Propagation of Dissolution/Precipitation Waves in Porous Media

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The transport of a chemically reactive fluid through a permeable medium is governed by many classes of chemical interactions. Dissolution/precipitation (D/P) reactions are among the interactions of primary importance because of their significant influence on the mobility of aqueous ions. In general, D/P reactions lead to the propagation of coherent waves.

This paper provides an overview of the types of wave phenomena observed in one-dimensional (1D) and two-dimensional (2D) porous media for systems in which mineral D/P is the dominant type of chemical reaction. It is demonstrated that minerals dissolve in sharp waves in 1D advection-dominated transport, and that these waves separate zones of constant chemical compositions in the aqueous and mineral phases. Analytical solutions based on coherence methods are presented for solving 1D advection-dominated transport problems with constant and variable boundary conditions. Numerical solutions of diffusion-dominated transport in porous media show that sharp D/P fronts occur in this system as well. A final example presents a simple dual-porosity system with advection in an idealized fracture and solute diffusion into an adjacent porous matrix. The example illustrates the delay of contaminant release from the 2D domain due to a combination of physical retardation and chemical retardation.

Chemical transport through porous media by advection and diffusion occurs by propagation of concentration waves. These waves can cause local build-up of concentration in the aqueous and mineral phases, but can also cause local reductions in concentrations. A decrease in concentration may be desirable if it leads to contaminant concentrations below recognized hazard levels. An increase in concentration might aid removal of a contaminant by concentrating the contaminant in a relatively small region. This paper focuses on waves caused by mineral dissolution and precipitation, and the effect of

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mineral dissolution/precipitation on the transport of contaminants across a monitored boundary.

Transport through porous media has applications in environmental systems such as contaminant transport away from waste disposal sites and radionuclide migration from radioactive waste repositories, as well as in other areas such as ore body formation and oil reservoir stimulation. Multiple variations on these and other systems are given by, to list a few, Cussler (1982), Cussler et al. (1983), Gruber (1990), Lichtner (1991), Lichtner et al. (1986), Ortoleva et al. (1987a; 1987b), and Weare et al. (1976). This chapter interprets transport from the perspective of propagating waves, and is based in part on the work of Novak et al. (1988, 1989), Schechter et al. (1987), Walsh and Lake (1989), and Walsh et al. (1984). Wave phenomena are demonstrated through two 1D examples and one 2D example. The 1D systems are advection-dominated transport and diffusion-dominated transport; the 2D example is a dual-porosity system where transport is advection-dominated in fractures and diffusion-dominated in the adjacent porous matrix.

PARTIAL DIFFERENTIAL EQUATIONS FOR TRANSPORT

The term advection signifies transport by flow; the equations that describe transport in porous media are referred to as advection-dispersion, or advection-diffusion (AD) equations. The AD equations are material balance equations for a set of chemical element. The equations are coupled by chemical reaction terms that are nonlinear functions of element concentrations in the aqueous and mineral phases. The nonlinear coupling due to chemical reactions results in the wave behavior discussed in this chapter.

Following Novak and Gelbard (1991), the AD equations for a set of I chemical elements can be expressed as

$$\frac{\partial}{\partial t} [\phi_1 C_{i1} + \phi_2 C_{i2}] = \frac{\partial}{\partial x} [D\phi_1 \frac{\partial C_{i1}}{\partial x}] + \frac{\partial}{\partial y} [D\phi_1 \frac{\partial C_{i1}}{\partial y}] - \frac{\partial(C_{i1}u)}{\partial x} - \frac{\partial(C_{i1}v)}{\partial y}$$

$i=1,\dots,I \quad (1)$

where

C_{ip} = concentration of element i in phase p , μmolar
 p = phase subscript, 1: aqueous (flowing), 2: mineral (nonflowing)
 ϕ_p = volume fraction of phase p
 D = effective diffusion coefficient, m^2/s
 u = fluid velocity in x -direction, m/s
 v = fluid velocity in y -direction, m/s
 t = time, s

Although the units listed above will be used throughout this chapter, any consistent set can be used. In Equation 1, mineral phases are not allowed to diffuse or advect. Also, the effective diffusion coefficient was assumed to be the same for all species, obviating the need for writing chemical species balances, and allowing electromigration effects to be ignored. Although Equation 1 allows for spatial and temporal variation in flow velocity, all calculations and discussions in this chapter use constant velocity. Equation 1 does not contain information on the coupling of element concentrations through chemical reactions. This issue is discussed in the following section.

For a one-dimensional domain of length L_x , with constant porosity and constant velocity, Equation 1 can be simplified to the dimensionless form

$$\frac{\partial (C_{i1} + \bar{C}_i)}{\partial t_D} = \frac{1}{N_{Pe}} \frac{\partial^2 C_{i1}}{\partial (X_D)^2} - \frac{\partial C_{i1}}{\partial X_D} \quad i=1, \dots, I \quad (2)$$

where

$$X_D = \frac{x}{L_x} \quad \text{dimensionless distance}$$

$$t_D = \frac{ut}{L_x \phi_1} \quad \text{dimensionless time}$$

$$N_{Pe} = \frac{uL_x}{D\phi_1} \quad \text{Peclet number}$$

$$\bar{C}_i = \frac{\phi_2}{\phi_1} C_{i2} \quad \text{moles } i \text{ in the mineral phases per liter aqueous volume}$$

When μM units are used for mineral concentrations, these refer to the symbol $\bar{C}_i$. The Peclet number indicates the relative importance of advection to diffusion/dispersion; a large Peclet number signifies an advection-dominated system while a small Peclet number signifies a diffusion/dispersion dominated system. Dimensionless time is often referred to as "pore volumes," PV, because

a dimensionless time of $t_D=1$ is required to completely replace all the fluid in the domain; these terms are used interchangeably. The transformation to dimensionless variables defines the fluid velocity as unity, or $V_D=1$. Concentration waves in the systems discussed herein cannot travel faster than the fluid, and thus have dimensionless velocities between 0 and 1.

For transport of elements in the aqueous phase that do not interact with the mineral phases, Equation 2 reduces to the linear PDE given in Equation 3.

$$\frac{\partial C_{i1}}{\partial t_D} = \frac{1}{N_{Pe}} \frac{\partial^2 C_{i1}}{\partial (X_D)^2} - \frac{\partial C_{i1}}{\partial X_D} \quad i=1,\dots,I \quad (3)$$

For a semi-infinite domain ($0 < x < \infty$) with uniform initial conditions and constant boundary conditions, Equation 3 has an exact solution (Marle, 1981) which shows that the initially abrupt concentration change becomes less abrupt as it propagates. Such waves are called *tracer waves* because they propagate with the fluid velocity. When a tracer wave is initiated in response to a step change, the sharpness of the tracer wave decreases with time (for constant value of dispersion, the wave will become more diffuse as it propagates) and also as function of dispersion (a tracer wave in a system with smaller dispersion will be sharper than a tracer wave in an equivalent system with more dispersion).

COUPLING THE A/D EQUATIONS THROUGH CHEMICAL REACTIONS

The relationships among concentrations in the aqueous and mineral phases can be given by either a kinetic or a local equilibrium description of chemical reactions. The local equilibrium description assumes that the time required for chemical reactions to reach equilibrium is much shorter than the time required for transport. The kinetic description is more general, and allows reactions to occur on any time scale. The local equilibrium description requires basic thermodynamic data (generally Gibbs free energies of formation or equilibrium constants, and data for activity coefficient models), and the kinetic description requires information on reaction rates in addition to the

basic thermodynamic data necessary for reactions that are not kinetically controlled.

This paper focuses only on the local equilibrium description. However, the mathematical description of transport with kinetically controlled chemical reactions, and numerical solution methods, are well developed (see for example Lichtner, 1985).

Nonlinear chemical coupling, as noted earlier, greatly increases the complexity of solving the AD equations. To obtain an analytical solution, the AD equation could be linearized by assuming that the mineral concentration of element i is proportional to the aqueous concentration of element i .

$$C_{i2} \approx K_d C_{i1} \quad (4)$$

This equation is a linear isotherm and the proportionality "constant" K_d is called the distribution coefficient. Defining C_{i2} in this way in Equation 2 transforms the nonlinear Equation 2 into the linear PDE Equation 3 with an additional constant term. This allows simplified rock/water interactions to be incorporated into the analytical solution. However, the approximation in Equation 4 is frequently an inadequate description of aqueous/mineral interactions because the ratio of C_{i2} to C_{i1} varies significantly with aqueous and mineral composition. The K_d model is particularly poor at describing dissolution/precipitation phenomena. The linear isotherm model, while appealing in its simplicity in transport calculations, does not adequately describe the chemical aspects of transport in many systems (Brown et al., 1991; Novak, 1992; Gruber, 1990; Payne and Waite, 1991).

Thermodynamic models for chemical equilibrium are based on minimization of the total Gibbs free energy of the system, and result in sets of nonlinear algebraic equations describing the equilibrium concentrations. Detailed discussions of the principles of chemical equilibrium can be found in books such as Garrels and Christ (1990), Smith and Van Ness (1975), and Stumm and Morgan (1981). Numerical algorithms for solving chemical equilibrium problems are given in Smith (1980) and Smith and Missen (1982).

A solubility product expression for mineral equilibria results from simplifying assumptions about the chemical system. For a dissolution reaction describing aqueous/mineral equilibria, such as

has the equilibrium expression

$$[A^+][X^-] \leq K_{AX(s)}^{sp} \quad (4b)$$

where $[A^+]$ and $[X^-]$ represent molal (moles per kg H_2O) concentrations of aqueous species A^+ and X^- , respectively, and $K_{AX(s)}^{sp}$ is a constant called the solubility product for mineral $AX(s)$. As indicated by the inequality, Equation 4 places no constraint on the aqueous concentrations of A^+ and X^- when no mineral $AX(s)$ is present. When $AX(s)$ is present, the product of A^+ and X^- concentrations must equal the solubility product; the actual amount $AX(s)$ is unconstrained by equilibrium but is controlled by the mass balance equations. For dilute solutions, molar and molal concentrations are effectively the same (molar quantities are used in Equations 1, 2, and 3), so these will be taken as identical in this chapter. However, this assumption is not valid for concentrated (brine) solutions, where conversion between these units is required.

The mathematical complexity introduced by chemical nonideality and reactions in the aqueous phase do not qualitatively change the wave phenomena observed during propagation of dissolution/precipitation waves (Novak, 1990), so these will not be considered here. However, phenomena such as ion exchange and adsorption, because of the different forms of reactions and equilibrium expressions (e.g., of corresponding Equations 4) do cause different wave propagation character, and are considered in papers such as Brown et al. (1991) and Bryant et al. (1986).

ONE-DIMENSIONAL SOLUTIONS: D/P WAVE PROPAGATION

Walsh et al. (1984) performed numerical simulations of transport systems with uniform initial conditions and constant boundary conditions,

called Riemann problems, and noted that mineral dissolution/precipitation waves propagate with constant velocity. These observations led to an analytical solution in the absence of diffusion/dispersion based on the concept of coherence (Helferich and Klein, 1970). A noncoherent disturbance is introduced into the domain at the inlet as the change from initial to boundary conditions. The noncoherence resolves into a series of coherent waves that are step changes in aqueous and mineral phase concentrations. These abrupt changes in concentration separate the domain into regions of constant aqueous and mineral composition.

The dimensionless velocity of element i in a coherent wave is given by a material balance across the shock wave,

$$V_{Di} = \frac{1}{1 + \frac{\Delta \bar{C}_i}{\Delta C_{i1}}} \quad (5)$$

where the delta indicates the difference in concentration across the wave. The *coherence condition* requires that the velocity of each element in the wave be the same; thus $V_{D1} = V_{D2} = \dots = V_{DI}$.

Along with the coherence condition and local chemical equilibrium, the general solution to these problems often requires a condition relating concentrations upstream of a wave to concentrations downstream of the wave. The *Downstream Equilibrium Condition*, DEC, (Walsh et al., 1984) requires the aqueous compositions downstream of a wave to be in equilibrium with the minerals upstream of the wave, whether or not those minerals are present in the downstream region. The DEC can be derived from a detailed analysis of the structure of dissolution/precipitation waves including diffusion/dispersion (Schechter et al., 1987); the DEC arises from the matching condition at a wave requiring continuity of aqueous concentrations. The description of the DEC as given here is sufficient for most situations but is not complete. A more thorough discussion is given by Bryant et al. (1987), although that interpretation must be modified by considerations given by Dria (1988) and Novak (1990).

Analytical solutions to 1D advection-dominated transport problems with dissolution/precipitation reactions can be calculated using coherence, local

Table 1. Chemical species, equilibrium data, and initial and boundary compositions for all examples

Species	Solubility Product (μM) ²	IC: Initial Concentration (μM)	BC: Boundary Concentration (μM)
A ⁺	-	1.0	0.0
B ⁺	-	0.0	1.0
X ⁻	-	1.0	0.0
Y ⁻	-	0.0	1.0
T(aq)	-	0.0	1.0
T(aq)	-	0.0	1.0
AX(s)	1.0	4.0	0.0
AY(s)	0.60	0.0	0.0
BX(s)	0.10	0.0	0.0

equilibrium, and downstream equilibrium, provided the order in which the minerals dissolve and precipitate is known (Bryant et al., 1987). When this order is unknown, candidate mineral sequences can be tested until the answer is found. A rule-based method for generating candidate sequences is given by Novak et al. (1988), along with heuristics that speed calculation through candidate sequences; simulators to perform these calculations are discussed in Novak (1990).

Example: Dissolution/Precipitation Waves in 1D Advective Transport for Constant Boundary Conditions

Consider advection-dominated transport in a 1D permeable medium of length L_x . The initial concentrations/conditions, IC, are uniform throughout the domain and are given along with the boundary concentrations/conditions, BC, in Table 1; solubility product data is given as well. The boundary concentrations/conditions will also be referred to as the injected concentrations/conditions. As indicated in Table 1, the initial aqueous phase is saturated with respect to AX(s) and undersaturated with respect to AY(s) and BX(s), while the boundary composition is undersaturated with respect to all minerals. Because the BC is undersaturated with respect to AX(s), AX(s)

would be expected to dissolve during transport. This does indeed happen (see solution below), and this dissolution causes $AY(s)$ and $BX(s)$ to precipitate. Because the BC is undersaturated with respect to $AY(s)$ and $BX(s)$, these minerals eventually dissolve as well. Also shown in Table 1 is the inert tracer $T(aq)$, which provides a means for tracking the bulk water flow and distinguishing between the initial water and the water that flows into the domain.

The analytical solution using the coherence methods outlined above is given in Figure 1 for $t_D=1$; the compositions in each of the regions are given in Table 2. The tracer wave, moving with $V_D=1$, is located at $X_D=1$ at $t_D=1$ and is thus not visible in the figure. The fastest D/P wave shows $AX(s)$ dissolution and precipitation of $AY(s)$ and $BX(s)$; $AY(s)$ dissolves at the next wave, moving more slowly, followed by $BX(s)$ dissolution at the slowest wave. The waves partition the domain into regions of constant composition containing different minerals. The resulting mineral sequence from the initial to boundary compositions, regions IC-R1-R2-R3-BC in Table 2, is

$$IC - \{AX(s)\} - \left\{ \begin{matrix} AY(s) \\ BX(s) \end{matrix} \right\} - \{BX(s)\} - BC$$

where minerals in a region are enclosed in curly brackets and the waves between regions are indicated by hyphens.

Contaminants Y^- and B^+ undergo *chemical retardation* through incorporation into the mineral phase at the R1-R2 wave. In R1, downstream of this wave, Y^- and B^+ are at about 50% and 12% of the boundary concentrations, respectively; in R2, upstream of this wave, the total (aqueous plus mineral) concentrations of Y^- and B^+ are about 360% and 340% of the boundary concentrations. Thus, the precipitation of $AY(s)$ and $BX(s)$ caused by dissolution of $AX(s)$ has reduced Y^- and B^+ concentrations in one region while causing an increase in another.

The wave structure of these problems is more easily recognized on a distance-time, or X-T, diagram, as shown in Figure 2; however only the portion of Figure 2 from $0 \leq t_D \leq 1$ applies to this example as discussed thus far. In X-T coordinates, the slope of the line separating two regions of constant composition represents the dimensionless velocity of the wave between the regions. A

vertical slice on an X-T diagram results in a profile of the domain (i.e., at a constant time) such as in Figure 1, while a horizontal slice yields a history (i.e., the time-evolution of concentrations at constant position). An effluent history, the concentrations leaving the domain versus time, is obtained by a slice at $X_D=1$ on an X-T diagram. The point $(X_D=0, T_D=0)$ can be considered as an intersection between waves carrying information on the initial and boundary conditions. The X-T diagram illustrates that this point of noncoherence is resolved into the four coherent waves shown in Figure 2. The dimensionless velocity of any wave can be calculated from Equation 5, which for Y^- across the R2-R3 wave is

$$V_{Di} = \frac{1}{1 + \frac{(2.164 - 0.0)}{(1.422 - 1.0)}} = 0.163$$

Example: D/P Waves in 1D Advective Transport for a Step Change in Boundary Conditions

The example thus far simulates continuous injection of one pore volume aqueous phase contaminated with Y^- and B^+ . Often, contaminants are introduced for a finite period of time in a pulse, after which an uncontaminated aqueous phase flows into the medium. We continue the example by imposing for $t_D \geq 1$ a new boundary condition with the same aqueous composition as the initial condition, call it BC' . Dria et al. (1987) show that such a problem results in intersecting waves, and that each wave intersection can be considered as an independent Riemann problem. The X-T diagram for the example extended through $t_D=2$, resulting from application of this theory, is shown in Figure 2. Compositions for each region appearing after $t_D=1$ are given in Table 3.

Figure 2 illustrates the wave-wave intersections resulting from a faster wave overtaking slower waves. When the tracer wave initiated by the second injection intersect waves caused by the first injection, the waves refract and produce additional waves. In addition to the dissolution/precipitation and tracer waves already seen in this problem, the wave intersections cause stationary waves to form. These waves do not propagate and occur when there is a change in mineral identities and/or mineral concentrations with no change in aqueous concentrations. The stationary wave closest to the inlet

Table 2. Analytical solution to 1D advection example through $t_D=1$, based on coherence methods

	IC: Initial Condition	R1: Region 1	R2: Region 2	R3: Region 3	BC: Boundary Condition
Species					
A ⁺	1.000	1.206	0.4220	0	0
B ⁺	0	0.1206	1.092	1.092	1.000
X ⁻	1.000	0.8292	0.09161	0.09161	0
Y ⁻	0	0.4975	1.422	1.000	1.000
T(aq)	0	1.000	1.000	1.000	1.000
AX(s)	4.000	4.000	0	0	0
AY(s)	0	0	2.164	0	0
BX(s)	0	0	2.273	2.273	0

forms because BX(s) dissolution causes AX(s) precipitation, yet the boundary condition is saturated with respect to mineral AX(s) so it cannot dissolve. The stationary waves (BC'-R3a; R3b-R2a; R2b-R1b) represent changes in mineral concentrations but not in aqueous concentrations. This completes the set of three wave types observed in these systems as discussed by Helfferich (this publication). Other types of waves can result from wave-wave intersections as discussed by Dria et al. (1987).

Figure 1. Concentration profiles at $t_D=1$ for the analytical solution to the advection example

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Figure 2. Distance-time diagram for the advection example

Table 3. Analytical solution to 1D advection example for regions created between $t_D=1$ and $t_D=2$, based on coherence methods

Species	BC'	R3a	R3b	R2a	R2b	R1b
A+	1.000	1.000	0.9535	0.9535	1.206	1.206
B+	0	0	0.09535	0.09535	0.1206	0.1206
X-	1.000	1.000	1.049	1.049	0.8292	0.8292
Y-	0	0	0	0	0.4975	0.4975
T(aq)	0	0	0	0	0	0
AX(s)	0	1.110	0	1.065	0	4.000
AY(s)	0	0	0	0	2.164	0
BX(s)	0	0	2.273	2.163	2.273	0

Because of the complexity associated with calculating concentration profiles using Riemann invariants and coherent wave theory, a numerical solution is often helpful if not essential. It is not our purpose here to discuss the details of the numerical solution, which can be found in such places as Gambolati et al. (this publication) and Novak and Gelbard (1991). Figure 3 shows concentration profiles at $t_D=2$, as calculated with the finite-difference simulator FMT (Novak and Gelbard, 1991). Because the numerical solution gives nonphysical oscillations in solid concentrations when

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Figure 3. Concentration profiles at $t_D=2$ for the numerical solution to the advection example

dispersion/diffusion is identically zero, there is a small amount of numerical dispersion in the simulation, resulting in the smoothing of waves most noticeable in the $T(aq)$ profile. These numerical solutions were generated with 50 nodes, $\Delta X_D=0.02$, $\Delta t_D=0.01$, and with numerical dispersion resulting in an equivalent Peclet number of 200 (Lantz, 1971).

The profile in Figure 3 corresponds to a vertical slice of the X-T diagram in Figure 2 at $t_D=2$, and the concentrations in each region from Table 3. The aqueous concentration in Figure 3 change in three places, $X_D \sim 0.05$, ~ 0.3 , and 1.0 , corresponding to the waves between R3a-R3b, R2a-R2b, and R1b-R1, respectively. While it is a little more difficult to discern the constant state zones for mineral at $t_D=2$ in Figure 3, the analytical and numerical solutions compare well. Profiles from the analytical solution at $t_D=2$ are shown in Figure 4 for comparison.

Contaminants undergo chemical retardation by reacting chemically with the mineral phases present (e.g., by dissolution/precipitation, adsorption, ion exchange, etc.). The effluent history and cumulative release diagrams (Figure 5) illustrate chemical retardation for the above example. The pulse of contaminant was injected for $0 \leq t_D \leq 1$, after which water with the initial composition was injected. The effluent history reflects the tracer pulse moving with the fluid velocity, and thus advecting out of the domain between $1 \leq t_D \leq 2$,

Figure 4. Concentration profiles at $t_D=2$ for the analytical solution to the advection example

with slight spreading due to numerical dispersion. The peak concentration of contaminant Y^- is reduced to ~50% of the boundary value because of $AY(s)$ precipitation, and is advected out of the domain between $1 \leq t_D \leq 3$. Contaminant B^+ undergoes more chemical retardation in this example, with peak concentration reduced to ~10% of the boundary concentration; it is retarded to such an extent that ~9% of the mass that entered the domain remains in the domain after a dimensionless time of ten.

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Figure 5. Effluent concentration histories and cumulative releases through $t_D=10$ from the numerical solution to the advection example

Example: Dissolution/Precipitation Waves in 1D Diffusive Transport for Constant Boundary Conditions

Shock waves are commonly found as solution to advection and convection equations such as the AD equation, but are less common as solutions to the diffusion equation (Equation 1 with $u=v=0$). Thus it is noteworthy that similar step changes in mineral concentration are observed during diffusion-only transport in porous media with mineral dissolution/precipitation (Lichtner et al., 1986; Kim and Cussler, 1987; Kopinsky et al., 1988; Novak et al., 1989). The sharp waves are caused by the nonlinear coupling of the transport equations through D/P reactions. Because this issue is discussed in detail in a separate chapter (Neretnieks, this publication), it is only briefly given here. In diffusion systems, transport partitions the domain into regions with distinct mineral assemblages, but the zones of constant concentration seen in the advection-dominated system are not present. This system is amenable to an analytical treatment, but the solution appears to be much less generalizable than the advection-dominated case.

Concentration profiles calculated using FMT are shown in Figure 6 for transport by diffusion-only with the initial and boundary conditions of Table 1 and a no-flux boundary condition at $Y=L_y$. The simulation used a 15-node variable grid given by $\Delta Y_1 = 5.014 \times 10^{-4}$ m, $\Delta Y_i = 1.3209 \Delta Y_{i-1}$, shown in Figure

Figure 6. Concentration profiles at equivalent $t_D=1$ for the numerical solution to the diffusion example

7, a time step $\Delta t=50$ seconds, and the diffusion coefficient $D=10^{-9} \frac{\text{m}^2}{\text{s}}$. The results of integration through 2.5×10^4 seconds are given. Only 20% of the domain is shown because beyond that there are no changes by this time. There are again sharp fronts where minerals dissolve and precipitate, and at these locations there is a discontinuity in aqueous concentrations for species that comprise the affected minerals, as required by a material balance about the wave (Novak et al., 1989).

TWO-DIMENSIONAL SOLUTIONS: D/P WAVE PROPAGATION

One practical application for transport in porous media involves geologic disposal of nuclear waste. The concept of geologic disposal involves emplacing nuclear waste underground within a series of manmade and natural barriers designed to prevent or delay radionuclide migration away from the repository. One of the more likely mechanisms for radionuclides to migrate away from a

Figure 7. Domain and discretization used for 1D diffusion example (Y-direction only) and for the 2D example

repository involves radionuclide dissolution and subsequent transport with the aqueous phase by advection and/or diffusion.

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy facility intended to demonstrate safe containment of transuranic (TRU) nuclear waste. The WIPP is located in Southeastern New Mexico within thick halite, NaCl(s) , beds chosen for their geologic stability and low porosity/permeability. Overlying the repository is a stratigraphic layer called the Culebra Dolomite Member of the Rustler Formation. Hydrologic testing has indicated that the Culebra is the most transmissive unit above the repository, yet the flow velocities are less than one meter per year. Calculations assessing repository performance with respect to environmental regulations for radionuclide containment indicate that radionuclides might reach the accessible environment through transport in the Culebra should a repository breach occur (Bertram-Howery, 1990).

Both hydrologic and geologic observations have demonstrated that the Culebra is appreciably fractured, and suggest that transport in the Culebra may occur by a dual porosity mechanism. Dual porosity systems are so named because advection occurs primarily through fracture networks, with diffusion of solutes from the fracture into the porous matrix. The fracture porosity allows flow to occur while the matrix porosity provides the bulk of solute storage capacity. A contaminant introduced into a dual-porosity system will undergo *physical retardation*, that is, the contaminant rate of transport will be slowed relative to the bulk water flow, because the contaminant will diffuse out of the fractures where it is present in high concentration and into the matrix.

For the final example advection and diffusion are occurring orthogonally in a 2D domain. The idealized domain consists of one planar fracture coupled to a porous matrix. One boundary is along the centerline of the fracture where a no flux boundary condition is imposed. The half-width of the fracture is represented by the ΔY_1 . The domain and the discretization used in the numerical solution are given in Figure 7. A no diffusive flux boundary condition is imposed on all boundaries. However, there is advection into and out of the domain at the fracture inlet and outlet. The fluid velocity is constant in the fracture and there is no advection in the matrix. The parameters for this example are: $u=4 \times 10^{-6}$ m/s; $D=1 \times 10^{-9}$ m²/s; $L_x=0.1$ m; $L_y=0.1$ m; $\Delta X=0.005$ m; $\Delta Y_1=5.014 \times 10^{-4}$ m; $\Delta Y_i=1.321 \Delta Y_{i-1}$; and $\Delta t=50$ seconds. Dimensionless

parameters can be calculated based on the fracture, giving: $\Delta t_D = 0.002$; $\Delta X_D = 0.05$; $\Delta Y_{D1} = 5.014 \times 10^{-3}$; $\Delta Y_{Di} = 1.321 \Delta Y_{Di-1}$; and a fracture Peclet number of 40.

This example uses the initial and boundary compositions of Table 1. Analogously with the 1D advection example, the contaminant boundary condition is imposed for one pore volume (based on fracture volume), after which the boundary condition is set equal to the initial condition. Mineral concentration profiles for $AX(s)$, $AY(s)$, and $BX(s)$ at $t_D = 1$ are shown in Figures 8, 9, and 10, respectively, and for $AX(s)$ at $t_D = 10$ in Figure 11. Effluent history and cumulative release through $t_D = 10$ are shown in Figure 12.

Consider first the mineral concentration profiles at $t_D = 1$, Figures 8 through 10, plotted in three dimensions versus the quantity $1 - X_D$ instead of X_D . Only a subset of the domain is shown to increase resolution and because mineral concentrations are constant outside the range plotted. The fracture inlet is at the left-most edge of these figures. Since at $t_D = 1$ no additional contaminants Y^- , B^+ , or $T(aq)$ can enter the domain, these mineral profiles represent the approximate maximum mineral concentrations in this example. There might be slight additional increases in these mineral concentrations until the waves propagating the boundary compositions for $t_D \geq 1$ have reached the regions of precipitation. Because Y^- and B^+ were incorporated into the mineral phase, we expect to observe chemical retardation of the elements, and more so for B^+ because the amount of B^+ incorporated into the minerals is greater.

The mineral concentration profile for $AX(s)$ at $t_D = 10$, given in Figure 11, shows the long-time response of the minerals in the domain to the new boundary condition. All $AY(s)$ and $BX(s)$ have dissolved by this time. There has also been precipitation of $AX(s)$ near the inlet to the domain, just as observed in the 1D multiple-injection example. The aqueous concentration profiles (not shown) are within ~6% of their steady-state values by this time.

Figure 12 shows the incremental and normalized cumulative releases (effluent histories) of the tracer and the two contaminants that undergo chemical retardation in this example. Also shown for reference on these figures are the incremental and normalized cumulative releases for a system

Figure 8. Concentration profile for mineral AX(s) at $t_D=1$.

Figure 9. Concentration profile for mineral AY(s) at $t_D=1$.

Figure 10. Concentration profile for mineral BX(s) at $t_D=1$.

Figure 11. Concentration profile for mineral AX(s) at $t_D=10$.

with the same geometry but in which there is no diffusion out of the fracture into the matrix (i.e., the 1D analogous case). These effluent curves represent waves of chemical concentrations passing through the domain. Comparison of the curves for T(aq)-1D and T(aq) reveals the effect physical retardation can have on species composition. Recall that species T(aq) does not react chemically in this system. The curve T(aq)-1D represents the two step changes in concentration that entered the domain at $t_D=0$ and $t_D=1$, and exited the domain at $t_D=1$ and $t_D=2$, respectively with slight spreading because of

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Figure 12. Effluent concentration histories and cumulative releases through $t_D=10$ from the numerical solution to the 2D example

dispersion. The tracer wave is more diffuse for T(aq)-1D, Figure 12, than for T(aq) in the 1D example, Figure 5, because there is more dispersion; the Peclet numbers are 40 and 200, respectively. The peak in concentration for T(aq) (Figure 12) occurs at a slightly later time than for T(aq)-1D and at a significantly reduced concentration, both of which are common observation for dual porosity systems (Grisak and Pickens, 1980). Also, although in the 1D case most of the T(aq) has left the system after $t_D \sim 2.5$ PV, about 19% of the tracer remains in the domain after $t_D = 10$ in the 2D case. Thus the physical retardation due to fracture flow with matrix diffusion is significant.

Consider the Y^- effluent profiles relative to the T(aq) profiles. Here there is a slight delay of maximum Y^- concentration relative to T(aq) concentration because Y^- undergoes both chemical and physical retardation in this system. The amount of chemical retardation of species Y^- in this example is slight, as demonstrated by the cumulative release curves. However, there is significant retardation compared to the 1D case in Figure 5.

Element B undergoes a significant amount of chemical retardation in this system due to incorporation into the mineral phase. Figure 12 shows that the release concentration of B^+ never exceeds $\sim 10\%$ of its inlet concentration, just as observed in the 1D case in Figure 5, and consequently takes a much longer time to leave the domain than T(aq) or Y^- . The combined effect of chemical and physical retardation cause $\sim 30\%$ of the injected B^+ to remain in the domain even after $t_D = 10$, which is appreciably more than the $\sim 9\%$ remaining in the 1D domain after $t_D = 10$, Figure 5.

CONCLUDING REMARKS

The analytical and numerical solutions presented here demonstrate that physical and chemical retardation caused by mineral precipitation can delay and/or reduce peak concentrations, and thus limit the release concentration of contaminants from simple one-dimensional and two-dimensional systems. These results are generalizable to systems with more complicated representations of the important chemical reactions. Acting separately, mineral precipitation (i.e., one for the mechanisms for chemical retardation) can reduce the release concentrations, and diffusion of a contaminant from a

fracture into a porous matrix (i.e., physical retardation) can both reduce release concentrations and delay the breakthrough time. The combination suggest significant retardation of radionuclides may occur in dual-porosity transport systems if radionuclide precipitation occurs.

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