Effect of kinetic limitations on colloid-facilitated radionuclide transport at the field scale

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Colloids and transport of strongly sorbing elements

- Contaminants bound to colloids have reduced interactions with host rock
- Transport by colloids observed or inferred at several sites and in experiments
- Most previous modeling focused on laboratory time/space scales
- Parameter and model sensitivities for long time and space scales are needed

Figure Source: DOE
Sorption kinetics

- Kinetic models for sorption/desorption of radionuclides onto colloids are important for interpreting laboratory experiments.
- Kinetics usually ignored in field-scale modeling.
- Analyses of laboratory data suggest multiple sorption rates.
- Slowest observed rates may not be negligible at field scale (e.g. Painter et al. 2002).
- Use minimalist model to understand potential role of sorption kinetics on field scale transport.
Objectives

- Develop colloid facilitated transport models
  - Focus on long time and space scales
  - Stochastic framework for uncertainty
  - Minimalist model for broad-scope sensitivity analysis
- Identify important modeling assumptions
  - Key parameters and ranges
  - Dominant processes
  - Focus on role of kinetic sorption/desorption onto colloids
- Use the alluvial aquifer near the potential Yucca Mountain repository to illustrate effect
Outline

- Modeling approach
- Generic sensitivity studies
- Stochastic simulation for the Yucca Mountain alluvial aquifer
- Conclusions
Transport scenario

- 1-D transport pathway
- Colloid concentration is constant in space and time
- Pathway initially free of radionuclide
- Specified input flux of radionuclide in solution
- Pathway properties (e.g., travel time) may be uncertain
- Monitor radionuclide discharge at pathway outlet (expected value versus time)
Modeled transport processes

- Colloids
  - Advection and dispersion
  - Sorption (temporary immobilization)
  - Filtration (permanent immobilization)

- Radionuclide
  - Advection and dispersion on 1-D pathway
  - Sorption on host rock (equilibrium)
  - Sorption on colloids (kinetic)
  - Use plutonium as example
Radionuclide states and exchange rates

Free colloids

S

S**
Permanently immobilized colloids

S*
Reversibly attached colloids

Solution

C

C*
Host rock

Mobile
Immobile

ε
κ_f
κ_r
α_f
α_r
α_r**
α_r*
κ_f
κ_r

8
Transport equations: General form

in solution
\[ \frac{\partial C}{\partial t} + \nabla C = -\psi^{C\rightarrow S}(C,S) - \psi^{C\rightarrow S*}(C,S*) - \psi^{C\rightarrow S**}(C,S**) - \psi^{C\rightarrow C*}(C,C*) - \lambda C \]

on mobile colloids
\[ \frac{\partial S}{\partial t} + \nabla S = \psi^{C\rightarrow S}(C,S) - \psi^{S\rightarrow S*}(S,S*) - \psi^{S\rightarrow S**}(S,S**) - \lambda S \]

on porous matrix
\[ \frac{\partial C^*}{\partial t} = \psi^{C\rightarrow C*}(C,C*) - \lambda C^* \]
\[ \frac{\partial S^*}{\partial t} = \psi^{S\rightarrow S*}(S,S*) + \psi^{C\rightarrow S*}(C,S*) - \lambda S^* \]

on permanently immobile colloids
\[ \frac{\partial S^{**}}{\partial t} = \psi^{S\rightarrow S**}(S,S**) + \psi^{C\rightarrow S**}(C,S**) - \lambda S^{**} \]
Transport equations:
Equilibrium sorption on porous matrix

Rapid transfers to/from porous matrix

\[ R = \text{radionuclide retardation factor} \]
\[ R_c = \text{colloid retardation factor} \]

in solution and sorbed to porous matrix

\[ \frac{d}{dt} R C + \tau C = -\psi^{C\rightarrow S}(C, S) - \psi^{C\rightarrow S^*}(C, K'_c S) - \psi^{C\rightarrow S**}(C, S^{**}) - \lambda R C \]

on mobile colloids and sorbed colloids

\[ \frac{d}{dt} R_c S + \tau S = \psi^{C\rightarrow S}(C, S) + \psi^{C\rightarrow S^*}(C, K'_c S) - \psi^{S\rightarrow S**}(S, S^{**}) - \lambda R_c S \]

on permanently immobile colloids

\[ \frac{d}{dt} S^{**} = \psi^{S\rightarrow S**}(S, S^{**}) + \psi^{C\rightarrow S**}(C, S^{**}) - \lambda S^{**} \]
Linear exchange model

\[ \psi^{C \to S}(C, S) = \alpha_f C - \alpha_r S \quad \text{solution – mobile colloid} \]

\[ \psi^{C \to S^*}(C, S^*) = \alpha^*_f C - \alpha^*_r S^* \quad \text{solution – temporarily immobile colloid} \]

\[ \psi^{C \to S**}(C, S**) = -\alpha_r S** \quad \text{solution – permanently immobile colloid} \]

\[ \psi^{S \to S**}(S, S**) = \varepsilon S \quad \text{mobile colloid – permanently immobile colloid} \]
Parameters in exchange model

- Assume desorption from colloids is independent of colloid state
  \[ \alpha_{r}^{**} = \alpha_{r}^{*} = \alpha_{r} \]

- Rate constant for sorption onto colloids
  - Proportional to sorption site density
    \[ \alpha_f \propto C_c \quad \alpha_f^{*} = K'_c \alpha_f \]
  - Linked to \( K_d \) for sorption on porous matrix (Contardi et al. 2001)
    \[ \frac{\alpha_f}{\alpha_r} = F C_c K_d \quad F = \frac{\text{Specific surface area colloids}}{\text{Specific surface area porous matrix}} \]
Transport operator in Lagrangian form

Usual form

\[ T = v \frac{\partial}{\partial x} - D \frac{\partial^2}{\partial x^2} \]

Assume dispersivity proportional to travel distance: \( D = f L v \)

\[ T = v \frac{\partial}{\partial x} - f L |v| \frac{\partial^2}{\partial x^2} \]

Make the substitution

\[ \tau = \frac{x}{v} \]

\[ T = \frac{\partial}{\partial \tau} - f \tau \frac{\partial^2}{\partial \tau^2} \]

Travel distance, porosity, and darcy flux now replaced by a single parameter: \textbf{global travel time.} Three uncertain parameters reduced to one.
Transport equations: Dimensionless form

- Normalize radionuclide concentrations by $C(0,0)$
- Normalize times and rates by $\tau_L = \text{global travel time}$
- Keep same symbols for clarity (except $\alpha = \alpha_f \tau_L$)

\[
\begin{align*}
R \frac{\partial C}{\partial t} + T C &= -\alpha R_c C + \frac{\alpha}{C_c'K_d'} R_c S + \frac{\alpha}{C_c'K_d'} S'' - \lambda RC \\
R_c \frac{\partial S}{\partial t} + TS &= \alpha R_c C - \frac{\alpha}{C_c'K_d'} R_c S - \varepsilon S - \lambda R_c S \\
\frac{\partial S''}{\partial t} &= \varepsilon S - \frac{\alpha}{C_c'K_d'} S'' - \lambda S''
\end{align*}
\]

\[
\begin{align*}
C_c' &= \frac{FC_c \theta}{\rho(1-\theta)} \\
\tau' &= \frac{\partial}{\partial \tau} - f \frac{\partial^2}{\partial \tau^2}
\end{align*}
\]
Generic sensitivities: Steady-state

Focus on sensitivity to models and parameters
Monitor steady-state discharge of Pu-239
Linear, bi-linear, and Langmuir sorption models
CFT is dominant transport mechanism for strongly sorbing species
Colloid retardation is relatively ineffective at reducing transport
Permanent removal more effective, but very sensitive to desorption rate

Cvetkovic, Painter, Turner, Pickett, Bertetti.
Generic sensitivity analysis: Transient discharge

- Deterministic pathway
- \( C(0,t) = \text{constant}; \ S(0,t) = 0 \)
- Radionuclide retardation factor: \( R = 2000 \)
- Colloid retardation factor: \( R_c = 20 \)
- Dimensionless colloid concentration: \( C'_c = 2 \times 10^{-4} \)
- Normalized decay constant: \( \lambda = 2.9 \times 10^{-3} \)
- No permanent removal: \( \varepsilon = 0 \)
- Scan the (normalized) forward rate constant \( \alpha \)
Generic sensitivity analysis

Normalized breakthrough for various values of the sorption rate constant $\alpha$.

- $\alpha = 0$ is no-colloids case

- Non-monotonic dependence on sorption rate constant
- Colloids cause early breakthrough for small fraction of plume
- Effect on bulk of plume is modest
Generic sensitivity analysis: Effect of sorption kinetics

- Dimensionless Damköhler number
  \[ Da = \alpha_r \tau_L R_c = \frac{\alpha_f \tau_L R_c}{F C_c K_d} = \frac{\alpha R_c}{C'_c K'_d} \]

- Sorption/desorption onto colloids is near equilibrium process for \( Da > 10 \)

- Critical range for sorption rate is
  \[ \frac{1}{R} < \alpha_f \tau_L < 10 \frac{C'_c K'_d}{R_c} \]
Generic sensitivity results: Effect of permanent colloid removal

- Reduces early breakthrough if product of removal rate constant and travel time is greater than 1
- Little effect on late-time breakthrough
Kinetic limitations and CFT in Yucca Mountain alluvial aquifer

- Transport parameters are uncertain
- With median values of uncertainty distribution, Da is estimated in equilibrium range (200 – 2000)
- With travel time and colloid retardation factor at 20th percentile, Da is near kinetic range (5 – 50)
- Use Monte Carlo analysis
Monte Carlo simulations

- Expected value for breakthrough (discharge versus time)
- 500 realizations sampling
  - Colloid concentration
  - Colloid retardation
  - Plutonium retardation
  - Global travel time
- Intrinsic rate constant $\alpha_0$
  - 0 (no colloids)
  - large (equilibrium)
  - 10 m$^3$/kg-yr
  - 100 m$^3$/kg-yr
- Two release scenarios
  - $C(x=0,t) = \text{constant}$
  - $C(x=0,t) = C_0 \exp(-t/1000)$
Uncertainty distributions

- Colloid parameter distributions
  - Saturated zone colloid transport AMR (Bechtel SAIC 2003).
  - Truncation at retardation factor of 8 removed.
- Plutonium retardation factor from NRC/CNWRA TPA code (Mohanty et al. 2002)
Uncertainty distribution: global travel time

- Calculated from TPA 4.0 input parameters (Mohanty et al. 2002)
- Incorporates uncertainty in
  - Travel distance
  - Porosity
  - Hydraulic conductivity
  - Regional hydraulic gradients
Forward rate for sorption on colloids

- Second slower rate apparent in sorption data (Painter et al. 2002)
- Intrinsic rate $\alpha_f = \alpha_0/C_c = 10 – 100 \text{ m}^3/\text{kg-yr}$
- About $\alpha_f = 0.1 \text{ yr}^{-1}$ after scaling to relevant colloid concentrations
- Reimus (2003) also observes 2-rate sorption/desorption
- > 2 rates possible

Painted et al. 2002 EST reinterpreting sorption data of Lu et al. 1998
Expected breakthrough curves: Constant input scenario

\[ C(0,t) = \text{constant} \]
Expected breakthrough curves: Exponentially decaying input

\[ C(0,t) = C_0 \exp(-t/1000) \]
Conclusions: Colloid-facilitated transport on the field scale

- Colloid-facilitated transport is likely an important transport mechanism for strongly sorbing contaminants.
- Exchanges between solution and immobilized colloids reduce effectiveness of colloid retardation.
- High sensitivity to:
  - Rate of desorption from colloids
  - Colloid permanent removal rate
- Permanent immobilization:
  - Difficult to demonstrate for natural colloids
  - If invoked, then need to know slow desorption rate
  - Currently using assumption of no permanent immobilization
Conclusions: Role of kinetic limitations

- Laboratory experiments show clear evidence for multiple sorption rates
- Main effect is to cause small amounts of mass to move ahead of the main plume
- Little effect on bulk of plume
- Damköhler number provides quick screening tool
- Colloids likely exist as heterogeneous population governed by multiple rates
  - Need multi-rate models
  - Longer experiments needed
Disclaimer

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