Oak Ridge IFRC

Bioreduction of Uranium with Slow Release Substrates

Presenter: David Watson

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Lansdowne, Virginia
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Objectives

• Conduct laboratory and field studies and modeling of slow release substrates:
  – Ca-oleate precipitates and emulsified vegetable oils
  – Is reduction of U(VI) and nitrate possible?
  – Is it sustainable?

• Assess substrate delivery and subsurface distribution issues

• Test direct and remote sensing measurement methods
Bioreduction of Uranium with Slow Release Substrates

Tasks and Contributors

- Task leaders – David Watson (ORNL) and Weimin Wu (Stanford)
- Batch rate studies to assess substrates - Weimin Wu (Stanford)
- Column break through and electrical resistivity studies (LBNL) – Yuxin Wu and Susan Hubbard
- Bromide tracer test and injection of emulsified vegetable oil (ORNL) – Field, lab, analytical and data analysis support: Tonia Mehlhorn, Kenneth Lowe, Sally Mueller, Jana Phillips, Kirk Hyder and Jennifer Earles
- Surface ERT geophysics (UT) – Greg Baker et. al.
- PELCAPs and dissolved gases (ORNL) – Brian Spalding and Jennifer Earles
- Microbiology (ORNL) – Chris Schadt and Gengxin Zhang
- Spectrographic (ANL) – Ken Kemner and Max Boyanov
- Modeling (ORNL) – Fan Zhang
**Low pH Shale Path**
- High U (5 – 60 ppm)
- Tc99 (>5000 pCi/L)
- Nitrate (<200 – 50,000 ppm)
- Low pH (3.2 – 5.5)
- High DOC (200 ppm)

**Site Conditions**

**Gravel Path**
- U (1 ppm)
- Tc99 (<100 pCi/L)
- Low NO₃ (40 ppm)
- High pH (6.5)
- Low DOC (<50 ppm)
Groundwater Flow Path

**Source Zone (S-3 Ponds)**

- **NO₃⁻**: Al, Mn, Fe
- **SO₄²⁻**: pH = 3.2
- **U(VI)**
- **Tc(VII)**

**FW408**

<table>
<thead>
<tr>
<th>Solid Phase</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>U(VI) coated gravel</td>
</tr>
<tr>
<td>pH</td>
<td>pH grades from 5.9 to 3.2</td>
</tr>
<tr>
<td>NO₃</td>
<td>NO₃⁻ 162 ppm</td>
</tr>
<tr>
<td>U</td>
<td>U(VI) 1,000 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>pH 3.4</td>
</tr>
<tr>
<td>NO₃</td>
<td>NO₃⁻ 14,000 ppm</td>
</tr>
</tbody>
</table>

**Depth Below Ground Surface (ft)**

- Gravel Fill: 12,000 ppm U, pH 5.9 - 6.8, NO₃⁻ 162 ppm
- Saprolite: 1,000 ppm U, pH 3.4, NO₃⁻ 14,000 ppm

**Bear Creek**

**Discharge**

**Tank**

**Gravel Fill**

**Fig 1**
Past studies suggest need to explore substrates that can sustain reducing conditions and decrease costs

“Scheibe” Site

- Daily injections of ethanol for 1 year
- U conc. below MCL of 0.03 mg/L can be achieved
- Rapid rebound observed when injections stopped in 09/2006
Remobilization of U during storm event within previously bioreduced zone

4” rain event from 37-73 hours

U response

Outside bioreduced zone

Within bioreduced zone

GW836

U response

Within bioreduced zone

DP13

MLSE
Laboratory Studies (with site GW and core material)

Acetate production from ethanol, Ca-oleate precipitates, and emulsified vegetable oil (EVO)

The rate of acetate accumulation suggests that EVO degradation is slow compared to other substrates.

The acetate production for all substrates depends on initial sulfate concentration.
The rate of U(VI) removal in microcosms: ethanol > oleate >> EVO.

U speciation using XANES showed significant (>50%) U(IV).

From 16s analysis we infer that *Desulforegula* oxidizes EVO and Ca-oleate and reduces sulfate with by-products of short fatty acids and hydrogen sulfide. The biogenerated hydrogen sulfide of FeS may abiotically reduce U(VI).
Effects of Donor Amendments and Sulfate Conc. on Delta-Proteobacteria Populations different for SRS and oleate compared to control and ethanol
- 900 gallons of a 20% SRS™ solution (mixed with site GW) injected in 3 wells in @1.5 hours on 2/9/09

-Bromide tracer test (450 ppm) conducted on 12/8/09 in similar manner to SRS injection

5.9 times the amount of COD injected in 2 hours than for the entire year of ethanol injections

**SRS™ composition**

- Soybean oil (%) 60
- Yeast extract (%) 0.3
- Surfactant (%) 6
- (NH₄)₃PO₄ (%) 0.05
- Remainder water
- Density (kg/L) 0.93
- COD (g/L) 1620
Br and SRS injections

Electrical resistivity surface arrays for tracking SRS plume

Sampling >50 GW wells and seeps
Analyses

- Visual indicator of % SRS
- Specific conductance (both bromide and SRS solutions have a signal), pH, DO
- Sulfide odor
- Field Hach kit (nitrite, Fe(II), sulfide, COD)
- Volatile solids by drying/ashing
- IC (anions), ICP/MS (metals), TIC/TOC after SRS lower and indication of bioreduction

Fluid conductivity of SRS mixture

\[ y = 31.063x + 819.52 \]
\[ R^2 = 0.9981 \]

This will serve as reference plot for dilution

Volatile solid (VS) analysis by oven drying and ashing (Borden, 2007)
Comparison of Br to SRS C/C₀ concentration contours

- Highest concentration port used for MLS wells
- Fewer time intervals sampled for SRS
- General distribution through center of well field
- SRS slower and more to the left (Impact of SRS floating?)
- Poorly constrained downgradient but reached creek
Comparison of Br to SRS
C/C_0 concentration contours

No data for this time step
Comparison of Br to SRS
$C/C_0$ concentration contours

Max Bromide 2.71 hours after injection

3 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide  7.17 hours after injection

7 hours after SRS Injection
Comparison of Br to SRS C/C₀ concentration contours

Max Bromide 12.3 hours after injection

11 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

No data for this time step
Comparison of Br to SRS
C/C₀ concentration contours

No data for this time step
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 27.24 hours after injection

25 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 32.78 hours after injection

32 hours after SRS Injection
Comparison of Br to SRS C/C₀ concentration contours

No data for this time step
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 50.59 hours after injection

50 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

No data for this time step
Comparison of Br to SRS C/C₀ concentration contours

No data for this time step

Max Bromide 64.3 hours after injection
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 79.18 hours after injection

Legend
- 0 - 0.007
- 0.007 - 0.03
- 0.03 - 0.07
- 0.07 - 0.12
- 0.12 - 0.2
- 0.2 - 0.3
- 0.3 - 0.4
- 0.4 - 0.6
- 0.6 - 0.8
- 0.8 - 1

Legend
VS C/C₀
- 0 - 0.007
- 0.007 - 0.03
- 0.03 - 0.07
- 0.07 - 0.12
- 0.12 - 0.2
- 0.2 - 0.3
- 0.3 - 0.4
- 0.4 - 0.6
- 0.6 - 0.8
- 0.8 - 2

74 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

No data for this time step
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 101.64 hours after injection

97 hours after SRS Injection
Comparison of Br to SRS
C/C₀ concentration contours

Max Bromide 119.77 hours after injection

122 hours after SRS Injection
Comparison of Br to SRS
$C/C_0$ concentration contours

No data for this time step
Comparison of Br to SRS C/C₀ concentration contours

Max Bromide 168.26 hours after injection

174 hours after SRS Injection
Surface electrical resistivity tomography surveys
Surface electrical resistivity tomography surveys

SRS Injection. Injection Began \( \sim 8\)am on 2/9

Shown are TLERT sections, all differenced from a pre-injection ERT section

Notes: Survey duration is \( \sim 8\) hours

Integerated dipole-dipole and Wenner/Schlumberger survey, 0.75 m electrode spacing.
SRS breakthrough compared to Br suggests SRS floating

**Bromide**

- **MLS-H Wells**: Shallow port
- **MLS-C Wells**: Deep port
- **MLS-E Wells**: Shallow port

**SRS**

- **MLS-H Wells**: Deep port
- **MLS-C Wells**: Shallow port
- **MLS-E Wells**: Deep port

Maximum detected bromide
Reduction of U achieved!

Initial zone of >80% U reduction

Current zone after 70 days

Release of Fe from solid phase cause of initial increase in U?
Acetate produced and nitrate removed

Initial zone of >80% U reduction

Current zone after 70 days

Small rebound in nitrate to 1 ppm

Yeast extract use?

Oil use?

Small rebound in nitrate to 1 ppm
In Situ Groundwater communities during SRS stimulation in our initial analysis using 16S libraries

Delta Proteobacteria increased in abundance through stimulation timecourse

Like the bottle tests Desulforegula and Geobacter are present together. Likely a syntrophic interaction where Desulforegula ferments fatty acids to acetate used by Geobacter

Desulforegula conservatrix (Rees and Patel, IJSEM, 2001)
XANES analysis of surge samples

- Up to 85% U(IV) measured in down gradient monitoring wells
- U(VI) observed in control samples

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample ID</th>
<th>U, mg/kg</th>
<th>U6%</th>
<th>U4%</th>
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<tbody>
<tr>
<td>1</td>
<td>FWB-124 core 17-20 section #1 (before)</td>
<td>nd</td>
<td>90</td>
<td>10</td>
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<tr>
<td>2</td>
<td>FW202 3/17/09 (after)</td>
<td>nd</td>
<td>85</td>
<td>15</td>
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<tr>
<td>3</td>
<td>FW215 1/16/09 Control, before</td>
<td>nd</td>
<td>95</td>
<td>5</td>
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<tr>
<td>4</td>
<td>FW215 3/17/09 (Control, after)</td>
<td>519.4</td>
<td>95</td>
<td>5</td>
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<td>5</td>
<td>FW216 1/27/09 (before)</td>
<td>112.4</td>
<td>100</td>
<td>0</td>
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<td>6</td>
<td>FW234 1/16/09 (before)</td>
<td>nd</td>
<td>100</td>
<td>0</td>
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<td>7</td>
<td>FW234 from 3/12/09 (after)</td>
<td>441.9</td>
<td>60</td>
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<td>8</td>
<td>FWB-234 core March 2009(after)</td>
<td>nd</td>
<td>55</td>
<td>45</td>
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<td>9</td>
<td>GP01 1/16/09 (before)</td>
<td>nd</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>GP01 3/17/2009 (after)</td>
<td>96.4</td>
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<td>85</td>
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<td>11</td>
<td>GP03 1/16/09 (before)</td>
<td>nd</td>
<td>85</td>
<td>15</td>
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<tr>
<td>12</td>
<td>GP03 3/17/09 (after)</td>
<td>152.3</td>
<td>15</td>
<td>85</td>
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</table>
Significant reduction of U concentration in seeps and flux to Bear Creek observed.

Seep is 50 meters from injection wells.
Conclusions

- EVO injection achieved sequential reduction of nitrate, Fe(III), sulfate and U(VI) in the subsurface. Acetate was generated after about 2 weeks. U(VI) reduction to U(IV) was confirmed by XANES analysis.
- Microbial community depends on electron donor source and sulfate concentration but *Desulforegula* seems to play an important role in oil breakdown.
- Comparison of bromide to oil breakthrough curves suggests some floating of the SRS occurs.
- Reducing conditions have been sustained for over 70 days and has significantly reduced U flux to Bear Creek the primary exit pathway at the site.
- Oil droplet size is important consideration for subsurface delivery.
- Identified effective monitoring techniques that we will use to continue to monitor response.