Vadose Zone Geochemistry Primer

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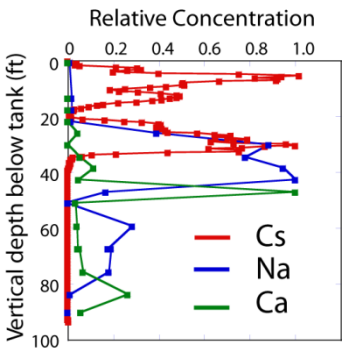
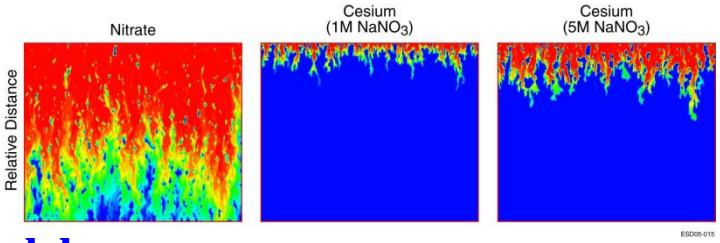
Topics for Discussion

- Geochemical processes to be considered
- Linkage with flow and transport
- Characterization
- Modeling approaches

Geochemical Processes I

- **Sorption**
  - **Non-competitive models**
    - **Linear distribution coefficient (or K_d)**
    - **Langmuir or Freundlich**
  - **Competitive models**
    - **Multicomponent ion exchange**
    - **Multicomponent surface complexation**
      - **Electrostatic versus non-electrostatic models**
  - **Generalized Composite versus Component Additivity**
    - **Generalized Composite Model considers properties of whole sediment**
    - **Component Additivity Model builds a composite model by summing individual phases (e.g., Fe hydroxide, clay)**





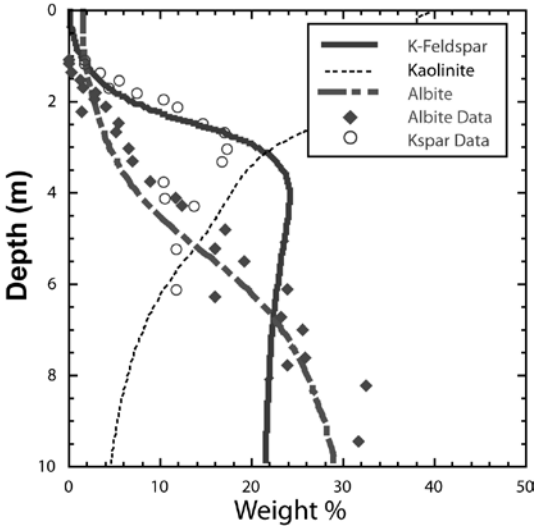
Hanford Tank Leak

Steefel et al., 2005

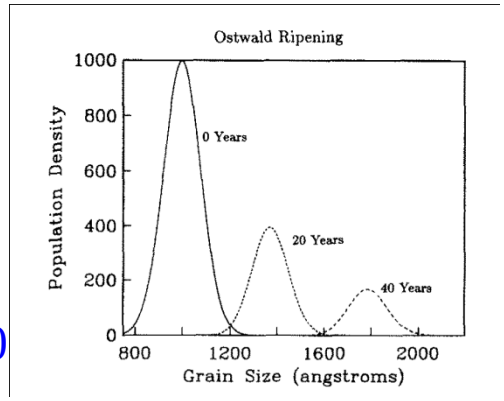
Geochemical Processes II

- **Mineral dissolution**
  - **Proton or base promoted**
  - **Organic ligand promoted**
  - **Reductive dissolution**
  - **Effect of Gibbs energy (reaction affinity)**
- **Mineral precipitation**
  - **Nucleation**
  - **Crystal rowth**
  - **Mineral ripening or aging (transformation)**
  - **Treatment of evolving reactive surface area**

Santa Cruz weathering profile



Steefel and Maher, 2009



Steefel and Van Cappellen, 1990

Geochemical Processes III

- **Gas-water exchange**
  - **O_2 in vadose zone may control redox state**
  - **CO_2 produced from organic carbon degradation**
    - **Can have a marked effect on mobility of some radionuclides, <u>especially</u> <u>uranium</u>**
- **Linked to fast gas transport**
  - **Gas diffusion rates may be 4 orders of magnitude faster than diffusion in aqueous phase**
- **Gaseous reaction products may influence local geochemistry and/or hydraulic conductivity**
  - **H_2S, methane…**

Redox Processes in the Vadose Zone

- **Normally the vadose zone is oxidizing due to the presence and rapid transport of O_2, but…**
  - **Transient fully saturated conditions (e.g., tank leaks) may allow for reducing conditions (e.g., from Fe silicate dissolution)**
  - **O_2 gas may be depleted even in the gas phase (e.g., sulfide mine tailings)**
- **Mobility of contaminants post-reductive event depends on their kinetic behavior**
  - **Uranium normally is normally easily reoxidized**
  - **Chromium reoxidation is kinetically limited**
- **Microbially-mediated processes may be important**

Linkage to Flow and Transport

- Most of the geochemical reactions are driven by the flux of reactive constituents, either in the gas or aqueous phase
- Rates, therefore, may be determined by transport
- Reactions may be close to equilibrium
- Liquid/gas saturation plays a key role through gas geochemistry (O_2, CO_2)

Characterization

- Different conceptual models are associated with different characterization requirements
  - pH or CO_2 dependence of sorption
  - Competitive ion effects on sorption
  - Reversibility (or lack thereof) of sorption
  - Different reactive pools
    - Poorly crystalline Fe-hydroxide
    - Crystalline Fe-oxides and hydroxides
  - Sorption properties of individual minerals
  - Gas phase geochemistry
  - Aqueous phase geochemistry

Modeling Approaches

- Linear versus nonlinear models
  - Most multicomponent systems involve nonlinear, competitive reactions
  - Treatment of multicomponent reaction networks
- Kinetic versus equilibrium models
- Multi-rate models
- Multi-domain models
- Uncertainty Quantification