Uranium Immobilization via Phosphate Injection into the Subsurface at the Hanford 300 Area

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Project History

- Demonstrate the control provided by polyphosphates over the precipitation kinetics of insoluble phosphate minerals for subsurface remediation
- Autunite stability

EM-22 (2006 – present) – “300 Area Treatability Test: In Situ Treatment of Uranium Contaminated Groundwater by Polyphosphate Injection”
- Site specific evaluation and optimization for the efficacy of using polyphosphate technology

ERSP (new start) – “An Integrated Approach to Quantifying the Coupled Biotic and Abiotic Mechanism, Rates and Long-Term Performance of Phosphate Barriers for In Situ Immobilization of Uranium”
- Determine the affect of dominant microbial metabolites on the long-term durability of autunite and apatite
- Incorporate fundamental data quantifying the effect of microbial activity on the durability of autunite and apatite into a kinetic rate equation allowing reactive transport codes to model the long-term fate of phosphate amendments for the in situ immobilization of uranium
Hanford 300 Area in 1962

- North & South Process Pond Inventory
  37,000 – 65,000 kg of uranium
- 1944 – 1954: Effluents from REDOX and PUREX process development
- 1978 – 1986: N-reactor fuels fabrication wastes
- Enriched, natural, and depleted uranium
The Problem: Persistent Elevated Uranium in 300 Area Groundwater

300 Area Uranium Plume
Uranium-Phosphate (Autunite) Minerals

- Very low solubility.
- Formation does NOT depend on changing the redox conditions of the aquifer.
- Not subject to reversible processes such as reoxidation or desorption.
Challenges to Phosphate Amendments: Rapid Precipitation Kinetics

- Injection of monophosphate molecules results in rapid flocculation and precipitation of phosphate phases
- Sharp decrease in hydraulic conductivity.

- Polyphosphate precludes rapid precipitation
- No measurable decrease in hydraulic conductivity
Solution to Deployment Challenges:
Use of Long-Chain Polyphosphates

- Slow reaction with water to yield orthophosphate
- Rate of hydrolysis is related to chain length
  - Time release - Controllable kinetics based on polymer length
- Rate of phosphate mineral formation is directly related to the rate of polyphosphate hydrolysis.
  - Direct treatment of uranium
  - Provides immediate and long-term control of aqueous uranium

Polyphosphate amendment can be tailored to delay formation of autunite and apatite.
Uranium Immobilization via Tripolyphosphate Application

Column tests with U-contaminated sediments (300 Area)

- Sustained release of uranium with groundwater
- Rapid decrease of aqueous uranium concentrations (near drinking water limits) in presence of polyphosphate
Single-Pass Flow-Through (SPFT) System

- Establishes steady-state conditions between the mineral and the aqueous solution
  - Constant chemical affinity
    - Minimizes reaction products
  - Ensures constant pH
  - Invariant concentration with respect to time
- Allow investigation over a range of experimental conditions
- Directly measured the dissolution rates
Autunite Minerals

- One of the most stable uranyl minerals
  - Natural ore deposits
  - Contaminated sites

- Thermodynamically, most likely uranyl phosphates to precipitate
  - \((M^{1\text{ or }2^+})[(UO_2)(PO_4)]_{1-2} \cdot x\ H_2O\)

- Structure is similar to micas
  - Polyhedra forming sheets
    - uranyl (yellow)
    - phosphate (blue)

- Not redox sensitive

Adapted from Locock and Burns, 2003
Autunite Dissolution Kinetics

- Linear pH-dependence, $\eta = 1.13$
- Uranium release rates from sodium and calcium autunite minerals are within experimental error (Wellman et al., 2006)
- The additional bond provided by the incorporation of a divalent cation (Ca$^{2+}$), relevant to a monovalent cation (Na$^+$), affords little increase in the overall structural stability of autunite minerals
- Uranium release from autunite ~ 6 orders of magnitude less than from UO$_2$ under similar conditions (Pierce et al. 2005)
Deployment of Phosphate Amendment for In-Situ Immobilization of Uranium

- Injection of soluble polyphosphate
- Lateral plume treatment
- Uranyl phosphate mineral (autunite) formation
  - Immediate sequestration
- Apatite formation
  - Sorbent for uranium
  - Conversion to autunite
- Enhancement of MNA
Uranium Stabilization through Polyphosphate Injection: Field Studies
Seasonal Dynamics of 300 A Uranium Plume

300 Area Uranium, December 2005

300 Area Uranium, June 2006
Treatability Test Site Location

300 Area Uranium, June 2006

Test Site Location
Geologic Cross Section

- Hanford formation
- Ringold Formation Unit 5
- Undesignated Fine-Grained Unit
- Ringold Formation Unit 8
- Lower Mud (Confining Unit)
- Basalt

Key:
- Screened Groundwater Sampling Interval
- Perforated Pipe Groundwater Sampling Interval
- Depth Discrete Sample Interval and Result (μg/L)
- Uranium data from 399-1-7
- Water Level from 399-1-3,7,8

K_h = Hydraulic Conductivity

Elevation (m) m/NA88

Pacific Northwest National Laboratory
U.S. Department of Energy
Hanford formation at this site ranges from silty sandy gravel to open framework gravels.

\[ K_h > 1000 \text{ m/d} \]

\[ K_h \sim 1 \text{ m/d} \]
300 Area Tracer Injection Test

- NaBr tracer test on Dec. 13, 2006
  - Injection Well: 399-1-23
  - Targeted 60 ft diam. treatment volume
  - Injected Volume: 143,000 gallons
  - 200 gpm for 11.9 hrs
- Inline tracer mixing with water from Well 399-1-7 (620 ft DG)
- Br\(^{-}\) conc. measured in injection stream and surrounding monitoring wells
  - Samples analyzed on site with ISE
  - Archive samples→ verification by IC
  - Downhole ISE probes installed in all monitoring wells
Tracer Test Results within Targeted Treatment Volume

\[ \bar{n}_{\text{eff}} \text{ (based on tracer arrival)} = 0.18 \]
- Consistent with LFI porosity estimates based on physical property analysis
Tracer Results for Downgradient Wells 399 1-32 and 399-1-7

399-1-32 tracer drift data
- Arrival in ~ 2 days
- \( v = 50 \text{ ft/d (15 m/d)} \)
- \( K = 14,000 \text{ ft/d (4,300 m/d)} \)
- \( K_{\text{fast}} = 20,000 \text{ ft/d (6,100 m/d)} \)

399-1-7 tracer drift data
- First arrival after ~ 12 days
- Tracer plume well dispersed

** Tracer drift data will be evaluated using a local-scale flow and transport model.**
Uranium Stabilization through Polyphosphate Injection: Bench Scale Testing
Laboratory Testing Strategy

31P NMR Hydrolysis Experiments
- Quantified the degradation of polyphosphates in groundwater and heterogeneous systems
  - Homogeneous degradation
    - Aqueous HCO$_3^-$, Ca$^{2+}$, Na$^+$, Al$^{3+}$, Fe$^{3+}$, and Mg$^{2+}$, pH = 6.5 – 8.0 at 23°C
  - Heterogeneous degradation

Batch Tests
- Amendment Optimization
  - Down selected potential polyphosphate compounds
- Uranium Sequestration
  - Kinetics of uranium sorption on apatite as a function of pH
  - Loading density of uranium per mass of apatite as a function of pH
  - Kinetics and stability of sorbed uranium

Column Tests
- Emplacement Efficiency
  - Amendment Transport
  - Autunite/Apatite Formation
Possible Amendment Components

<table>
<thead>
<tr>
<th>Amendment Source</th>
<th>Formula</th>
<th>Solubility, g/L cold H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Orthophosphate</td>
<td>Na₃PO₄ • 12H₂O</td>
<td>40.2</td>
</tr>
<tr>
<td>Sodium Pyrophosphate</td>
<td>Na₄P₂O₇ • 10H₂O</td>
<td>54.1</td>
</tr>
<tr>
<td>Sodium Tripolyphosphate</td>
<td>Na₅P₃O₁₀</td>
<td>145.0</td>
</tr>
<tr>
<td>Sodium Trimetaphosphate</td>
<td>(NaPO₃)₃ • 6H₂O</td>
<td>Soluble</td>
</tr>
<tr>
<td>Sodium Hexametaphosphate</td>
<td>(NaPO₃)₆ • 6H₂O</td>
<td>Very Soluble</td>
</tr>
<tr>
<td>Calcium Dihydrogen Phosphate</td>
<td>Ca(H₂PO₄)₂ • H₂O</td>
<td>18</td>
</tr>
<tr>
<td>Calcium Hydrogen Phosphate</td>
<td>CaH₂PO₄ • 2H₂O</td>
<td>0.32</td>
</tr>
<tr>
<td>Calcium Pyrophosphate</td>
<td>Ca₂HPO₄ • 5H₂O</td>
<td>Slightly Soluble</td>
</tr>
<tr>
<td>Calcium Hypophosphite</td>
<td>Ca(H₂PO₂)₂</td>
<td>154</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂</td>
<td>743</td>
</tr>
</tbody>
</table>
Site Relevant Speciation

Jenkins et al., 1971

- Log concentration, moles l

pH

HPO₄⁻²
H₂PO₄⁻
H₂P₃O₁₀⁻³
HP₃O₁₀⁻⁴
H₂P₂O₇⁻²
HP₂O₇⁻³

Total-P = 3 x 10⁻⁹ M  Pyro-P = 1.8 x 10⁻⁵ M  Ortho-P = 1.5 x 10⁻⁴ M  Triply-P = 3.8 x 10⁻⁵ M
Phosphate Relationships

Phosphate

- Tripolyphosphate
  - Sorbs to sedimentary material (calcite, Fe and Al oxide, clay)
  - Forms fine ppt. w/ Ca

- Orthophosphate
  - Sorbs to sediment bound tripolyphosphate complexes increasing rate and degree of precipitation

- Pyrophosphate
  - Forms heavy, fast settling ppt. w/ Ca

Calcium
Column Testing

Test Parameters

- $[P]_{\text{ortho/pyro/tripoly}}$
- Calcium/phosphorus ratio
- $[\text{Ca}]_{\text{total}}$ & $[\text{P}]_{\text{total}}$
- pH of amendment solution

Column Length = 1 ft
Cross Sectional Area = 0.005 ft$^2$
Porosity = 0.25
Flow Rate = 1.5 L/day
$[\text{U}]_{\text{aq}} = 1000 \ \mu\text{g/L}$
Uranium Column Testing

Total $[P]_{aq} = 1.05 \times 10^{-2}$ M
Pyro $[P]_{aq} = 2.63 \times 10^{-3}$ M
$[Ca]_{aq} = 2.32 \times 10^{-2}$ M

Tripoly $[P]_{aq} = 3.94 \times 10^{-3}$ M
Ortho $[P]_{aq} = 3.94 \times 10^{-3}$ M
pH adj. to 7
Uranium Column Testing

Total $[P]_{aq} = 5.26 \times 10^{-2}$ M
Pyro $[P]_{aq} = 6.58 \times 10^{-3}$ M
$[Ca]_{aq} = 9.98 \times 10^{-2}$ M  pH = 7

Tripoly $[P]_{aq} = 8.77 \times 10^{-3}$ M
Ortho $[P]_{aq} = 1.32 \times 10^{-2}$ M
RT = 56 min  PV = 52 mL  PV = 1 Ca/ 1P
Post-Test Preliminary Analysis
Aqueous Uranium During Treatment
Rate of Uranium Sequestration with Apatite

Graph showing the rate of uranium sequestration over time with different pH levels (pH 6, pH 6.5, pH 7) and the concentration of uranium (µg L⁻¹) decreasing over time (min). The graph indicates a rapid decrease in uranium concentration as time increases, with the rate being faster at lower pH levels.
Stability of Uranium Sequestered with Apatite

Cumulative Volume (mL)

% U Desorbed

-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6

pH 6
pH 6.5
pH 7
pH 7.5

Cumulative Volume (mL)
Ongoing Injection Design Activities

- Intermediate scale column test (i.d. = 4”, L = 10’)
- Develop hydraulic property zonation in the vicinity of the test site
  - Lithologic descriptions
  - Hydraulic test data
  - Changes in hydraulic gradient
  - EBF testing (vertical distribution of $K_h$)
  - Tracer arrival data
- Perform predictive simulations to evaluate transport under high river stage conditions
- Polyphosphate injection planned for June 07 (high water table conditions)
Acknowledgements

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