Hydrologic Transport Equations:

$$\theta \frac{\partial T_j}{\partial t} + \mathbf{V} \cdot \nabla T_j + K(T_j) + \frac{\partial \theta}{\partial t} T_j = \mathbf{V} \cdot \nabla (S+P) + K(S_j + P_j) + QC_{jin}, \quad j \in N_a \tag{1a}$$

$$K(!) = \left(-\nabla \cdot \theta \mathbf{D} \cdot \nabla + Q - \frac{\partial \theta}{\partial t} \right) \tag{1b}$$

$$\theta \frac{\partial W_j}{\partial t} + \frac{\partial \theta}{\partial t} W_j = 0, \quad j \in N_s \tag{2}$$

$$\theta \frac{\partial N_{eq}}{\partial t} + \frac{\partial \theta}{\partial t} N_{eq} = 0 \tag{3}$$

where

Q	=	source rate of injecting water, ($L^3/L^3/T$),
θ	=	moisture content, (dimensionless),
T_j	=	total analytical concentration of the j-th aqueous component (M/L^3),
C_j	=	total dissolved concentration of the j-th aqueous component (M/L^3),
S_j	=	total sorbed concentration of the j-th aqueous component (M/L^3),
P_j	=	total precipitated concentration of the j-th aqueous component (M/L^3),
C_{jin}	=	concentration of the j-th component in the injecting fluid (M/L^3),
M_j^a	=	total rate of source/sink of the j-th aqueous component ($M/L^3/T$),
W_j	=	total analytical concentration of the j-th adsorbent component (M/L^3),
M_j^s	=	total rate of source/sink of the j-th adsorbent component ($M/L^3/T$),
N_{eq}	=	number of equivalents of the ion-exchange sites per liter of solution (M/L^3),
M_{eq}	=	total rate of source/sink of the ion-exchange site ($M/L^3/T$),

Initial Conditions of Hydrologic Transport Equations:

$$T_j = T_{jo} \quad \text{at } t = 0 , \quad j \in N_a , \tag{4}$$

$$W_j = W_{jo} \quad \text{at } t = 0 , \quad j \in N_s , \tag{5}$$

$$N_{eq} = N_{eqo} \quad \text{at } t = 0 \tag{6}$$

where

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

Boundary Conditions of Hydrologic Transport Equations:

Dirichlet Boundary Conditions (Specified Concentrations)

$$T_j = T_{jD} \quad \text{on} \quad B_D , \quad j \in N_a , \tag{7}$$

Neumann Boundary Conditions (Specified Gradient Fluxes)

$$- \mathbf{n} \cdot \theta \, \mathbf{D} \cdot \nabla C_j = q_{jN} \quad \text{on} \quad B_N , \quad j \in N_a , \tag{8}$$

Cauchy Boundary Conditions (Specified Total Fluxes)

$$\mathbf{n} \cdot (\mathbf{V} C_j - \theta \mathbf{D} \cdot \nabla C_j) = q_{jC} \quad \text{on} \quad B_C , \quad j \in N_a , \tag{9}$$

Variable Boundary Conditions (Flow-in/Flow-put Boundaries)

$$- \mathbf{n} \cdot \theta \mathbf{D} \cdot \nabla C_j = q_{jV} \text{ if } V \cdot n > 0 \text{ on } B_V , \ j \in N_a , \tag{10}$$

and

$$\mathbf{n} \cdot (\mathbf{V} C_j - \theta \mathbf{D} \cdot \nabla C_j) = q_{jV} \text{ if } V \cdot n < 0 \text{ on } B_V , \ j \in N_a \tag{11}$$

where

T_{jD} = prescribed Dirichlet total analytical concentration of the j-th component (M/L^3),
q_{jN} = normal Neumann flux of the j-th component ($M/L^2/T$),
q_{jC} = normal Cauchy flux of the j-th component ($M/L^2/T$),
$\mathbf{n}$ = an outward unit vector normal to the boundary.
q_{jv} = prescribed flux at the variable boundary of the j-th component.

Geochemical Equilibrium Reaction Equations

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i + \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i \ , \quad i \in N_a \tag{12}$$

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^y y_i \ , \quad j \in N_s \tag{13}$$

$$\kappa_{iJ} = \frac{(z_i/s_T)^{\nu_J}}{(z_J/s_T)^{\nu_i}} \frac{a_J^{\nu_i}}{a_i^{\nu_J}} \ , \quad i \in M_z$$

$$N_{eq} = \sum_{i=1}^{M_z} \nu_i z_i \tag{14}$$

$$1 = \alpha_i^p \prod_{k=1}^{N_a} c_k^{a_{ik}^p} \ , \quad i \in M_p \tag{15}$$

$$x_i = \alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x} \ , \quad i \in M_x \tag{16}$$

$$y_i = \alpha_i^y \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^y} \right) \ , \quad i \in M_y \tag{17}$$

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^{x} x_i \ , \quad j \in N_a \tag{18}$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^{y} y_i + \sum_{i=1}^{M_z} a_{ij}^{z} z_i \ , \quad j \in N_a \tag{19}$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^{p} p_i \ , \quad j \in N_a \tag{20}$$

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

Step 1 - Solve Eqs. (2) and (3) for W_j's and N_{eq}.

Step 2 - Make guesses of T_j's.

Step 3 - Solve Eqs. (12) through (20) to obtain all species concentrations and S_j's and P_j's.

Step 4 - Solve Eq. (1) one by one for T_j's using S_j's and P_j's obtained from Step 3 to evaluate the right-hand terms in Eq. (1).

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

Step 6 - If the difference is within the error tolerance, proceed to the next time step. If the difference is greater than the tolerance, repeated steps 2 through 5 until the system converges.