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 effect 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

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Autunite Minerals

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

► Thermodynamically, most likely uranyl phosphates to precipitate
  - \((M^{1\text{ or }2^+})[(UO_2)(PO_4)]_{1-2} \cdot xH_2O\)

► 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
Local-Scale Geologic Cross Section

Hanford formation at this site ranges from *silty sandy gravel* to *open framework gravels*

- $K_h > 1000 \text{ m/d}$
- $K_h \sim 1 \text{ m/d}$

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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

- \( \bar{n}_{\text{eff}} \) (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 $\text{HCO}_3^-$, $\text{Ca}^{2+}$, $\text{Na}^+$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$, and $\text{Mg}^{2+}$, 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>Na₄P₃O₁₀ • 10H₂O</td>
<td>54.1</td>
</tr>
<tr>
<td>Sodium Triorthophosphate</td>
<td>Na₅P₃O₁₀</td>
<td>145.0</td>
</tr>
<tr>
<td>Sodium Tripolyphosphate</td>
<td>(NaPO₃)₃ • 6H₂O</td>
<td>Soluble</td>
</tr>
<tr>
<td>Sodium Hexametaphosphate</td>
<td>(NaPO₃)₆ • ½H₂O</td>
<td>Very Soluble</td>
</tr>
<tr>
<td>Calcium Dihydrogen Phosphate</td>
<td>Ca(H₂PO₂)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 Pyroorthophosphate</td>
<td>Ca₃P₂O₇ • 5H₂O</td>
<td>Slightly Soluble</td>
</tr>
<tr>
<td>Calcium Hypophosphate</td>
<td>Ca₃P₂O₇ • 5H₂O</td>
<td>154</td>
</tr>
<tr>
<td>Calcium Hypophosphate</td>
<td>Ca₃P₂O₇ • 5H₂O</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

\[ \text{Total-P} = 3 \times 10^{-4} \text{ M} \]
\[ \text{Pyro-P} = 1.8 \times 10^{-5} \text{ M} \]
\[ \text{Ortho-P} = 1.5 \times 10^{-4} \text{ M} \]
\[ \text{Triply-P} = 3.8 \times 10^{-5} \text{ M} \]

- log concentration, moles L

- pH

- HPO_4^{\text{-2}}

- H_2PO_4^{-}

- H_2P_3O_{10}^{\text{-3}}

- HP_3O_{10}^{\text{-4}}

- H_2P_2O_7^{-2}

- HP_2O_7^{\text{-3}}

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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
- \([\text{Ca}]_{\text{total}} & [P]_{\text{total}}\)
- pH of amendment solution

- Column Length = 1 ft
- Cross Sectional Area = 0.005 ft\(^2\)
- Porosity = 0.25
- Flow Rate = 1.5 L/day
- \([U]_{\text{aq}} = 1000 \ \mu\text{g/L}\)
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 \([P]_{aq} = 5.26 \times 10^{-2} \text{ M}\)
Pyro \([P]_{aq} = 6.58 \times 10^{-3} \text{ M}\)
\([Ca]_{aq} = 9.98 \times 10^{-2} \text{ M}\)  \(\text{pH} = 7\)
Tripoly \([P]_{aq} = 8.77 \times 10^{-3} \text{ M}\)
Ortho \([P]_{aq} = 1.32 \times 10^{-2} \text{ M}\)
RT = 56 min  PV = 52 mL  PV = 1 Ca/ 1P
Post-Test Preliminary Analysis
Aqueous Uranium During Treatment

![Graph showing aqueous uranium during treatment](image_url)
Rate of Uranium Sequestration with Apatite
Stability of Uranium Sequestered with Apatite

Cumulative Volume (mL)
0 10 20 30 40 50
% 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
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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