{\substack{surf.\\cmplx}} = \frac{\partial S_X^\alpha}{\partial t} + \sum_i \nu_i^\alpha \frac{\partial S_i^\alpha}{\partial t} = 0. \tag{4.9}$$

However, precipitation/dissolution reactions can lead to a change in ω_α:

$$\left(\frac{\partial \omega_\alpha}{\partial t}\right)_{\substack{precip.\\/diss.}} = \eta_m^\alpha \mathcal{A}_m \rho_m \frac{\partial \varphi_m}{\partial t}, \tag{4.10}$$

$$= \eta_m^\alpha \mathcal{A}_m \rho_m \overline{V}_m I_m. \tag{4.11}$$

4.1.2 Electric Double Layer

Diffuse layer concentration C_i^m associated with the surface of the mth mineral is related to the bulk concentration C_i^b through the Boltzmann factor

$$C_i^m(x) = C_i^b \, e^{-z_i F \Phi_m(x)/RT}, \tag{4.12}$$

where Φ_m denotes the electric potential resulting from sorption on the surface of the mth mineral. The potential satisfies the Poisson equation

$$\frac{d^2 \Phi_m}{dx^2} = -\frac{1}{\epsilon \epsilon_0} \rho_m(x). \tag{4.13}$$

In this equation ϵ_0 denotes the permitivity of free space, ϵ represents the dielectric constant of pure water, and ρ_m refers to the charge density of the diffuse layer defined by

$$\rho_m(x) = F \sum_i z_i C_i^m. \tag{4.14}$$

Table 2: Fundamental constants at 25°C.

N_A	6.023×10^{23}	mol^{-1}
ϵ	78.5	
ϵ_0	8.854×10^{-14}	Coul/(Vcm)
F	96485	Coul/mol

The sorbed surface charge σ_m is related to the bulk concentration and potential by the expression

$$\sigma_m = \sqrt{2 \epsilon \epsilon_0 RT \sum_i C_i^b \left(e^{-z_i F \Phi_m^0/RT} - 1\right)}, \tag{4.15}$$

where Φ_m^0 denotes the value of the potential at the mineral surface. For a $z{:}z$ electrolyte with concentration C_0 the expression for the surface charge reduces to

$$\sigma_m = \sqrt{8\epsilon\epsilon_0 RTC_0}\,\sinh\left[\frac{zF\Phi_m^0}{RT}\right].$$

(4.16)

This result is obtained from the identity

$$\sinh\left[\frac{x}{2}\right] = \frac{1}{2}\sqrt{e^x + e^{-x} - 2}.$$

(4.17)

The volumetric sorbed charge density q_m is given by the sum of sorbed ion concentrations multiplied by their respective valencies as

$$q_m = F\sum_{s\alpha} z_{s\alpha}^m \overline{C}_{s\alpha}^m,$$

(4.18)

where the sum is taken over all sorbed species on all sorption sites corresponding to the mth mineral. The relation between volumetric charge density q_m and surface charge density σ_m can be derived as follows

$$\begin{aligned}
q_m &= \frac{Q_m}{V}, \\
&= \frac{Q_m}{A_m}\frac{A_m}{M_m}\frac{M_m}{N_m}\frac{N_m}{V_m}\frac{V_m}{V}, \\
&= \sigma_m \mathcal{A}_m W_m \overline{V}_m^{-1}\phi_m.
\end{aligned}$$

(4.19)

Therefore

$$\sigma_m = \frac{Q_m}{A_m} = \frac{q_m}{\mathcal{A}_m W_m \overline{V}_m^{-1}\phi_m}.$$

(4.20)

In the presence of the electric double layer potential the unoccupied site concentration $\overline{C}_\alpha^m$ becomes

$$\overline{C}_\alpha^m = \frac{\omega_\alpha^m}{1 + \sum_s K_{s\alpha}^m \prod_j \left(\gamma_j C_j \mathcal{P}^{z_j}\right)^{\nu_{js}^{m\alpha}}},$$

(4.21)

and the sorbed concentration is given by

$$\overline{C}_{s\alpha}^m = \frac{\omega_\alpha^m K_{s\alpha}^m \prod_j \left(\gamma_j C_j \mathcal{P}^{z_j}\right)^{\nu_{js}^{m\alpha}}}{1 + \sum_{s'} K_{s'\alpha}^m \prod_j \left(\gamma_j C_j \mathcal{P}^{z_j}\right)^{\nu_{js'}^{m\alpha}}},$$

(4.22)

where the factor $\mathcal{P}$ is defined by

$$\mathcal{P} = e^{-F\Phi_m^0/RT}.$$

(4.23)

Noting that

$$\prod_j \mathcal{P}^{z_j \nu_{js}^{m\alpha}} = \mathcal{P}^{\sum_j z_j \nu_{js}^{m\alpha}} = \mathcal{P}^{z_{s\alpha}^m},$$

(4.24)

using the identity

$$\sum_j z_j \nu_{js}^{m\alpha} = z_{s\alpha}^m, \tag{4.25}$$

these relations become

$$\overline{C}_\alpha^m = \frac{\omega_\alpha^m}{1 + \sum_s K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j (\gamma_j C_j)^{\nu_{js}^{m\alpha}}}, \tag{4.26}$$

and the sorbed concentration is given by

$$\overline{C}_{s\alpha}^m = \frac{\omega_\alpha^m K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j (\gamma_j C_j)^{\nu_{js}^{m\alpha}}}{1 + \sum_{s'} K_{s'\alpha}^m \mathcal{P}^{z_{s'\alpha}^m} \prod_j (\gamma_j C_j)^{\nu_{js'}^{m\alpha}}}. \tag{4.27}$$

In the presence of the electric double layer potential the expression for the kinetic reaction rate based on a pseudo-kinetic description of sorption takes the form

$$I_{s\alpha}^m = k_{s\alpha}^{fm} \frac{\omega_\alpha^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}}}{1 + \sum_{s'} K_{s'\alpha}^m \mathcal{P}^{z_{s'\alpha}^m} \prod_j a_j^{\nu_{js'}^{m\alpha}}} - k_{s\alpha}^{bm} \overline{C}_{s\alpha}^m. \tag{4.28}$$

The potential at the mth mineral surface may be obtained by solving a nonlinear equation equating the diffuse layer charge to the sorbed charge. Substituting for q_m the surface charge density can be expressed as

$$\sigma_m = \frac{F}{N_A} \sum_\alpha \frac{\eta_\alpha^m}{\mathcal{D}_\alpha^m} \sum_s z_{s\alpha}^m K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}}, \tag{4.29}$$

where

$$\mathcal{D}_\alpha^m = 1 + \sum_s K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}}. \tag{4.30}$$

With this result the following equation is obtained for the potential

$$\begin{aligned} f(\Phi_m^0) &= \sqrt{\sum_i C_i^b (\mathcal{P}^{z_i} - 1)} - \frac{\sigma_m}{\sqrt{2RT\epsilon\epsilon_0}}, \\ &= \sqrt{\sum_i C_i^b (\mathcal{P}^{z_i} - 1)} - \frac{1}{\sqrt{2RT\epsilon\epsilon_0}} \left[\frac{1}{N_A} \sum_\alpha \frac{\eta_\alpha^m}{\mathcal{D}_\alpha^m} \sum_s z_{s\alpha}^m K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}} \right], \\ &= 0. \end{aligned} \tag{4.31}$$

Setting $\xi = F\Phi_m^0/RT$, the Jacobian is found to be

$$\frac{df}{d\xi} = -\frac{\sum_i z_i C_i^b \mathcal{P}^{z_i}}{2\sqrt{\sum C_i^b \mathcal{P}^{z_i}}} - \frac{1}{\sqrt{2RT\epsilon\epsilon_0}} \frac{d\sigma_m}{d\xi}, \tag{4.32}$$

with

$$\frac{d\sigma_m}{d\xi} = -\frac{F}{N_A} \sum_\alpha \frac{\eta_\alpha^m}{\mathcal{D}_\alpha^m} \left\{ \sum_s (z_{s\alpha}^m)^2 K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}} \right.$$

$$\left. -\frac{1}{\mathcal{D}_\alpha^m} \left(\sum_s z_{s\alpha}^m K_{s\alpha}^m \mathcal{P}^{z_{s\alpha}^m} \prod_j a_j^{\nu_{js}^{m\alpha}} \right)^2 \right\}. \tag{4.33}$$

The potential is computed from the Newton-Raphson algorithm

$$\xi_{k+1} = \xi_k - \frac{f_k}{df_k/d\xi}. \tag{4.34}$$

4.1.3 Bulk Properties

In many cases surface complexation properties are specified in terms of bulk properties of the porous medium: η_b, $\mathcal{A}_b$, ρ_b, φ. To represent this situation a fictitious mineral $\mathcal{M}_{m_0}$ may be entered with properties that reproduce the bulk density of the system by taking $W_{m_0} \overline{V}_{m_0}^{-1} \varphi_{m_0} = \rho_b$.

4.1.4 Implementation

Implementing surface complexation involves summing over complexes associated with different sites on different minerals. The structure of the sum has the form

$$\sum_{i\alpha} S_i^\alpha = \sum_{m=1}^{M} \sum_{s=s_1(m)}^{s_2(m)} \sum_{i=i_1(l)}^{i_2(i)} S_i^{ms} \tag{4.35}$$

Local Equilibrium:

$$S_i^\alpha = K_i^\alpha Q_i^\alpha (S_X^\alpha)^{\nu_i^\alpha}, \tag{4.36}$$

$$Q_i^\alpha = \prod_j a_j^{\nu_{ji}^\alpha}, \tag{4.37}$$

$$\omega_\alpha = S_X^\alpha + \sum_i \nu_i^\alpha (S_X^\alpha)^{\nu_i^\alpha} K_i^\alpha Q_i^\alpha. \tag{4.38}$$

Jacobian:

$$C_l \frac{\partial S_X}{\partial C_l} = -\frac{\sum \nu_{li} \nu_i S_i}{1 + \frac{1}{S_X} \sum \nu_i^2 S_i} \tag{4.39}$$

$$C_l \frac{\partial S_i}{\partial C_l} = \nu_{li} S_i + \nu_i S_i \frac{C_l}{S_X} \frac{\partial S_X}{\partial C_l}, \tag{4.40}$$

$$= \nu_{li} S_i - \nu_i S_i \frac{\sum\limits_{i'} \nu_{li'} \nu_i S_{i'}}{S_X + \sum\limits_{i'} \nu_{i'}^2 S_{i'}}, \tag{4.41}$$

$$= S_i \left\{ \nu_{li} - \frac{\nu_i \sum\limits_{i'} \nu_{li'} \nu_{i'} S_{i'}}{S_X + \sum\limits_{i'} \nu_{i'}^2 S_{i'}} \right\} \tag{4.42}$$

$$C_l \frac{\partial \Psi_j^S}{\partial C_l} = C_l \sum_i \nu_{ji} \frac{\partial S_i}{\partial C_l}, \tag{4.43}$$

$$= \sum_i \nu_{ji} S_i \left[\nu_{li} - \frac{\nu_i \sum_{i'} \nu_{li'} \nu_{i'} S_{i'}}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}} \right], \tag{4.44}$$

$$= \sum_i \nu_{ji} \nu_{li} S_i - \frac{1}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}} \left(\sum_i \nu_{ji} \nu_i S_i \right) \left(\sum_{i'} \nu_{li'} \nu_{i'} S_{i'} \right) \tag{4.45}$$

Special Case: $\nu_i^\alpha = 1$

$$\omega_\alpha = S_X^\alpha + \sum_i S_i^\alpha \tag{4.46}$$

$$S_X^\alpha = \frac{\omega_\alpha}{1 + \sum_i K_i^\alpha Q_i^\alpha} \tag{4.47}$$

$$S_i^\alpha = \frac{\omega_\alpha K_i^\alpha Q_i^\alpha}{1 + \sum_{i'} K_{i'}^\alpha Q_{i'}^\alpha} \tag{4.48}$$

$$C_l \frac{\partial S_i}{\partial C_l} = \nu_{li} S_i - \frac{\omega Q_i^\alpha}{\left(1 + \sum Q_{i'}\right)^2} \sum \nu_{li'} Q_{i'}^\alpha, \tag{4.49}$$

$$= \nu_{li} S_i - S_i \frac{1}{\omega} \sum \nu_{li'} S_{i'}, \tag{4.50}$$

$$= S_i \left[\nu_{li} - \frac{1}{\omega} \sum \nu_{li'} S_{i'} \right]. \tag{4.51}$$

$$C_l \frac{\partial \Psi_j^S}{\partial C_l} = C_l \sum_i \nu_{ji} \frac{\partial S_i}{\partial C_l}, \tag{4.52}$$

$$= \sum_i \nu_{ji} S_i \left[\nu_{li} - \frac{1}{\omega} \sum \nu_{li'} S_{i'} \right], \tag{4.53}$$

$$= \sum_i \nu_{ji} \nu_{li} S_i - \frac{1}{\omega} \left(\sum \nu_{ji} S_i \right) \left(\sum \nu_{li'} S_{i'} \right). \tag{4.54}$$

Residual:

$$R_j \mathrel{+}= \sum_i \nu_{ji} I_i V_n \tag{4.55}$$

$$R_i = \left(S_i^{k+1} - S_i^k \right) \frac{V_n}{\Delta t} - I_i V_n \tag{4.56}$$

$$R_X = \left(S_X^{k+1} - S_X^k \right) \frac{V_n}{\Delta t} + \sum_i I_i V_n \tag{4.57}$$

Jacobian:

$$\frac{\partial R_j}{\partial C_l} \mathrel{+}= \sum_i \nu_{ji} \frac{\partial I_i}{\partial C_l} V_n \tag{4.58}$$

$$\frac{\partial R_j}{\partial S_i} \mathrel{+}= \sum_i \nu_{ji} \frac{\partial I_i}{\partial S_i} V_n \tag{4.59}$$

$$\frac{\partial R_j}{\partial S_X} \mathrel{+}= \sum_i \nu_{ji} \frac{\partial I_i}{\partial S_X} V_n \tag{4.60}$$

$$\frac{\partial R_i}{\partial C_l} = -\frac{\partial I_i}{\partial C_l} V_n \tag{4.61}$$

$$\frac{\partial R_i}{\partial S_i} = \frac{V_n}{\Delta t} - \frac{\partial I_i}{\partial S_i} V_n \tag{4.62}$$

$$\frac{\partial R_i}{\partial S_X} = -\frac{\partial I_i}{\partial S_X} V_n \tag{4.63}$$

$$\frac{\partial R_X}{\partial C_l} = \sum_i \frac{\partial I_i}{\partial C_l} V_n \tag{4.64}$$

$$\frac{\partial R_X}{\partial S_i} = \sum_i \frac{\partial I_i}{\partial S_i} V_n \tag{4.65}$$

$$\frac{\partial R_X}{\partial S_X} = \frac{V_n}{\Delta t} + \sum_i \frac{\partial I_i}{\partial S_X} V_n \tag{4.66}$$

$$C_l \frac{\partial I_i}{\partial C_l} = \nu_{ji} k_i^f S_X Q_i \tag{4.67}$$

$$\frac{\partial I_i}{\partial S_i} = -k_i^b \tag{4.68}$$

$$\frac{\partial I_i}{\partial S_X} = k_i^f Q_i \tag{4.69}$$

4.1.5   Input File Structure

F77 programing style:

```
SURFACE_COMPLEX
min1 area1
  >fsite1 den1
    >srf1
    >srf2
    >srf3
    END
  >fsite2 den2
    >srf4
```

```
    >srf5
      END
   END
min2 area2
  >fsite3 den3
     >srf6
     >srf7
     END
   END
END
```

F90 object oriented programming style:

```
SORPTION
  SURFACE_COMPLEXATION_RXN
    MINERAL min1
    SITE    >fsite1 den1
    SURFACE_COMPLEXES
    >srf1
    >srf2
    >srf3
    END
  END
  SURFACE_COMPLEXATION_RXN
    MINERAL min1
    SITE    >fsite2 den2
    SURFACE_COMPLEXES
    >srf4
    >srf5
    END
  END
  SURFACE_COMPLEXATION_RXN
    MINERAL min2
    SITE    >fsite3 den3
    SURFACE_COMPLEXES
    >srf6
    >srf7
    END
  END
END
```

4.2 Ion Exchange Reactions

Ion exchange reactions may be represented either in terms of bulk- or mineral-specific rock properties. Changes in bulk sorption properties can be expected as a result of mineral reactions. However, only the mineral-based formulation enables these effects to be captured in the model. The bulk rock sorption site concentration ω_α, in units of moles of

sites per bulk sediment volume (mol/dm^3), is related to the bulk cation exchange capacity Q_α (mol/kg) by the expression

Ion exchange reactions can be expressed in the form

$$\frac{1}{z_j}\mathcal{A}_j + \frac{1}{z_i}X^\alpha_{z_i}\mathcal{A}_i \;\rightleftharpoons\; \frac{1}{z_i}\mathcal{A}_i + \frac{1}{z_j}X^\alpha_{z_j}\mathcal{A}_j, \tag{4.70}$$

with valencies z_j, z_i of cations $\mathcal{A}_j$ and $\mathcal{A}_i$, respectively. The reference cation is denoted by the subscript j and the subscript $i \neq j$ represents all other cations. The mass action equation is given by

$$K_{ji} \;=\; \left(\frac{X^\alpha_j}{a_j}\right)^{1/z_j} \left(\frac{a_i}{X^\alpha_i}\right)^{1/z_i}, \tag{4.71}$$

where, using the Gaines-Thomas convention, the equivalent fractions X^α_k are defined by

$$X^\alpha_k = \frac{z_k S^\alpha_k}{\sum_l z_l S^\alpha_l} = \frac{z_k}{\omega_\alpha} S^\alpha_k, \tag{4.72}$$

with

$$\sum_k X^\alpha_k = 1, \tag{4.73}$$

The site concentration ω_α is defined by

$$\omega_\alpha = \sum_k z_k S^\alpha_k, \tag{4.74}$$

where ω_α is related to the cation exchange capacity Q_α (CEC) by the expression

$$\omega_\alpha = (1 - \varphi)\rho_s Q_\alpha, \tag{4.75}$$

with solid density ρ_s and porosity φ.

For equivalent exchange ($z_j = z_i = z$), an explicit expression exists for the sorbed concentrations given by

$$S^\alpha_j \;=\; \frac{\omega_\alpha}{z} \frac{k^\alpha_j C_j}{\sum k^\alpha_l C_l}, \tag{4.76}$$

where C_k denotes the kth cation concentration. This expression follows directly from the mass action equations and conservation of exchange sites.

4.2.1   Kinetic Formulation of Ion Exchange

The simplest approach to developing a kinetic formulation of ion exchange is to assume simple reaction kinetics in which the rate is equal to the difference between the forward and backward rates with concentrations raised to powers of the reaction stoichiometric coefficients. This form of the rate law, however, is not unique (with the exception of monovalent exchange) and depends on the stoichometry used to write the exchange reaction. As long as the same final equilibrium state is obtained, the correctness of the form of the rate law cannot be ascertained without further experiment effort.

4.2.2   Kinetic Rate Laws

The kinetic reaction rate for reaction (4.70) has the following form

$$I_{ji}^\alpha = k_{ji}^f a_j^{1/z_j} (X_i^\alpha)^{1/z_i} - k_{ji}^b a_i^{1/z_i} (X_j^\alpha)^{1/z_j}. \tag{4.77}$$

The ratio of the forward and backward rate constants are equal to the equilibrium constants according to

$$K_{ji} = \frac{k_{ji}^f}{k_{ji}^b}. \tag{4.78}$$

4.2.3   Mass Conservation Relations

Mass conservation equations including homogeneous aqueous reactions, mineral precipitation and dissolution, and ion exchange with the form (4.70) using cation $\mathcal{A}_j$ as reference cation have the form

$$\frac{\partial}{\partial t}\varphi\Psi_j + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j = -\frac{1}{z_j}\sum_\alpha\sum_{k\neq j} I_{jk}^\alpha - \sum_m \nu_{jm}I_m + \sum_r \widetilde{\nu}_{jr}I_r, \tag{4.79a}$$

$$\frac{\partial}{\partial t}\varphi\Psi_k + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_k = \frac{1}{z_k}\sum_\alpha I_{jk}^\alpha - \sum_m \nu_{km}I_m + \sum_r \widetilde{\nu}_{kr}I_r, \tag{4.79b}$$

for aqueous primary species with mineral reaction rates I_m. Sorbed concentrations obey the conservation equations

$$\frac{\partial S_j^\alpha}{\partial t} = \frac{1}{z_j}\sum_{i\neq j} I_{ji}^\alpha, \tag{4.80a}$$

$$\frac{\partial S_k^\alpha}{\partial t} = -\frac{1}{z_k}I_{jk}^\alpha. \tag{4.80b}$$

Eliminating the exchange rates from the primary species equations gives the equation

$$\frac{\partial}{\partial t}\left(\varphi\Psi_j + \sum_\alpha S_j^\alpha\right) + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j = -\sum_m \nu_{jm}I_m + \sum_r \widetilde{\nu}_{jr}I_r, \tag{4.81}$$

valid for all exchangeable cations.

It follows that exchange sites are conserved according to the result

$$\frac{\partial \omega_\alpha}{\partial t} = 0. \tag{4.82}$$

implying that the cation exchange capacity of the porous medium is constant with respect to exchange reactions as must be the case.

4.2.4 Finite Difference Form

For a system with N_{ex} exchangeable cations, in a kinetic formulation there are $2 \times N_{\text{ex}}$ independent variables: $\{C_1, \cdots, C_{N_{\text{ex}}}, S_1, \cdots, S_{N_{\text{ex}}}\}$, consisting of the cation aqueous and sorbed concentrations.

The contribution of ion exchange to the residual function R_{kn}^{ex} for finite difference equations for the jth primary species at the nth node is given by:

$$R_{jn}^{\text{ex}} = V_n \frac{\Delta S_j}{\Delta t}, \tag{4.83}$$

and for sorbed concentrations

$$R_{N_{\text{ex}}+j,n} = \frac{V_n}{\Delta t}\left(S_{jn}^{t+\Delta t} - S_{jn}^t\right) - \frac{V_n}{z_j}\sum_{i \neq j} I_{ji,n}, \tag{4.84a}$$

$$R_{N_{\text{ex}}+i,n} = \frac{V_n}{\Delta t}\left(S_{in}^{t+\Delta t} - S_{in}^t\right) + \frac{V_n}{z_i} I_{ji,n}. \tag{4.84b}$$

The Jacobian equations in matrix form for the contribution of exchange reactions have the structure

$$\begin{bmatrix} 0 & \dfrac{\partial R_j}{\partial S_k} \\[2ex] \dfrac{\partial R_{N_{\text{ex}}+j}}{\partial C_k} & \dfrac{\partial R_{N_{\text{ex}}+j}}{\partial S_k} \end{bmatrix} \begin{bmatrix} \delta C_j \\[2ex] \delta S_k \end{bmatrix} = - \begin{bmatrix} R_j \\[2ex] R_{N_{\text{ex}}+j} \end{bmatrix}, \tag{4.85}$$

with

$$\frac{\partial R_j}{\partial S_k} = \delta_{jk}\frac{V}{\Delta t}, \tag{4.86}$$

and

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial \ln C_{jn}} = \frac{V_n}{z_j}C_j \sum_{i \neq j} \frac{\partial I_{ji,n}}{\partial C_{jn}}, \tag{4.87a}$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial \ln C_{in}} = \frac{V_n}{z_j}C_i \frac{\partial I_{ji,n}}{\partial C_i}, \tag{4.87b}$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial \ln C_{jn}} = \frac{V_n}{z_i}C_j \frac{\partial I_{ji,n}}{\partial C_{jn}}, \tag{4.87c}$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial \ln C_{in}} = \frac{V_n}{z_i}C_i \frac{\partial I_{ji,n}}{\partial C_{in}}, \tag{4.87d}$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial S_{jn}} = \frac{V_n}{\Delta t} - \frac{V_n}{z_j}\sum_{i \neq j} \frac{\partial I_{ji,n}}{\partial S_{jn}}, \tag{4.88a}$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial S_{in}} = \frac{V_n}{\Delta t} - \frac{V_n}{z_j}\frac{\partial I_{ji,n}}{\partial S_i}, \tag{4.88b}$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial S_{jn}} = \frac{V_n}{\Delta t} + \frac{V_n}{z_i}\frac{\partial I_{ji,n}}{\partial S_{jn}}, \tag{4.88c}$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial S_{in}} = \frac{V_n}{\Delta t} + \frac{V_n}{z_i}\frac{\partial I_{ji,n}}{\partial S_{in}}. \tag{4.88d}$$

Logarithmic derivatives of the exchange reaction rates are given by

$$C_j \frac{\partial I_{ji}}{\partial C_j} = \frac{1}{z_j} k_{ji}^f a_j^{1/z_j} S_i^{1/z_i}, \tag{4.89a}$$

$$C_i \frac{\partial I_{ji}}{\partial C_i} = -\frac{1}{z_i} k_{ji}^b a_i^{1/z_i} S_j^{1/z_j}, \tag{4.89b}$$

$$S_j \frac{\partial I_{ji}}{\partial S_j} = -\frac{1}{z_j} k_{ji}^b a_i^{1/z_i} S_j^{1/z_j}, \tag{4.89c}$$

$$S_i \frac{\partial I_{ji}}{\partial S_i} = \frac{1}{z_i} k_{ji}^f a_j^{1/z_j} S_i^{1/z_i}. \tag{4.89d}$$

Note that: $\dfrac{df}{d \ln x} = x \dfrac{df}{dx}$, for any function f.

4.2.5 Input File Structure

F77 programing style:

```
ION_EXCHANGE
min1
  cec1
    >cat1
    >cat2
    >cat3
    END
  cec2
    >cat4
    >cat5
    END
  END
min2
  cec3
    >cat6
    >cat7
    END
  END
END
```

F90 object oriented programming style:

```
SORPTION
  ION_EXCHANGE_RXN
    MINERAL min1
    SITE    cec1
    CATION
    >cat1
    >cat2
```

```
      >cat3
    END
  END
  ION_EXCHANGE_RXN
    MINERAL min1
    SITE      cec2
    CATION
    >cat4
    >cat5
    END
  END
  ION_EXCHANGE_RXN
    MINERAL min2
    SITE      cec3
    CATION
    >cat6
    >cat7
    END
  END
END
```

5   Colloid-Facilitated Transport

The above formulation for heterogeneous reactions also apply to colloids, represented as $\mathcal{A}_c$. This presents an added complication since now the solid phase is moving with the fluid. In this case the primary species transport equation contains contributions from both reactions with stationary solid grains and colloids. The colloids themselves may react with the fluid through mineral precipitation and dissolution reactions. In addition, sorption through ion exchange and surface complexation may occur on the surfaces of colloids. These processes are described through the reactions

$$\sum_j \nu_{jc}\mathcal{A}_j \ \rightleftharpoons \ \mathcal{A}_c, \tag{5.1}$$

for precipitation and dissolution (formation and degradation), and

$$>X_c + \sum_j \nu^c_{ji}\mathcal{A}_j \ \rightleftharpoons \ >\mathcal{A}^c_i, \tag{5.2}$$

for surface complexation, and

$$\frac{1}{z_j}\mathcal{A}_j + \frac{1}{z_i}X^c_{z_i}\mathcal{A}_i \ \rightleftharpoons \ \frac{1}{z_i}\mathcal{A}_i + \frac{1}{z_j}X^c_{z_j}\mathcal{A}_j, \tag{5.3}$$

for ion exchange, with sorption sites X_c and $X^c_{z_l}$.

The colloid concentration C_c is equal to the number of moles of colloids of type c, N^{coll}_c, divided by the pore volume V_p

$$C_c \ = \ \frac{N^{coll}_c}{V_p}. \tag{5.4}$$

In the case of surface complexation reactions, the site concentration equal to the number of sorption sites N_c^{sites} associated with colloid $\mathcal{A}_c$ divided by the pore volume is defined as

$$\omega_c = \frac{N_c^{\text{srf}}}{V_p}. \tag{5.5}$$

The site concentration is related to the colloid concentration according to the equation

$$\omega_c = \frac{N_c^{\text{srf}}}{A_c} \frac{A_c}{M_c} \frac{M_c}{N_c^{\text{coll}}} \frac{N_c^{\text{coll}}}{V_p}, \tag{5.6}$$

$$= \eta_c A_c^M W_c C_c, \tag{5.7}$$

$$= \Gamma_c C_c, \tag{5.8}$$

where η_c denotes the site density, A_c^M the colloid area per mass of colloid, and W_c represents the formula weight of the colloid, and Γ_c is defined as

$$\Gamma_c = \frac{N_c^{\text{sites}}}{N_c^{\text{coll}}} = \eta_c A_c^M W_c. \tag{5.9}$$

From the site conservation equation

$$\omega_c = S_c + \sum_i S_i^c, \tag{5.10}$$

and mass action equation

$$K_i^c = \frac{S_i^c}{S_c Q_i^c}, \tag{5.11}$$

where

$$Q_i^c = \prod_j \left(\gamma_j C_j \right)^{\nu_{ji}^c}, \tag{5.12}$$

the free site and surface complex concentrations are found to be

$$S_c = \frac{\Gamma_c C_c}{1 + \sum_i K_i^c Q_i^c}, \tag{5.13}$$

and

$$S_i^c = \frac{K_i^c Q_i^c}{1 + \sum_i K_{i'}^c Q_{i'}^c} \Gamma_c C_c. \tag{5.14}$$

In the case of ion exchange, the cation exchange capacity is related to the colloid concentration by the expression

$$Q_c = \frac{N_c^{\text{ex}}}{V_p}, \tag{5.15}$$

$$= \frac{N_c^{\text{ex}}}{M_c} \frac{M_c}{N_c^{\text{coll}}} \frac{N_c^{\text{coll}}}{V_p}, \tag{5.16}$$

$$= \text{CEC}_c W_c C_c, \tag{5.17}$$

where CEC_c denotes the cation exchange capacity in units of mol sites/kg colloid.

The aqueous phase primary species transport equations thus have the form

$$\frac{\partial}{\partial t}\varphi\Psi_j + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j \; = \; -\sum_m \nu_{jm}\big(I_m + I_m^c\big) - \sum_k \nu_{jk}\big(I_k + I_k^c\big) + \sum_r \nu_{jr}^{\mathrm{kin}} I_r^{\mathrm{kin}}, \qquad (5.18)$$

where mineral precipitation and dissolution and surface complexation reactions are considered. The superscript c refers to colloids. Ion exchange can be handled similarly. In addition to the stationary solid inventory, transport equations for colloids are needed of the form

$$\frac{\partial}{\partial t}\varphi\mathcal{R}_c\varphi_m^c + \boldsymbol{\nabla}\cdot(\boldsymbol{q}\varphi_m^c) \; = \; \overline{V}_m I_m^c, \qquad (5.19)$$

and for surface complexes

$$\frac{\partial}{\partial t}\varphi\mathcal{R}_c S_k^c + \boldsymbol{\nabla}\cdot(\boldsymbol{q}S_k^c) \; = \; I_k^c, \qquad (5.20)$$

analogous to Eqns.(**??**) and (**??**) for stationary solid phases, but with an added flux term. The factor $\mathcal{R}_c$ in the accumulation term represents retardation of colloids due to filtration. Eliminating the surface complexation rates gives

$$\frac{\partial}{\partial t}\left(\varphi\Psi_j + \sum_k \nu_{jk}\big(S_k + \varphi\mathcal{R}_c S_k^c\big)\right) + \boldsymbol{\nabla}\cdot\left(\boldsymbol{\Omega}_j + \boldsymbol{q}\sum_k \nu_{jk}S_k^c\right) \; = \; -\sum_m \nu_{jm}\big(I_m + I_m^c\big)$$
$$+ \sum_r \nu_{jr}^{\mathrm{kin}} I_r^{\mathrm{kin}}. \qquad (5.21)$$

Note that colloids are only transported by advection and not diffusion in this formulation. The same Darcy flow rate is assumed for the colloids as for the fluid phase, although colloids have been shown to actually move slightly faster because of their tendency to be concentrated away from the pore walls due to electrostatic repulsion.

From the primary species transport equations it is possible to define a retardation factor assuming constant aqueous and sorbed concentrations and neglecting diffusion. It follows that the transport equations can be expressed in the form

$$\frac{\partial}{\partial t}\big(\varphi\Psi_j\big) + \boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{q}}{R_j}\Psi_j\right) \; = \; -\frac{1}{1 + K_j + \mathcal{R}_c K_j^c}\left[\sum_m \nu_{jm}\big(I_m + I_m^c\big) + \sum_r \nu_{jr}^{\mathrm{kin}} I_r^{\mathrm{kin}}\right], \quad (5.22)$$

where the retardation factor R_j is defined as

$$R_j \; = \; \frac{1 + K_j + \mathcal{R}_c K_j^c}{1 + K_j^c}, \qquad (5.23)$$

where the distribution coefficients K_j for the stationary solid and K_j^c for colloids are defined by

$$K_j \; = \; \frac{1}{\varphi\Psi_j}\sum_k \nu_{jk}S_k, \qquad (5.24)$$

and

$$K_j^c \; = \; \frac{1}{\Psi_j}\sum_k \nu_{jk}S_k^c. \qquad (5.25)$$

For $\mathcal{R}_c = 1$, Eqn.(5.23) reduces to

$$R_j = 1 + \frac{K_j}{1 + K_j^c}, \tag{5.26}$$

Note that if $K_j^c \geq K_j \gg 1$, $R_j \leq 2$, and there is little or no retardation. However, there still remains a reduction in kinetic homogeneous and heterogeneous rates. Finally, it should be noted that if colloids are to compete with stationary solid phase, they must be sufficiently concentrated to provide an equivalent surface site density (or cation exchange capacity).

6 Solid Solutions

7 Biogeochemical Reactions

Microbial processes are playing an increasingly important role in our understanding of the subsurface geochemical environment (Lovley and Chapelle, 1995). An excellent introduction into modeling microbially induced processes has been given by Rittmann and VanBriesen (1996). They derive overall reactions for biomass synthesis resulting from biodegradation reactions based on H_3NTA as the electron-donor primary substrate. Two different electron-acceptor substrates $O_{2(aq)}$ and NO_3^- are considered by the authors. In addition to these species, other important electron-acceptor primary substrates include SO_4^{2-}, $CO_{2(aq)}$ and Fe^{3+}.

The approach used by Rittmann and VanBriesen (1996) is somewhat cumbersome in that mass- rather than mole-based measures are used to represent organic substances. Their approach complicates the derivation of overall reactions describing biomass synthesis. The discussion presented here provides a unified treatment of organic reactions coupled to the usual aqueous acid-base, complexing, and mineral reactions employing mole-based quantities. A important feature of many biologically induced reactions is that they are strictly irreversible. As a consequence these reactions do not go to equilibrium. The reactions stop when either all donor or acceptor substrate material or biomass is completely utilized. As noted by Rittmann and vanBriesen (1996), biologically catalyzed reactions are affected by non-biological reactions and vice versa and their interaction can affect the fate of contaminants and the effectiveness of bioremediation schemes.

Rittmann and VanBriesen (1996) present a derivation of overall reactions governing biomass synthesis based on considerations of molecular biology at the cell level. Bacteria oxidize the electron-donor substrate to produce NADH (nicotinanaide adenine dinucleotide). With H_3NTA ($C_6H_9O_6N_{(aq)}$) as primary electron-donor substrate, 18 electrons are transferred according to the reaction

$$6\,CO_{2(aq)} + NH_4^+ + 17\,H^+ + 18\,e^- - 6\,H_2O \longleftarrow C_6H_9O_6N_{(aq)}. \tag{7.1}$$
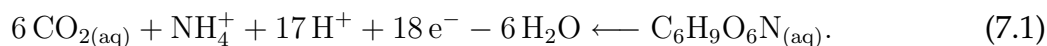
Biomass synthesis, with biomass represented as $C_5H_7O_2N_{(s)}$, results in the transfer of 20 electrons

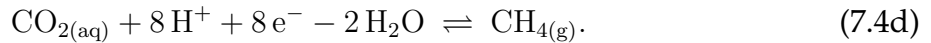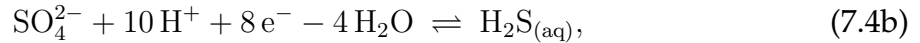$$5\,CO_{2(aq)} + NH_4^+ + 19\,H^+ + 20\,e^- - 8\,H_2O \longrightarrow C_5H_7O_2N_{(s)}. \tag{7.2}$$
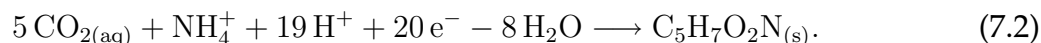
With oxygen as the electron acceptor substrate, 4 electrons are transferred

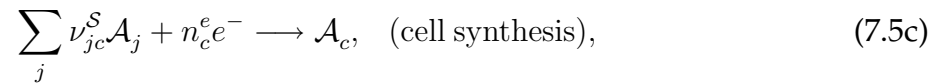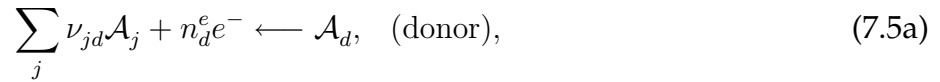$$2\,H_2O - 4\,H^+ - 4\,e^- \;\rightleftharpoons\; O_{2(aq)}. \tag{7.3}$$
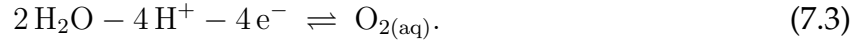
The overall reaction for biomass synthesis is derived by combining these reactions to balance electrons taking into account intra-cell process.

Electron acceptors other than oxygen may be involved in biomass synthesis. For example, reaction (7.3) may be replaced by any one of the reactions

$$2\,NO_3^- + 12\,H^+ - 10e^- - 6\,H_2O \;\rightleftharpoons\; N_2, \tag{7.4a}$$

$$SO_4^{2-} + 10\,H^+ + 8\,e^- - 4\,H_2O \;\rightleftharpoons\; H_2S_{(aq)}, \tag{7.4b}$$

$$Fe^{3+} + e^- \;\rightleftharpoons\; Fe^{2+}, \tag{7.4c}$$

$$CO_{2(aq)} + 8\,H^+ + 8\,e^- - 2\,H_2O \;\rightleftharpoons\; CH_{4(g)}. \tag{7.4d}$$
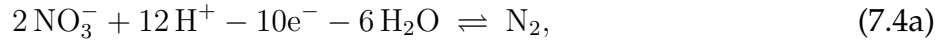
These reactions may occur simultaneously or individually depending on the nature of the geochemical system. Within a flow column they may occur in different, possibly overlapping, regions along the flow path.

In terms of a given set of primary species $\{A_j\}$ excluding electron donor A_d and acceptor A_a species, the reactions for oxidation of the primary electron-donor substrate, reduction of the primary electron-acceptor substrate, and biomass synthesis can be written as half-cell reactions in the general form

$$\sum_j \nu_{jd} A_j + n_d^e e^- \;\longleftarrow\; A_d, \quad \text{(donor)}, \tag{7.5a}$$

$$\sum_j \nu_{ja} A_j + n_a^e e^- \;\rightleftharpoons\; A_a, \quad \text{(acceptor)}, \tag{7.5b}$$

$$\sum_j \nu_{jc}^S A_j + n_c^e e^- \;\longrightarrow\; A_c, \quad \text{(cell synthesis)}, \tag{7.5c}$$

where A_c represents biomass. A fourth reaction describes biomass decay expressed as the overall reaction

$$\nu_{ac}^{\mathcal{D}} A_a + \sum_j \nu_{jc}^{\mathcal{D}} A_j \;\longleftarrow\; A_c, \quad \text{(decay)}. \tag{7.5d}$$

Note that the electron donor primary substrate does not appear in this reaction.

The transfer of electrons from the electron donor substrate must be conserved by cell processes of synthesis and respiration generating more biomass and energy. If the quantity f_s° represents the fraction of electrons going to biomass synthesis, then the fraction of electrons for respiration providing energy is

$$f_e^\circ \;=\; 1 - f_s^\circ. \tag{7.6}$$

The flow of electrons from the donor substrate and their partitioning between biomass synthesis and energy production is illustrated in Figure 1. The overall reaction for biomass systhesis is constructed from a linear combination of reactions (7.5a), (7.5b) and (7.5c) with
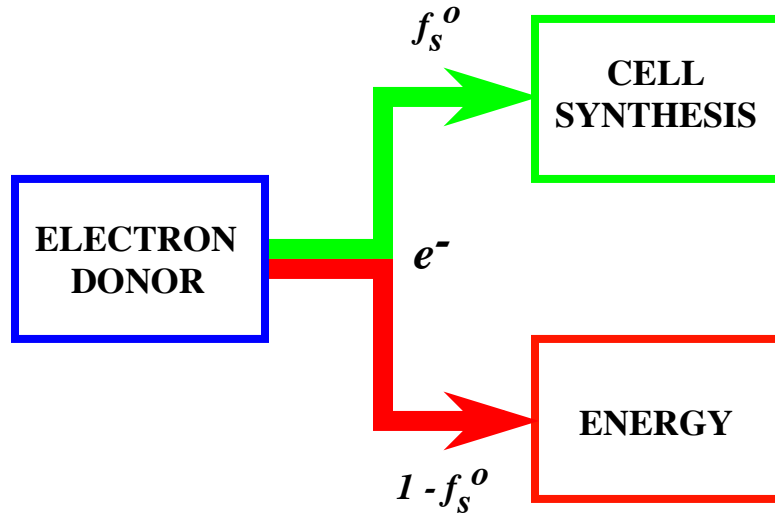
Figure 1: Schematic diagram illustrating the partitioning of electrons from the donor substrate to form biomass and create energy.

weighting factors f_s° and f_e° (Christensen and McCarty, 1975; Pavlostathis and Giraldo-Gomez, 1991). This may be accomplished by first writing these reactions in terms of a single electron brought to the right-hand side

$$\frac{1}{n_d^e}\mathcal{A}_d - \frac{1}{n_d^e}\sum_j \nu_{jd}\mathcal{A}_j \longrightarrow e^-, \tag{7.7}$$

$$\frac{1}{n_a^e}\mathcal{A}_a - \frac{1}{n_a^e}\sum_j \nu_{ja}\mathcal{A}_j \rightleftharpoons e^-, \tag{7.8}$$

$$\frac{1}{n_c^e}\mathcal{A}_c - \frac{1}{n_c^e}\sum_j \nu_{jc}^{\mathcal{S}}\mathcal{A}_j \longleftarrow e^-. \tag{7.9}$$

Combining these reactions with weighting factors f_s° and $1 - f_s^\circ$ according to

$$\mathcal{R}_{(7.7)} - (1 - f_s^\circ)\mathcal{R}_{(7.8)} - f_s^\circ\mathcal{R}_{(7.9)}, \tag{7.10}$$

yields the following overall reaction for biomass synthesis

$$\frac{1}{n_d^e}\mathcal{A}_d - \frac{1 - f_s^\circ}{n_a^e}\mathcal{A}_a + \sum_j \left[\frac{f_s^\circ}{n_c^e}\nu_{jc}^{\mathcal{S}} + \frac{1 - f_s^\circ}{n_a^e}\nu_{ja} - \frac{1}{n_d^e}\nu_{jd}\right]\mathcal{A}_j \longrightarrow \frac{f_s^\circ}{n_c^e}\mathcal{A}_c. \tag{7.11}$$

From this reaction an expression for the yield $\mathcal{Y}_c^d$ for biomass synthesis is obtained as the ratio of the rate of cell production to the rate of donor substrate utilization

$$\mathcal{Y}_c^d = f_s^\circ \frac{n_d^e}{n_c^e}. \tag{7.12}$$

The yield is proportional to the electron synthesis factor f_s° and the ratio of electrons transferred in the donor and biomass systhesis reactions. The biomass yield may be different for different electron acceptor substrates as well.

With oxygen as the electron acceptor substrate, and taking $f_s^\circ = 0.64$, $n_c^e = 20$, $n_d^e = 18$, and $n_a^e = -4$, reaction (7.11) becomes

$$0.0555556\,C_6H_9O_6N - 0.173333\,CO_{2(aq)} + 0.0235556\,H^+ - 0.102667\,H_2O$$
$$- 0.0235556\,NH_4^+ + 0.09\,O_{2(aq)} \longrightarrow 0.032\,C_5H_7O_2N. \qquad (7.13)$$
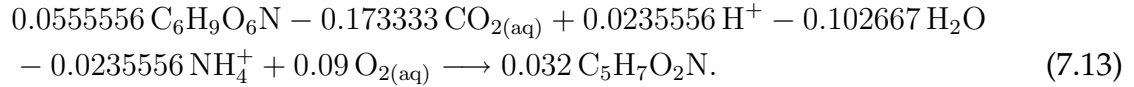
The yield $\mathcal{Y}$ has the value $\mathcal{Y}=0.576$. Using as electron acceptor NO_3^- with $f_s^\circ=0.62$ gives

$$0.0555556\,C_6H_9O_6N - 0.178333\,CO_{2(aq)} + 0.100556\,H^+ - 0.142667\,H_2O$$
$$- 0.038\,N_2 - 0.0245556\,NH_4^+ + 0.076\,NO_3^- \longrightarrow 0.031C_5H_7O_2N. \qquad (7.14)$$

For this reaction the yield $\mathcal{Y}$ has the value $\mathcal{Y}=0.558$.

Reactions (7.13) and (7.14) are linearly independent provided the intra-cell electron synthesis factor f_s° is different for different electron acceptors. Otherwise the reactions are linearly dependent. Provided local equilibrium prevails within the aqueous phase between different redox couples, catalyzed by bacteria, reactions based on different electron-acceptor substrates with equal intra-cell electron factors f_s° are linearly dependent and as a consequence the stoichiometry of the linearly-dependent reactions does not play a role in the transport equations, their rates being additive [see Eqn.(**??**)]. Only if disequilibrium of redox couples persists does the stoichiometry of the overall reaction come into play according to Eqn.(**??**).

Kinetic Rate Law. Introducing the yield, reaction (7.11) can be written as

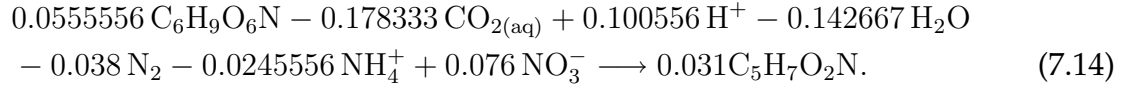$$\frac{1}{\mathcal{Y}_c^d}\,\mathcal{A}_d - \frac{1-f_s^\circ}{f_s^\circ}\frac{n_c^e}{n_a^e}\,\mathcal{A}_a + \sum_j \left[\nu_{jc}^{\mathcal{S}} + \frac{1-f_s^\circ}{f_s^\circ}\frac{n_c^e}{n_a^e}\,\nu_{ja} - \frac{1}{\mathcal{Y}_c^d}\,\nu_{jd}\right]\mathcal{A}_j \longrightarrow \mathcal{A}_c, \qquad (7.15)$$

in which the stoichiometric coefficient multiplying biomass is normalized to unity. The kinetic rate law for biomass synthesis is presumed to be adequately described by the Monod rate law

$$I_c = k_c\,\chi_c\,\frac{C_d}{K_d+C_d}\frac{C_a}{K_a+C_a}, \qquad (7.16)$$

for single acceptor and donor substrates with concentrations C_a and C_d, respectively, and where k_c represents the rate constant and χ_c denotes the concentration of cells. Note that an affinity factor, present in mineral precipitation and dissolution reactions, is absent from the Monod rate law. The rate law describing biomass decay is assumed to be first order of the form

$$I_c^{\mathcal{D}} = -\lambda_c\chi_c, \qquad (7.17)$$

where λ_c denotes the decay constant.

Mass Transport Equations. To set up the mass transport equations the first step is to identify an appropriate set of primary and secondary species to represent the reactions taking place in the particular system at hand. The primary electron donor substrate must be chosen as primary species as well as at least one on the primary electron acceptor substrates. If redox reactions are described through kinetic rate laws then all electron acceptors become primary species. On the other hand if redox reactions are represented by local equilibrium constraints, catalyzed by the presence of bacteria, then only one electron acceptor can be chosen as primary species, with the remaining electron acceptors included as aqueous secondary species. In addition to the biomass synthesis reaction (7.15)

and decay reaction (7.5d), and possibly electron acceptor equilibria, additional reactions including homogeneous reactions

$$\nu_{di}^{aq} \mathcal{A}_d + \nu_{ai}^{aq} \mathcal{A}_a + \sum_j \nu_{ji}^{aq} \mathcal{A}_j \; \rightleftharpoons \; \mathcal{A}_i, \tag{7.18}$$

and mineral precipitation and dissolution reactions

$$\nu_{di}^{min} \mathcal{A}_d + \nu_{ai}^{min} \mathcal{A}_a + \sum_j \nu_{jm}^{min} \mathcal{A}_j \; \rightleftharpoons \; \mathcal{M}_m, \tag{7.19}$$

must also be accounted for in a geochemical system. In these reactions allowance is made for participation by both the electron donor and acceptor substrates. For the set of primary species $\{\mathcal{A}_d, \; \mathcal{A}_a, \; \mathcal{A}_j\}$, the mass transport equations have the following form for primary species

$$\widehat{\mathcal{L}} C_d \; = \; -\frac{1}{\mathcal{Y}_c^d} I_c^{\mathcal{S}} - \sum_i \nu_{di}^{aq} I_i^{aq} - \sum_m \nu_{dm}^{min} I_m^{min}, \tag{7.20}$$

$$\widehat{\mathcal{L}} C_a \; = \; \frac{1 - f_s^\circ}{f_s^\circ} \frac{n_c^e}{n_a^e} I_c^{\mathcal{S}} + \nu_{ac}^{\mathcal{D}} \lambda_c \chi_c - \sum_i \nu_{ai}^{aq} I_i^{aq} - \sum_m \nu_{am}^{min} I_m^{min}, \tag{7.21}$$

$$\widehat{\mathcal{L}} C_j \; = \; -\left[\nu_{jc}^{\mathcal{S}} + \frac{1 - f_s^\circ}{f_s^\circ} \frac{n_c^e}{n_a^e} \nu_{ja} - \frac{1}{\mathcal{Y}_c^d} \nu_{jd} \right] I_c^{\mathcal{S}} + \nu_{jc}^{\mathcal{D}} \lambda_c \chi_c$$
$$- \sum_i \nu_{ji}^{aq} I_i^{aq} - \sum_m \nu_{jm}^{min} I_m^{min}, \tag{7.22}$$

secondary species

$$\widehat{\mathcal{L}} C_i \; = \; I_i^{aq}, \tag{7.23}$$

biomass

$$\frac{\partial \chi_c}{\partial t} \; = \; I_c^{\mathcal{S}} - \lambda_c \chi_c, \tag{7.24}$$

and finally for minerals

$$\frac{\partial \phi_m}{\partial t} \; = \; \overline{V}_m I_m^{min}. \tag{7.25}$$

Mineral reaction rates are denoted by I_m^{min}, and homogeneous aqueous reaction rates by I_i^{aq}.

    For the case in which the rates I_i^{aq} for homogeneous reactions are in local equilibrium, their rates may be eliminated by replacing the corresponding transport equations with mass action equations. This results in the primary species transport equations

$$\widehat{\mathcal{L}} \Psi_d \; = \; -\frac{1}{\mathcal{Y}_c^d} I_c^{\mathcal{S}} - \sum_m \nu_{dm}^{min} I_m^{min}, \tag{7.26a}$$

$$\widehat{\mathcal{L}} \Psi_a \; = \; \frac{1 - f_s^\circ}{f_s^\circ} \frac{n_c^e}{n_a^e} I_c^{\mathcal{S}} + \nu_{ac}^{\mathcal{D}} \lambda_c \chi_c - \sum_m \nu_{am}^{min} I_m^{min}, \tag{7.26b}$$

$$\widehat{\mathcal{L}} \Psi_j \; = \; -\left[\nu_{jc}^{\mathcal{S}} + \frac{1 - f_s^\circ}{f_s^\circ} \frac{n_c^e}{n_a^e} \nu_{ja} - \frac{1}{\mathcal{Y}_c^d} \nu_{jd} \right] I_c^{\mathcal{S}} + \nu_{jc}^{\mathcal{D}} \lambda_c \chi_c - \sum_m \nu_{jm}^{min} I_m^{min}, \tag{7.26c}$$

where

$$\Psi_d = C_d + \sum_i \nu_{di}^{aq} C_i, \tag{7.27a}$$

$$\Psi_a = C_a + \sum_i \nu_{ai}^{aq} C_i, \tag{7.27b}$$

$$\Psi_j = C_j + \sum_i \nu_{ji}^{aq} C_i. \tag{7.27c}$$

Parallel Reactions. So far the discussion has focused on the presence a single electron donor and acceptor substrate. However, in natural systems it is common for a number of different electron donor and acceptor substrates to be present at any one time. In such cases several parallel reactions representing biosynthesis may take place simultaneously. For the case of multiple electron acceptors indexed by β, these reactions may be written collectively in the general form

$$\sum_j \nu_{jc}^\beta \mathcal{A}_j \longrightarrow \mathcal{A}_c, \tag{7.28}$$

where the sum over the index j includes electron donor and acceptor substrates in addition to the other primary species. The reaction rate is given by the Monod rate law

$$I_c^\beta = k_c^\beta \chi_c \frac{C_{a_\beta}}{K_{a_\beta} + C_{a_\beta}} \frac{C_d}{K_d + C_d}, \tag{7.29}$$

with electron acceptor concentration C_{a_β}. The total rate for biomass synthesis is given by the sum over all parallel reactions related to different electron acceptors

$$I_c = \sum_\beta I_c^\beta,$$

$$= \chi_c \frac{C_d}{K_d + C_d} \sum_\beta \frac{k_c^\beta C_{a_\beta}}{K_{a_\beta} + C_{a_\beta}} \tag{7.30}$$

For example, for parallel reactions based on $O_{2(aq)}$ and NO_3^- as electron acceptors the total rate for biomass synthesis is equal to the sum of the individual rates

$$I_c = I_{O_{2(aq)}} + I_{NO_3^-},$$

$$= \chi_c \frac{C_d}{K_d + C_d} \left[\frac{k_{O_{2(aq)}} C_{O_{2(aq)}}}{K_{O_{2(aq)}} + C_{O_{2(aq)}}} + \frac{k_{NO_3^-} C_{NO_3^-}}{K_{NO_3^-} + C_{NO_3^-}} \right]. \tag{7.31}$$

The primary species mass transport equations can be written in the form

$$\widehat{\mathcal{L}}\Psi_j = -\sum_{c\beta} \nu_{jc}^\beta I_c^\beta - \sum_{jm} \nu_{jm} I_m^{min}, \tag{7.32}$$

and for biomass synthesis as

$$\frac{\partial \chi_c}{\partial t} = \sum_\beta I_c^\beta = I_c. \tag{7.33}$$

The equations may be further generalized to more than one electron donor substrate if desired.

8   Pitzer Activity Coefficient Algorithm

9   Species-Dependent Diffusion

9.1   Species-Independent Diffusion Coefficients

For the case of species-independent diffusion coefficients, because the homogeneous and heterogeneous reactions conserve charge, expressed by Eqn.(**??**), the mass conservation equations also conserve charge. The total charge density ρ_e in solution must vanish

$$\rho_e \;=\; \mathcal{F} \sum_j z_j \Psi_j \;=\; \mathcal{F} \sum_j z_j C_j + \mathcal{F} \sum_i z_i C_i \;=\; 0, \tag{9.1}$$

where $\mathcal{F}$ denotes the Faraday constant (96,485.3415 Coulombs/mol). Multiplying the primary species transport equations Eqn.(**??**) by z_j and summing over all primary species noting that $\sum_{jm} z_j \nu_{jm} I_m = \sum_m z_m I_m = 0$ from Eqn.(**??**), gives

$$\frac{\partial}{\partial t} \varphi \rho_e + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_{\rho_e} \;=\; 0, \tag{9.2}$$

where $\boldsymbol{\Omega}_{\rho_e}$ is defined as

$$\boldsymbol{\Omega}_{\rho_e} \;=\; \big(\boldsymbol{q} - \varphi \boldsymbol{D} \cdot \boldsymbol{\nabla} \big) \rho_e. \tag{9.3}$$

Thus the flux can be expressed in terms of ρ_e alone, and therefore if $\rho_e = 0$ initially, it must remain zero as the system evolves in time.

9.2   Species-Dependent Diffusion Coefficients

Real aqueous electrolyte solutions consist of charged species that diffuse at different rates. This requires consideration of electrochemical effects on transport in order to maintain charge balance. For charged species the solute flux is obtained from the Nernst-Planck equation involving the sum of gradients of the chemical and electric potentials as (Newman, 1991)

$$\boldsymbol{F}_i \;=\; -\tau \phi \frac{D_i C_i}{RT} \boldsymbol{\nabla} \big(\mu_i + \mathcal{F} z_i \Phi \big) + \boldsymbol{q} C_i, \tag{9.4}$$

where chemical potential μ_i [J/mol] is defined by

$$\mu_i \;=\; \mu_i^\circ(T, \, p) + RT \ln \gamma_i C_i, \tag{9.5}$$

with standard state potential $\mu_i^\circ(T, \, p)$, and the last term refers to bulk advective transport. Here z_i, γ_i and D_i denote the valence, activity coefficient and diffusivity of the ith species, respectively. The quantity Φ [J/Coul] represents the electrical potential, $\mathcal{F}$ [Coul/mol] denotes the Faraday constant, τ refers to the tortuosity of the porous medium, and $\mathbf{q}$ denotes the Darcy fluid velocity.

Table 3: Tracer diffusion coefficients of ions at infinite dilution in deionized water at 25°C (modified from Lasaga, 1998).

Cations $D_i \times 10^5$ cm^2/s		Anions $D_i \times 10^5$ cm^2/s	
H^+	9.31	OH^-	5.27
Li^+	1.03	F^-	1.46
Na^+	1.33	Cl^-	2.03
K^+	1.96	Br^-	2.01
Rb^+	2.06	I^-	2.00
Cs^+	2.07	IO_3^-	1.06
NH_4^+	1.98	HS^-	1.73
Ag^+	1.66	HSO_4^-	1.33
Mg^{2+}	0.705	NO_2^-	1.91
Ca^{2+}	0.793	NO_3^-	1.90
Sr^{2+}	0.794	HCO_3^-	1.18
Ba^{2+}	0.848	$H_2PO_4^-$	0.846
Mn^{2+}	0.688	$H_2AsO_4^-$	0.905
Fe^{2+}	0.719	$H_2SbO_4^-$	0.825
Co^{2+}	0.699	SO_4^{2-}	1.07
Ni^{2+}	0.679	SeO_4^{2-}	0.946
Cu^{2+}	0.733	CO_3^{2-}	0.955
Zn^{2+}	0.715	HPO_4^{2-}	0.734
Cd^{2+}	0.717	CrO_4^{2-}	1.12
Pb^{2+}	0.945	MoO_4^{2-}	0.991
UO_2^{2+}	0.426	PO_4^{3-}	0.612
Cr^{3+}	0.594		
Fe^{3+}	0.607		
Al^{3+}	0.559		

As is apparent from the form of the solute flux Eqn.(9.4), electrochemical migration leads to a species-dependent velocity field v_i^e superimposed on the bulk fluid flow, defined by

$$v_i^e = -\tau\phi\frac{z_i D_i}{RT}\mathcal{F}\nabla\Phi. \qquad (9.6)$$

The electrochemical velocity is proportional to the charge on the ion, the diffusivity and the electric potential gradient. The minus sign ensures that positively charged ions migrate in the direction of the electric field. Electrochemical effects may have several different origins. One possible contribution comes from diffusion of ionic species with differing diffusion coefficients. An electric field is established which acts on the charged species and influences their rates of migration in order to maintain electroneutrality of the aqueous solution. Another contribution is the electrochemical reaction of solids involving the transfer of electrons. Half-cell reactions are not in general balanced locally, but may occur at spatially distinct locations resulting in the formation of an electric current in both the aqueous solution and solid porous matrix.

To account for effects of pH and aqueous complexing reactions it is necessary to al-

low for homogeneous equilibrium reactions with the possibility of charged secondary species. Note that from Table (3) the species H^+ and OH^- have the largest tracer diffusion coefficients. It is assumed that homogeneous reactions are fast and local equilibrium conditions may be assumed. As for the case of equal diffusivities, it is also possible in the case of species-dependent diffusivities to derive mass conservation equations for the primary species taking into account homogeneous equilibrium relations. However, in this case it is no longer possible to express the primary species transport equations in terms of the total concentration Ψ_j alone, but in this case each individual species now occurs in the transport equations. To derive the form of the primary species transport equations, first separate equations are written for primary and secondary species including rates of the homogeneous reactions I_i as before [see Eqns.(**??**) and (**??**)], but with the solute flux $\boldsymbol{F}_l$ now given by Eqn.(9.4). Substituting Eqn.(9.4) into Eqn.(**??**), the total primary species flux is found to be after rearranging terms

$$\boldsymbol{\Omega}_j = -\tau\varphi\frac{\mathcal{F}\boldsymbol{\nabla}\Phi}{RT}\left(z_j D_j C_j + \sum_i \nu_{ji} z_i D_i C_i\right)$$

$$- \tau\varphi\left(D_j\boldsymbol{\nabla}C_j + \sum_i \nu_{ji}D_i\boldsymbol{\nabla}C_i\right.$$

$$\left. + D_j C_j \boldsymbol{\nabla}\ln\gamma_j + \sum_i \nu_{ji}D_i C_i \boldsymbol{\nabla}\ln\gamma_i\right) + \boldsymbol{q}\Psi_j. \tag{9.7}$$

Defining the quantities

$$\Lambda_j = z_j D_j C_j + \sum_i \nu_{ji} z_i D_i C_i, \tag{9.8}$$

$$\Gamma_j^C = D_j\boldsymbol{\nabla}C_j + \sum_i \nu_{ji}D_i\boldsymbol{\nabla}C_i, \tag{9.9}$$

and

$$\Gamma_j^\gamma = D_j C_j \boldsymbol{\nabla}\ln\gamma_j + \sum_i \nu_{ji}D_i C_i \boldsymbol{\nabla}\ln\gamma_i \tag{9.10}$$

the flux may be expressed in the more compact form

$$\boldsymbol{\Omega}_j = -\tau\varphi\left(\frac{\mathcal{F}\boldsymbol{\nabla}\Phi}{RT}\Lambda_j + \Gamma_j^C + \Gamma_j^\gamma\right) + \boldsymbol{q}\Psi_j. \tag{9.11}$$

It is possible to eliminate the potential Φ from the total flux by introducing the current density $\boldsymbol{i}_e$ defined as

$$\boldsymbol{i}_e = \mathcal{F}\sum_j z_j\boldsymbol{\Omega}_j. \tag{9.12}$$

Substituting for $\boldsymbol{\Omega}_j$ from Eqn.(9.11), the current density becomes

$$\boldsymbol{i}_e = -\tau\varphi\mathcal{F}\left(\frac{\mathcal{F}\boldsymbol{\nabla}\Phi}{RT}\sum_j z_j\Lambda_j + \sum_j z_j\left(\Gamma_j^C + \Gamma_j^\gamma\right)\right) + \boldsymbol{q}\rho_e. \tag{9.13}$$

Assuming the aqueous solution is electrical neutral the last term vanishes according to Eqn.(9.1). Solving Eqn.(9.13) for $\boldsymbol{\nabla}\Phi$ yields the expression

$$\boldsymbol{\nabla}\Phi = -\frac{1}{\kappa}\left(\boldsymbol{i}_e - \boldsymbol{q}\rho_e + \tau\varphi\mathcal{F}\sum_j z_j\left(\Gamma_j^C + \Gamma_j^\gamma\right)\right), \tag{9.14}$$

where the conductivity κ is defined as

$$\kappa = \frac{\tau\varphi\mathcal{F}^2}{RT}\sum_j z_j\Lambda_j. \tag{9.15}$$

Note that the sum on the right-hand side can be simplified to

$$\sum_{j=1}^{N_c} z_j\Lambda_j = \sum_{k=1}^{N} z_k^2 D_k C_k, \tag{9.16}$$

using the identity $\sum_j z_j\nu_{ji} = z_i$, where the sum over k includes all species, primary and secondary. The solute flux Ω_j may now be expressed in terms of the current $\boldsymbol{i}_e$ as

$$\Omega_j = \frac{t_j}{z_j\mathcal{F}}(\boldsymbol{i}_e - \boldsymbol{q}\rho_e) - \tau\varphi\sum_l \beta_{jl}(\Gamma_l^C + \Gamma_l^\gamma) + \boldsymbol{q}\Psi_j, \tag{9.17}$$

where the matrix β_{jl} is a projection operator ($\boldsymbol{\beta}^2 = \boldsymbol{\beta}$) defined by

$$\beta_{jl} = \delta_{jl} - \frac{z_l}{z_j}\Upsilon_j, \tag{9.18}$$

with the property

$$\sum_j z_j\beta_{jl} = 0, \tag{9.19}$$

and where the generalized transference number Υ_j is defined as

$$\Upsilon_j = \frac{z_j\Lambda_j}{\sum_l z_l\Lambda_l}. \tag{9.20}$$

To demonstrate that charge is indeed conserved, the primary species transport equations Eqn.(**??**) with flux given by Eqn.(9.17) are multiplied by the valence z_j and summed over all primary species to yield

$$\frac{\partial}{\partial t}\varphi\rho_e + \boldsymbol{\nabla}\cdot\boldsymbol{i}_e = 0. \tag{9.21}$$

In order for the electroneutrality condition Eqn.(9.1) to be satisfied, Eqn.(9.21) implies that the divergence of the current must vanish

$$\boldsymbol{\nabla}\cdot\boldsymbol{i}_e = 0, \tag{9.22}$$

which in turn requires that $\boldsymbol{i}_e = 0$. This will be the case if both ρ_e and $\boldsymbol{i}_e$ vanish initially. These results assume that corrosion processes which result in a source/sink term and nonzero current are not applicable.

10   Multiple Interacting Continua

A fundamental problem facing efforts to model subsurface reactive flows is characterizing and incorporating a multitude of spatial scales that are typical of natural systems into multicomponent-multiphase numerical models. Spatial scales may range from nanoscale surface chemistry, to pore and fracture apertures of millimeters to centimeters, to fracture spacing and matrix block sizes of tens of centimeters to meters, to reservoir or basin scales of kilometers to tens of kilometers. To illustrate the technical challenges involved in modeling multi-scale subsurface processes, consider a basin scale reservoir with an areal extent of one square kilometer and depth of 500 meters. Modeling this system as a single continuum on a grid with one million nodes results in an average grid block size of 10m by 10m by 5m—or roughly the size of a large conference room. Within this grid block, physical and chemical processes occur at much smaller sub-grid scales. Such processes involve, for example, diffusive and advective mass transfer between fractures and rock matrix, or more generally diffusion between macro- and micro-pore scales, accompanied by chemical reactions. Characteristic of these systems is mass transport and chemical reactions occurring at disparate spatial scales that cannot be captured within a single continuum description. In particular, localized chemical environments may be vastly different from the bulk fluid and lead to dramatically different results compared to a single continuum description. It is clearly impossible to capture this range of scales within a single continuum framework because of the large computational expense that would be required to resolve the smallest scale. One approach that appears feasible to describe such systems is to incorporate sub-grid scale processes through multiple interacting continua representing fine scale processes. Besides the difficulty developing conceptual models of such systems, characterization at the laboratory and field scales adds additional challenges. In addition, this approach carries a significant computational cost as well because of the increase in the number of degrees of freedom associated with the additional continua and the necessity to carry out calculations over engineering and geologic time spans within feasible computation times.

A considerable body of literature exists on multiscale descriptions of flow and transport in porous and fractured media. Such formulations range from structured soils (Murphy et al., 1986; van Genuchten and Wagenet, 1989; Brusseau and Rao, 1990; Gerke and van Genuchten, 1993; Gwo et al., 1995; and others), to fractured rock (Warren and Root, 1956; Barenblatt et al., 1960; Duguid and Lee, 1977; Pruess and Narisimhan, 1985; Bai et al., 1993; Lichtner, 2000). These works, however, have been largely confined to consideration of flow and simple single component systems with first order linear kinetics or a constant K_D model. Precipitation and dissolution reactions which result in a moving boundary problem associated with different mineral assemblages are usually not included in the description.

In the soil science literature these models are referred to as two-site and two-domain, or more generally multi-site and multi-domain models, and have been generalized to so-called multi-rate models by Haggerty and Gorelick (1995). In fractured rock studies, they have various names including dual permeability-dual porosity models or more generally dual and multiple continuum models. They may involve both saturated and partially saturated conditions.

Distinguishing between different domains is somewhat arbitrary and nonunique especially in soils (Lichtner and Kang, 2007). Which pores participate in flow depends on the degree of saturation of the medium. A typical approach is to divide pores into macro pores which carry the bulk fluid and micro pores which are connected to macro pores by diffusion. Inter- (between macro pores) and intra- (inside micro pores) mass transfer between the different pores is formulated as a set of coupled partial differential equations based on the generalization of a single continuum to interacting continua.

One of the primary difficulties in applying a multiscale formulation is obtaining values for the parameters that enter into the model. As has been demonstrated for linear single component systems these values may be nonunique (Sardin et al., 1991).

Multiscale processes play a significant role in many situations involving flow and reactive transport. However, because of the inherent nonlinearity of constitutive relations, for example, chemical rate laws and statements of equilibrium mass action relations in real multicomponent fluids, use of linear relations is of limited usefulness.

The formulation presented below is based on a multiple interacting continuum formulaiton. This formulaiton provides for local concentration gradients within a sub-continuum domain. The model places no restrictions on linear or nonlinear constitutive relations, and is completely general in its treatment of chemical and other physical processes.

In the following a multi-scale continuum formulation for reactive transport is developed based on multiple interacting continua. In this formulation the primary continuum, which may consist of one, two, or three spatial dimensions, is coupled to sub-grid scale domains that are presumed to form effective one-dimensional regions.

A control, or representative elemental volume V of the porous medium is subdivided into regions consisting of primary and secondary continua. A single volume is associated with the primary continuum although this assumption could be relaxed. The geometry of the system is assumed to be characterized by the primary continuum volume fraction ϵ_α, the intrinsic volume and surface area of each secondary continuum domain V_β^0 and A_β^0, respectively, and the fraction x_β of the number of the βth subdomain type

$$x_\beta = \frac{N_\beta}{N}, \tag{10.1}$$

where N is the total number of secondary domains in a control volume and N_β is the number of subdomains of type β. The total volume V may thus be represented as

$$V = V_\alpha + \sum_\beta V_\beta, \tag{10.2}$$

where the sum is over all secondary continua with volume V_β expressed as

$$V_\beta = N_\beta V_\beta^0, \tag{10.3}$$

in terms of the volume V_β^0 of a particular type and the number of such types within a control volume. The primary continuum volume fraction ϵ_α is related to the number density of secondary domains by the expression

$$\epsilon_\alpha = \frac{V_\alpha}{V} = 1 - \frac{1}{V} \sum_\beta N_\beta V_\beta^0, \tag{10.4}$$

or

$$\frac{N}{V} = \frac{1 - \epsilon_\alpha}{\sum_\beta x_\beta V_\beta^0}.$$

(10.5)

The volume fraction ϵ_β of each secondary continuum is given by

$$\epsilon_\beta = \left(1 - \epsilon_\alpha\right)\frac{x_\beta V_\beta^0}{\sum_{\beta'} x_{\beta'} V_{\beta'}^0}.$$

(10.6)

Also of interest is the specific interfacial surface area $a_{\alpha\beta}$ separating primary and secondary continua

$$a_{\alpha\beta} = \frac{A_{\alpha\beta}}{V} = \frac{1}{V}\sum_\beta N_\beta A_\beta^0 = \left(1 - \epsilon_\alpha\right)\frac{x_\beta A_\beta^0}{\sum_{\beta'} x_{\beta'} V_{\beta'}^0}.$$

(10.7)

Multi-scale, multicomponent, continuum-scale reactive transport equations for primary species $\mathcal{A}_j$ participating in reactions given in Eqns.(**??**) and (**??**) can be written in the general form as the set of coupled partial differential equations as follows (Lichtner and Kang, 2007)

$$\frac{\partial}{\partial t}\epsilon_\alpha \varphi_\alpha \Psi_j^\alpha + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j^\alpha = \sum_\beta a_{\alpha\beta}\Omega_j^{\alpha\beta} - \epsilon_\alpha \sum_s \nu_{js}I_s^\alpha,$$

(10.8)

for the primary continuum fluid, and

$$\frac{\partial}{\partial t}\varphi_\beta \Psi_j^\beta + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j^\beta = -\sum_s \nu_{js}I_s^\beta,$$

(10.9)

for the βth sub-grid domain. The quantity ϵ_α represents the volume fraction occupied by the primary continuum. The volume averaged kinetic mineral reaction rate $I_s^{\alpha,\beta}$ has the form

$$I_s^{\alpha,\beta} = -k_s^{\alpha,\beta}a_s^{\alpha,\beta}(1 - K_sQ_s^{\alpha,\beta}),$$

(10.10)

with rate constant $k_s^{\alpha,\beta}$ and mineral surface area $a_s^{\alpha,\beta}$ for primary continuum α and sub-grid continua β. The total concentration $\Psi_j^{\alpha,\beta}$ is given by Eqn.(**??**) for the primary and secondary continua. The total solute flux includes advective and diffusive terms

$$\boldsymbol{\Omega}_j^{\alpha,\beta} = -\varphi_{\alpha,\beta}\tau_{\alpha,\beta}D\boldsymbol{\nabla}\Psi_j^{\alpha,\beta} + \boldsymbol{q}_{\alpha,\beta}\Psi_j^{\alpha,\beta},$$

(10.11)

with tortuosity $\tau_{\alpha,\beta}$, diffusivity D, and Darcy flow rate $\boldsymbol{q}_{\alpha,\beta}$. For simplicity dispersion is not included, but in general would be necessary.

The boundary condition at the primary continuum-matrix fluid interface is given by

$$C_j^\beta(r = r_\beta, t; \boldsymbol{r}) = C_j^\alpha(\boldsymbol{r}, t),$$

(10.12)

where r_β denotes the boundary of the domain β. The flux at the primary continuum-matrix interface is presumed to only involve diffusion with the form

$$\Omega_j^{\alpha\beta} \;=\; -\varphi_\beta \tau_\beta D\, \boldsymbol{n}_\beta \cdot \boldsymbol{\nabla} \Psi_j^\beta \bigg|_{r_\beta}, \tag{10.13}$$

where $\boldsymbol{n}_\beta$ denotes the outward normal to the interface. The matrix equation is quite general and applies to various geometries including spheres and linear domains. As an approximation cubes and irregular shaped domains may be used. Because of computational considerations, the sub-grid domain equations are reduced to an equivalent 1D problem. For further discussion of numerical techniques for efficiently solving the multi-scale equations see Lichtner (2006).

11 References