

LINKING REACTION, TRANSPORT, AND HYDROLOGICAL PARAMETERS IN UNSATURATED FRACTURED ROCK: TOUGHREACT IMPLEMENTATION AND APPLICATION

Eric Sonnenthal, Nicolas Spycher, and Tianfu Xu

Lawrence Berkeley National Laboratory
Earth Sciences Division
Berkeley, CA, 94720, USA
e-mail: elsonnenthal@lbl.gov

INTRODUCTION

Modeling coupled water-gas-rock interactions in unsaturated fractured rock requires conceptual and numerical model considerations beyond those developed for saturated porous media. This paper focuses on the integration of the geological and hydrological parameters into the calculation of reactive-transport parameters and the feedback of mineral precipitation/dissolution to flow and transport. These basic relations have been implemented in the reactive transport code TOUGHREACT (Xu et al., 2003) that couples equilibrium and kinetic water-gas-rock interactions with multiphase flow and aqueous and gaseous species transport. Simulation results are presented illustrating the effects of water-rock interaction accompanying the heating of unsaturated heterogeneous fractured tuff.

Unknowns associated with modeling water-rock interaction in fractured unsaturated systems are the area of the fracture surface that is wetted and which fractures are active components of the overall flow system. The wetted fracture area is important not only to water-rock interaction but to flow and transport between fluids flowing in fractures and the adjacent matrix. The other unknown relations are those describing permeability and capillary pressure modification during mineral precipitation and dissolution. Here we discuss solely the relations developed for fractures and the fracture-matrix interface.

REACTIVE SURFACE AREAS

The fundamental parameter coupling kinetically-controlled mineral-water reactions to fluid flow is the reactive surface area. Rates of mineral dissolution and precipitation close to equilibrium can be described via a relationship of the rate to the saturation index (Q/K), as follows (based on Steefel and Lasaga, 1994):

$$R = \text{sgn} \left[\log \left(\frac{Q}{K} \right) \right] k A \left(\frac{Q}{K} \right)^m \quad (\text{Eq. 1})$$

where R is the rate ($\text{mol s}^{-1} \text{ kg}_w^{-1}$), w refers to water, m and n are empirically determined exponents, k is the rate constant, “ sgn ” refers to the sign of the reaction (dissolution is positive and precipitation is negative) and A is the reactive surface area expressed in units of $\text{m}_m^2 / \text{kg}_w$.

Fracture Mineral Reactive Surface Areas

Reactive surface areas of minerals on fracture walls can be calculated from the fracture-matrix interface area/volume ratio, the fracture porosity, and volume fractions of minerals. The total fracture-matrix interface areas can be based on measured fracture densities and an assumption of the fracture geometry, e.g., as planar disks. The wall of the fracture is treated as a surface covered by mineral grains and having some roughness. This geometric surface area of the fracture wall per unit volume of fracture can be approximated by:

$$A_r = \frac{\square A_{f-m}}{2 \square_f} \quad (\text{Eq. 2})$$

where A_r is the reactive surface area ($\text{m}^2 / \text{m}_f^3$), A_{f-m} is the fracture-matrix interface area/volume ratio ($\text{m}_f^2 / \text{m}_{f+m}^3$), \square_{f-m} is the fracture porosity of the rock, and $\square/2$ is the roughness factor. A_{f-m} is the surface area used as input to the model simulations as an approximation of the reactive surface area. This model for the fracture surface area considers that the areal coverage is approximately equivalent to the mineral volume fraction. A further modification, relates the 3-D cross-sectional area to the 2-D surface area in the fracture, yields a factor of $3/2$, i.e., an increase of 50% in the reactive surface area.

The reactive surface area of each mineral (A_i given in units of $\text{m}_m^2 / \text{kg}_w$) used in Equation 1 is then given by:

$$A_i (\text{m}_m^2 / \text{kg}_{\text{water}}) = \frac{A_r f_i}{\square_w \square_f} \quad (\text{Eq. 3})$$

where f_i is the volume fraction of the mineral in the

mineral assemblage, ρ_w is the density of water (taken as a constant 1,000 kg/m³), and ϕ_f is the porosity of the fracture medium, as opposed to the fracture porosity of the rock. This is the surface area/water mass ratio for a mineral in a liquid-saturated system.

To provide the correct rock/water ratio in an unsaturated system, the form of this surface area can be written as:

$$A_i \text{ (m}^2\text{/kg}_{\text{water}}\text{)} = \frac{A_r f_i}{\rho_w \phi_f S_w} \quad (\text{Eq. 4})$$

where S_w is the water saturation. However, as S_w goes to zero, the reactive surface area would tend to infinity. In this case, the question is whether the water takes the form of a thin film across much of the fracture surface, as narrow rivulets of water, covering only a portion of the surface, or as some combination. Under a condition of very small water flux and low liquid saturation, the surface area of the rock contacted by water is likely much smaller than the total area.

Two methods have been implemented to address this phenomenon. The first method considers that the surface area contacted by water is directly proportional to the liquid saturation. This yields the saturated surface area given by Equation 3. The second method employs the active-fracture-model concept (Liu et al., 1998) that has been modified to consider water-rock reactions taking place below the residual saturation. The form of the active fracture parameter for reaction is then given by the following set of equations:

$$S_{ar} = (S_w - S_m)/(1 - S_m) \quad (\text{Eq. 5})$$

$$a_{fmr} = S_{ar}^{(1+\beta)} \quad (\text{Eq. 6})$$

where S_m is the minimum liquid saturation for which water-rock reactions are considered and S_{ar} is the effective saturation available for reaction. The active fracture parameter, β , is determined through iTOUGH2 inversions to matrix saturation, assuming a known infiltration rate (Liu et al., 2003). The factor that reduces the surface area contacted by the water phase is given by a_{fmr} . S_m is usually set to a very small value around 10^{-4} , to ensure that reactions take place until virtually no water is left (e.g., during dry out via ventilation or heating). Finally, the reactive surface area, using this modified form of the active fracture model, is given by:

$$A_i \text{ (m}^2\text{/kg}_{\text{water}}\text{)} = \frac{A_r a_{fmr}}{\rho_w \phi_f S_w} \quad (\text{Eq. 7})$$

The surface area calculated in this way is applicable only to reactions taking place in the fracture medium.

In the dual permeability method, the porosity of the fracture medium can be taken as 1.0; however, for modeling of mineral dissolution and precipitation, there would then be no rock to dissolve. Therefore, an adequate volume of rock adjoining the open space of the fracture needs to be considered as the starting rock fraction.

HYDROLOGICAL PROPERTY CHANGES

Porosity

In this analysis, porosity changes in matrix and fractures are directly tied to the volume changes as a result of mineral precipitation and dissolution. The molar volumes of hydrous minerals, such as zeolites or clays, created by hydrolysis reactions with anhydrous phases, such as feldspars, are commonly larger than those of the primary reactant minerals. Therefore, constant molar dissolution-precipitation reactions can lead to porosity reductions. These changes are taken into account in TOUGHREACT. The porosity of the medium (fracture or matrix) is given by:

$$\phi = 1 - \sum_{m=1}^{nm} f r_m - f r_u \quad (\text{Eq. 8})$$

where nm is the number of minerals, $f r_m$ is the volume fraction of mineral m in the rock ($V_{\text{mineral}}/V_{\text{medium}}$, including porosity), and $f r_u$ is the volume fraction of nonreactive rock. As the $f r_m$ of each mineral changes, the porosity is recalculated at each time step. The porosity is not allowed to go below zero.

Fracture Permeability Changes

Fracture permeability changes can be approximated using the porosity change and an assumption of plane parallel fractures of uniform aperture (cubic law—Steeffel and Lasaga, 1994). Assuming no change in fracture spacing or density, the updated permeability, k , is given by:

$$k = k_0 \left(\frac{\phi}{\phi_0} \right)^3 \quad (\text{Eq. 9})$$

where k_0 and ϕ_0 are the initial permeability and porosity, respectively. This law yields zero permeability only under the condition of zero fracture porosity.

In most experimental and natural systems, permeability reductions to values near zero occur at porosities significantly greater than zero. This generally is the result of mineral precipitation preferentially closing the narrower interconnecting apertures. The hydraulic aperture, as calculated from the fracture spacing and permeability (as determined through air-permeability measurements) assuming a cubic law

relation, is a closer measure of the smaller apertures in the flow system. Using the hydraulic aperture, a much stronger relationship between permeability and porosity can be developed. This relationship can be approximated as follows:

The initial hydraulic aperture $b_{0,h}$ (m) is calculated using the following cubic law relation (Steeffel and Lasaga, 1994):

$$b_{0,h} = [12k_0s]^{1/3} \quad (\text{Eq. 10})$$

where k_0 is the initial fracture permeability (m^2) and s is the fracture spacing (m). The permeability (k') resulting from a change in the hydraulic aperture is given by:

$$k' = \frac{(b_{0,h} + \Delta b)^3}{12s} \quad (\text{Eq. 11})$$

where Δb is the aperture change resulting from mineral precipitation or dissolution. The aperture change resulting from a calculated volume change can be approximated by assuming precipitation of a uniform layer over the entire geometric surface area of the fracture, assuming also that this area (as well as the fracture spacing) remains constant. In geologic systems, the actual distribution of mineral alteration is much more heterogeneous and depends on many factors that are active at scales much smaller than the resolution of the model. The combined effect of the initial heterogeneities and localized precipitation processes can only be treated through model sensitivity studies and experiments. The initial aperture available for precipitation (b_g , the geometric, rather than the hydraulic, aperture) can be approximated from the ratio of the initial fracture porosity ($\varphi_{f,0}$) to the fracture surface area (A_f), as follows:

$$b_g = \frac{\varphi_{f,0}}{A_f} \quad (\text{Eq. 12})$$

For a dual-permeability model, changes in the fracture porosity are calculated based on the porosity of the fracture medium, so that Δb can be approximated by

$$\Delta b = \frac{(\Delta \varphi_m \varphi_{fm,0})}{\varphi_{fm,0}} b_g \quad (\text{Eq. 13})$$

Equations 10, 11, and 13 were implemented in TOUGHREACT with input parameters of b_g and s .

Changes to Capillary Pressures

Changing permeability and porosity also results in changes in the unsaturated flow properties of the rock. This effect is captured by modification of the calculated capillary pressure (P_c) using the Leverett

scaling relation to obtain a scaled P_c' as follows:

$$P_c' = P_c \sqrt{\frac{k_0 \Delta}{k \Delta}} \quad (\text{Eq. 14})$$

Simulations performed with TOUGHREACT have the maximum capillary pressure limited by the cutoff prescribed in the input file.

SIMULATION OF REACTIVE TRANSPORT IN HETEROGENEOUS FRACTURED TUFF

Here we present an example of the coupling between mineral-water reactions and unsaturated flow in heterogeneous fractured tuff. The model was developed to investigate processes accompanying the proposed emplacement of nuclear waste in emplacement drifts in the unsaturated welded tuffs at Yucca Mountain, Nevada. Detailed discussions of the model development and parameters are discussed in Sonnenthal and Spycher (2001) and Spycher et al. (2003).

The model represents a 2-D vertical cross-section perpendicular to a 5.5m emplacement drift that is heated according to a defined heat loading curve and considering an initial 50-year period of ventilation-induced heat removal. By symmetry the model is reduced to a half-drift and extends horizontally to the midpoint between two adjacent drifts (40.5m). The model extends upward to the ground surface and downward to the water table. An initial random heterogeneous fracture permeability distribution was created at a scale of 0.2 m, which was then averaged over the area of each numerical grid block. The initial range in fracture permeability was 4 orders of magnitude. A prescribed step-wise infiltration-rate was applied (6 mm/yr to 600y, 16 mm/yr to 2000y, and 25 mm/yr to 20,000y) to approximate a possible climate change scenario.

The geochemical model used for the simulation is a simplified system consisting of several primary aqueous, gaseous and mineral species, capturing the dominant effects of mineral precipitation on unsaturated flow. The primary aqueous species considered are Ca^{2+} , Na^+ , SiO_2 , HCO_3^- , Cl^- , F^- , and SO_4^{2-} . Gases include water vapor, air, and CO_2 . Minerals include silica polymorphs (quartz, tridymite, cristobalite, and amorphous silica), calcite, gypsum, and fluorite. The silica polymorphs and fluorite are treated as kinetic phases, whereas calcite and gypsum, being relatively fast-reacting, are set to react under equilibrium conditions. Aqueous and gaseous species are transported by diffusion and advection. The dual permeability model considered different mineralogical and geochemical properties for the fracture and matrix continua as well as unsaturated

flow properties.

In addition to the reactive surface area, fluid fluxes also control the rate and extent of mineral-water reactions. Liquid saturations and fluxes are strongly tied to the permeability and capillary properties, as shown in Figure 1, which exhibits the dry-out and a heterogeneous condensation zone around an above-boiling repository drift after 600y. Percolation fluxes above the drift are higher than below (capillary diversion effect) and therefore the condensation zone is developed more strongly above the drift. At the edge of the boiling front, mineral precipitation is driven by a combination of mineral-water-reactions and evaporative concentration.

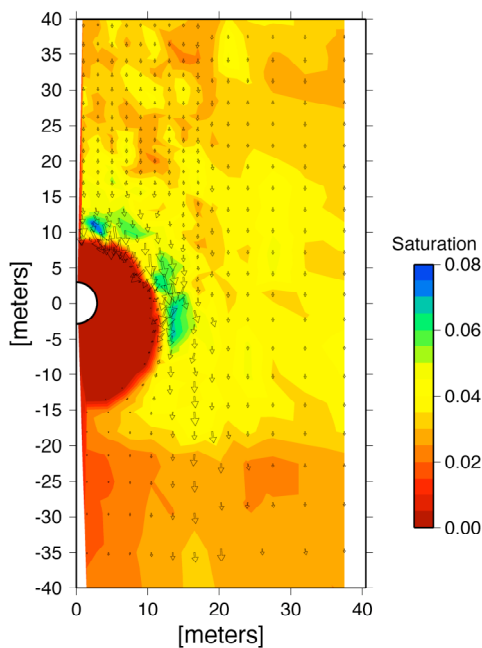


Figure 1. Fracture saturation and liquid flux vectors at 600y for a proposed above-boiling nuclear waste emplacement drift.

The net effect of these processes over 20,000y is a change in permeability that is strongest in areas of initially low permeability but high liquid fluxes and saturation (Figure 2). The distribution of permeability changes is, however, a combined effect of different minerals precipitating in varying patterns. For example, amorphous silica has an increased solubility at higher temperatures and only precipitates at the boiling front by evaporative concentration (Figure 3). Calcite also precipitates by evaporative concentration, but also by degassing of CO₂ and heating of percolating fracture water from the surface, thus leading to abundant precipitation well above the boiling zone (Figure 4).

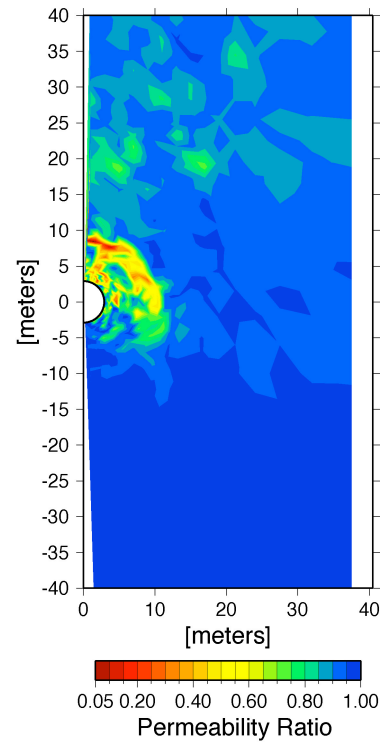


Figure 2. Ratio of fracture permeability at 20 ky to the initial value.

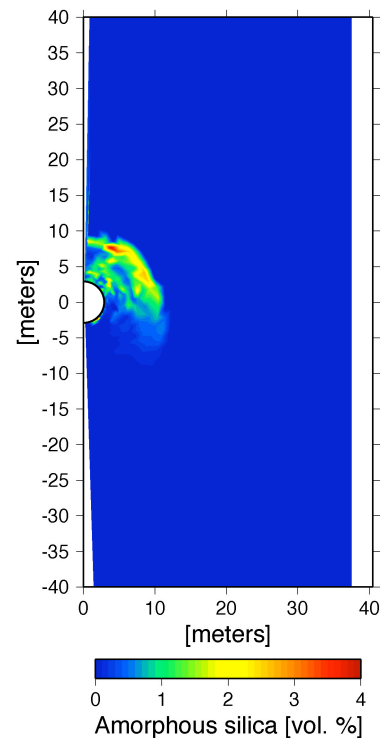


Figure 3. Amorphous silica precipitated in fractures (volume %) after 20 ky.

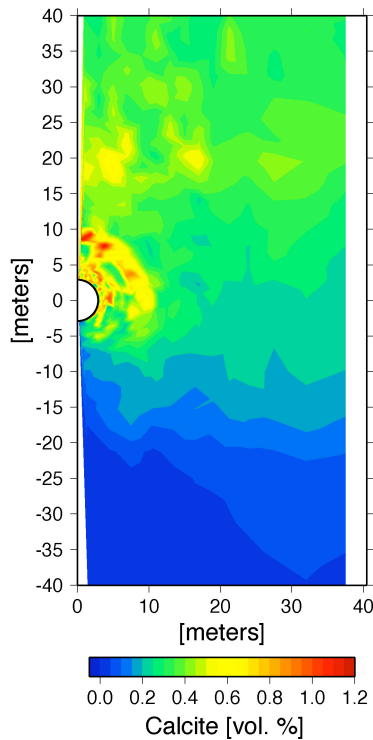


Figure 4. Calcite precipitated in fractures (volume %) after 20 ky for a proposed above-boiling nuclear waste emplacement drift.

CONCLUSIONS

Modeling water-rock interaction in unsaturated rock requires additional considerations for the calculation of reactive surface areas and the coupling of mineral precipitation and dissolution to flow. In this paper we have described some possible relationships between reactive surface areas in unsaturated fractures and the conceptual model of fracture geometry and the fracture-matrix interaction factor. The reactive surface area in unsaturated fractures has been related directly to the fracture-matrix interaction factor as given by the “active fracture model” (Liu et al., 1998). These relationships have been implemented into the reactive-transport code TOUGHREACT. Modeling of water-rock interaction in boiling unsaturated heterogeneous fractured rock exemplifies the strong feedbacks between water-rock interaction and unsaturated flow. In particular, increased liquid saturation as a result of higher capillary pressures in smaller aperture fractures leads to increased rates of reaction and further reductions in permeability.

ACKNOWLEDGMENTS

The authors wish to acknowledge input to various aspects of the model development by John Apps and Charles Haukwa and improvements through earlier reviews of related work by Pat Dobson and Peter Persoff. This work was supported by the Director, Office of Civilian Radioactive Waste Management, U.S. Department of Energy, through Memorandum Purchase Order EA9013MC5X between Bechtel SAIC Company, LLC and the Ernest Orlando Lawrence Berkeley National Laboratory (Berkeley Lab). The support is provided to Berkeley Lab through the U.S. Department of Energy Contract No. DE-AC03-76SF00098.

REFERENCES

- Liu, H.H., C.B. Haukwa, C.F. Ahlers, G.S. Bodvarsson, A.L. Flint, and W.B. Guertal. Modeling flow and transport in unsaturated fractured rock: an evaluation of the continuum approach *Journ. Contam. Hydrol.*, 62-63, 173-188, 2003.
- Liu, H.H., C. Doughty, and G.S. Bodvarsson. An active fracture model for unsaturated flow and transport in fractured rocks, *Water Resour. Res.*, 34(10), 2633–2646, 1998.
- Sonnenthal, E., and N. Spycher, N., 2001. *Drift-Scale coupled processes (DST and THC seepage) models. AMR N0120/U0110 Rev.01*, Yucca Mountain Project, Lawrence Berkeley National Laboratory, Berkeley, California.
- Spycher, N., E. Sonnenthal, and J. A. Apps. Prediction of fluid flow and reactive transport around potential nuclear waste emplacement tunnels at Yucca Mountain, Nevada, *Journ. Contam. Hydrol.*, 62-63, 653-673, 2003.
- Steefel, C.I. and A.C. Lasaga. A coupled model for transport of multiple aqueous species and kinetic precipitation/dissolution with application to reactive flow in single-phase hydrothermal systems. *Am. Jour. Sci.*, 294, 529-592, 1994.
- Xu, T., E. Sonnenthal, N. Spycher, and K. Pruess, TOUGHREACT User's Guide: A Simulation Program for Nonisothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media, Lawrence Berkeley National Laboratory, Berkeley, Calif., in prep.