Coupled Flow and Multicomponent Biogeochemical Reactive Transport Modeling: In Situ Biostimulation at the Rifle Site

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Engineering bioremediation for site-specific conditions will require a \textit{quantitatively predictive understanding} of the dominant processes and properties controlling contaminant behavior.

Complex natural environments make the reliable prediction of field scale behavior 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.
- Need to develop a quantitatively mechanistic understanding of field-scale behaviors by addressing the relevant range of scales and multiple interacting processes.

In the context of temporally and spatially variable conditions at the site, use \textit{modeling to develop understanding} of the interplay between the dominant flow, transport, and biogeochemical processes.
Presentation Outline

- Previous modeling
- Knowledge gaps & issues
- Path forward
Hypothesis: Dissimilatory metal-reducing bacteria grown on acetate can be used to immobilize U(VI) in a field setting

Continuous influx of elevated uranium (140 to 350 ug/L)

2002: Initial biostimulation
- 123-day release period
- 100 mM acetate, 10 mM bromide
- Average rate ~70 L/d (range 0 to 120 L/d)

2003: 2nd biostimulation
- 109-day release
- 300 mM acetate, 10 mM bromide
- Average rate ~80 L/d (range 0 to 400 L/d)
Proof of Principle

- Acetate stimulated growth of microbial populations that reduced aqueous U(VI) to U(IV), effectively removing uranium from groundwater through the precipitation of U(IV) mineral.
- Initial bioreduction of aqueous U(VI) was 75 to 85 percent efficient and attributed to iron reducing bacteria (*Geobacter* sp.).
- Subsequent onset of sulfate reduction, coincided with less efficient U(VI) removal from groundwater.
Modeling Approach

- Use mechanistic coupled process simulators as a systematic framework to
  - gain insight on the dominant processes and properties responsible for observed behaviors in the field
  - identify knowledge gaps that need to be addressed

Philosophy
- Start simple to isolate major behaviors
- Systematically add process complexity and detail

Field-scale flow and biogeochemical reactive transport simulation of biostimulation experiments
- consistent gradient direction and magnitude: 1-D steady flow
- iron and sulfate reducers: Fe(III), U(VI), and sulfate TEAPS
- 2002 field experiment data set: calibrate flow, transport, and biogeochemical reaction parameters
- 2003 field experiment: strict application of 2002 calibrated parameters
Flow and Transport Modeling

2002

Row 1

2003

Row 2

Row 3
Uranium

2002

Row 1

2003

Row 1

Row 2

Row 3
Summary of Results

Observations during 2002 & 2003 biostimulation experiments are consistent with:

- 2 dominant microbial populations: iron reducers (i.e., Geobacter) and sulfate reducers
- 3 TEAPs: Fe(III) mineral, U(VI), sulfate
- Iron reducers concomitantly responsible for U(VI) reduction
- Onset of sulfate reduction triggered by consumption of threshold amount of Fe(III) mineral by iron reducers
- Lower U(VI) removal rate during sulfate reduction due to competition for acetate
2002 Simulation: Day 38, 52

SOLID PHASE

Mineral Distribution at 38 Days

Mineral Distribution at 52 Days

AQUEOUS PHASE

Acetate and Sulfate at 38 Days

Acetate and Sulfate at 52 Days

SOLID PHASE

AQUEOUS PHASE
Principal Knowledge Gaps: Processes and Properties

Large gap ("THE GAP") between fundamental research in geochemistry, microbial ecology and molecular biology, and field-scale reactive transport modeling

- Need development of detailed biogeochemical reaction network models
- Need to link new knowledge of cell reactions/metabolism to kinetics and constraints of enzymatic processes

Need for 3-D characterization of spatially-variable model parameters

- controls flow paths, sediment reactivity, rate-limited mass transfer between pore domains, gas entrapment during water table fluctuation
- simulation will play a key role in characterizing spatially variable parameters
  - testing and linking process models
  - accommodating a variety of data types from different scales
  - joint inverse modeling approaches
Biogeochemical Issues

- Are there other microorganisms consuming acetate?
- What factors control the stoichiometry and rates for TEAP reactions?
  - nutrient limitations
  - water chemistry
  - mineral form
- What factors control the onset of sulfate reduction?
  - “bioavailable” iron (e.g., poorly crystalline iron)
  - redox potential
  - metabolic lag
- What is the role of biomass in controlling U mobility?
  - production/consumption/decay
  - attachment/detachment
  - contribution to microbial reaction rates
  - effect on reactivity of mineral surfaces
  - sorption effects
- What is the role of U surface complexation before, during, and after biostimulation?
Preferential Flow and Transport Paths

- Considerable variability in bromide concentrations in the same row
- Row 2 has highest concentrations and maximum variability
- Some wells bypassed

**Issues**
- Heterogeneous sediments
- Nonuniform metering of injectate to gallery wells

**Graphs:**
- Row 1: 3.66 m downgradient
- Row 2: 7.32 m downgradient
- Row 3: 14.63 m downgradient
Spatially & Temporally Variable Uranium

- Spatially variable pre-biostimulation aqueous concentrations in 2002
  - U ranged from 0.3 to 1.5 uM
  - Fe(II) ranged from 18 to 250 uM

- Initial uranium distribution in G-28 sediments is strongly depth dependent
Density-Dependent Transport

- Acetate – bromide injectate is denser than GW
- Multilevel samplers show effect in 2003
- 3D modeling of individual gallery wells is necessary to accurately represent phenomenon
  - Modeling identifies sensitivity to anisotropy

![Acetate Concentration (depth & distance)](image1)

![Bromide Concentration (depth & distance)](image2)

![2d isotropic (vertical view)](image3)

![3d isotropic (vertical view)](image4)

![3d Anisotropic (vertical view)](image5)
Stratified Water Chemistry

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
- Screened interval of wells
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
Oxygen Entrapment during Water Table Fluctuation

- 2-phase flow model of aquifer-vadose zone system
- Hysteretic saturation function calculates entrapped gas during 2003 transient
- Oxygen entrapped during water table rise dissolves into GW
- Water table recession moves enhanced DO deeper in the aquifer
Coupling the Processes

2002 Field Experiment
- 2-phase 3D flow simulation
- Oxygen entrapment during water table transients
- Transient influent water chemistry
- Transient acetate injection
- Density effects
- Biogeochemical reactions

Acetate Concentrations (M)

- 30 Days
- 40 Days
- 50 Days
Path Forward

- Plenty of issues identified by earlier work
- Providing opportunity to begin to holistically address the goal of a quantitative field-scale understanding of uranium bioremediation
- Paradigm shift from extension of laboratory studies to field-scale context of site-specific conditions
- Address “THE GAP” between fundamental research and field-scale reactive transport modeling
- Collaborative modeling expertise
  - Carl Steefel, biogeochemical reactive transport from Hubbard et al. EMSP project
  - Mahadevan/Scheibe, in silico modeling from Lovley et al. ERSP project