Model for Precipitation and Dissolution Processes with Precipitate Migration

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Chemical precipitation can cause permeability reduction during the injection or mixing of ionic solutions in a permeable medium. The permeability reduction has been attributed to the migration and plugging of pore throats by solid precipitates. A few studies have been conducted so far to model the precipitation/dissolution processes by neglecting precipitate migration and pore plugging processes (Walsh et al., 1982; Keith et al., 1984; Lichtner, 1985). Such studies have macroscopically predicted the permeability loss in terms of the traditional permeability and porosity correlations. Walsh et al. (1984) developed a geochemical flow model for both mineral dissolution and precipitation processes during convective transport. The model was based on the assumptions of local equilibrium (large Damkohler number), negligible dispersion (large Peclet number), no surface adsorption/ion exchange, and no migration of solids. Later, Bryant et al. (1986) and Stohs (1986) extended Walsh's model to include surface adsorption/ion exchange. This model VCSFLOW does not allow for solid migration, an assumption that severely limits the model because several experimental studies have demonstrated that precipitated solids can migrate with the fluid (Patton, 1977; Boon et al., 1983; Walsh et al., 1983).

The model presented here incorporates the migration of precipitated solids in VCSFLOW. As a basic theory, the new model also attempts to characterize the local permeability reduction by incorporating precipitated solid-size and pore-size distribution into one of the two dominant pore plugging (or solid trapping) mechanisms: particle size exclusion by pore throats. A fractional flow function for each migrating mineral has been developed and coupled with the mass conservation of each element. These, together with an assumption of local equilibrium between the solid and aqueous species, provide a complete description of flow and reaction in permeable media. Because the conservation laws are hyperbolic equations, we also formulate an analytical solution procedure based on coherence conditions (Helfferich and Klein, 1970). Thus, the solution can be written in terms of waves between zones of constant composition which move at different velocities. The model is illustrated by means of an example flow problem.

Model Formulation

The model is formulated on the same basis as Walsh's model (Walsh et al., 1984). To simplify the formulation, the following additional assumptions have been added.

1. The mobile solid-phase is transported at the same superficial velocity as the aqueous phase.
2. The flowing solid minerals have a single size (r_s), that is comparable to the mean pore throat size, so that the size exclusion trapping mechanism dominates.
3. The trapping length, defined as the dimensionless distance a particle travels before being captured, is small. This is shown to be the case when size exclusion is the dominant mechanism for particle capture (Sharma and Yortsos, 1987).

Subject to the assumptions, the dimensionless mass conservation of element i can be written as a differential hyperbolic equation:

$$\frac{\partial}{\partial t_D}(C_i + \hat{C}_i) + \frac{\partial}{\partial x_D}(C_i + \hat{C}_i^f) = 0 \quad i = 1, \ldots, N. \tag{1}$$

The initial and boundary conditions are:
Initial Composition:

$$C_i(x_D, 0) = (C_i)_I \text{ and } \hat{C}_i^f(x_D, 0) = 0; \quad x_D > 0, i = 1, \ldots, N$$

Injected Composition:

$$C_i(0, t_D) = (C_i)_J \text{ and } \hat{C}_i^f(0, t_D) = (\hat{C}_i^f)_J; \quad t_D > 0, i = 1, \ldots, N$$

No solid phase flows initially. However, a flowing solid phase may be injected.

Two major types of chemical reactions occur: intraaqueous

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and dissolution/precipitation reactions. The equilibrium constant K_r for the r^{th} intraaqueous reaction is defined as:

$$K_r = \prod_{j=1}^{J} C_j^{\nu_{rj}} \quad r = 1, \ldots, R. \tag{2}$$

The chemical equilibrium between the solid and aqueous species can be represented by a solubility product (K_k^{sp}) for each mineral k:

$$K_k^{sp} \geq \prod_{j=1}^{J} C_j^{\nu_{kj}} \quad k = 1, \ldots, K. \tag{3}$$

The inequality in Eq. 3 holds when the mineral k dissolves, and the equality applies if it precipitates. K_r and K_k^{sp} are functions of temperature (T) and pressure (P) which are specified.

To complete the formulation, a fractional flow function for each precipitated solid species is derived and combined with the effective medium theory. Sharma and Yortsos (1987) have recognized two basic trapping mechanisms: 1) solid deposition on pore walls because of attractive surface forces (surface adsorption); and 2) straining or size exclusion by pore throats smaller than the particles. If the solid size is comparable to the mean pore throat size, the dominant mechanism for particle trapping is size exclusion. In this study, we will not consider the case where the solid size is much smaller than the pore throat size where surface adsorption becomes important. We also assume that a single particle completely plugs a smaller pore. This means that 'pore bridging' is not accounted for. Consequently, the reduction of some pore sizes owing to solid deposition and the occurrence of some plugged pores because of bridging are ignored and the model, therefore, will predict a smaller-than-observed permeability reduction.

Consider the flow of uniform-sized particles, r_s, through a permeable medium. Then the minimum number fraction of pore throats that can be open to flow is:

$$a = \int_{r_s}^{\infty} f_p(r)\, dr$$

If the number of pore throats with radii less than r_s is greater than the number of particles, some of the smaller pores ($r < r_s$) will be open to flow and the number fraction of open throats will exceed a. For a given particle size, however, the number fraction of open pore throats is no less than a. The maximum possible number fraction of plugged pores is then $(1 - a)$.

Let n_o be the original number of pore throats per unit bulk volume. Based on the assumption that a single particle completely plugs a smaller pore, the maximum number of trapped particles per unit bulk volume N^* is:

$$N^* = (1 - a)n_o.$$

If the total number of solid particles per unit bulk volume in the medium is less than N^*, all the particles will instantaneously be trapped. If the total number of particles per unit bulk volume exceeds N^*, the particles in excess of N^* will flow. Therefore, N^* forms a threshold for particle flow. A threshold concentration, denoted by C^*, for particle flow is then expressed as:

$$C^* = \frac{(1 - a)n_o\rho_s}{\phi}. \tag{4}$$

The above argument suggests a straight-line fractional flow function between flowing and total solid concentrations:

$$\frac{\sum_{k=1}^{p} \hat{C}_k^f}{\sum_{k=1}^{p} \hat{C}_k} = \begin{cases} \left(1 - \dfrac{C^*}{\sum_{k=1}^{p} \hat{C}_k}\right) & \sum_{k=1}^{p} \hat{C}_k > C^* \\ 0 & \sum_{k=1}^{p} \hat{C}_k \leq C^*. \end{cases} \tag{5}$$

Since all precipitated minerals are assumed to have the same particle size (r_s), they are indistinguishable from a trapping standpoint. Therefore, the concentration of each mineral k that is flowing is proportional to its total concentration, and the proportionality factor will be the same for all minerals. We can, therefore, write,

$$\frac{\hat{C}_1^f}{\hat{C}_1} = \cdots = \frac{\hat{C}_k^f}{\hat{C}_k} = \cdots = \frac{\hat{C}_p^f}{\hat{C}_p} = \frac{\sum_{k=1}^{p} \hat{C}_k^f}{\sum_{k=1}^{p} \hat{C}_k}. \tag{6}$$

In general, Eq. 6 will be statistically true and has been shown to be consistent with the coherence condition (Wu, 1988). From Eq. 6, it is also evident that the trapped mineral concentration is

$$\hat{C}_k^t = \hat{C}_k - \hat{C}_k^f, \quad \text{for} \quad \sum_{k=1}^{p} \hat{C}_k > C^*. \tag{7}$$

Equations 6 and 7 are the two conditions used in the analytical solution presented in the next section. We refer to Eqs. 5 and 6 as the mineral fractional flow function (FFF) and to Eq. 7 as the trapped mineral concentration constraint (TMC).

The advantage of formulating the problem of particle capture and migration at a pore level is that such local properties as the permeability can be directly calculated. Use is made of the pore throat distribution of the permeable medium after trapping has occurred. Effective medium theory (EMT) is then used to estimate the permeability loss with the permeable medium represented as a three-dimensional network of pore throats and pore bodies (Sharma and Yortsos, 1987).

For our purpose, the quantity of interest is the ratio of permeability in the damaged zone k_D to the initial permeability k_I,

$$k_{\text{ratio}} = \frac{k_D}{k_I} = \frac{g_{mD}}{g_{mI}} \tag{8}$$

Calculation of the effective conductances is achieved by solving the equation for either g_{mI} or g_{mD},

$$\int_0^{\infty} G(g)\, \frac{g_m + g}{g + \alpha g_m}\, dg = 0 \tag{9}$$

where $\alpha = z/2 - 1$ and z is the coordination number. The conductance distribution $G(g)$ can be obtained from the pore throat size distribution

$$G(g) = f_p(r)\left|\frac{dr}{dg}\right|. \tag{10}$$

We assume $g \propto r^4$ in our calculations.

In the damaged zone $G(g)$ consists of a fraction Y of nonconductive pores (blocked pores) and a fraction $(1 - Y)$ of conductive pores. $G(g)$ is then given by:

$$G(g) = Y\delta(g) + (1 - Y)\tilde{G}(g) \tag{11}$$

where $\delta(g)$ is the Dirac delta function, which is zero if $g \neq 0$, and $\tilde{G}(g)$ is the probability distribution of conductive pores, which is related to the damaged-pore throat-size distribution $f_{pD}(r)$ through Eq. 11 with $\tilde{G}(g)$ and f_{pD} replacing $G(g)$ and f_D, respectively.

The damaged-pore throat-size distribution can be related to the initial-pore throat-size distribution $f_{pI}(r)$ by the following equation:

$$f_{pD}(r) = \begin{cases} \dfrac{1 - \dfrac{\sum_{k=1}^{p} \hat{C}_k^t}{C^*}}{1 - \dfrac{\sum_{k=1}^{p} \hat{C}_k^t}{C^*} + \dfrac{a\sum_{k=1}^{p} \hat{C}_k^t}{C^*}} f_{pI}(r) & r < r_s \\[2ex] \dfrac{1}{1 - \dfrac{\sum_{k=1}^{p} \hat{C}_k^t}{C^*} + \dfrac{a\sum_{k=1}^{p} \hat{C}_k^t}{C^*}} f_{pI}(r) & r > r_s. \end{cases} \tag{12}$$

Solutions and Discussion

In this section, we use an example to illustrate the solution features. A key concept in solving the reducible hyperbolic differential Eq. 1 is that of *coherence* (Helfferich and Klein, 1970). For shock composition changes in our model, the concentration steps of all elements must advance at the same rate according to the integral coherence condition (ICC) $v_1 = \cdots v_i = \cdots v_N$. Therefore,

$$\frac{\Delta(C_1 + \hat{C}_1^f)}{\Delta(C_1 + \hat{C}_1)} = \cdots = \frac{\Delta(C_i + \hat{C}_i^f)}{\Delta(C_i + \hat{C}_i)} = \cdots = \frac{\Delta(C_N + \hat{C}_N^f)}{\Delta(C_N + \hat{C}_N)} \tag{13}$$

If the correct set of solids in each region and correct number of waves, known as the solid sequence, is specified, the ICC, along with the other equations, will give a system of algebraic equations to compute the aqueous and solid concentrations in the constant state region as well as the velocities for all the waves between the regions (Bryant, 1986). Determining the correct solid sequence for a given condition is not straightforward and is discussed elsewhere (Novak et al., 1988). The application of the algebraic method is also provided in detail elsewhere (Wu, 1988).

In the example flow problem, we consider a precipitation/dissolution process composed of four aqueous species A, B, C, D and three minerals AB, AC, and BD. For example, A may stand for Ca^{++}, B for $OH-$, C for CO_3^-, and D for Fe^{++}. Figures 1 and 2 show the numerical results by concentration profiles and a time-distance diagram. The solution resolves into constant state regions separated by sharp waves. Across the precipitation/dis-

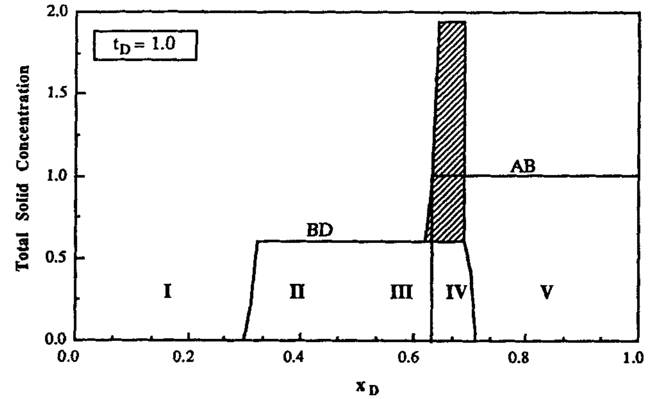

Figure 1a. Minerals *BD* and *AB* concentration profile for the example flow problem.
Shading indicates flowing solid *BD*.

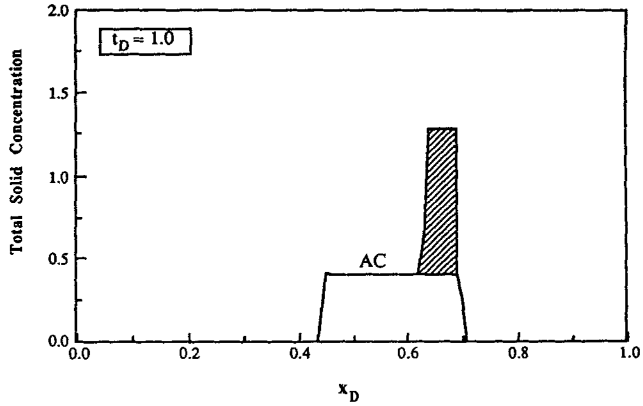

Figure 1b. Minerals *AC* concentration profile for the example flow problem.
Shading indicates flowing solid *AC*.

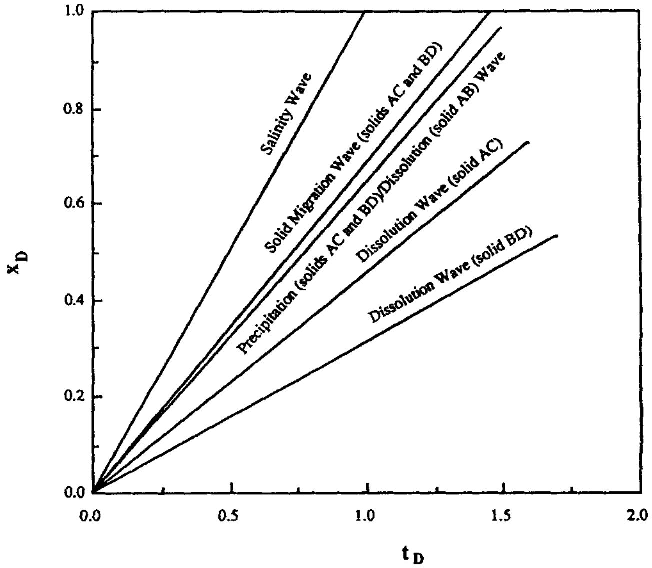

Figure 2. Time-distance diagram for the example problem.

solution wave between region III and IV, solid *AB* is first dissolved, and at the same time solids *AC* and *BD* are precipitated and start to flow with the fluid. Because an instantaneous reaction rate is assumed, the precipitation/dissolution wave is sharp as expected. As solids *AC* and *BD* flow forward some particles start being trapped, forming constant trapped solid concentrations for two minerals. Hence, region IV consists of two kinds of particles: flowing particles and trapped particles. The total trapped particle concentration is equal to C^* according to the fractional flow function. As a result, a wave is formed dynamically; the wave between region IV and V is termed the solid migration wave. Since the fractional flow function of the solids is a straight line, the solid migration wave is also sharp. However, the solid migration wave can spread out if the fractional flow curve is concave-down. Across the dissolution wave, which is located between region I and II, and region II and III in this example, the trapped solid is dissolved. The salinity wave with unit velocity marks the movement of furthest advance of the injected fluid. In this example it is located at the outflow end ($x_D = 1.0$) when one pore volume of the fluid ($t_D = 1.0$) is injected.

There are some interesting features of the solution. From the *coherence condition*, the velocity of the solid migration wave is determined by the ratio of any flowing mineral concentration to its total concentration in that region, i.e. $\hat{C}^f_k/\hat{C}_k$. This is consistent with Eq. 6 used in deriving the mineral fractional flow function. Large $\hat{C}^f_k$ (or small trapped mineral k) implies a large wave velocity; small $\hat{C}^f_k$ (or large trapped mineral k) implies a low wave velocity. The highest solid migration wave velocity, equal to salinity wave velocity, is attained when all minerals flow, i.e., $\hat{C}^f_k = \hat{C}_k$. The smallest solid migration wave velocity, which is the precipitation/dissolution wave velocity, is obtained when no solids flow. Hence, solid migration is always retarded when solid trapping occurs across the migration wave.

The precipitated mineral concentrations are independent of the threshold concentration C^*. Mineral precipitation occurs across a shock wave and the amount of mineral k precipitated depends only on the chemical compositions on either side of the precipitation wave. By introducing solids migration, we do not incur any chemical reaction and therefore the compositions are not changed. As a result, the total amount of mineral k precipitated is the same as when solids do not move.

In multiple precipitation/dissolution wave problems, another observation can be made. The number of solid migration waves is equal to or less than the number of precipitation/dissolution waves. This is because the source of solids migration is the continuous precipitation of solids across a precipitation/dissolution wave. The number of migration waves could be less than the number of precipitation/dissolution waves, if there are regions downstream of those migration waves where the total trapped solid concentration is equal to C^*. If the total trapped solid concentration is equal to C^* in a region and there is a migration wave upstream of this region, this migration wave may merge into the next migration wave in the downstream direction assuming there exists such a migration wave downstream. Two precipitation/dissolution waves may be obtained by changing equilibrium conditions or the injected composition. Figure 3 shows the case where the number of migration waves equals the number of precipitation/dissolution waves in an ABCDE problem (by adding an aqueous species *E* to the *ABCD* problem to generate an additional mineral *BE* we can formulate an *ABCDE* problem).

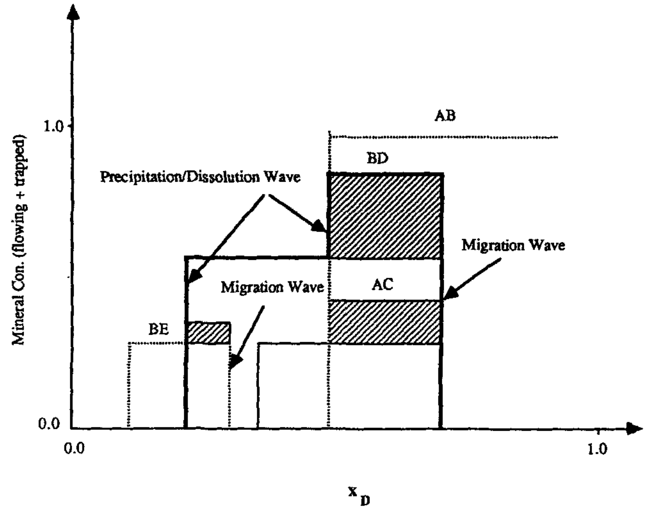

Figure 3. Example problem with two precipitate migration waves.
Shading indicates flowing solids.

We now use the EMT model discussed earlier to calculate k_{ratio} for the *ABCD* flow problem. Let us suppose that the original pore throats are normally distributed with a mean pore size of 35 μm and a standard deviation of 10 μm and that the coordination number is 6. The particle size r_s is assumed to be 43 μm. Because of the nonuniform trapped solid concentration profile in the example problem, the damaged-pore throat-size distribution in region II, and region III and IV differ according to Eq. 12. The damaged-pore throat-size distribution in region II is shown in Figure 4. Figure 5 shows the damaged permeability ratio (k_{ratio}) profile. The number of precipitation/dissolution waves determines the number of damaged regions. The more the number of precipitation/dissolution waves, the larger the number of damaged regions. The permeability recovery region I will always exist if no flowing solid phase is injected. The damaged permeability regions I and II expand as more fluid is injected.

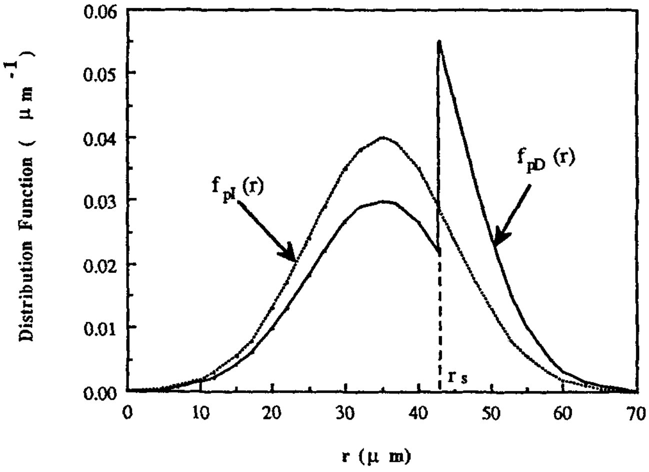

Figure 4. Pore throat size distribution in damaged region II.

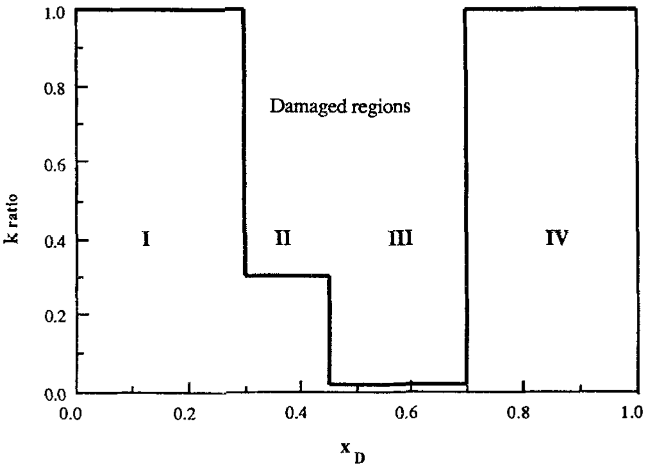

Figure 5. Damaged permeability ratio profile for the example problem.

This means that the extent of formation damage will increase as more volume of fluid is injected until the damaged regions are "produced" (reach $x_D = 1$).

Finally, the effect of relative pore and particle size on wave behavior can be investigated. For the sake of simplicity, we will consider the mineral *AC* concentration profile only since the same effects occur for the mineral *BD*. When the particle size (r_s) is larger than the maximum pore size ($r_{\max}$), all precipitated *AC* is trapped and no migration of solid *AC* occurs. The solution here is identical to the solution disallowing solid migration. When the particle size is less than the minimum pore size ($r_{\min}$), all precipitate *AC* migrates and there is no trapped solid *AC*. At this condition, the solid migration wave coincides with the salinity wave. We refer to this solution as the complete solid migration solution where no permeability impairment occurs. When the particle size is comparable to the mean pore size ($r_{\max} > r > r_{\min}$), the partial solid migration solution is obtained. The mineral *AC* profile under these conditions is the same as in Figure 1b as the value of r_s is chosen with C^* being 1. By reducing the particle size, we reduce the magnitude of trapped mineral concentration and increase the solid migration wave velocity and the dissolution wave velocity. Meanwhile, the flowing mineral concentration remains constant.

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Notation

a = fraction of open pores
C^* = threshold concentration
$C_i = \Sigma_{j=1}^{J} h_{ij} C_j$ = concentration of element i in aqueous phase
$\hat{C}_i = \Sigma_{k=1}^{K} g_{ik} \hat{C}_k$ = concentration of element i in total solids
$\hat{C}_i^f = \Sigma_{k=1}^{p} g_{ik} \hat{C}_k^f$ = concentration of element i in flowing solids
C_j = aqueous concentration of species j
$\hat{C}_k$ = total solid concentration of mineral k
$\hat{C}_k^f$ = flowing solid concentration of mineral k
$\hat{C}_k^t$ = trapped solid concentration of mineral k
$f_p(r)$ = pore throat size distribution
$f_{pD}(r)$ = damaged pore throat size distribution
$f_{pI}(r)$ = initial pore throat size distribution
g = conductance of a bond in the network
g_{ik} = mineral-phase stoichiometric constant
g_m = effective conductance
g_{mD} = damaged effective conductance
g_{mI} = initial effective conductance
$G(g)$ = conductance distribution function over the network
$\tilde{G}(g)$ = conductance distribution function of conductive pores
h_{ij} = aqueous-phase stoichiometric constant
J = maximum number of aqueous species in the system (subscript J = injected conditions)
K = maximum number of mineral species in the system
k_D = permeability in the damaged zone
k_I = permeability in the initial permeable medium
K_k^{sp} = solubility product of mineral k
K_r = thermodynamic equilibrium constant of reaction r
k_{ratio} = damaged permeability ratio
N = maximum number of aqueous elements in the system
n_o = original number of pores per unit bulk volume
N^* = maximum number of trapped particles per unit bulk volume
P = pressure
p = maximum number of injected and precipitated minerals
r = pore radius
R = total number of intraaqueous reactions
r_s = particle radius
t_D = dimensionless time
T = temperature
v_i = specific concentration velocity of element i
Y = fraction of closed pores
x_D = dimensionless distance
z = coordination number

Greek letters

$\alpha = (z/2) - 1$
$\delta(g)$ = Dirac delta function
ν_{kj} = stoichiometric reaction coefficient for species j in mineral k
ν_{rj} = stoichiometric reaction coefficient for species j in reaction r
ρ_s = number-averaged density of solids
ϕ = porosity

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