

P O S T E R   S E S S I O N   I I

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THE INFLUENCE AND MODELING OF WASTE NUCLIDE  
AQUEOUS SPECIATION ON GEOSPHERE RETARDATION  
PROCESSES RELEVANT TO RISK ASSESSMENT

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INTRODUCTION

In a recent paper,<sup>1</sup> we have demonstrated how risk assessment and sensitivity analysis techniques can be used to identify parameters which contribute most to risk and to uncertainty associated with risk predictions in nuclear waste disposal site performance assessment. Retardation in the transport of radionuclides in groundwater was shown to be one of the most significant of these parameters. This paper is intended to examine the physical processes involved in retardation in more detail than is currently involved in risk assessment modeling being done at Sandia, with the intention of developing further insights into the mechanisms involved. This should provide the basis for improved retardation modeling in the risk assessment methodology being developed.

The retardation process in geologic media is commonly modeled using the nuclide distribution coefficient  $K_d$ . The  $K_d$  of an element is defined as the ratio of the concentration of that element in the solid and aqueous phases at a point in the system:

$$K_d = \frac{C_{\text{solid}} \text{ (moles/g)}}{C_{\text{solution}} \text{ (moles/ml)}} \quad (\text{in ml/g}) \quad (1)$$

This ratio may vary with temperature, with characteristics of the solid phase (e.g., chemical and mineralogical composition, ion exchange capacity and specific surface), with characteristics of the solution (e.g., pH, Eh and concentration and speciation of natural elements, of other waste elements and of the element in question) and with time (in systems not at chemical equilibrium at that point or in systems undergoing dynamic chemical

evolution). It has been shown<sup>2</sup> that because of this variability, the notion of a constant distribution coefficient for describing the migration of waste radionuclides in groundwater systems is unrealistic. Rather than dealing with a lumped parameter such as  $K_d$ , it is proposed that developing an understanding of and modeling the actual processes responsible for radionuclide retardation can provide a better means of describing contaminant migration in groundwater.

Accurate hydraulic transport or flow models currently exist for predicting the transport of water through geologic media. The transport of an unretarded nuclide, one which is indistinguishable from the water, could be predicted by such codes if the source strength were known. If the difference between the transport behavior of water and of the retarded solute can be taken into account, these models could also serve to predict the transport of waste nuclides.

Let us consider the transport of water through a geologic medium by tracking a small parcel or molecule of water through the system. This molecule traces a path of a given length per unit time  $t$ , reflecting its actual mean velocity over the path,  $\bar{v}$ . Flow models approximate this value with  $\bar{v}_i$ , the mean interstitial velocity.<sup>a</sup> If another molecule of water is released at the starting point of the path, the molecule need not necessarily be at the same position as was the first particle after the same transport time interval. This is due to hydrodynamic dispersion, for which flow models can also account. In Fig. 1 the straightened path is represented by the solid line and the uncertainty about that path due to dispersion is shown by the shaded area.

Next, consider a rigid control volume of fluid at a point along the path, oriented so that flow occurs only through opposite faces. Water traverses the length of this volume at  $\bar{v}$ .

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<sup>a</sup>The Darcy velocity of the fluid  $\bar{v}_d$  is the volumetric flow rate through a groundwater flow tube divided by its cross-sectional area ( $\bar{v}_d = Q/A$ ). The interstitial velocity adjusts this value by accounting for flow only in the voids ( $\bar{v}_i = \bar{v}_d/\phi_e$  where  $\phi_e$  is the effective porosity of the medium). This is equivalent to assuming the water takes the shortest path through the connected voids of the volume of the flow tube and therefore  $\bar{v}_i$  is not necessarily equal to  $\bar{v}$ . In media of only primary porosity,  $\bar{v}_i$  well approximates  $\bar{v}$  in small volumes.

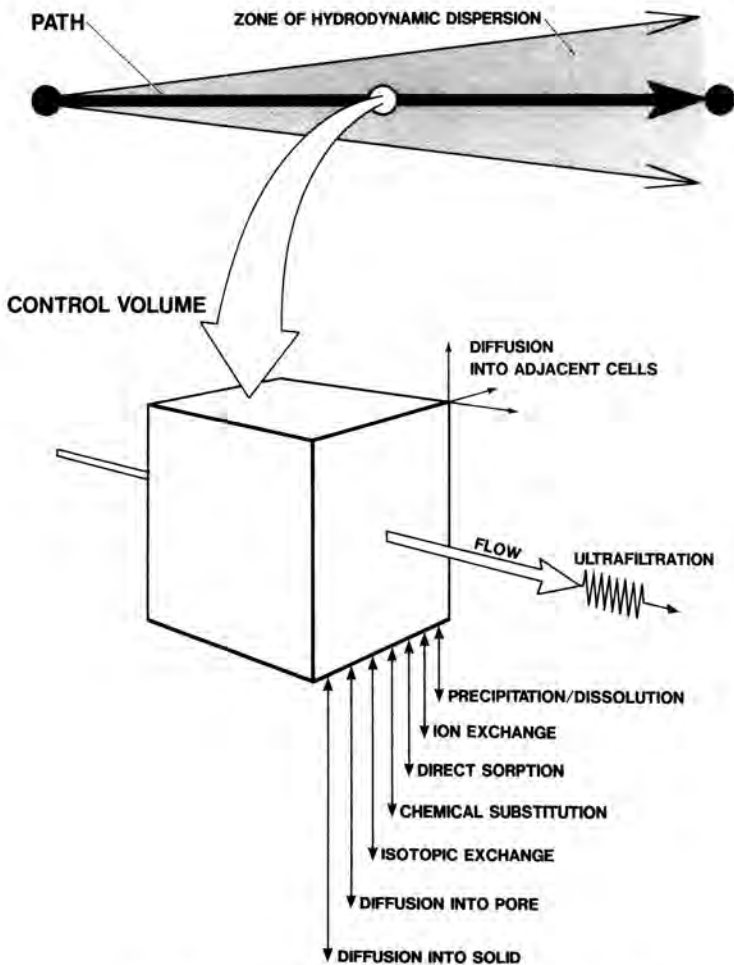


Fig. 1 Conceptual model of processes involved in the retardation of solutes in a ground-water system.

Thus, due to continuity, the water mass flux  $q_w$  through the upstream face of the volume and out through the opposite face both equal  $v\rho a$ , where  $a$  is the area of each face and  $\rho$  is the density of water. Notice that the areas of the two faces are equal and that the flux is independent of the volume of the cell being considered. Given the inflow concentration of a solute into the control volume, the outflow concentration may be calculated if a solute mass balance can be made for the volume.

The major physicochemical processes which can cause the solution within the control volume to gain or lose solute are:

- 1) Chemical precipitation/dissolution reactions
- 2) Cation or anion exchange reactions
- 3) Direct sorption processes
- 4) Chemical substitution reactions
- 5) Isotopic exchange reactions
- 6) Diffusion into an adjacent cell
- 7) Diffusion into fluid not involved in flow
- 8) Diffusion into the solid matrix
- 9) Ultrafiltration

Although the control volume is "rigid" to water, it need not be "rigid" to the solute, i.e., the concentration of solute within the volume need not be constant. Processes changing the amount of solute stored within the volume should also be considered. The most significant of these processes is ultrafiltration.

The amount of mass transferred (or stored) by each of these processes is a function of a set of physicochemical conditions and is controlled by a constant or kinetic parameter. Each of the processes is extremely sensitive to the aqueous chemical speciation of the solute. In the following section we will discuss these processes and their dependence on speciation and will propose a method by which an accountability of mass transfers due to the processes may be made.

#### PROCESSES RESPONSIBLE FOR RETARDATION

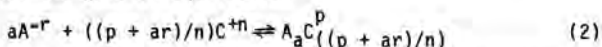
Each of the processes in the list above is driven by an activity gradient (usually a concentration gradient) between the control volume and a reservoir in contact with and outside that volume. The first five reaction processes tend to reach equilibrium rather rapidly, in general, and transfer mass between thermodynamically distinct reservoirs across the control volume boundary only while the inflow water is seeking equilibrium.

The next four processes reach equilibrium much more slowly, tending toward a steady-state during which mass is transferred between thermodynamically identical reservoirs during the total cell transport time. Because of these inherent differences in the processes, the mass balance for the two types of processes will be treated separately.

### Reaction Processes

Two types of computer codes have been used to model the geochemical interactions of natural ground waters and their geologic environment.<sup>3</sup> The original ion-speciation/solubility codes use data on pH, Eh, temperature and observed elemental chemical compositions to calculate the chemical activities of species formed in solution according to the law of mass action. Saturation indices of mineral phases are also computed. The more powerful reaction-path-simulation codes determine changes in the aqueous solution caused by variations in temperature and by the precipitation/dissolution of mineral phases. Activities of all aqueous species, Eh, pH, ionic strength and the amount of mass lost, or gained, from solution are calculated from temperature and pressure corrected equilibrium constants compared to ion-activity products. It is this mass balance feature of reaction-path-simulation codes which makes them suitable in modeling the chemical precipitation/dissolution reactions involved in solute retardation.

Consider the general equilibrium



where  $a$  and  $((p + ar)/n)$  are the stoichiometric coefficients of the anion  $A^{-r}$  and cation  $C^{+n}$  and where  $A_aC_{((p + ar)/n)}^p$  can be an ionic or uncharged complex in solution or a solid phase. The law of mass action defines the equilibrium constant of the reaction as

$$K = \frac{[A_aC_{((p + ar)/n)}^p]}{[A^{-r}]^a [C^{+n}]^{((p + ar)/n)}} \quad (3)$$

where the brackets indicate chemical activities. This equilibrium constraint is a function of temperature which is obtained either empirically, or from the enthalpy of reaction and the Van't Hoff equation. Replacing activities by the product of

activity coefficient and molality ( $\gamma_i m_i$  for species  $i$ ) and solving for one of the concentration terms, arbitrarily selected here as that of the anion yields

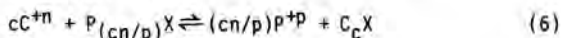
$$m_{A-r} = \left( \frac{\gamma_{AC} m_A^A C^P ((p + ar)/n)}{K \gamma_A^a (\gamma_C m_C^{+n}) ((p + ar)/n)} \right)^{1/a} \quad (4)$$

where the activity coefficients can be determined by the Debye-Huckel method or by another ionic interaction model. In addition to this expression which may be written for all reactions not involving oxidation/reduction, a general mass balance equation

$$A_{\Sigma} = \sum_j m_{Aj} \quad (5)$$

may be written over all aqueous species and mineral phases containing the element A. The  $A_{\Sigma}$  may be the input mass (concentration) of A into the control volume before reaction. Consider a system of  $i$  aqueous species and  $j$  mineral phases composed of a total of  $k$  elements. Since the activities of the mineral phases are unity, by definition, the  $(i + j - k)$  possible equilibrium expression have  $i$  unknown terms (i.e., the molalities of the  $i$  aqueous species). The  $k$  possible elemental mass balance equations have  $j$  unknown terms (i.e., the  $j$  mineral mass balance terms, since the  $i$  aqueous mass terms may be obtained by summing over the molalities of all species containing the given element). The simultaneous solution of the  $i$  equations for the  $i$  unknowns is obtained by iterative techniques. This completely models the speciation/precipitation/dissolution process and can thus be used to determine the mass transfer across the control volume boundary caused by chemical precipitation/dissolution reactions, the first of the reaction retardation mechanisms in the list above. Further, by applying the constraints of electroneutrality and of the conservation of electrons, two additional degrees of freedom may be gained. This permits the calculation of the pH and Eh of the solution rather than having these parameters as required input variables.

The second set of retardation mechanisms, the ion exchange reactions, may be treated in an analogous way. Consider the general cation exchange reaction



described by the equilibrium constant

$$K = \frac{[P^{+p}]^{(cn/p)} [C_c X]}{[C^{+n}]^c [P_{(cn/p)} X]} \quad (7)$$

Here  $X$  represents the anionic substrate,  $-cn$  is the site charge and  $P^{+p}$  and  $C^{+n}$  are the cations being exchanged. If the aqueous terms already appear in the chemical equilibrium expressions, this equation introduces the two unknowns  $[C_c X]$  and  $[P_{(cn/p)} X]$ . Let the activity of the sorbed species  $C_c X$  be defined

$$[C_c X] = \lambda_c N_c \quad (8)$$

where  $\lambda_c$  and  $N_c$  are respectively its rational activity coefficient and mole fraction in the sorbed phase (i.e., moles of  $C$  sorbed on  $X$  per total moles of  $X$  available for sorption,  $(C_c X)/(X)$ ). Since the cation exchange capacity, CEC, is defined as the total charge available for exchange (per unit mass of solid),

$$CEC = cn \sum_i (C_c X_i) = cn(X) \quad (9)$$

and

$$(X) = \frac{CEC}{cn} \quad (10)$$

Thus Eq. (8) may be written

$$[C_c X] = \lambda_c (C_c X) cn / CEC \quad (11)$$

and Eq. (7) becomes (after a similar analysis for  $[P_{(cn/p)} X]$ )

$$K = \frac{[P^{+p}]^{(cn/p)} (C_c X) \lambda_c}{[C^{+n}]^c (P_{(cn/p)} X) \lambda_p} \quad (12)$$

Solving for one of the exchanged terms, here arbitrarily for  $(C_c X)$  gives

$$(C_c X) = \frac{K (P_{(cn/p)} X) (\gamma_c m C^{+n})^c}{(\gamma_p m P^{+p})^{(cn/p)}} \quad (13)$$



which is analogous to Eq. (4). For parallel treatment, the exchanged terms must be added to the appropriate element balance equations and the additional "element balance" equation, representing the conservation of sites must be considered as it is in Eq. (9). The treatment for anion exchange reactions is similar, when the anion exchange coefficient AEC is known. Reaction-path-simulation codes which treat chemical precipitation/dissolution processes can thus also treat ion exchange processes when the sorbed phase is considered analogous to a precipitate.

Unfortunately, in practice, the initial surface activities (or concentrations) are extremely difficult to determine. In this case the assumption of a constant activity ratio in the solid phase must be made. If the constraint that

$$K' = \frac{[C_c X]}{[P(cn/p)X]} \quad (14)$$

is made in Eq. (7), the absolute initial concentrations and the CEC (or AEC) need not be specified. This is analogous to assuming that the reservoir of exchanging solution is infinite relative to the number of sites available for exchange and that the ratios of surface concentrations are constant over the range of aqueous concentrations encountered.

The third type of retardation process, that is, direct sorption reactions not involving exchange, are a special subset of the ion exchange process just described. The reaction in Eq. (6) reduces to the form



Note that these processes usually involve very weak intermolecular forces such as hydrogen bonding, and are probably very minor contributors to retardation. Nevertheless, reversible direct sorption reactions are directly analogous to precipitation/dissolution since

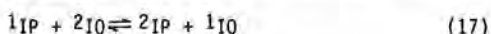
$$K = \frac{[C_c X^{+n}]}{[c^{+n}]c} \quad (16)$$

Since the activity of the solid X is unity, Eq. (16) introduces only one unknown. This type of reaction is therefore directly treatable by reaction-path-simulation codes.

The next type of retardation process, involving the chemical substitution of a portion of the solid phase by another substance from solution, is also completely analogous to ion exchange. They differ simply in that ionic forces retain the exchanged species in the latter, while the former involves the breaking and re-establishment of covalent bonds. An example of such a process is the dolomitization of calcite in a magnesium-bearing solution. Although the bonding mechanisms involved are different, the processes can be considered thermodynamically identical, and substitution is therefore treatable by the method described above.

The last retardation mechanism involving reaction processes is isotopic exchange. In such a process there is no macroscopically, or even chemically apparent, redistribution of mass. An isotope of a given element in the solid phase is simply replaced by a different isotope of that element from solution. An example of such an exchange is the substitution of  $^{12}\text{C}$  in  $\text{CaCO}_3(\text{s})$  by  $^{14}\text{C}$  from  $\text{HCO}_3^-(\text{aq})$ . No changes occur in the total amount of  $\text{CaCO}_3(\text{s})$  or  $\text{HCO}_3^-(\text{aq})$  present.

Consider the fractionation equilibrium of two isotopes  $^1\text{I}$  and  $^2\text{I}$  between two phases X and Y:



The equilibrium constant for this reaction is

$$K = \frac{[^2\text{IP}] [^1\text{IQ}]}{[^1\text{IP}] [^2\text{IQ}]} \quad (18)$$

but since substances differing only in isotopic composition have virtually identical chemical behavior, the terms in brackets need not be activities, but could represent concentrations. The concentration of a heavy or rare isotope in a reservoir containing a common lighter one of the same element is expressed as the abundance ratio R, such that

$$R_p = \frac{^2\text{IP}}{^1\text{IP}} \quad \text{and} \quad R_q = \frac{^2\text{IQ}}{^1\text{IQ}} \quad (19)$$

The experimentally determined fractionation factor  $\alpha_{PQ}$  describes the equilibrium isotopic distribution between phases P and Q as

$$\alpha_{PQ} = \frac{R_P}{R_Q} \quad (20)$$

Combining the expressions in Eq. (19) with Eq. (20) shows that

$$\alpha_{PQ} = \frac{2_{IP} \ 1_{IQ}}{1_{IP} \ 2_{IQ}} \quad (21)$$

and the fractionation factor is equivalent to, and can be used as, the equilibrium constant for the reaction in Eq. (17). Notice that this relationship need not be applied only between aqueous and solid phases, but may be applied among aqueous phases to describe the isotopic distribution in solution. Unlike ion exchange, the surface activities (concentrations) are not difficult to determine, and the simplifying solid phase distribution assumption need not be made. On the other hand, in analogy to the elemental mass balance equation, an isotopic balance equation must be introduced for each isotope so that the number of equations and unknowns is equal.

In each case, the speciation of the element in solution determines the appropriate reaction and integrates the many factors upon which radionuclide distribution is dependent. By using this approach, no major changes in the logic used by a reaction-path-simulation code need be made to account for this or any of the other retardation processes.

The fundamental assumption in this approach is that the processes detailed above go rapidly to equilibrium. This assumption is necessitated by the paucity of kinetic data (rate constants) available for all five of the processes. If rate constants were known, the residence time  $t$  in the control volume could be used to calculate the actual degree of equilibrium reached. In this way the mass transfer by each mechanism could be obtained. The treatment of kinetics can simply and advantageously be added to a reaction-path-simulation code even in light of the poor data since, if done, sensitivity analysis could be used to determine the relative importance of the rate constants (i.e., of the equilibrium assumption) and to identify the critical terms which most warrant measurement.

## Non-Reaction Processes

Of the remaining four processes which do not involve reactions, we will discuss the three diffusional processes together. Consider the control volume whose faces are adjacent to similar but separate volumes or cells. A solute molecule within the control volume may diffuse through the cell boundary into the adjacent cells. In addition, the control volume may gain mass by diffusion from any of the adjacent cells. This, of course, describes a standard Fick's Law type diffusional process.

This process may be extended to include other diffusional mechanisms. For instance, the control volume can be in contact with the solid matrix or with fluid contained in a volume not actively involved in the flow such as a dead-end pore. Both of these reservoirs can act as sources or sinks of solute, depending on the direction of the driving gradient. In a generalized treatment, they can, therefore, be represented by source/sink terms of variable strength. A mathematical representation of the actual physical process involved may replace this term when available.

All three of the diffusional processes may be expressed in a generalized diffusion equation as

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + \sum_j \left[ \frac{\rho_j}{\phi_j} \frac{\partial S_j}{\partial C_i} \frac{\partial C_i}{\partial t} + \frac{\rho_j}{\phi_{nj}} \frac{\partial S_{wj}}{\partial C_w} \frac{\partial C_w}{\partial t} \right] \quad (22)$$

where  $C_i$  is the aqueous concentration of species  $i$  (as obtained from the equilibrium calculations),  $C_w$  is the amount of non-flowing fluid,  $D_i$  is the aqueous diffusion constant for the  $i$ th species, the summation index  $j$  represents, as above, the separate mineral phases,  $\rho_j$  is the bulk mass density of the  $j$ th mineral phase,  $S_j$  and  $S_{wj}$  represent the mass of the species present in the solid phase and the corresponding non-flowing fluid phase, respectively, per unit mass of solid or of fluid, and  $\phi_j$  and  $\phi_{nj}$  are the effective porosity and the contribution to the total porosity as defined by

$$\phi_{\Sigma j} = \phi_j + \phi_{nj} \quad (23)$$

from voids not involved in fluid flow.

The first term on the right-hand-side of Eq. (22) represents the diffusion into the adjacent cells with a species-dependent aqueous diffusion constant,  $D_1$ . The terms in the summation are a generalized form of the adsorption-diffusion expression. The first term in the summation represents diffusion into the bulk solid and is dependent upon both the solute species and the particular solid phase  $j$ . The  $\partial S_j / \partial C_1$  part of this term is the general source/sink expression for the solid medium. The second summation term refers to diffusion into the dead-end pores of the  $j$ th solid phase.

This form of the diffusion equation gives considerable flexibility when treating these three processes. The source/sink terms, being dependent on both the aqueous species and the solid phase, are certainly the most difficult to quantify. However, by writing this term in this specific manner, we may discard particular species-solid phase combinations which are negligible and make suitable approximations for those combinations which are important but which lack the required experimental data. In addition, Eq. (22) can treat porous or fractured media equally well. In the case of planar fractured media, the Laplacian operator may be modified to appropriately treat diffusion relative to the fracture plane.

Ultrafiltration results from the preferential retention of solute, over that of water. There are two mechanisms which dominate this process. First, in fine grain geologic media of high surface charge, the large polarized hydration spheres of some ions cause their preferential retention by physical or electrostatic filtration effects. Second, colloids which have sorbed species from solution may be preferentially retained in this way. This process can be modeled by simply retaining a fraction of the mass, determined by the filtration coefficient, from the mass to be convectively transported from the control volume during that time step. This is a suitable treatment for modeling the hydration sphere ultrafiltration mechanism, where another term containing a transport velocity dependent negative diffusion coefficient can be added along the axis of flow in Eq. (22). Although the transport behavior of colloids is outside the scope of the chemical model being proposed here, the loss of solute from solution to a colloid sorbed phase may be described by equilibrium expressions such as those in the first part in this section. Therefore, if the hydraulic transport code also treats colloid transport, both of the main ultrafiltration mechanisms can be modeled.

## COMPUTATIONAL SEQUENCE AND COUPLING TO HYDRAULIC TRANSPORT CODES

The discussion to this point has been limited to describing the physicochemical processes which distinguish a solute from the water solvent, as they occur within a single control volume. To be useful in macroscopic transport modeling of solutes, a computational scheme must be developed for the cell, a chemical model must be developed for coupling cells and the chemical model must be coupled to a hydraulic model which is used to predict the flow of water.

Hydraulic transport models generally consist of a set of nodes, in two or three dimensions, joined by legs which represent hydraulic connections. The path in Fig. 1 may be considered one such leg. Each leg in such a system can be considered to be made up of one or more cells. Convective transport can occur only along the legs, although cells may share solid phase reservoirs or may exchange material by diffusion along paths not described by legs. The volume of cells is limited only by the consistency of the physicochemical environment and by the intensity of spatial variability in dynamic systems. When the cell volume is made sufficiently small so that it is not influenced by spatial or dynamic variations of these environmental conditions, the control volume can be considered a simple mixing/reaction cell. Such a cell outputs a volume of solution, determined by the transport model, which is equal to the inflow volume which displaces it during one time step. The concentration of the outflow is equal to that of the homogeneous (well mixed cell) at the end of the time interval.

The computational sequence for a single cell during one time step is shown in Fig. 2. First the input concentrations are calculated by mixing the inflow solutions and adding any mass gained by diffusion during the last time step. The system of equilibrium expressions, which may be written with only one independent variable (the master species concentration) for each element, is then solved for the amount of mass in each species. The results are used to determine if the element mass balance constraints are satisfied, and to calculate any mass loss or gain from solution. If the mass balance restrictions are not satisfied, the concentrations of the master species are adjusted and the system equilibrium expression is resolved. If the mass balance restrictions are not met, the electroneutrality and conservation of

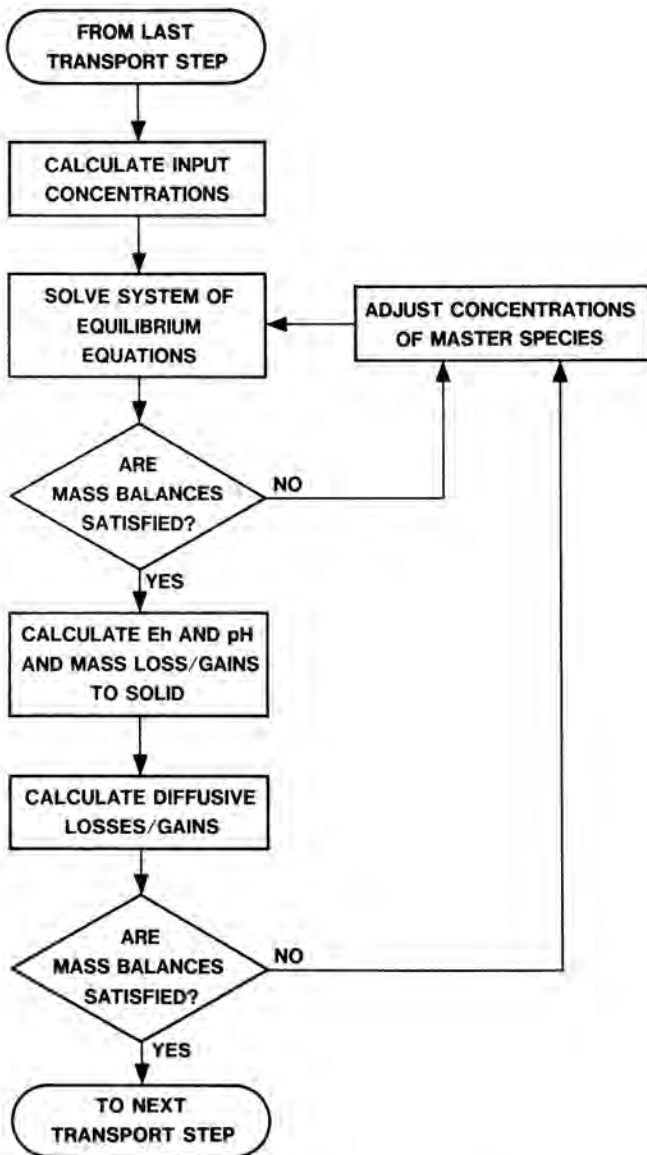


Fig. 2 Computational sequence for retardation mechanisms within a single cell during one time step.

electron equations are used to solve for pH and Eh. The mass losses/gains to the solid phase due to reaction processes are then calculated. Next, the losses/gains due to the non-reaction processes occurring during that transport interval are calculated among all communicating cells, based on results of the concentration and speciation calculation. If this does not satisfy the mass balance constraints, the master species are readjusted and the system equilibrium expressions are resolved. If conservation of mass is satisfied, another transport step can be executed. The diffusional losses and the outflow concentrations are used to calculate the concentration of the input solution for the appropriate cells for the next time step.

In this way a modified reaction-path-simulation model can be coupled to a hydraulic transport model. The result can be used to determine the speciation and concentration of solutes in the system at various locations and times. The hybrid chemical/physical code proposed is potentially cumbersome since a nested loop through an equilibrium reaction-path-simulation code is to be coupled to an already complex hydraulic transport code. The full hybrid code with all its generalized features is clearly of unmanageable proportions and unacceptable running times, particularly in a risk assessment situation where repeated runs are required. This problem is resolved by using only features of the generalized hybrid code which are particularly applicable to the problem at hand. This requires a firm understanding of the system being considered. Such simplified forms of transport codes are already in use. Two areas of simplification can much reduce the complexity of the chemical codes. First, only species making up significant mass fractions of an element in solution need be considered. This would be only a few species for an element such as technetium, and only a few tens of species even for uranium (rather than the several hundred potential aqueous forms). These could be identified by a predominant ion (calculational) code. Second, only dominant retardation mechanisms in the given geomedium need be considered (e.g., ultrafiltration in a highly fractured granite can be neglected). Thus, by selecting the most important species and mineral phases, and by disregarding processes having minor contributions to retardation, an efficient, problem specific code can be developed.



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