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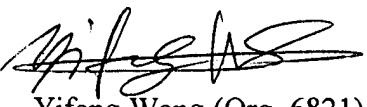
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subject: On Matrix Pore Plugging Issue

Introduction

A fractured geologic formation can be viewed as a dual porosity medium consisting of low porosity matrix blocks separated by high porosity fracture domains. Diffusion is a dominant mass transport mechanism in matrix blocks. This diffusion coupled with the sorption by matrix minerals plays an important role in radionuclide retardation in the far field of a nuclear waste repository. A contaminant plume may react with the surrounding rocks of the repository after entering the ambient environment. The reaction may cause extensive changes in rock properties, particularly in rock porosity. An issue has arisen that secondary mineral precipitation may significantly reduce rock porosity and consequently shut down matrix diffusion (Steefel and Lichtner, 1994), thus rendering the far-field radionuclide retardation ineffective. In this memorandum, I want to (1) identify the conditions under which matrix pore plugging can occur and (2) evaluate the possibility of the occurrence of matrix pore plugging in the far-field of the Waste Isolation Pilot Plant.

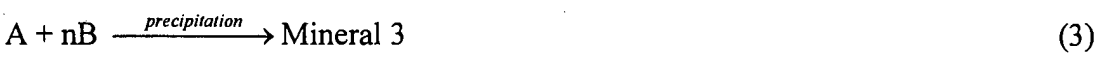
Scenarios of Mineral Precipitation in Matrix

Let's focus on one matrix block. According to the sources of reactants, mineral precipitation reactions can be divided into two scenarios:

(1) One reactant (A) is supplied by diffusion from fractures and another (B) is from the initial pore water in the matrix:



(2) One reactant (A) is supplied by diffusion from fractures and another (B) is from matrix mineral dissolution:



where n is the stoichiometric coefficient of B in the reaction. Here I assume that the volume of mineral 3 precipitated is larger than the empty volume created by the dissolution of mineral 1. Otherwise, there would be no matrix pore plugging. As shown below, the two scenarios of chemical reactions can have very different consequences in matrix porosity reduction.

Matrix pore plugging requires sufficient quantities of reactants to be supplied. Matrix pore plugging is also likely to occur if mineral precipitation is limited in a narrow zone. Let's assume that the concentration of reactant A in the fractures is maintained constant by advective flow. Then, mineral precipitation in both scenarios is limited by reactant B. Scenario 1 is equivalent to the mixing of two brines. In this scenario, reactant B is directly from the initial pore water in the matrix and thus the quantity of this component is very limited. In contrast, in scenario 2, reactant B is derived from the dissolution of a matrix mineral. Based on the consideration that the ratio of the concentration of a dissolved component to the concentration of this component in a solid phase is much, much less than 1, reactant B in scenario 2 is thus much more abundant than it in scenario 1. Thus, intuitively, matrix pore plugging is most likely to happen in scenario 2, as demonstrated by Steefel and Lichtner (1994) for the Swiss low-level nuclear waste repository. In the following, I use a bounding calculation to demonstrate that matrix pore plugging is unlikely to occur in scenario 1. Scenario 1 is directly relevant to the WIPP repository.

Bounding Calculation

In the bounding calculation, for simplicity, I make the following conservative assumptions:

- (1) Reaction (1) is instantaneous and the solubility of the precipitating mineral is zero. This assumption ensures the precipitation front to be infinitely sharp.
- (2) The matrix block under consideration is a semi-infinite domain Figure 1. Extending the matrix block to a semi-infinite domain causes more mineral precipitation because more reactant B is available.

The concentrations of A and B in the matrix can be described by:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial X^2} - k C_A C_B^n \quad (4)$$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial X^2} - n k C_A C_B^n \quad (5)$$

with boundary and initial conditions:

$$\begin{aligned} C_A(0,t) &= C_A^0 \\ C_B(0,t) &= 0 \\ C_A(X,0) &= 0 \\ C_B(X,0) &= C_B^0 \end{aligned} \quad (6)$$

where C_A and C_B are the concentrations of aqueous species A and B respectively; D is the effective diffusion coefficient; t is the time; k is the rate constant of reaction (1).

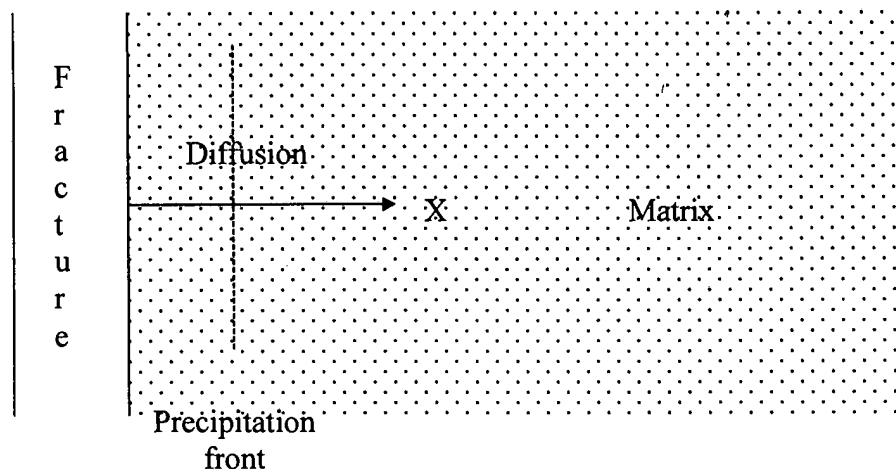


Figure 1. A semi-infinite matrix block bordering a fluid-filled fracture. Component A diffuses from the fracture into the matrix and reacts component B initially in the matrix pore water.

By defining :

$$C \equiv nC_A - C_B + C_B^0 \quad (7)$$

we obtain from equations (4) and (5):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \quad (8)$$

with boundary and initial conditions:

$$\begin{aligned} C(0, t) &= nC_A^0 + C_B^0 \\ C(X, 0) &= 0. \end{aligned} \quad (9)$$

Let $k \rightarrow \infty$, and the chemical equilibrium constraint on reaction (1) is then imposed as:

$$C_A C_B'' = 0. \quad (10)$$

The solution to equation (8) can be obtained analytically (Crank, 1986):

$$C = (nC_A^0 + C_B^0) \left(1 - \operatorname{erf} \left(\frac{X}{2\sqrt{Dt}} \right) \right) \quad (11)$$

where erf is the error function:

$$erf(r) = \frac{2}{\sqrt{\pi}} \int_0^r e^{-r^2} dr. \quad (12)$$

Due to the assumption of instantaneous chemical reaction, the mineral precipitation front becomes infinitely sharp. From equation (10), C_A must be zero on the right side of the front and C_B must be zero on the other side. Because any aqueous species concentration must be continuous across the reaction front in a diffusion-dominated system, both C_A and C_B must be zero at the reaction front. The reaction front position (X_f) can then be determined from equations (7) and (11):

$$X_f = 2\sqrt{Dt}\beta \quad (13)$$

where

$$\beta = erf^{-1}\left(\frac{nC_A^0}{nC_A^0 + C_B^0}\right). \quad (14)$$

The front advances at a velocity:

$$V_f = \frac{dX_f}{dt} = \sqrt{\frac{D}{t}}\beta. \quad (15)$$

As the front advances, the precipitated mineral is left behind, causing rock porosity reduction in the left side of the front. The change in rock porosity ($\Delta\phi$) is determined from mass balance at the precipitation front:

$$\frac{\Delta\phi V_f}{v_m} = D \left. \frac{\partial C_A}{\partial X} \right|_{X=X_f} \quad (16)$$

where v_m is the molar volume of the precipitating mineral. From equations (7) and (11), for $X \leq X_f$, where $C_B = 0$, we have:

$$C_A = C_A^0 - \frac{nC_A^0 + C_B^0}{n} erf\left(\frac{X}{2\sqrt{Dt}}\right) \quad (17)$$

and

$$\left. \frac{\partial C_A}{\partial X} \right|_{X=X_f} = -\frac{nC_A^0 + C_B^0}{n\sqrt{\pi Dt}} e^{-\frac{X_f^2}{4Dt}} = -\frac{nC_A^0 + C_B^0}{n\sqrt{\pi Dt}} e^{-\beta^2} \quad (18)$$

Solving for $\Delta\phi$ from equations (15-16) and (18), we obtain:

$$\Delta\phi = -\frac{v_m(nC_A^0 + C_B^0)e^{-\beta^2}}{n\sqrt{\pi}\beta} \quad (19)$$

Equation (19) indicates that the porosity reduction depends on two factors: $v_m(nC_A^0 + C_B^0)$ and β . Because of solubility limit, $nC_A^0 + C_B^0$ is usually small, say, < 0.01 M. Given a typical value of $100 \text{ cm}^3/\text{mole}$ for v_m , $v_m(nC_A^0 + C_B^0)$ is generally less than 0.001. For the cases where $C_A^0 \geq 0.1 C_B^0$ (i.e., $\beta \geq 0.1$), the porosity reduction by mineral precipitation is estimated to be less 1%, and matrix pore plugging is thus unlikely to occur. For the cases where $C_A^0 < 0.1 C_B^0$, equation (19) indicates the possibility of large porosity reduction near the fracture-matrix interface. In reality, however, this may not occur. First, bear in mind that this model is used only for bounding calculations and the model assumption of a semi-infinite domain for the matrix is very conservative. The actual matrix blocks are finite in size, the supply of reactant B is limited, and the precipitation front cannot stay close to the fracture-matrix for a long time because the depletion of B forces the precipitation front to continuously move inward. Second, the actual interface should start at the hydraulic boundary layer in the fracture. This boundary layer separates the advection-dominated transport regime from the diffusion-dominated transport regime. For $C_B^0 \gg C_A^0$, the predicted precipitation at $X = 0$ may actually occur in the boundary layer, i.e., in the fracture, instead of the fracture-matrix interface. At any rate, since $C_B^0 < C_A^0$ in the WIPP (see below), the sealing of fracture-matrix interface by mineral precipitation will not occur.

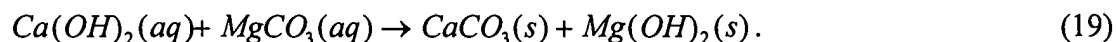
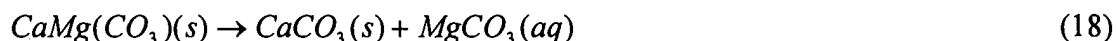
We have assumed above a constant concentration of A in the fracture. The reaction front movement is then unidirectional. Mineral precipitation at a point occurs only once and produces a finite volume of mineral as the front passes. However, if the concentration in the fracture varies, the reaction front may possibly oscillate in space, and multiple precipitation events may occur at the same location. The multiple precipitation events may increase the possibility for pore plugging. This phenomenon, however, seems unlikely to occur, at least, in the WIPP. First, there are no conceivable mechanisms that can cause cyclic variations in WIPP brine composition. Second, actual matrix blocks are finite in size, and the reactant B is limited. Even if the composition in the fracture fluid varies cyclically for an infinite time, the oscillation of the mineral precipitation front will stop after a few cycles, when the whole matrix blocks become prevailed by fracture fluids. From the bounding calculation with WIPP-relevant conditions conducted below, the porosity reduction by one cycle of precipitation will be $\ll 1\%$. Thus, a few cycles of mineral precipitation, if they would ever occur, is not enough to plug matrix pore space.

Application of Modeling Results to WIPP Far-Field Transport

A major far-field radionuclide release pathway of the WIPP is the overlying fractured Culebra dolomite formation. A thermodynamic calculation shows that brine in the WIPP repository will be saturated with dolomite and therefore dolomite will not dissolve as the repository brine percolates in the Culebra formation. The brine, however, will dissolve gypsum, which is present as a minor component in the Culebra formation. The brine containing dissolved gypsum will mix with the pore water originally in the matrix blocks by

diffusion, causing calcite precipitation in the matrix. Calcite precipitation in this case is then similar to mineral precipitation scenario 1 described above. Here calcium cation is supplied by diffusion from the fracture fluid, while carbonate is from the original pore water in the matrix. By assuming that the fracture fluid is saturated with gypsum, EQ3/6 v7.2a (Wolery and Daveler, 1992) calculations estimate Ca concentration in the fracture fluid and carbonate concentration in the original matrix pore water to be 0.01 M and 0.002 M respectively. Given $v_m = 37 \text{ cm}^3/\text{mole}$ for calcite (CaCO_3), from equation (19), the maximum porosity reduction due to calcite precipitation in Culebra matrix blocks is estimated to be much less than 0.1%. Obviously, such small porosity changes will have a negligible impact on radionuclide transport in the Culebra formation.

Which mineral precipitation scenario will occur depends on both repository chemical conditions and ambient rock chemical properties. The above discussion is based on the assumption that the chemical conditions in the WIPP repository will be controlled by MgO backfill reactions. However, if cementitious materials were used as backfill, the solution from the repository would be much more reactive, and mineral precipitation scenario 2 would occur in the WIPP far field. Mineral precipitation can be roughly described by



Based on molar volume data from Robie et al. (1978), the above two reactions will cause solid volume expansion by a factor of 150% and matrix pore plugging will occur. This is exactly what has been described by Steefel and Lichtner for the Swiss low-level nuclear waste repository. Therefore, the compatibility of repository chemical conditions with ambient rock properties should be considered as an important criterion for selection of backfill materials. In the WIPP, since the repository chemical conditions will be dominated by MgO backfill reactions, matrix pore plugging in the Culebra formation seems unlikely to occur.

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