Predicting Coupled Process Behavior in Field-Scale Systems

Recent Workshops

- “A Science-Based Case for Large-Scale Simulation,” DOE-SC, June 2003

Reliable prediction of field scale behavior is a scientific challenge
- Many field-scale issues are difficult to address at the lab scale
- Many processes and properties are difficult to monitor in the field

Reactive transport models integrate fundamental earth science research and focus on complex natural environments where individual time and space-dependent processes are linked

Need for multidisciplinary research teams dedicated to developing a quantitatively mechanistic understanding of behaviors at a particular field site to address the range of scales and multiple interacting processes

Build field-scale process models on a framework of understanding from fundamental experiments and characterization studies at complementary length scales in the field
Conceptual Model: Old Rifle Biostimulation Experiments

- Bulk of uranium and sulfate in the aquifer originated as leachate from mill tailings
- Uranium transported as U(VI) with the bulk adsorbed to the sediments under background geochemical conditions
- Acetate stimulates the growth of microbial populations that remove aqueous U(VI) from solution via homogeneous reduction reactions that form uraninite
- Initial bioreduction of aqueous U(VI) is 75 to 85 percent efficient and is attributed to iron reducing bacteria that use Fe(III) minerals as a terminal electron acceptor
- Once bioavailable iron is depleted, the iron reducing bacteria are succeeded by sulfate reducing bacteria, which are less efficient at U(VI) removal from groundwater
How do spatial and temporal variations in hydrogeology and chemistry affect uranium behavior?

- Heterogeneous materials
  - Permeability
  - Iron and uranium
- Depth-dependent U(VI) and DO
  - Highest DO and U(VI) near the water table
  - Issues
    - Oxygen diffusion through water table
    - Background utilization of DO
How do seasonal and episodic hydrologic events affect uranium behavior?

Seasonal and event-driven changes
- Velocity field
- Oxidation of zones affected by water table fluctuations

Issues
- Rapid oxidation of zones affected by water table fluctuations
- Highest U concentrations bypassing treatment zones
What controls the post-amendment uranium behavior?

- Residual enzymatic reductive capacity of biomass
- Uranium surface complexation
- Fe(II) adsorption / desorption
- Mineral precipitation and dissolution [Fe(III) oxides/hydroxides, uraninite, FeS(am), siderite, calcite]
  - Coprecipitation
  - Alteration in surface reactivity
  - Alteration of access to reactive surfaces
Goal and Objectives

Goal
Systematic and quantitatively predictive understanding of the mechanistic contribution by individual subsurface processes to the observed uranium behavior at the Old Rifle UMTRA field site.

Objectives
- Determine the interplay between microbial and abiotic reactions governing field-scale bioremediation in the context of site-specific hydrologic and geochemical conditions
- Determine the impact of biostimulation on the geochemical controls (Eh, carbonate speciation and complexation, pCO2, mineral solubility, adsorption, pH) governing the mobility and long-term fate of uranium
Approach

- **Build field-scale conceptual process models**
  - Flow and transport
  - Biogeochemistry of biostimulation
  - Uranium surface complexation

- **Systematically integrate process models into a comprehensive field-scale flow and biogeochemical reactive transport simulation capability**
  - TEAPs and abiotic consequences of biostimulation affecting uranium mobility
  - Reoxidation and uranium mobility
    - Latent capacity for removal of aqueous U(VI)
    - Evolving surface chemistry (mineral precipitation/dissolution, adsorption/desorption)

- **Philosophy**
  - Start simple to isolate major behaviors
  - Systematically add process complexity and detail
  - Use modeling to gain insight and target knowledge gaps
2002 Flow Field

- 2002 field experiment
  - No prior augmentation
  - Steady flow field
  - Injection June 22 – Oct 23

- Modeling assumptions
  - 1-D domain
  - Constant velocity and dispersivity based on bromide transport
  - Bulk tank release rate distributed uniformly over injection gallery
  - Injection averaged over saturated thickness
10 mM Bromide injected

Breakthrough at monitoring wells

- General trends reproduced with constant velocity and dispersivity
- Row 2 has highest concentrations and maximum variability missed by average injection
  - Preferential flow paths
  - Release not uniform or fully mixed

Row 1
3.66 m downgradient

Row 2
7.32 m downgradient

Row 3
14.63 m downgradient

Old Rifle Test Plot

Injection Gallery

Control Wells

Acetate

GW flow

M-01 M-06 M-11

M-05 M-10 M-15

6.1m

16m

24m
Biologically Mediated Reactions

0.125CH$_3$COO$^- + 0.6$FeOOH(s) + 1.155H$^+ + 0.02$NH$_4^+$ = 0.02BM$_{\text{iron}} + 0.6$Fe$^{2+} + 0.96$H$_2$O + 0.15HCO$_3^-$

0.125CH$_3$COO$^- + 0.0057H$^+ + 0.0038$NH$_4^+$ + 0.1155SO$_4^{2-}$ = 0.0038BM$_{\text{sulfate}} + 0.0114$H$_2$O + 0.231HCO$_3^-$ + 0.1155HS$^-$

0.125CH$_3$COO$^- + 0.3538$H$_2$O + 0.0113NH$_4^+$ + 0.775UO$_2^{2+}$ = 0.0113BM$_{\text{iron}} + 0.855$H$^+ + 0.1938$HCO$_3^-$ + 0.775UO$_2$(s)
Sulfate / Sulfide Behavior

- 3-4 mM/L sulfide generation
- Typical field aqueous sulfide measurement 3 uM/L
- Implies sulfide associated with sediment
- 2003 AVS: equivalent to ~15 mM/L, 5 mM/L, 4 mM/L, 1.5 mM/L
Insights: Need for additional Fe++

- FeS formation on surface inferred
- Need 3-4 mM/L Fe++ to react sulfide
- Maximum aqueous Fe++ measurement is 196 uM/L
- Additional Fe++ would have to be associated with solid phases
- Fe++ adsorption
  - Consistent with other investigators

PNC-CAT x-ray microprobe
- Blackened sediment
- Fe and Sulfur
- No XRD for sulfide minerals
- Evidence for FeS(am)
Expansion of the Biogeochemical Reaction Network

42 total reactions

- Aqueous
  - Ca$$^{++}$$, Fe$$^{++}$$, K$$^{+}$$, Mg$$^{++}$$, Na$$^{+}$$, H$$^{+}$$, NH$_4$$^{+}$$, Cl$$^{-}$$, CO$_3$$^{-}$$, HS$$^{-}$$, SO$_4$$^{--}$

- Mineral
  - CaCO$_3$, FeOOH, FeCO$_3$, FeS, UO$_2$

- Sorption
  - Fe$$^{++}$

- Biologically-mediated (by acetate)
  - Fe(III), U(VI), sulfate TEAPs
Acetate injected for 123 days

In Row 1, acetate concentrations diminish significantly after 40 days
  - Decrease in sulfate
  - Decrease in Fe^{++}

Model: acetate peak diminishes with travel distance

Acetate concentrations are spatially and temporally variable
  - Multiple peaks with later arrivals in Row 1
  - Highest concentration in Row 2
  - Row 3 has much lower acetate than predicted
Uranium Bioreduction

- Initial aqueous U(VI) spatially variable
- Initial timing of aqueous U(VI) removal reproduced by model
Iron Bioreduction, Dissolution, and Sorption

- Initial Fe\(^{++}\) increase followed by decrease after onset of sulfate reduction
- Model predicts cumulative peak which is not obvious in well data
- Effect is observed in 2004 experiment

**Issues**
- Fe\(^{++}\) adsorption
- Fe\(^{++}\) production may be much higher
Sulfate Bioreduction

- Sulfate reduction begins after 40 days of iron reduction
- Rapid and complete utilization of acetate
- Sulfate reduction limited by acetate supply
- 3 - 4 mM sulfate removed underestimated by model
Uranium Experiments on Rifle Sediments

- Rifle Aquifer Background Sample (RABS)
- Sediment sample collected December 2004
  - 10 gallons of < 2 mm prepared
  - Experiments
    - Grand Junction
    - Princeton (Jaffe)
- Issues
  - High background U
  - Break off point between labile and nonlabile
  - Kinetics

<table>
<thead>
<tr>
<th></th>
<th>NABS</th>
<th>RABS</th>
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<tbody>
<tr>
<td>Particle size, mm</td>
<td>&lt; 3</td>
<td>&lt; 2</td>
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<tr>
<td>Surface area, m²/g</td>
<td>5.15</td>
<td>4.256</td>
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<tr>
<td>Labile U(VI), ug/g</td>
<td>0.208</td>
<td>1.12</td>
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<tr>
<td>Elapsed time, h</td>
<td>504</td>
<td>530</td>
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Set of batch equilibrium adsorption experiments
- RABS+AGW-3
- 10⁻⁸ to 10⁻⁵ M/L U(VI)

<table>
<thead>
<tr>
<th></th>
<th>Solid to Solution</th>
<th>TIC</th>
<th>pCO2</th>
<th>pH</th>
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<tbody>
<tr>
<td>ADS-1</td>
<td>25 g/L</td>
<td>8.25 mg/L</td>
<td>0.10%</td>
<td>7.62</td>
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<tr>
<td>ADS-2</td>
<td>820</td>
<td>108.35</td>
<td>2.39</td>
<td>7.33</td>
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<tr>
<td>ADS-3</td>
<td>125</td>
<td>92.7</td>
<td>2.23</td>
<td>7.28</td>
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<tr>
<td>ADS-4</td>
<td>125</td>
<td>100.2</td>
<td>3.62</td>
<td>7.06</td>
</tr>
<tr>
<td>ADS-5</td>
<td>250</td>
<td>238.4</td>
<td>22.8</td>
<td>6.52</td>
</tr>
<tr>
<td>ADS-6</td>
<td>125</td>
<td>100.8</td>
<td>5.23</td>
<td>6.90</td>
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<tr>
<td>ADS-7</td>
<td>250</td>
<td>213.6</td>
<td>20.8</td>
<td>6.52</td>
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Comparison of experimental results with Naturita surface complexation model
- RABS appears to be more sorptive
- Adsorption of lower U(VI) concentrations sensitive to labile U(VI)
Uranium Surface Complexation Modeling

Generalized composite surface complexation model

- Preliminary fit of formation constants for 2 surface reactions, 3 site types
- 1.92 µM/m² site density (bidentate)
- 23 aqueous uranium complexation reactions
  - Includes Ca-UO₂-CO₃ ternary complexes

<table>
<thead>
<tr>
<th>U(VI) Surface Reaction</th>
<th>Log K_f</th>
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<tr>
<td>SSOH + UO₂²⁺ = SSOUO₂⁺ + H⁺</td>
<td>12.28</td>
</tr>
<tr>
<td>SOH + UO₂²⁺ = SOUO₂⁺ + H⁺</td>
<td>6.95</td>
</tr>
<tr>
<td>WOH + UO₂²⁺ = WOUO₂⁺ + H⁺</td>
<td>2.74</td>
</tr>
<tr>
<td>SSOH + UO₂²⁺ + H₂O = SSOUOOH + 2 H⁺</td>
<td>0.033</td>
</tr>
<tr>
<td>SOH + UO₂²⁺ + H₂O = SOUOOOH + 2 H⁺</td>
<td>-2.12</td>
</tr>
<tr>
<td>SOH + UO₂²⁺ + H₂O = SOUOOOH + 2 H⁺</td>
<td>-5.01</td>
</tr>
</tbody>
</table>

Total site concentration of 1.92 _moles/m²_.

SSOH denoting very strong binding sites: 0.01% of total sites
SOH denoting strong binding sites: 0.1% of total sites
WOH denoting weak binding sites: 99.89% of total sites
Dissolved Oxygen Stratification: Framework for 2-D Reactive Transport

~20 cm layer of higher DO near water table
- Transported in from upgradient conditions
- Diffusion through water table

- O$_2$ influent with GW
- O$_2$ microbial TEAP
- O$_2$ diffusion at WT

Flow
Next Steps

- 2-D simulations to investigate depth-dependent issues
  - Incorporate new information on permeability distribution in the vertical
  - Incorporate new information from geophysics

- Refine uranium surface complexation model
  - Assess labile uranium and adsorption kinetics
  - Consider other combinations of uranium surface complexation reactions and site types in calibration
  - Identify additional experiments for model refinement

- Incorporate new process models into comprehensive reactive transport simulator
  - Datasets
    - 2003 and 2004 field experiments
    - Laboratory experiments
  - Impacts of biostimulation on iron chemistry
    - dissolution of uranium-bearing Fe(III) minerals
    - generation of Fe(II) and effect of adsorbed Fe(II) on bioavailability of Fe(III) minerals
    - effect of precipitation and dissolution on the accessibility of Fe(III) and U(IV) mineral surfaces to aqueous components
  - Post-amendment uranium mobility
    - conditions for residual capacity to remove U(VI) from groundwater
    - conditions where ambient geochemistry is being re-established
Acknowledgments

- University of Massachusetts
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- Dick Dayvault and Stan Morrison, SM Stoller Corporation

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Backup Slides
Adsorption Experiments

Experiments with AGW-3

- Approach based on Davis et al 2004
- Assess applicability of GC-SCM approach
- Compare with Naturita results

Adsorption Kinetics

<table>
<thead>
<tr>
<th>AGW-3</th>
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<tbody>
<tr>
<td>in air at 0.8547 atm</td>
</tr>
<tr>
<td>pH 7.79</td>
</tr>
<tr>
<td>pCO2 0.06%</td>
</tr>
<tr>
<td>CaSO₄</td>
</tr>
<tr>
<td>MgSO₄</td>
</tr>
<tr>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>CaCl₂</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>NaHCO₃</td>
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Depth-Dependent Transport

Acetate Concentration (depth & distance)

Bromide Concentration (depth & distance)