A Lagrangian Reactive Transport Simulator with Successive Paths and Stationary-States: Concepts, Implementation and Verification

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A LAGRANGIAN REACTIVE TRANSPORT SIMULATOR WITH SUCCESSIVE PATHS AND STATIONARY-STATES: CONCEPTS, IMPLEMENTATION AND VERIFICATION

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A geochemical software package which models static, single-path kinetic water-rock interactions, EQ3/6 [Wolery, 1979], has been modified to incorporate successive-paths and stationary states under high Peclet number transport conditions in a Lagrangian reference frame [Lichtner, 1988]. These modifications permit calculation of reactive transport with reasonable computational requirements. Results from the new option in EQ3/6 have been compared with analytical results for the simple HCl - SiO2 system; excellent agreements were achieved. Results have also been compared with published results [Lichtner, 1988] for a portion of the Al2O3 - HCl - K2O - SiO2 system. The results are in good qualitative and, in some cases, good quantitative agreement. However, the values of some variables differ substantially; these differences can be attributed to use of a different set of Al and Si aqueous species.
INTRODUCTION

Emplacement of high-level radioactive waste into the subsurface is expected to cause a thermal perturbation, convective fluid flow and, possibly, the release of radionuclides into the flowing fluid phase [e.g. Brueton, 1987; Nitao, 1988]. Consequently, fluids may move across isotherms and lithologic boundaries causing a state of overall chemical disequilibrium between the fluid and rock. This will result in kinetic dissolution of minerals initially present in the rock and precipitation of secondary minerals, some of which may contain radionuclides. Dissolution and precipitation produce changes in porosity and permeability which may, in turn, alter the flow field. Thus, there is an intimate coupling among the fluid flow, solute transport and heterogeneous reaction processes; these coupled processes have been called reactive transport by various authors [e.g. Rosner, 1986; Orin and Boris, 1987].

Two different reference frames can be chosen in any consideration of reactive transport: Lagrangian and Eulerian. A Lagrangian reference frame is one where the evolution of a single hypothetical fluid packet is followed. This is the reference frame selected for this study where we will examine the chemical evolution of successive fluid packets as they move along the same curvilinear trace in space. An Eulerian reference frame is, in contrast, tied to a particular point in the porous medium. During the chemical evolution of an individual fluid packet, the aqueous phase may become saturated with respect to some mineral phases and precipitation can commence. It appears that the location of these precipitation points, fronts, moves very slowly through time; they can be considered stationary in space for significant amounts of time. It is the purpose of this work to be able to calculate the locations of precipitation fronts, the duration of their stationarity and the steady-state aqueous chemistry associated with them. These conditions are called stationary-states.

The purpose of reactive transport simulation, within the context of radioactive waste disposal, is to predict aqueous radionuclide concentrations at various times and locations in a system of interest. Predicted concentrations are compared with regulatory limits to assess the viability of particular disposal strategies. It is anticipated that maximum aqueous radionuclide concentrations will be less than 0.01 ppm and that their potential to be sequestered in solid phases will be a function of solution pH and Eh [Brueton, 1987]. In contrast, the major elements (e.g. Ca, Cl, Fe, K, Mg, Na and Si) may have maximum concentrations on the order of 10 - 100 ppm. At these concentrations, the major elements, their heterogeneous reactions and their transport through the system will control solution pH.
and Eh; aqueous radionuclides will merely respond in a passive fashion to these key variables. It may be possible to separately examine the evolution of the major element and radionuclide aqueous chemistry. Results of major element reactive transport modeling can be used in radionuclide migration calculations as imposed conditions to which the radionuclides respond.

In the following report, we will present the conceptual and mathematical foundation for a particular reactive transport simulator, discuss the implementation of this model and, finally, examine its application to two simple hypothetical systems.

**CONCEPTUAL AND MATHEMATICAL MODEL**

There are an abundance of approaches to reactive transport simulation reported in the literature and many of these are summarized by Yeh and Tripathi [1989] and Knapp [1988]. This study will closely follow the methodology presented by Lichten [1988] as applied to steady flow in a fully saturated porous medium where transport is dominated by advection and heterogeneous reactions are restricted to irreversible dissolution and equilibrium precipitation. With these restrictions, the mass conservation of an aqueous chemical component in an isothermal, homogeneous volume can be expressed as

\[
\frac{\partial \bar{c}_i}{\partial t} + \bar{v} \cdot \nabla \bar{c}_i - \nabla \left( D_{\text{eff}}^* (I + D) \right) \nabla \bar{c}_i + \bar{R}_i = 0
\]

(1)

where the barred quantities denote averages over the volume and

- \( \bar{c}_i \) = concentration of the \( i \)th component (mol/m\(^3\)),
- \( D_{\text{eff}}^* \) = effective porous media diffusion coefficient (m\(^2\)/s),
- \( D \) = dispersion tensor (m\(^2\)/s),
- \( I \) = unit tensor
- \( t \) = time (s),


\[
\mathbf{\bar{R}}_i \text{ represents gain and loss of solute component mass due to heterogeneous reaction processes. These processes may include dissolution and precipitation of solid phases, ion exchange and adsorption. Attention in the current study will be limited to one-dimensional, constant velocity environments where dissolution and precipitation reactions occur irreversibly in a nonlinear manner. The exact form of } \mathbf{\bar{R}}_i \text{ is still uncertain but relationships similar to }
\]

\[
\mathbf{\bar{R}}_i = \sum_{j=1}^{n_s} v_{ij} k_j S_j a_{ir} \left( 1 - \frac{Q_j}{K_j} \right)
\]

(2)

where

- \( a_{ir} = \text{hydrogen ion activity} \)
- \( k_j = \text{intrinsic dissolution rate for } j\text{th mineral (mol } / \text{m}^2 / \text{s)} \)
- \( K_j = \text{equilibrium constant for hydrolysis of } j\text{th mineral} \)
- \( n_j = \text{exponent to hydrogen ion activity for } j\text{th mineral} \)
- \( n_s = \text{total number of solid phases in system} \)
- \( Q_j = \text{ion activity product for } j\text{th mineral} \)
- \( S_j = \text{specific surface area (m}^2 \text{of mineral } j / \text{m}^3 \text{of bulk rock)} \)
- \( v_{ij} = \text{stoichiometry of the } i\text{th component in the } j\text{th mineral} \)

have been proposed [Helgeson et al., 1984; Knauss and Wolery, 1986; Lichtner, 1988]. The sum in (2) is taken over all heterogeneous reactions since a chemical component often occurs in more than one mineral.

Equation (1) can be made dimensionless and put into a 1-D Lagrangian reference frame (Appendix 1)

\[
\frac{D C_i}{D \tau} - \frac{1}{P e} \mathbf{\bar{R}}_i - \sum_{j=1}^{n_s} v_{ij} a_{ir} \left( 1 - \frac{Q_j}{K_j} \right) = 0
\]

(3)

where

\( C_i = \frac{\mathbf{\bar{R}}_i}{a_{ir}}, \)
with \( q \) being a reference concentration for the \( i \)th chemical component, \( Da \) the Damköhler number, \( Pe \) the Peclet number, \( L \) a characteristic length and \( x \) the dimensioned length scale. Then as \( Pe \to \infty \),

\[
\frac{D C_i}{D \tau} + \sum_{j=1}^{n} \left[ Da_j \left( 1 - \frac{C_j}{K_j} \right) \right] = 0
\]

(4)

Though the governing equation (4) can treat both kinetic dissolution and precipitation, we will assume in the following implementation that all product phases are in equilibrium with the fluid phase; thus, the precipitation rate adjusts to prevent supersaturation. This follows the suggestions of Helgeson [1979].

Equation (4) forms a system of ordinary differential equations with there being one equation for each chemical component. This system of equations describes the chemical evolution within a fluid packet resulting from heterogeneous reactions that occur as fluid migrates along a predetermined pathline [Norton, 1978; Bear, 1988]. Initial compositions for the aqueous and solid phases must be supplied; the aqueous phase is initially out of equilibrium with at least one of the solid phases and initial solid phase abundances are usually homogeneously distributed in space. However, this homogeneity will be disrupted as product phases, not initially present in the rock, are precipitated at various times and locations as a result of coupled fluid migration and reaction; a distinct sequence of altered mineral assemblages is produced along the fluid pathline in this manner. In addition, dissolution of initial minerals and precipitation of new products cause temporal and spatial changes in the source term through changes in solid phase surface area, \( S_i \), and when reactants are completely dissolved, i.e., \( n_s \) decreases. Therefore, subsequent fluid
packets with the same starting solution composition will experience a separate and distinct chemical evolution due to these modified coefficients and due to reaction with an altered rock. Subsequent fluid packets will not, in general, attain equilibrium with product phases at the same time and location of previous fluid packets. Previously deposited minerals will then become reactants until the new fluid packet reaches equilibrium with them and begins precipitation downstream. Thus there is a continual dissolution of previously precipitated phases and a continual migration of precipitation fronts. Precipitation fronts are defined to be the first occurrence of product phase precipitation in space with increasing x from the origin.

From the preceding discussion it would appear that the system of equations would need to be solved for each and every fluid packet in the system and for the duration of the time period of interest. This would require an exceedingly large number of solutions. However, Lichtner [1988] presents a stationary-state concept that permits large time steps to be taken in a system where the initial fluid composition is constant. The basis for the stationary-state concept is that mineral dissolution rates ($10^{-11} \text{ mol/m}^2/\text{s}$) and precipitation front movement ($< \text{mm/yr}$) in natural fluid-rock systems are exceedingly slow. The precipitation fronts are effectively stationary for time frames of practical interest. This permits development of steady-state fluid compositions, dissolution rates and precipitation rates upstream of each precipitation front. These rates can be linearly extrapolated through time; after a significant amount of time has elapsed there changes in mineral abundance and specific surface areas will cause significant rate changes which will translate into a movement of the precipitation fronts. Until there is an appreciable change in the location of precipitation fronts, the chemical evolution of only one fluid packet per stationary-state is required. In this scheme, frontal movement is caused by complete dissolution of a reactant, by significant changes in surface area or by porosity changes which induce significant fluid velocity changes; porosity changes are not incorporated in the present implementation. The time duration of a stationary-state limited by complete dissolution is [Lichtner, 1988]

$$\Delta t_{ij}^* = \frac{X_j \rho_j}{k_j S_j a_{ij}^* \left[ 1 - \frac{Q_j}{K_j} \right]}$$

(5)

where

$$\Delta t_{ij}^* = \text{duration of stationary-state for jth mineral in ith grid block (s)}$$
\[ X_j \quad = \quad \text{mole fraction of jth mineral} \]
\[ \rho_s \quad = \quad \text{molar density of solid phases (mol/m}^3 \text{)} \]

The numerator in (5) is the total amount of mineral \( j \) per unit pore volume and the denominator represents the rate of dissolution of one mole of mineral \( j \) per unit pore volume. The time duration of a stationary-state limited by surface area changes is \([\text{Lichtner, 1988}]\)

\[
\Delta t_{ij}^* = \frac{e_j \left(1 - f_x\right)^{1.5}}{V_j \rho_{H2O} k_j S_j \frac{\Delta S}{\Delta t}} \left(1 - \frac{Q}{K_j}\right)
\]

where
\[ f_x \quad = \quad \text{maximum fractional change in surface area permitted; } f_x = \frac{[S(t) - S(t+\Delta t)]}{S(t)} \]
\[ V_j \quad = \quad \text{molar volume of jth solid phase (m}^3/\text{mol)} \]
\[ e_j \quad = \quad \text{volume fraction of jth mineral} \]
\[ \rho_{H2O} \quad = \quad \text{water density (kg/m}^3 \text{)} \]

The surface area relationship (6) is highly empirical due to an assumed relationship between the number of moles dissolved and the net change in pore volume and mineral surface area; (6) can only be considered as a first approximation. For an entire path, consisting of a number of grid blocks, the duration of a stationary-state is the minimum of (5) and (6) for all minerals in the system and at all points in the system. This defines the interval between the next fluid packet that needs to be considered. The duration of stationary-states are typically on the order of hundreds or even thousands of years and depend, in part, on the time scales-of-interest. In natural systems, the time step is most likely limited by deviations from steady flow conditions or by changes in the initial fluid composition. In hypothetical systems, the duration is most often limited by the amount of a mineral that is precipitated; precipitation amounts are small and subsequent fluid packets, under-saturated with this mineral, will dissolve the small amounts precipitated in a relatively short period of time. In the following section, an implementation of this successive path, stationary-state concept is described.
EQ3/6 MODIFICATION

A geochemical modeling code, EQ3/6 [Wolery, 1979], has been modified to simulate the chemical evolution of successive fluid packets in a fully saturated, isothermal porous medium where advection is the dominant transport process. EQ3/6 is a comprehensive and flexible static equilibrium model that solves the system of equations (4) for multiple components, multiple simultaneous kinetic reactions and one fluid packet. It also assumes the aqueous phase is in complete internal equilibrium. Though other options are available, the chemical evolution of a single fluid packet in a Lagrangian reference frame can be simulated if the open thermodynamic system option is selected [Wolery, 1979]. The objective in the modification was to add the capability to treat successive paths, i.e., successive fluid packets, and the stationary-state concept. Details of the EQ3/6 software package can be found in Wolery [1979] and these will not be discussed further here.

The modifications were effected by first setting up a user defined computational time grid (figure 1); time is transformed to space in the Lagrangian reference frame through fluid velocity. Each grid has identical initial conditions for the solid phases. Computations commence for the first grid with the initial fluid composition read in from an input file; computations are terminated when the grid boundary is reached or when the fluid comes into equilibrium with a product phase. If a product phase is encountered, a new grid is created such that a grid boundary and the precipitation front coincide; in this manner discretization in time can change from fluid packet to fluid packet and also during the computations for one fluid packet. Computations proceed from one grid to the next with the effluent from the previous grid serving as the initial fluid composition for the next grid. Each grid is treated as if it were a separate and distinct run by this scheme. Computations proceed for this path until a user defined time and space limit is achieved. This method permits the user to define a minimum temporal and spatial resolution; resolution is greatest near precipitation fronts where there is the greatest change in variables and also where there is the greatest interest. Discontinuities in fluid composition often occur near precipitation fronts, making continuous computation across them difficult [Lichtner, 1985]; the method of terminating computations at a precipitation front, creating a new grid boundary to coincide with this front and then recommencing computations circumvents this difficulty.

At the end of a path computation, effluent solution composition, reaction rates, solid compositions and porosity are known. The duration of the stationary-state is computed from these; the duration is limited by either complete
dissolution of a solid phase (5), a change in reactive surface area to a user defined level (6) or a user defined maximum duration. Rates are linearly extrapolated to calculate solid abundances and porosity within each grid block at the end of the stationary-state; these serve as initial conditions for the next path. Computations for subsequent paths repeat the steps of the first path; the initial fluid composition for the first grid is still read in from an input file and computations proceed from one grid to the next. A significant difference between different path runs is the initial solid composition; product minerals may be deposited during the first path and in subsequent runs these become part of the initial solid assemblage and are available for dissolution. This procedure is repeated for a specified number of stationary-states.

These new capabilities were added as an option in EQ3/6. The logic of the data flow is described in Appendix 2, a selected glossary of terms is given in Appendix 3 and a sample input file is given in Appendix 4. Two examples are described in the next section which serve as model verification.

EXAMPLES

$H_2O - SiO_2$ System: Quartz Reactant

The new option was applied to a hypothetical $H_2O - SiO_2$ system and results were compared with analytical solutions to the governing equation as a partial verification of the model. The initial conditions (Table 1) represent a dilute fluid, initially undersaturated with all solid phases, flowing through and reacting with a homogeneous porous medium where the initial solid phase is pure quartz. Dissolution rates are from Knauss and Wolery [1988]. As time increases the silica concentration in the fluid packet will increase, due to dissolution, until equilibrium is achieved. This simple one-dimensional, homogeneous, single-component system can easily be represented mathematically by equation (4) with $i = Q$, for SiO$_2$, and $n_s = 1$, where $n_s$ is the number of heterogeneous reactions. The dimensioned solution is [Knapp, 1988]

$$c_Q(t) = c_Q + [c_Q(0) - c_Q] e^{-Q t}$$

(7)
where \( n_j = 0 \) in equation (2) for the chosen pH range [Knauss and Wolery, 1988].

Results from the new EQ3/6 option and analytical results using (7) are essentially equivalent (figure 2). This serves as a partial verification of the new option. It is a partial verification due to the highly simplified nature of the problem. In addition, only the first stationary state has been examined; results for subsequent fluid packets would yield results of comparable fidelity since the only change in the system is in the \( S_Q \) parameter.

**Al₂O₃ - HCl - H₂O - K₂O - SiO₂ System: Quartz and Feldspar Reactants**

An additional verification example was run and compared with the published results of Lichtner [1988]. This case is for a dilute acid solution reacting with a quartz-potassium feldspar porous medium; it serves as a stringent test of the new EQ3/6 option since it encompasses multiple aqueous species, reactants and products. Initial conditions and parameter values used (Table 2) are identical to those given in Lichtner [1988]. The medium has an initial homogeneous solid phase assemblage consisting of quartz and potassium feldspar; potential product phases are limited to gibbsite, kaolinite and muscovite in addition to the initial reactants. The initial fluid composition is dilute and undersaturated with all solid phases. Lichtner [1988] computed results to almost \( 10^5 \) years; in contrast, the current study only examines results to \( 10^3 \) years due to time considerations. A qualitative and quantitative comparison of the location of precipitation fronts, the paragenetic sequence, precipitation and dissolution rates, mineralogic zone widths and solution compositions will be conducted over the coincident time period in the following paragraphs. In addition, a description and interpretation of some of the observed phenomena will be provided. It should be noted that Lichtner [1988] does not report the aqueous species or the thermodynamic data utilized or other details of the implementation of the theory. While this limits some of the quantitative comparisons, it still permits qualitative, and in some cases quantitative comparison of the overall chemical evolution of each fluid packet.

There is good qualitative agreement between the new EQ3/6 option and Lichtner [1988] with respect to the location of precipitation fronts as well as paragenetic sequences at the end of the first reaction path (figures 3 and 4). The predicted paragenetic sequence in both cases is gibbsite, kaolinite, quartz and muscovite. The gibbsite
precipitation front location is identical in both models; the new EQ3/6 option slightly under-predicts the kaolinite precipitation front location relative to Lichtner's model but over predicts the location for quartz and muscovite (figure 3). The discrepancy in the location of the muscovite front is substantial, being about 1 m. Though there are several possible explanations for the discrepancies, the most likely is the use of a different set of aqueous species in the two models. This will be examined in greater detail later. The evolution of the various mineralogic zones for subsequent fluid packets and stationary-states is also qualitatively similar (compare figure 5 with Lichtner's [1988] figure 10). The precipitation fronts for all products migrate downstream; these fronts are all preceded by dissolution of the mineral which was precipitated by previous fluid packets. Dissolution of previous products by subsequent fluid packets reflects a temporal decrease in upstream dissolution rates. This is caused by a decrease in reactive surface areas (6); each succeeding fluid packet will be increasingly undersaturated with respect to a mineral phase as it approaches a previous precipitation front; the previously precipitated mineral will become a reactant until equilibrium is achieved.

Dissolution rates for k-feldspar and quartz are nearly identical for the two models (compare figure 6 with Lichtner's [1988] figure 8). In addition, there is good qualitative agreement for precipitation rates of gibbsite, kaolinite and muscovite; each has an initially high rate followed by a decay to lower rates. Precipitation rates are controlled by dissolution rates of minerals which serve as a source of components for the product minerals and by speciation within the fluid phase. The gibbsite (Al(OH)_3) precipitation rate remains essentially constant up to the kaolinite (Al_2Si_2O_5(OH)_4) precipitation front; this reflects the relatively constant dissolution rate of feldspar, which is the only source of Al for gibbsite. When kaolinite begins to precipitate there is competition for aqueous Al; most of the Al will go to kaolinite, causing a rapid decrease in the gibbsite precipitation rate until it is no longer a product. This scenario is repeated for kaolinite which fails to precipitate shortly after the muscovite (KAl_3Si_3O_10(OH)_2) front is encountered. A quantitative comparison of precipitation rates reveals significant discrepancies; the rates appear to be greater by about a factor of two in the new EQ3/6 option than in Lichtner's model; in addition, the new EQ3/6 option shows no precipitation of quartz after it reaches equilibrium whereas Lichtner's [1988] model displays a small precipitation rate. While the reasons for these discrepancies are not entirely clear, it is suspected that treatment of instantaneous equilibrium with product phases and the set of aqueous species used is different in the two models. This can not be verified because Lichtner [1988] does not report the details of his chemical system.
In general, there is good agreement in mineralogic zone thicknesses between the two models (compare figure 7 with Lichtner's [1988] figure 8). However, the gibbsite zone and gibbsite-kaolinite zone are exceptions. The new EQ3/6 option calculates thicknesses of about 0.4 m and 0.02 m for these, respectively, whereas Lichtner [1988] calculates thicknesses of about 1 m for each zone. It appears the increased thickness compensates for the decreased precipitation rate so that the same amount of gibbsite is precipitated in both models though over different distances. This cannot be quantitatively checked due to lack of pertinent information in Lichtner [1988].

There is good qualitative and, in some cases, quantitative agreement between the two models for the solid phase data. The discrepancies in some of the computed values can be attributed to differences in the sets of aqueous species. This explanation can be checked by comparing the aqueous data. Unfortunately, Lichtner [1988] provides only total elemental molalities and not species molalities or activities. Comparison between total molalities can serve as an additional verification exercise and as a qualitative check on the suggested differences in the aqueous species set.

There is excellent quantitative agreement in the total concentration of K between the two methods (compare figure 8 with Lichtner's [1988] figure 11); the log molality of K levels off at a value of about -4.0 in both cases. There is also good qualitative agreement for Al, pH and SiO₂. Al displays a rapid increase and commences to decrease at the onset of gibbsite precipitation; this decrease is interrupted by a significant second-order discontinuity near the muscovite precipitation front; a second-order discontinuity is where the derivative of the function is discontinuous as opposed to the function itself. pH displays an initial moderate increase until gibbsite starts to precipitate; this is followed by a very gradual increase until the muscovite precipitation front is approached, at which time a very rapid increase occurs. SiO₂ shows a logarithmic-like increase to a fairly constant level. Though the geometries of the spatial variations are similar, there are significant differences in the concentrations of Al and SiO₂, as well as pH, between the two methods. In both models Al initially increases to a peak value of about -4.8; however, after muscovite precipitation Al from the new EQ3/6 option returns to a value of about -6.5 whereas Lichtner computes a value of about -7.0. SiO₂ log molality at quartz equilibrium is -4 (the new EQ3/6 option) whereas as Lichtner's SiO₂ value appears to be about -3.7. Finally, pH computed by the new EQ3/6 option reaches a value approaching 8.5 whereas Lichtner's value is about 7.8.
These discrepancies are consistent with differences in the aqueous species sets for Al and Si. The lower values of Al in Lichtner [1988] suggest the use of a subset of Al species that were used in the new EQ3/6 option; increasing the number of aqueous Al species increases the maximum amount of Al that can be held in solution. In contrast, Lichtner's greater value for SiO₂ suggests the opposite. The set of Al and Si species used in this study are given in Table 3 along with the dissociation constants.

The gradual decline in total Al molality and the second-order discontinuity near the muscovite precipitation front are interesting features of this simulation. Analysis of these features gives insight into general reactive transport phenomena as well as additional insight into the aforementioned discrepancies. The following discussion will be focussed on the region near the muscovite precipitation front. The driving force for the chemical phenomena is the irreversible dissolution of k-feldspar. The rate of dissolution is nearly constant for the entire path and decreases only slightly near the muscovite front (figures 6 and 9); this provides a nearly constant source of Al, K and Si into the aqueous phase. Kaolinite and quartz equilibria are additional controls on the aqueous phase; these buffer SiO₂ activity and the Al³⁺/H⁺ activity ratio (figure 10). Any change in pH (figures 8 and 10) must be accompanied by an equal and opposite change in Al³⁺ activity; as pH increases, Al³⁺ activity must decrease and, for nearly constant total Al in solution, the activities of the other Al species must increase relative to Al³⁺ (figure 11). However, the amount of Al in a solution in equilibrium with kaolinite and quartz changes with pH (figure 12). The equilibrium amount below a pH of about 6 is comprised predominantly of Al³⁺, which is the dominant Al species. Al molality will steadily decrease as pH increases in this region; this causes the steady decline in Al observed in figure 8. At pH between about 6 and 6.5 the abundances of the various Al species are nearly equivalent; the interplay of the various Al species gives rise to almost no change in Al concentration. However, as pH increases Al(OH)₃ becomes the dominant species causing the maximum Al content to increase with pH. This type of aqueous species behavior, with trough-shaped solubilities as a function of pH is commonly observed for alumino-silicates and also for oxides [Jackson and Helgeson, 1985]. This critical pH region is traversed very rapidly near the muscovite precipitation front in this simulation and causes the observed reversal (figure 8). The reversal is pH dependent and occurs just before muscovite begins to precipitate; it is the rapid increase in pH which causes the Al second-order discontinuity and not the precipitation front.
The overall good agreement between the new EQ3/6 option and Lichtner's [1988] results are encouraging. However, the discrepancies are significant enough to preclude a complete verification. It is likely that the discrepancies can be attributed to the use of a different set of aqueous species for Al and Si, especially in light of the previous discussion on the sensitivity of the results to Al species distribution. This suggestion can not be verified due to the lack of appropriate information in Lichtner [1988].

CONCLUSIONS

The geochemical software package EQ3/6 has been modified to treat reactive transport in a Lagrangian reference frame under the restriction of isothermal, steady flow and high Peclet number transport. The new EQ3/6 option has been successfully verified against an analytical solution for a very simple HCl - SiO₂ system. A verification exercise was also conducted on a more complicated system for which there is a published result [Lichtner, 1988]. Though good qualitative agreement was found between the two models, significant differences occur in some of the computed variables. These can, at least in part, be attributed to use of different sets of aqueous species; this would lead to the observed differences in equilibrium aluminum concentrations. It is not possible to unequivocally state that this is the source of the discrepancies; in complicated models such as these, there are a myriad of variables and options that would need to be checked in detail before such conclusions could be drawn. In addition, these are the first two computations of reactive transport in such a complicated system; additional experience in this field is required and each code package should undergo further testing before either can be considered as vetted packages.

The utility of the stationary-state concept as presented by Lichtner [1988] can not be over emphasized. It is an extremely useful scheme for taking large time steps in realistic systems. The rate of frontal propagation appears to be less than 1 mm/year, though this is highly dependent on the specifics of each system. Such rates suggest that a system can be considered stationary for the duration of a high-level nuclear repository; this could considerably simplify analyses in a system where there can be up to 40 chemical components [Brulon, 1987]. The stationary-state concept also has some interesting implications for systems where the time scale of interest is less than the duration of a stationary-state. It is possible to model these cases with a single fluid packet. Aqueous concentrations can then be
treated as steady-state variables and rates of precipitation and dissolution can be linearly extrapolated for the time period of interest.

There are some significant limitations of the stationary-state concept as implemented here. These limitations are related to the use of a Lagrangian reference frame and the restriction to high Peclet numbers. The initial condition for most systems is a state where there is overall chemical equilibrium between fluid and rock. This is perturbed by fluid flow from a boundary where the fluid composition is kept at some undersaturated level or by fluid flow past some region within the domain where the initial fluid composition is also undersaturated with all minerals. To effectively model the evolution of this system in three-dimensional space, every fluid packet from the boundary or undersaturated domain must be followed from zero time. For a steady flow environment then computations will proceed as described above for each fluid packet; the duration of the stationary-state will be the minimum for all of the fluid packets. In nonsteady flow the situation becomes quite complicated because fluid pathlines will cross at advanced times causing changes in the downstream rock composition. The approach described in this paper is of questionable utility in this case. The high Peclet number restriction also limits the utility of the current implementation. In many natural systems dispersion will be an important transport process; this will cause displacements of reaction fronts from their positions calculated by this method. The degree of displacement and its overall importance will be problem dependent.

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REFERENCES


APPENDIX 1: DERIVATION OF DIMENSIONLESS TRANSPORT EQUATION

The basic equation can be obtained by substituting (2) into (1) to give

\[
\frac{\partial \bar{c}_i}{\partial t} = - \vec{v} \cdot \nabla \bar{c}_i + \nabla \left[ D_{\text{eff}} I + D \right] \nabla \bar{c}_i + \sum_{j=1}^{n_s} \left[ v_{ij} k_j \bar{S}_j \bar{a}_i \left( 1 - \frac{Q}{K_j} \right) \right]
\]

(A1-1)

where the barred quantities denote averages over the volume and

- \( a_r \) = hydrogen ion activity,
- \( c_i \) = concentration of the \( i \)th component (mol/m\(^3\)),
- \( D_{\text{eff}} \) = effective porous media diffusion coefficient (m\(^2\)/s),
- \( D \) = dispersion tensor (m\(^2\)/s),
- \( I \) = unit tensor,
- \( k_j \) = intrinsic dissolution rate for \( j \)th mineral (mol/m\(^2\)/s),
- \( K_j \) = equilibrium constant for hydrolysis of \( j \)th mineral,
- \( n_j \) = exponent to hydrogen ion activity for \( j \)th mineral,
- \( n_s \) = total number of solid phases in system,
- \( Q_j \) = ion activity product for \( j \)th mineral,
- \( S_j \) = specific surface area (m\(^2\) of mineral \( j \)/m\(^3\) of bulk rock),
- \( t \) = time (s),
- \( v \) = fluid velocity (m/s),
- \( v_{ij} \) = stoichiometry of the \( i \)th component in the \( j \)th mineral.

For a one-dimensional system with a homogeneous velocity field (A1-1) becomes

\[
\frac{\partial \bar{c}_i}{\partial t} = - \frac{\partial \bar{c}_i}{\partial x} + \left[ D_{\text{eff}} + D \right] \frac{\partial^2 \bar{c}_i}{\partial x^2} + \sum_{j=1}^{n_s} \left[ v_{ij} k_j \bar{S}_j \bar{a}_i \left( 1 - \frac{Q}{K_j} \right) \right]
\]

(A1-2)
where $D$ is the scalar dispersion coefficient, $x$ the length coordinate and $v$ the scale velocity. Introducing an arbitrary length scale, $L$, and a dimensionless length, $\chi$ then $x = \chi L$, $\partial x = L \partial \chi$, $\partial x^2 = L^2 \partial \chi^2$ and upon substitution (A1-2) becomes

$$\frac{\partial \bar{C}_i}{\partial t} = -\frac{v}{L} \frac{\partial \bar{C}_i}{\partial x} + \left[ \frac{D_{\text{eff}} + D}{L^2} \right] \frac{\partial^2 \bar{C}_i}{\partial x^2} + \sum_{j=1}^{n} \left[ v_{ij} \frac{S_j}{\bar{v}} \frac{a_{ji}}{\bar{v}} \frac{L}{\bar{c}_i} \left[ 1 - \frac{Q_j}{K_j} \right] \right]$$

(A1-3)

A reference concentration, $c_i$, can also be defined as can a dimensionless concentration, $C_i$, then $\bar{C}_i = c_i C_i$, $\partial \bar{C}_i = c_i \partial C_i$, and upon substitution into (A1-3)

$$\frac{\partial C_i}{\partial t} = -\frac{v}{L} \frac{\partial C_i}{\partial x} + \left[ \frac{D_{\text{eff}} + D}{L^2} \right] \frac{\partial^2 C_i}{\partial x^2} + \sum_{j=1}^{n} \left[ v_{ij} \frac{S_j}{\bar{L}} \frac{a_{ji}}{\bar{v}} \frac{L}{\bar{c}_i} \left[ 1 - \frac{Q_j}{K_j} \right] \right]$$

(A1-4)

Dividing each term in (A1-4) by $\bar{v} / L$ gives

$$\frac{L}{\bar{v}} \frac{\partial C_i}{\partial t} = -\frac{v}{L} \frac{\partial C_i}{\partial x} + \left[ \frac{D_{\text{eff}} + D}{L^2} \right] \frac{\partial^2 C_i}{\partial x^2} + \sum_{j=1}^{n} \left[ v_{ij} \frac{S_j}{\bar{v}} \frac{a_{ji}}{\bar{v}} \frac{L}{\bar{c}_i} \left[ 1 - \frac{Q_j}{K_j} \right] \right]$$

(A1-5)

By defining a Damkohler number, $Da$, a Peclet number, $Pe$, and a dimensionless time, $\tau$ via

$$Da = \frac{v_{ij} \bar{S}_j \bar{a}_{ji} \bar{L}}{\bar{v} c_i} \frac{L}{\bar{v}} ,$$

$$Pe = \frac{\bar{v} L}{D_{\text{eff}} + D} ,$$

$$\tau = \frac{L \bar{v}}{L}$$

then upon substitution (A1-5) becomes

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The final step is to put (A1-6) into a Lagrangian reference frame. This is done by noting that the definition of the substantial time derivative is

$$\frac{D C_i}{D \tau} = \frac{\partial C_i}{\partial \tau} + \frac{1}{T_e} \frac{\partial^2 C_i}{\partial \tau^2} + \sum_{pi} \left\{ \mathcal{D}_{aij} \left[ 1 - \frac{Q_i}{K_{ij}} \right] \right\}$$  \hspace{1cm} \text{(A1-7)}$$

then

$$\frac{D C_i}{D \tau} = \frac{1}{T_e} \frac{\partial^2 C_i}{\partial \tau^2} + \sum_{pi} \left\{ \mathcal{D}_{aij} \left[ 1 - \frac{Q_i}{K_{ij}} \right] \right\}$$  \hspace{1cm} \text{(A1-8)}$$
APPENDIX 2: LOGIC CHART FOR THE NEW EQ3/6 OPTION*

A. Read Input Data for \( n_{\text{path}} \) and \( n_{\text{grid}} \)
   1. read run conditions and switches (mprdz)
   2. read mineral data (mprdm)
   3. reset mineral data if \( n_{\text{path}} > 1 \) (mpsetm & mpsetk)
   4. read computational switches (mprdz)
   5. read Lagrangian input (mprdl)
   6. save mineral data if \( n_{\text{path}} = 1 \) (mpsavm)
   7. read aqueous data (mprdz)
   8. reset matrix parameters if \( n_{\text{grid}} > 1 \) (mpsetp)
   9. save aqueous data if \( n_{\text{grid}} = 1 \) (mpsave)
  10. reset aqueous data if \( n_{\text{grid}} > 1 \) (mpsete)

B. Output Lagrangian Run Data to lagm and lagaq (mpout1)

C. Read Thermodynamic Data

D. Set Grids and Run Times

E. Initialize and Set Parameters

F. Distribute Aqueous Solution (ngcadv & eqcalc)

G. Compute Reaction Path for \( n_{\text{grid}} \)
   1. stop at time flag or when new product encountered
      a. time flag is time required for fluid to traverse the grid block
   2. save reaction rates at end of each step for averaging (mpavg)
   3. output key grid data at specified print increments to lagfjij (mpscrpz)

H. Shift Grids if New Product Encountered (mpshft)
   1. create new grid with boundary on new reaction front
   2. shift grid data to next higher grid number

I. Compute Duration of Stationary State for \( n_{\text{grid}} \) (mpndur)
   1. for both complete mineral dissolution and surface area change

J. Save Solid and Aqueous Data (mpsav)
   1. solid data are reactants for next path
   2. aqueous data are influent for next grid

K. Increment \( n_{\text{grid}} \) (mpeq6)

L. Go To A Unless Last Grid (mpeq6)

M. Reset Solid Abundances to End of Stationary State (mpcalc)
   1. duration of stationary state is minimum time for all grids
   2. linearly extrapolate dissolution and precipitation rates for duration of stationary state of \( n_{\text{path}} \)

N. Output Path and Grid Data to lagm and lagaq (mpout2)

O. Increment \( n_{\text{path}} \) (mpeq6)

P. Go To A Unless Last Path (mpeq6)

* In the above, names in parentheses, e.g., (mprdz), refer to subroutine names, names in italics, e.g., \( n_{\text{path}} \), refer to variable names and underlined names, e.g., lagm, refer to output file names.
**APPENDIX 3: SELECTED GLOSSARY FOR THE NEW EQ3/6 OPTION**

**cmoles(i,j)** . . . . . total number of moles of ith solid in jth grid block;
initially set in mpsavm for reactants so that cmoles(i,ngrd)=morr(i);
set for products in mpsav to either cmoles(i,ngrd)=morn(i)+mpmn(i) or 
cmoles(i,ngrd)=10**zvelg0(i);
reset for all solids in mpsave to represent values at end of stationary state;
used in mpout2, mpsetm and mpshift.

**cmoll(i,j)** . . . . . total number of moles of jth element in equilibrium system;
cmoll(i,j) = mte;
set in mpsav using effluent of grid i as influent of grid i + 1;
used in:
mpout2 to output influent composition of ith grid,
mpsave to save influent data of first grid and
mpsete to reset input aqueous data for i + 1 grid,
mpshift to shift data up one grid after a new reaction boundary has been located.

**cmoll2(i,j)** . . . . . total number of moles in aqueous phase;
cmoll2 = micaq for each grid block;
set in mpsav using effluent of grid i as influent of grid i + 1;
used in:
mpout2 to output influent composition of ith grid,
mpsave to save influent data of first grid and
mpsete to reset input aqueous data for i + 1 grid,
mpshift to shift data up one grid after a new reaction boundary has been located.

**cmoll3(i,j)** logarithmic starting estimate of basis variable for each grid block;
cmoll3 = mprmn for product minerals,
cmoll3 = zvelg1 for aqueous species
set in mpsav using effluent of grid i as influent of grid i + 1;
denh2o . . . . . . . . . . density of water (g/cm**3);
read in via mprdl;
distal . . . . . . . . . . duration of current stationary state;
distal = minimum of endure(i); for i = 1,ngrdmx;
reset in mpstep to 0;
set in mpscale;
used in mpout2.

**fsurf** . . . . . . . . . . fractional decrease in surface areas (S) required to terminate a stationary-state;

\[
fsurf = \frac{S(t+\Delta t) - S(t)}{S(t)}
\]
read in through mprdz;
utilized in mpdur.

**klim(i)** . . . . . code describing whether stationary state is limited by complete dissolution (klim(i) = 0), surface area change (klim(i) = 1) or total porosity change (klim(i) = 2) for each grid block;
initially set in mpdur for each grid block;
shifted in mpshift when necessary;
klim(ngrdmx+1) set to value of klim(j) where j is the index of the grid block limiting the step size;
used in mpout2.

**morn(i)** . . . . . accumulative number of moles precipitated in equilibrium system;
products are arbitrarily divided into an equilibrium (es) and physically removed (prs) subsystems;
al precipitated mass is put into prs except enough to keep matrix from bombing which is left in morn;
total accumulated moles precipitated is morn+mpmn

**morr(i)** . . . . . number of moles of ith reactant at end of grid block.

**mpmn(i)** . . . . . accumulative number of moles precipitated in physically removed system;

*bold-face* type denotes subroutine names in mpeq6 whereas *italic-face* type denotes names of actual variables in mpeq6.
products are arbitrarily divided into an equilibrium (cs) and physically removed (prs) subsystems: all precipitated mass is put into mpmmn except enough to keep matrix from bombing which is kept in cs; total accumulated moles precipitated is momm+mpmmn.

\[ nct \] number of basis elements.

\[ ngdms \] maximum number of grids at the beginning of a run; \[ \text{ngdms} \] can change as the run progresses due to the creation of additional grid blocks as phase boundaries are encountered; used in mpstep to set the maximum distance for computation via \[ x(\text{ngdms}+1) = x(1) + \text{ngdms} \times dx \] where \( x(1) = 0.0 \text{ and } dx = (\text{timemx} - \text{istr}) \times \text{vel}; \)

read in through mprdl.

\[ nprod \] total number of equilibrium minerals in input data; \[ \text{nprod} = kdim - \text{teq}; \]

set in mprdz after read of matrix dimensions; used in mpsav to increment nrcsv for current grid.

\[ nrc \] number of reactants; set in mprdz.

\[ \text{nrcsv}(i) \] number of reactants for current grid \((i)\) but next path; \[ \text{nrcsv}(i) = nct + nprod; \]

set in mpsav; used in mpsav to reset nrcsv on next path.

\[ nsol \] total number of solids allowed in this run; read in via mprdl.

\[ nstate \] total number of stationary states to calculate in this run; read in via mprdl.

\[ p8ch(i) \] effluent pH of ith grid; set in mpsscrpz; used in mpou2.

\[ \text{phi}(i) \] volume fraction of the ith mineral in the jth grid block; initially set in mpsavm: \[ \text{phi}(i) = \text{morr}(i) \times \text{vsave}(i) \times \text{denh2o} \times \text{por}\text{sty}(i) / 1000; \]

reset in mpsscalc to represent values at the end of a stationary state; used in mpndur, mpout2, mpsav and mpshft.

\[ \text{por}\text{sty}(i) \] porosity of the ith grid block; initially set in mpsavm to value read in from input file \((\text{prsty}); \)

reset in mpsscalc to represent value at end of stationary state; used in mpndur, mpout2 and mpshft.

\[ \text{prsty} \] initial porosity for this run; read in via mprdl.

\[ \text{rate} \] dissolution or precipitation rate averaged over entire stationary state duration for current grid (mol/s); \[ \text{rate} = (\text{cmoles(bgrij)} - \text{smoles(ngrdj)} ) / (\text{elapsed time}) \]; a local variable in mpou2.

\[ \text{rkdef} \] default mineral dissolution rate (mol/cm**2/s); read in via mprdl.

\[ \text{rksav}(i) \] dissolution rate for ith mineral (mol/cm**2/s); read in via mprdl; used to find rate when new reactant occurs.

\[ \text{rravg}(i) \] average reaction rate of ith mineral in jth grid block (mol/s); initially set for reactants in mpav to sum of \( rreacl(i) \times dtimc \) where \( rreacl \) is dissolution rate at current \( \xi \) step and \( \text{dtimc} \) is the incremental time for this \( \xi \) step; reset for reactants in mpndur to \( \text{rravg}(i) = \text{rravg}(i) / \text{dtimc} \) where \( \text{dtimc} \) is the transit time across the jth grid block;

set for products in mpsav to \( \text{rravg}(i) = \text{cmoles}(i) / \text{dtimc} \) where \( \text{dtimc} \) is the transit time across the jth grid block;

used in mpsscalc and mpshft.

\[ \text{sarca}(i) \] reactive surface area of the jth mineral in the ith grid block (cm**2); set in mpsavm to input values; reset in mpsscalc to values at end of stationary state; used in mpou1, mpou2 and mpsav.
smoles(i,j) . . . . moles of jth reactant in ith grid block at the beginning of a path;
    set in mprdz;
    used in mpout2 to calculate rate.

tend(i) . . . . . . cumulative fluid transit time (s) for ith grid block in current stationary-state; total elapsed time
    from 1st grid block to 1st stationary-state is obtained by summing duration of each stationary-
    state, except the current one, with tend(i);
    set in mpstep;
    shifted when necessary in mpshft.

time . . . . . . . . elapsed time (s) for this grid block and stationary-state; for each grid block calculation the time
    always starts at zero and goes to timemx or a phase boundary is encountered.

timemx . . . . . . fluid transit time across the current grid block (s);
    timemx is not changed if a phase boundary is encountered before the end of the current grid is
    reached and the current grid is subdivided into two grids;
    read in via mprdz;
    used in mpstep to set grid boundary locations via 
    \[ dx = (timemx - tstart) * \text{vel}. \]

tndur . . . . . . user specified maximum duration of stationary state;
    read in as years and immediately changed to seconds in mprdl;
    used in mpdur.

tolx . . . . . . . . tolerance for stopping a path calculation (s);
    computations will stop within the range 
    \[ \text{timemx} \pm \text{tolx} * \text{timemx}, \]
    read in through mprdz;
    used in chktmx.
tstart . . . . . . starting time for first Lagrangian path; always assumed to be 0.

ubase1(i,j) . . . name of ith element in jth grid block.

ulim(j) . . . . . . name of mineral limiting duration of stationary state in jth grid block;
    initially set in mpndur for each grid block;
    shifted in mpshft when necessary;
    used in mpout2.

umin(i) . . . . . . names of product phase for current grid block.

ureac(i) . . . . . . names of reactants for this grid block.

usave(i) . . . . . . names of all solids permitted in this run;
    read in via mprdl.

uxsil(i,j) . . . . name of each solid phase in jth grid block;
    set initially in mpsavm so that 
    \[ \text{uxsil}(i,j)=\text{umin}(i); \]
    reset in mpsav to reflect addition of product minerals;
    used in mpcalc, mpndur, mpout1, mpout2, mpsetm and mpshft.

vdef . . . . . . . default molar volume (mol/cm^3);
    read in via mprdl.

vel . . . . . . . . fluid velocity (cm/s);
    read in through mprdl.

vreac(i) . . . . . . molar volume of ith reactant (mol/cm^3).

vsave(i) . . . . . . molar volume of ith mineral (mol/cm^3);
    read in through mprdl.

x(i) . . . . . . . location of upstream boundary for ith grid (m);
    set in mpstep for npath = 1 and ngrid = 1 via 
    \[ x(n+1) = x(n) + dx \]
    where 
    \[ dx = (timemx - tstart) * \text{vel} \] and \[ x(1) = 0.0; \]
    changed in mpshft if phase boundary encountered and if not at downstream boundary of ith grid.

zvclg0(i) . . . . . accumulative log moles of product minerals precipitated from 1st step to step before
    current step

zvclg1(i) . . . . . accumulative log moles of product minerals precipitated from 1st step to current step

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APPENDIX 4:

SAMPLE INPUT FILE FOR QUARTZ - FELDSPAR EXAMPLE
input file name= qkfin

k-feldspar + quartz reactants, 25C, pH independent diss., LEQ ppt,
k-feldspar surf. area = 1.2 cm**2/cm**3 bulk rock;
quartz surf. area = 4.0 cm**2/cm**3 bulk rock.
endit.

nmod1= 3
temp0= 25.
tk1= 0.
zistr= 0.0
tstt= 0.
kstpmx= 2000
dzprnt= 1.000000e+00
dzplot= 0.
ifile= 60
iopt1-10= 1
iopt1= 1
iopdr= 1
iocbi= 1
nxopt= 1
uxopt= all
nxopex= 5

jcode= 0
morr= 22.006479
nsk= 0
rk1= 3.162278e-16
imech= 1
reactant= k-feldspar

jcode= 0
morr= 309 6352365
nsk= 0
rk1= 3.162278e-18
imech= 1
reactant= quartz

dlzidp= 0.
tolbt= 0.
tolsat= 1.000000e-04
csgr= 0

gibbsite
kaolinite
k-feldspar
muscovite
quartz
123456789*123456789*123456789*123456789*123456789*123456789*123456789*
mineral

123456789*123456789*123456789*123456789*123456789*123456789*123456789*
mineral

3.1688088e-5 0.1000000 50 0.99707 5 0.25 155. 1.000000e-14 500.

3.1688088e-5 0.1000000 50 0.99707 5 0.25 155. 1.000000e-14 500.

3.1688088e-5 0.1000000 50 0.99707 5 0.25 155. 1.000000e-14 500.

3.1688088e-5 0.1000000 50 0.99707 5 0.25 155. 1.000000e-14 500.

3.1688088e-5 0.1000000 50 0.99707 5 0.25 155. 1.000000e-14 500.
endit.

\[\begin{align*}
\text{ucion} &= \text{cl}^{-}, \\
\text{tempci} &= 0.25000e+02 \\
\text{nxmod} &= 0 \\
\text{iopgl} &= 0 \\
\text{iopg4} &= 0 \\
\text{iopg7} &= 0 \\
\text{iopg10} &= 0 \\
\text{kct} &= 6 \\
\text{kxt} &= 7 \\
\end{align*}\]

\[\begin{align*}
\text{o} &= 0.555091862429018e+02 \\
\text{al} &= 0.100300902673393e-08 \\
\text{cl} &= 0.101156718807777e-03 \\
\text{h} &= 0.111017464268698e+03 \\
\text{k} &= 0.100300902708124e-08 \\
\text{si} &= 0.100000000000000e-08 \\
\text{electr} &= -0.609863722023096e-18 \\
\text{h2o} &= \text{h2o} \\
\text{al+++} &= \text{al+++} \\
\text{cl}^{-} &= \text{cl}^{-} \\
\text{h}^+ &= \text{h}^+ \\
\text{k}^+ &= \text{k}^+ \\
\text{sic2(aq)} &= \text{sic2(aq)} \\
\text{o2(g)} &= \text{o2(g)}
\end{align*}\]
TABLE 1: INITIAL CONDITIONS FOR QUARTZ REACTANT EXAMPLE

**SYSTEM:**

<table>
<thead>
<tr>
<th>T</th>
<th>= 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>= 0.1 MPa</td>
</tr>
<tr>
<td>v</td>
<td>= 1000 cm/yr</td>
</tr>
<tr>
<td>φ</td>
<td>= 0.20</td>
</tr>
</tbody>
</table>

**FLUID:**

<table>
<thead>
<tr>
<th>Elements</th>
<th>log molality (mol/kg H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-3.9950</td>
</tr>
<tr>
<td>Si</td>
<td>-9.00</td>
</tr>
<tr>
<td>pH</td>
<td>3.9950</td>
</tr>
</tbody>
</table>

**SOLIDS:**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>volume fraction</th>
<th>surface area (cm²)</th>
<th>dissolution rate (mol/cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>0.80</td>
<td>1.00000×10⁴</td>
<td>3.162278×10⁻¹⁸</td>
</tr>
</tbody>
</table>

TABLE 2: INITIAL CONDITIONS FOR QUARTZ-FELDSPAR REACTANT EXAMPLE

**SYSTEM:**

<table>
<thead>
<tr>
<th>T</th>
<th>= 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>= 0.1 MPa</td>
</tr>
<tr>
<td>v</td>
<td>= 1000 cm/yr</td>
</tr>
<tr>
<td>φ</td>
<td>= 0.10</td>
</tr>
</tbody>
</table>

**FLUID:**

<table>
<thead>
<tr>
<th>Elements</th>
<th>log molality (mol/kg H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-9.00</td>
</tr>
<tr>
<td>Cl</td>
<td>-3.00</td>
</tr>
<tr>
<td>K</td>
<td>-9.00</td>
</tr>
<tr>
<td>Si</td>
<td>-9.00</td>
</tr>
<tr>
<td>pH</td>
<td>4.00</td>
</tr>
</tbody>
</table>

**SOLIDS:**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>volume fraction</th>
<th>surface area (cm²)</th>
<th>dissolution rate (mol/cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k-feldspar</td>
<td>0.20</td>
<td>1.203526×10⁵</td>
<td>3.162278×10⁻¹⁵</td>
</tr>
<tr>
<td>quartz</td>
<td>0.70</td>
<td>4.011754×10⁵</td>
<td>3.162278×10⁻¹⁸</td>
</tr>
</tbody>
</table>

**Potential Products**

- gibsise: 1.00×10⁻¹⁴
- kaolinite: 1.00×10⁻¹⁴
- muscovite: 1.00×10⁻¹⁴

TABLE 3: AL AND SI AQUEOUS SPECIES AND DISSOCIATION CONSTANTS

\[ \text{Al}_x \text{O}_y (\text{OH})_z + (2y + z)\text{H}^+ = x\text{Al}^{+3} + (y + z)\text{H}_2\text{O} \]

\[ \text{H}_x (\text{H}_2\text{SiO}_4)_y + (2y - x)\text{H}^+ = y\text{SiO}_2 + 2y\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(\log K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>4.9901</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td>10.1980</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
<td>16.1912</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>4</td>
<td>22.3751</td>
</tr>
<tr>
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Fig. 1: Schematic of how gridding operates in the new EQ3/6 option. a) Initially the user specifies a length, the number of grids and the fluid velocity. This yields the grid dimensions ($x_i$), the time it takes a fluid packet to traverse a grid and the total elapsed time from the boundary $x = 0$ to the end of the grid ($t_i$). The slant pattern represents the initial solid phase assemblage. b) As the first fluid packet traverses the grid, it reacts with the solid phases and eventually comes into equilibrium with a new product phase. A new grid boundary is created at this point and all downstream grid designations are incremented. In this manner the number of grids increases during computations. The cross-hatched pattern represents a phase assemblage consisting of the original solids plus an additional product mineral. c) As implemented in the new EQ3/6 option, each grid block is treated separately and distinctly. For the first grid block the user specified initial fluid composition is the starting fluid. This fluid reacts with the solid phase assemblage for the time period $t_1$, unless of course a product mineral is encountered. At $t_1$ computations are interrupted, some book-keeping for the first grid block is done and the ending fluid composition for the first grid block becomes the initial fluid composition for the next grid block. Computations continue in this manner through the last grid block. At this point, the duration of the stationary-state is calculated, solid phase abundances and rate parameters are updated and computations recommence for the first grid block again using the user specified initial fluid composition as the starting fluid.
Fig. 2: Comparison of silica concentrations computed by the new EQ3/6 option (dots) with concentrations calculated from an analytical solution (line) of (7). The differences between the two results is less than one part in $10^3$ which serves to verify the new EQ3/6 option for this particular example.

Fig. 3: Comparison of precipitation front locations from Lichtner's results [1988] and from the new EQ3/6 option for the first fluid packet. If the results are identical, the points would lie along the 45° line. Points above the line indicate Lichtner predicting fronts downstream of those predicted by the new EQ3/6 option; points below the line indicate Lichtner predicting fronts upstream of those predicted by the new EQ3/6 option. The gibbsite, kaolinite and quartz precipitation fronts are in good agreement whereas Lichtner predicts the muscovite precipitation front to occur somewhat downstream from the prediction by the new EQ3/6 option.
Fig. 4: Paragenesis with quartz and k-feldspar as initial reactants at 1 year as predicted by the new EQ3/6 option. Mineral dissolution is illustrated by the stippled pattern and precipitation is illustrated by the cross-hatched pattern. Gibbsite, kaolinite and muscovite are products at this time; quartz is a reactant upstream but becomes a product as quartz and feldspar dissolution increase dissolved silica concentration. There is a small zone where gibbsite and kaolinite coexist and there is also a small zone where kaolinite and muscovite coexist. The precipitation fronts move downstream with subsequent fluid packets (shown by arrows) due to a decrease in upstream dissolution rates.

Fig. 5: Paragenesis with quartz and k-feldspar as initial reactants predicted by the new EQ3/6 option at 1,000 years. Mineral dissolution is illustrated by the stippled pattern and precipitation is illustrated by the cross-hatched pattern. In contrast to the conditions at 1 year, the secondary minerals gibbsite, kaolinite and muscovite are both products and reactants at this time. An upstream decrease in quartz and k-feldspar dissolution rates retards the approach to equilibrium for each of these minerals; this causes precipitation fronts to propagate downstream (shown by arrows) and causes minerals previously deposited at the upstream margin to dissolve.
Fig. 6: Dissolution (-) and precipitation (+) rates of minerals after 1 year. Vertical lines are the precipitation fronts of gibbsite, kaolinite, quartz and muscovite, respectively.

Fig. 7: Thickness of product mineralogic zones up to 1,000 yrs. The total thickness of the gibbsite zone remains constant (0.427 m) for the duration of the numerical experiment; the thickness of the product muscovite zone is indeterminate since muscovite remains a reaction product from its precipitation front onward in space.
Fig. 8: pH and total concentration profiles along the fluid pathline at 1 year. The dotted lines denote precipitation fronts of gibbsite, kaolinite, quartz and muscovite in succession. Al concentration shows a second-order discontinuity near the muscovite precipitation front illustrating the computational difficulties in reactive transport and the necessity to incorporate kinematic shock fronts in Eulerian calculations.

Fig. 9: Dissolution (-) and precipitation (+) rates at 1 year and near the muscovite precipitation front (dotted line).

Fig. 10: Logarithm of the activity ratios for the base ions near the muscovite ppt. front (dotted line) after 1 year: \( \frac{a_{Al^{3+}}}{a_{H^+}}, \frac{a_{K^+}}{a_{H^+}} \) and \( a_{SiO_2} \).

Fig. 11: Log molalities of the five most abundant aluminum species after one year and near the muscovite precipitation front (dotted vertical line).

Fig. 12: Concentration of aluminum in a solution in equilibrium with kaolinite and quartz. At a given pH, the equilibrium concentration of Al with respect to quartz + kaolinite is unique.