Tracking high-pH reaction fronts in MX-80 bentonite using infiltration techniques and 4D CT

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Geological storage of radioactive waste foresees bentonite as backfill material enclosing spent fuel drums. Concrete is proposed as building material for tunnel reinforcement or as backfill. The emplacement of high-pH cementitious material next to clay generates a chemical gradient in pore water chemistry that drives diffusive transport. Laboratory studies and reactive transport modeling predict significant mineral alteration near interfaces [1].

We aim to characterize and quantify the cement/bentonite skin effects spatially and temporally, focusing on the advective-diffusive transport domain resolved at intermediate spatial scales. Equipment made of carbon fiber and plastics holds a cylindrical sample under confining pressure and imposes a constant hydraulic gradient to drive a small advective flux. Compacted and saturated MX-80 bentonite and sand/bentonite mixtures are used. Infiltration of high-pH pore-fluids into the bentonite plug alters the mineral assemblage over time. The related change in phase densities, porosity and local bulk density is tracked by CT scans during ongoing infiltration. The resulting micrographs describe the electron density distribution in 3D and as a function of time. Electron densities are transformed into material densities using reference materials and are calculated on the basis of the data of the NIST [2]. After 1-2 years the experiment is stopped and the samples subjected to post-mortem analysis.

In a first experiment running for >6 months, MX-80 bentonite (ϱ_{wet}=1.875 g/cm^3) is used as starting material, and a synthetic cement pore fluid of pH 13.4. The reaction front is tracked in the CT and appears as precipitations in the thin filter separating bentonite and infiltration fluid, and as an evolving zone of higher density in the bentonite next to it. Simultaneously, hydraulic conductivity is decreasing by 58% over 6 months.

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Estimating fluid fluxes from equilibrium properties and transport theory: pitfalls and solutions

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Aqueous fluids are efficient mass transport agents and reactive fluid flow occurs in diverse settings including compaction of porous sediments, thermal perturbations in oceanic crust, prograde metamorphic reactions in continental orogens and subduction zones, or during plutonic and volcanic degassing. We will address several issues pertaining to accuracy and extrapolability of thermodynamic data, magnitude of reaction progress in temperature and pressure gradients, and separation of equilibrium vs. disequilibrium effects, i.e., closed- vs. open-system fluid-mineral interaction. Standard reaction enthalpies and volumes directly provide gradients in mole amounts of reaction progress or mineral precipitated, n, per unit temperature or pressure. Evaluation of mineral solubilities reveals that $\partial n/dP$ are significant and critically moderate $\partial n/dT$ for fluid reactions along geotherms *vs.* at constant pressure. Highly charged species are responsible for retrograde solubility effects during isobaric (lateral) flow, but along geotherms (7-20 ºC km^{-1}) the $\partial n/dT$ are monotonous and nearly identical for a variety of rock-forming phases. Estimation of integrated fluid fluxes is frequently biased towards two limiting approaches: (i) local equilibrium with host rocks, with reaction progress driven by pressure and temperature gradients only, or (ii) dis-equilibrium fluid-rock interaction at constant or variable temperature and pressure. We extend conventional transport theory to include the disequilibrium effects and demonstrate that these two approaches yield the lower and upper limits of the flux, respectively, that may differ by several orders of magnitude. A model application to hydrolytic alteration of peraluminous granites reveals time-integrated fluid fluxes from 10^2 to 10^6 m^3 m^{-2}, which covers the plausible range observed globally. If the magnitude of disequilibrium is constrained by modal proportions or volume conservation, the fluid fluxes become bracketed and smaller, 10^{2-3} m_{fl}^3 m_r^{-2}. We conclude that vein-producing fluid fluxes may be several orders of magnitude lower than previously indicated for fracture- or shear zone-related flow, and low fluxes support alternating periods of episodic flow and stagnant fluid-rock interaction. Such discontinuous flow mechanism is more consistent with cycles of transient permeability enhancement and subsequent chemical or mechanical sealing.

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