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

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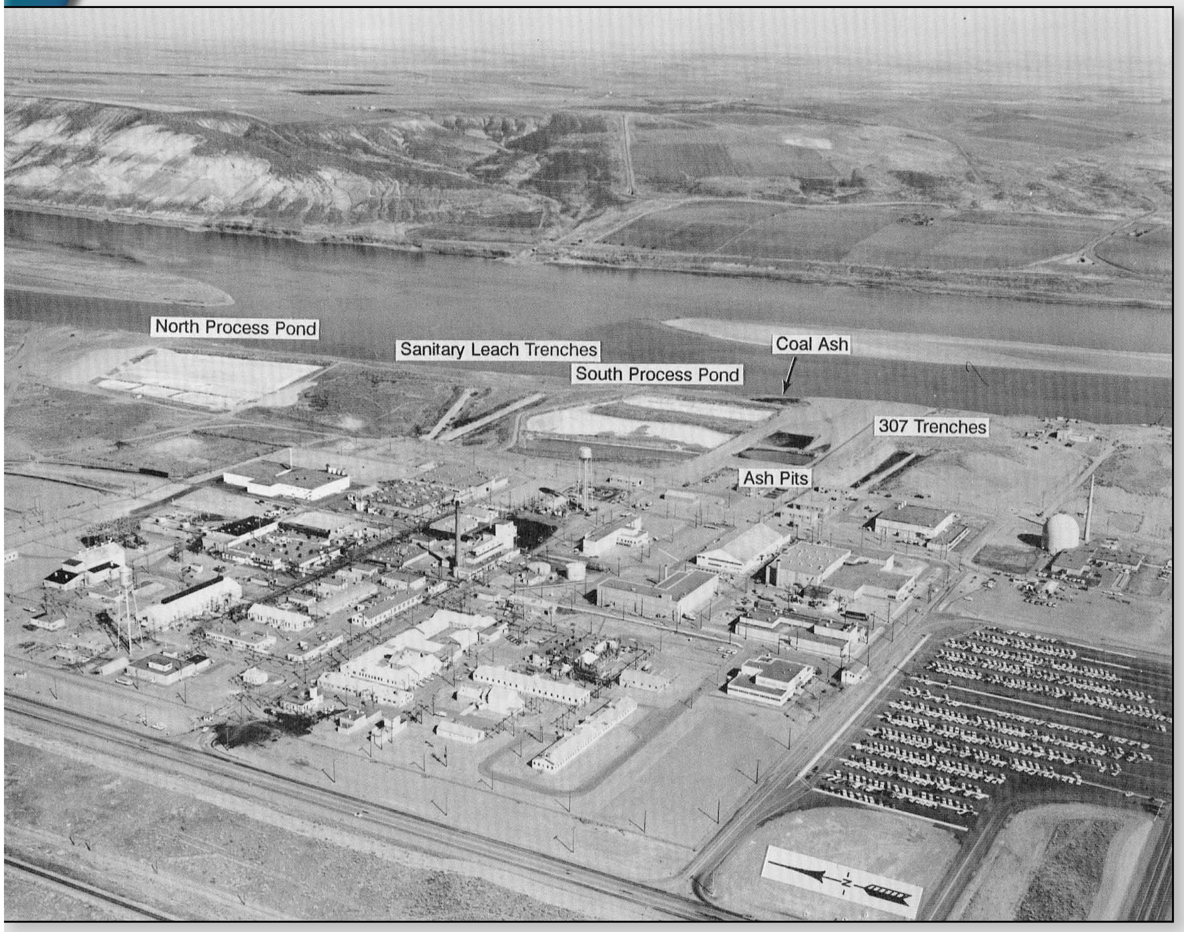
Project History

- EMSP (2002 - 2004) – “Phosphate Barriers for Immobilization of Uranium Plumes”
  - 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

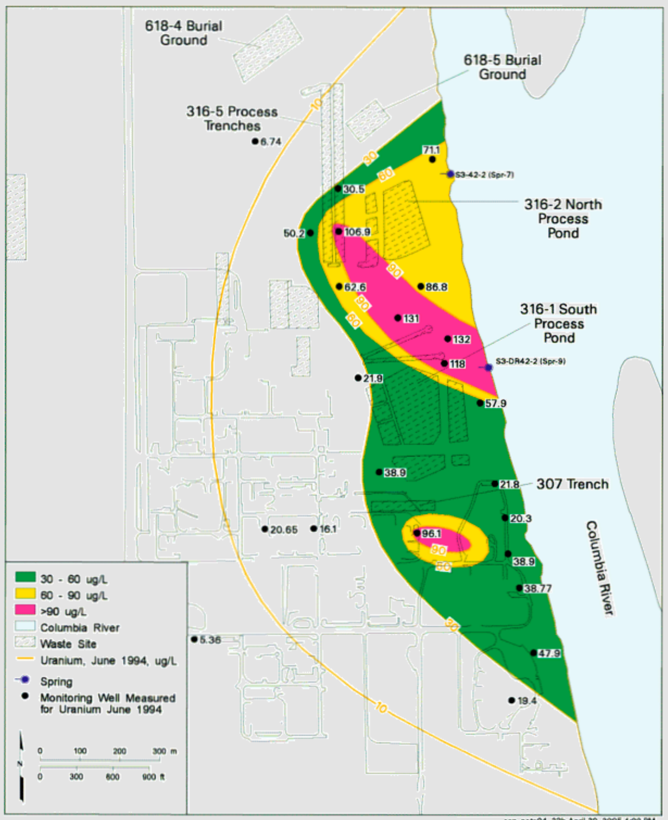


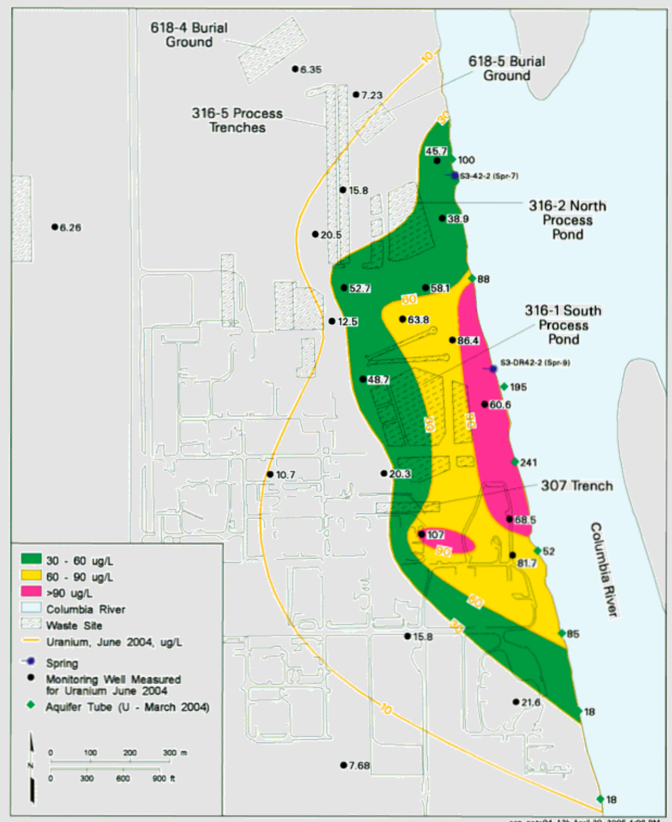
- North & South Process Pond Inventory 37,000 – 65,000 kg of uranium
  - 1944 – 1954: Effluents from REDOX and PUREX process development
  - 1978 – 1986: N-reactor fuels fabrication wastes
  - Enriched, natural, and depleted uranium

The Problem: Persistent Elevated Uranium in 300 Area Groundwater

300 Area Uranium Plume

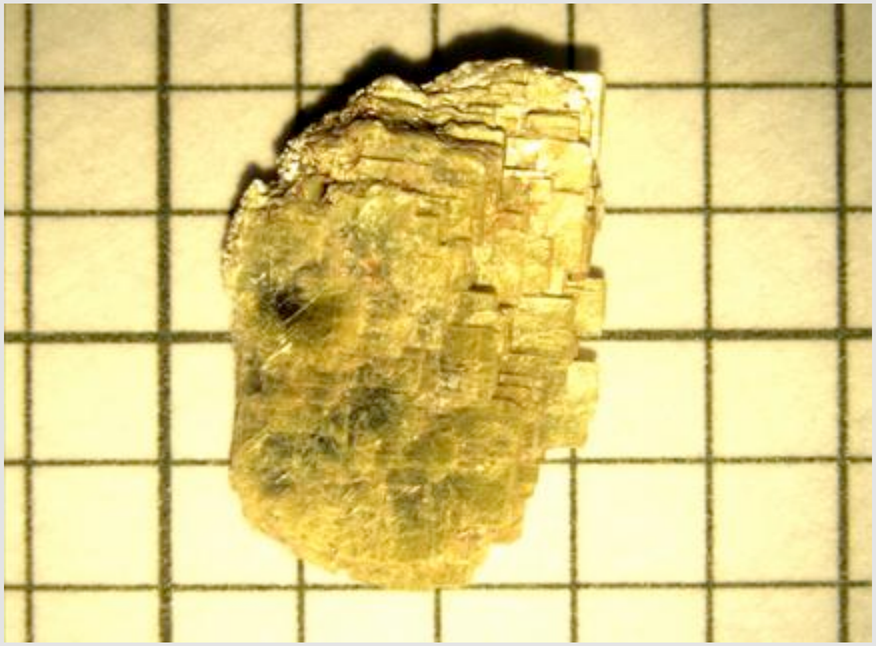
Exceeding Current Drinking Water Standard 1994 & 2004



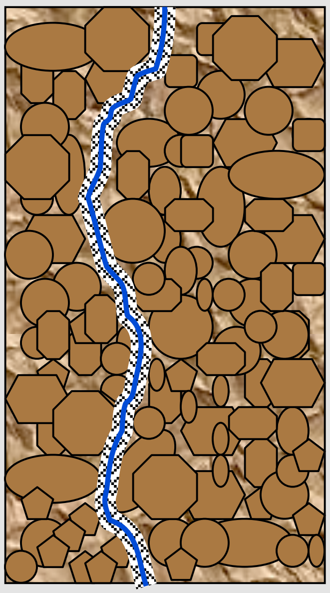


Uranium-Phosphate (Autunite) Minerals

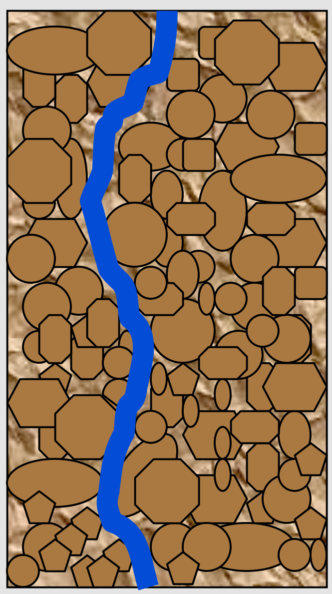
- Very low solubility.
- Formation does NOT depend on changing the redox conditions of the aquifer.
- Not subject to reversible processes such as reoxidation or desorption.



Challenges to Phosphate Amendments: Rapid Precipitation Kinetics



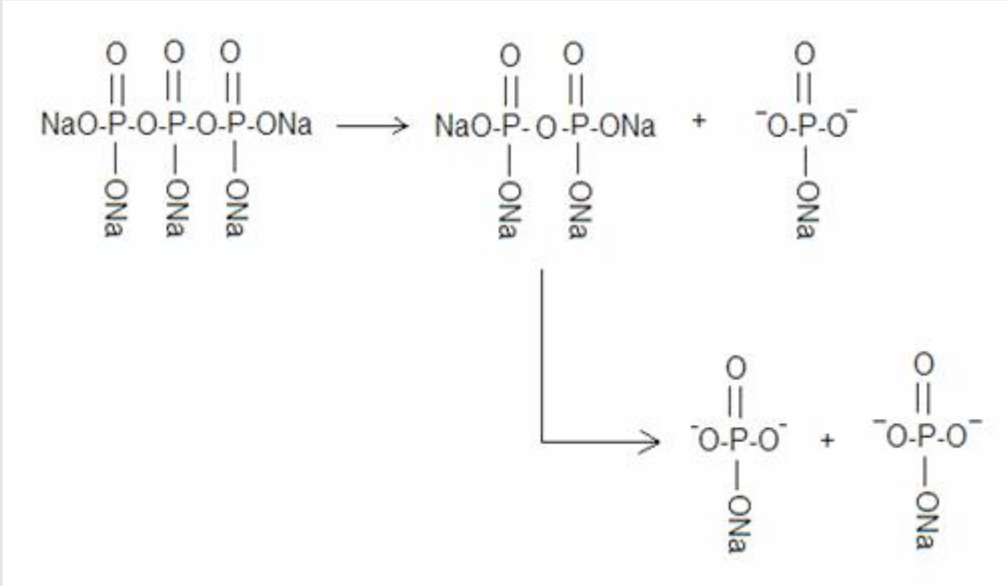
- Injection of monophosphate molecules results in rapid flocculation and precipitation of phosphate phases
- Sharp decrease in hydraulic conductivity.



- Polyphosphate precludes rapid precipitation
- No measurable decrease in hydraulic conductivity

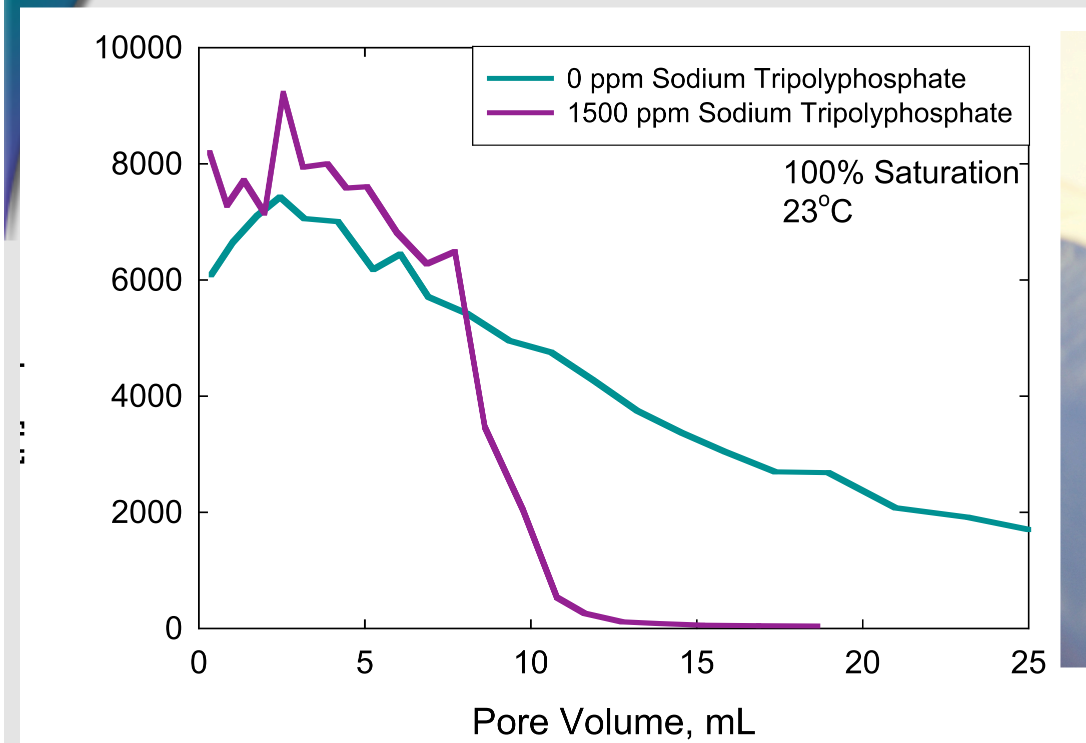
Solution to Deployment Challenges: Use of Long-Chain Polyphosphates

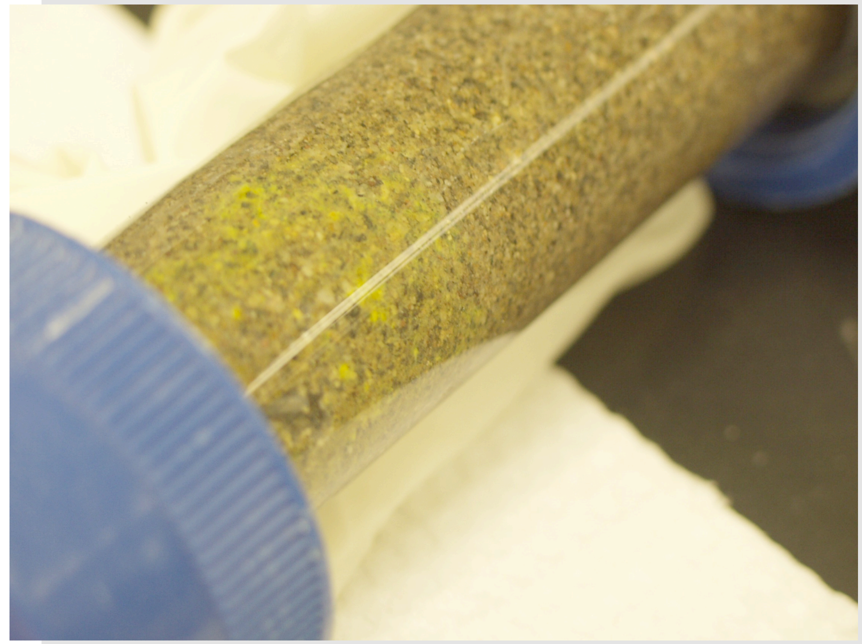
- Slow reaction with water to yield orthophosphate
- Rate of hydrolysis is related to chain length
  - Time release - Controllable kinetics based on to polymer length
- Rate of phosphate mineral formation is directly related to the rate of polyphosphate hydrolysis.
  - Direct treatment of uranium
  -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

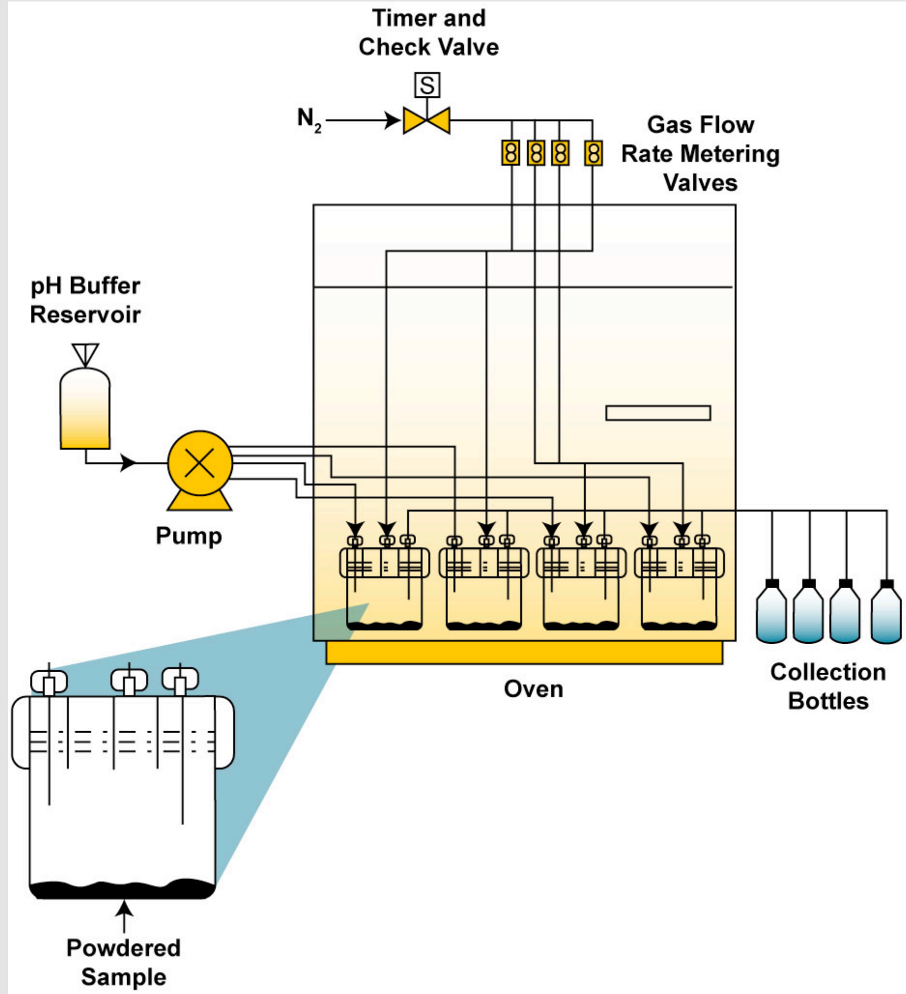




- Column tests with U-contaminated sediments (300 Area)
  - Sustained release of uranium with groundwater
  - Rapid decrease of aqueous uranium concentrations (near drinking water limits) in presence of polyphosphate

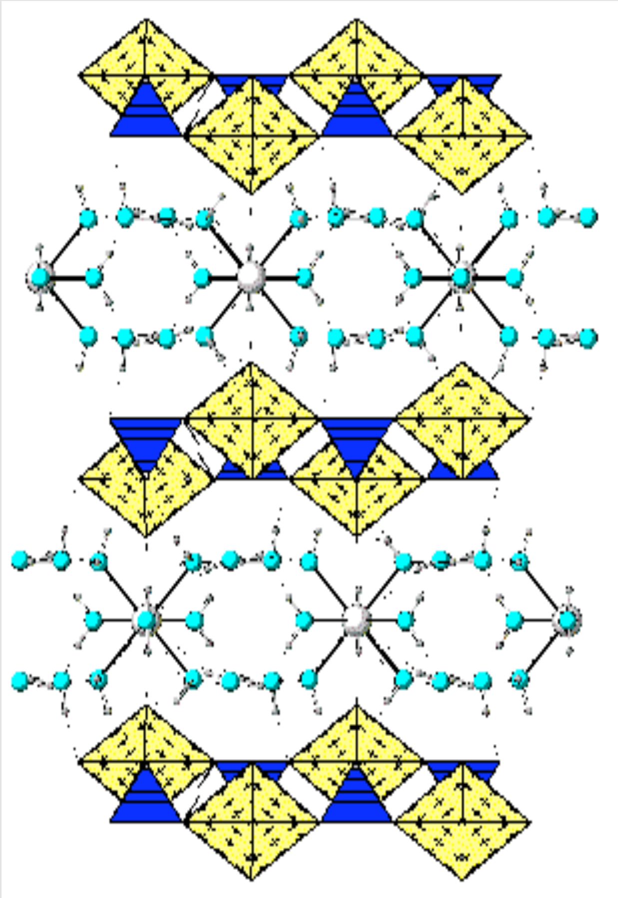
Single-Pass Flow-Through (SPFT) System

- 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

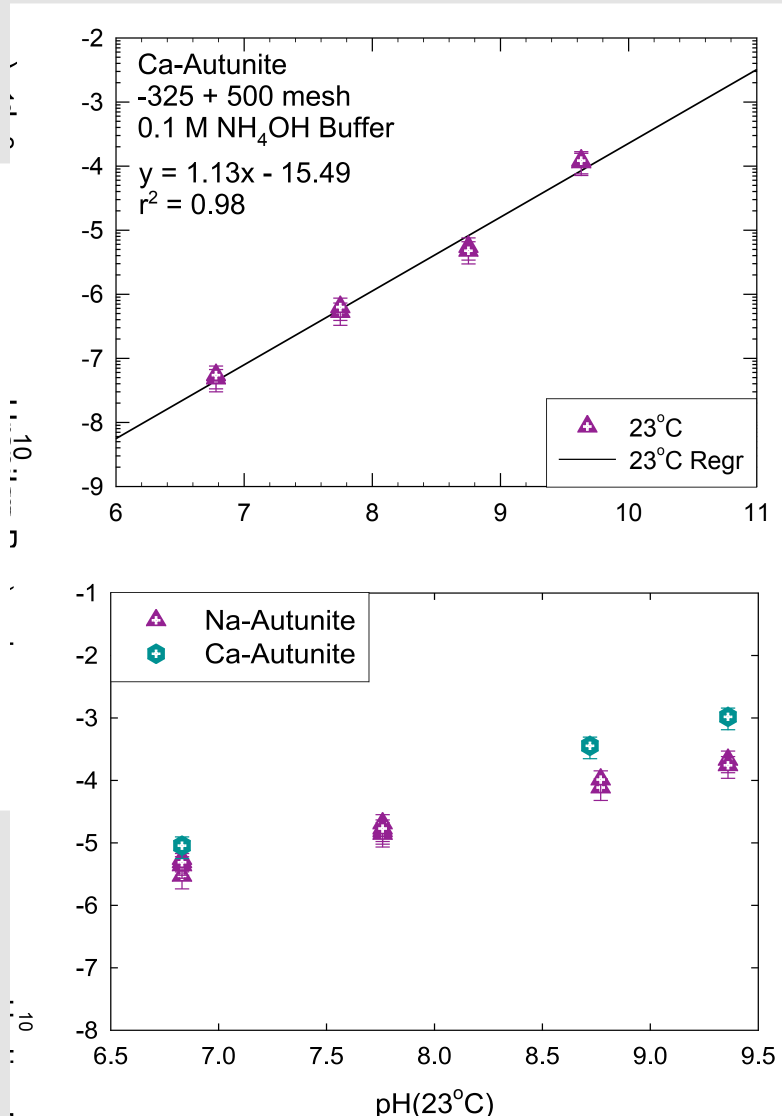
- One of the most stable uranyl minerals
  - Natural ore deposits
  - Contaminated sites
- Thermodynamically, most likely uranyl phosphates to precipitate
  - $(M^{1\text{ or }2+})[(UO_2)(PO_4)]_{1\text{-}2} \cdot x\, H_2O$
- Structure is similar to micas
  - Polyhedra forming sheets
    - uranyl (yellow)
    - phosphate (blue)
- Not redox sensitive



Adapted from Locock and Burns, 2003

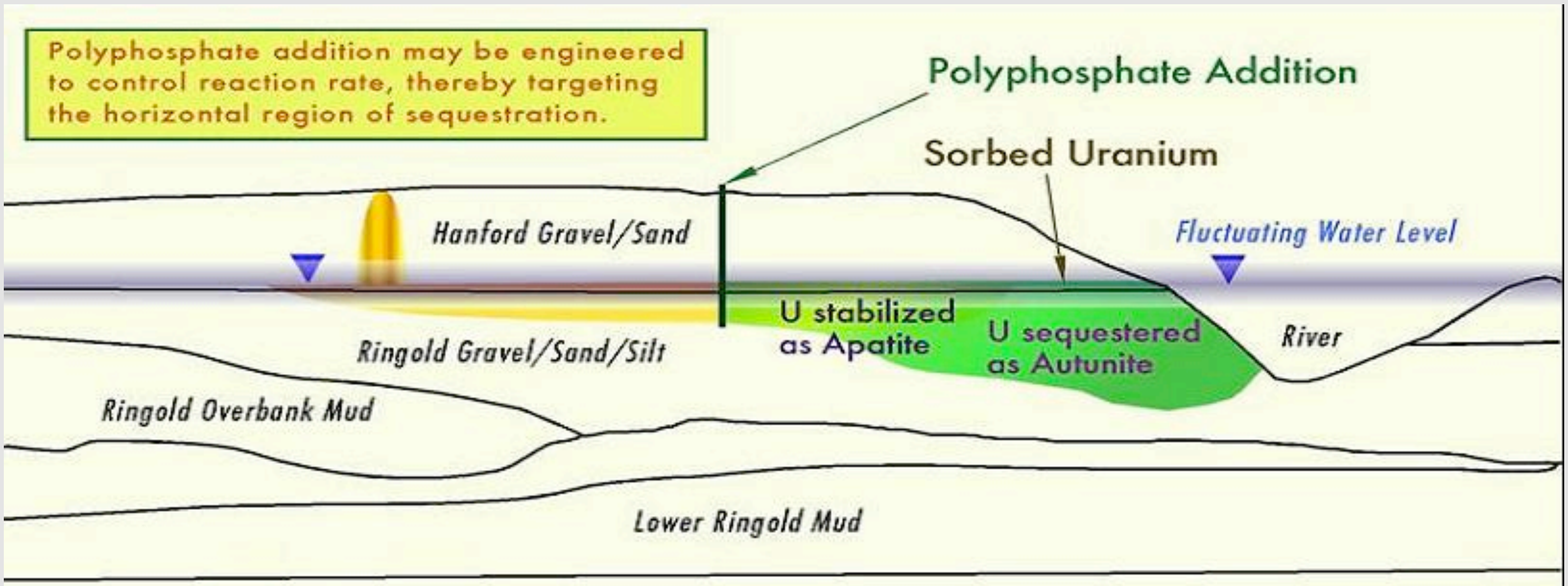
Autunite Dissolution Kinetics

- 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 provide 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)*



(Wellman et al., 2006)

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

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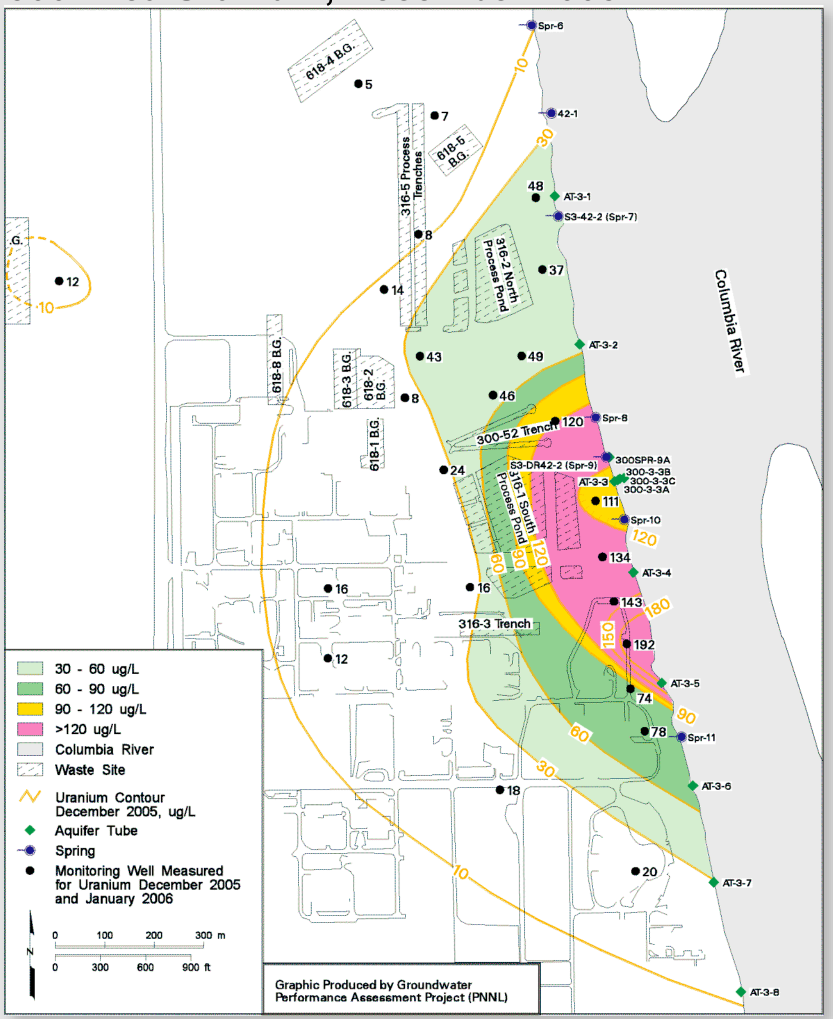
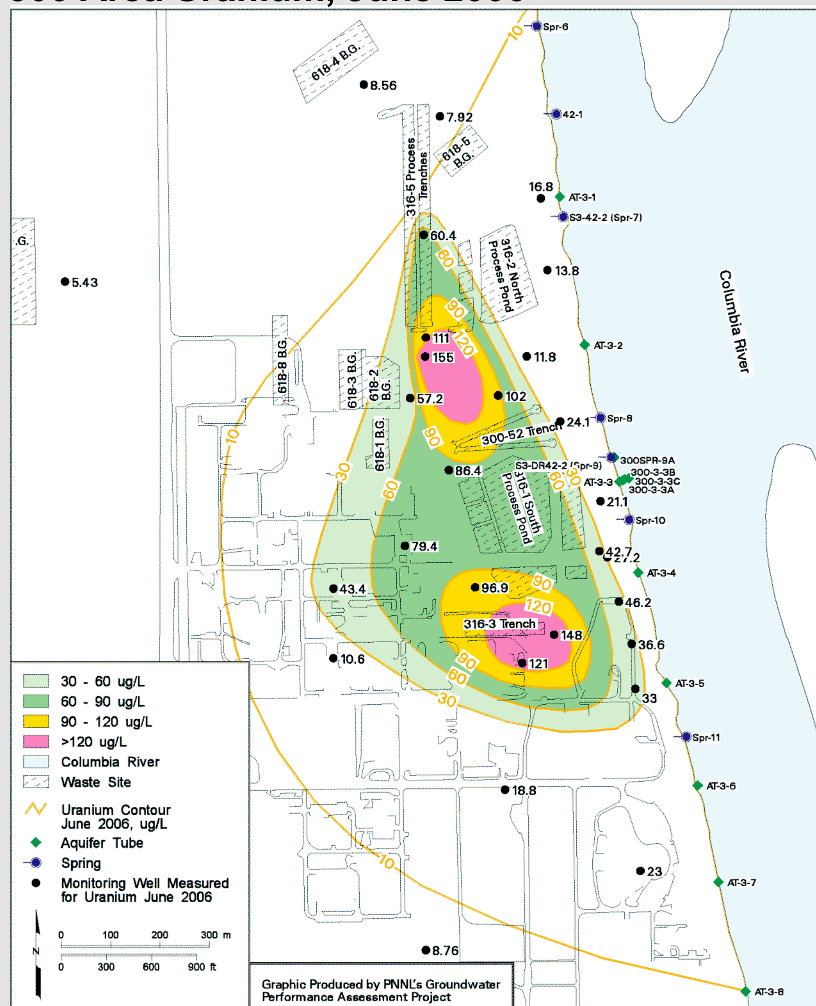
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Seasonal Dynamics of 300 A Uranium Plume

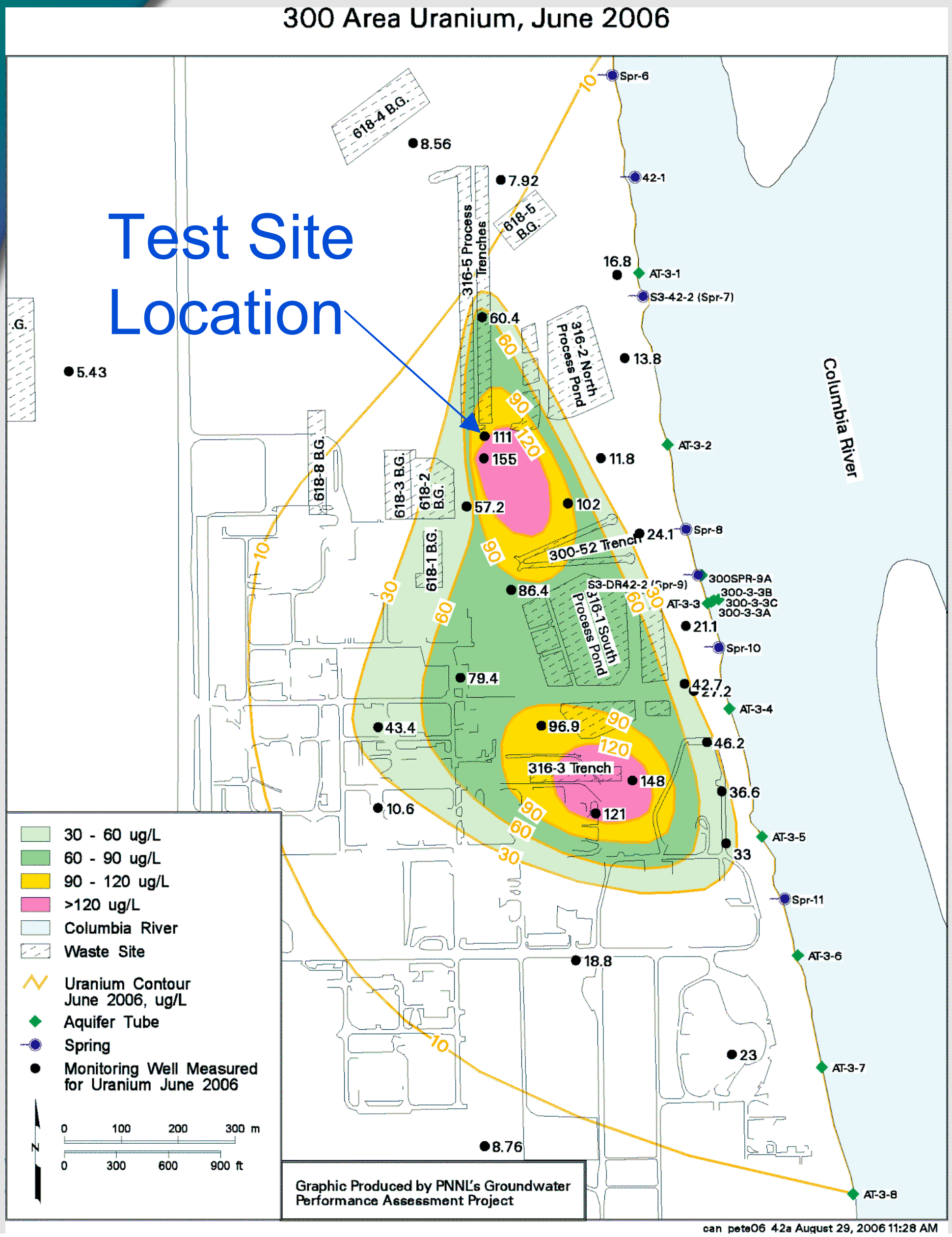
300 Area Uranium, December 2005

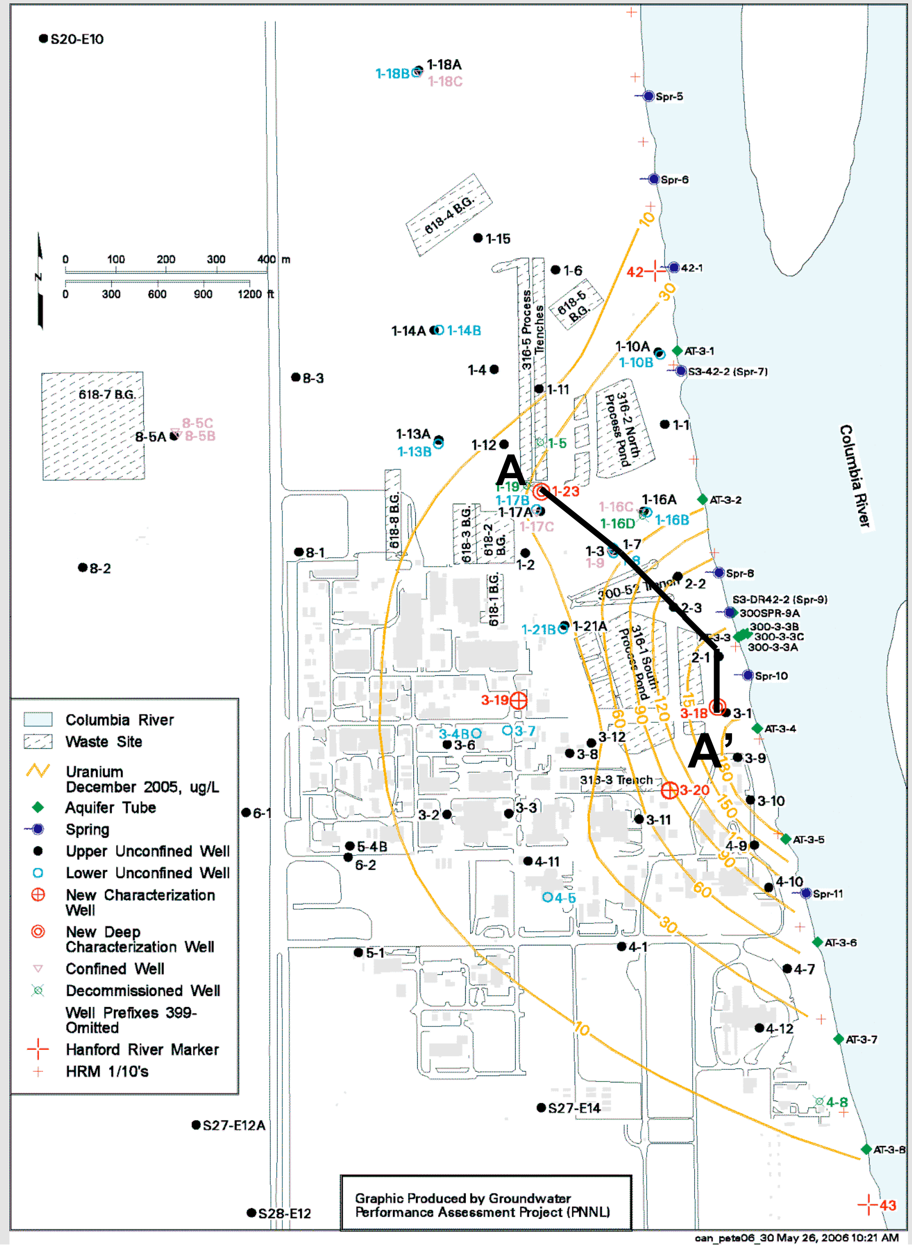


300 Area Uranium, June 2006

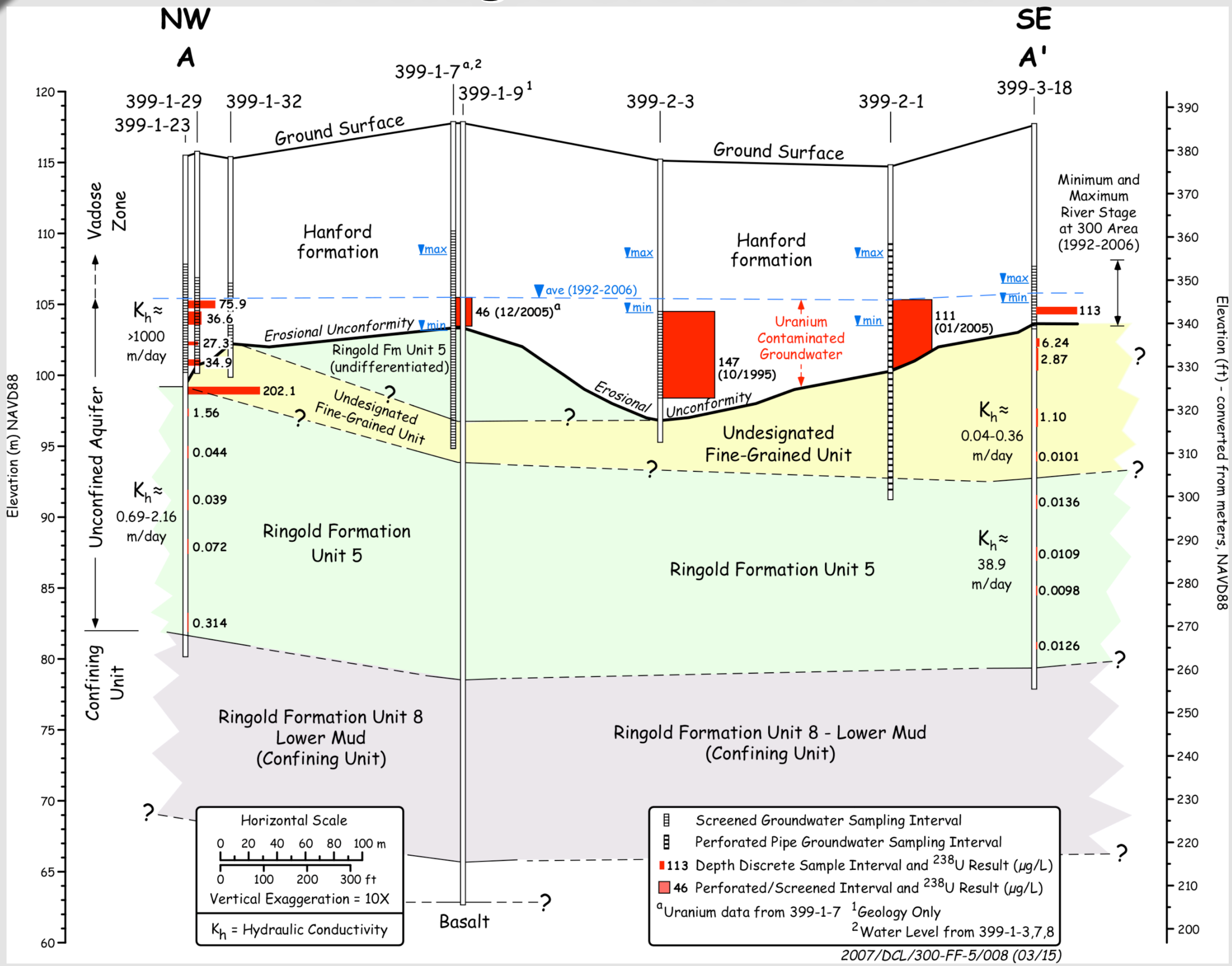


Treatability Test Site Location

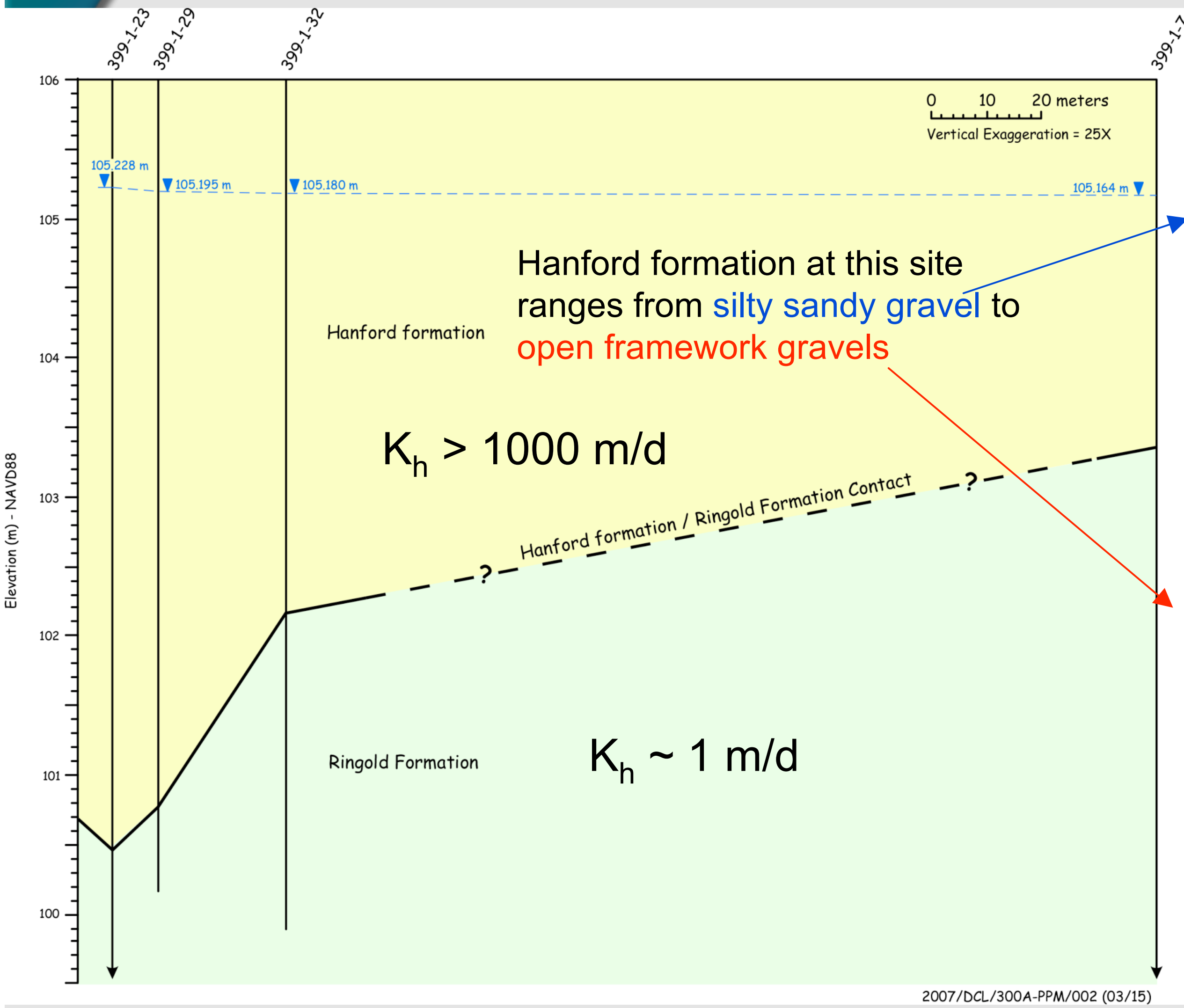




Geologic Cross Section



Local-Scale Geologic Cross Section



399-1-23, 33.5-34.5 ft

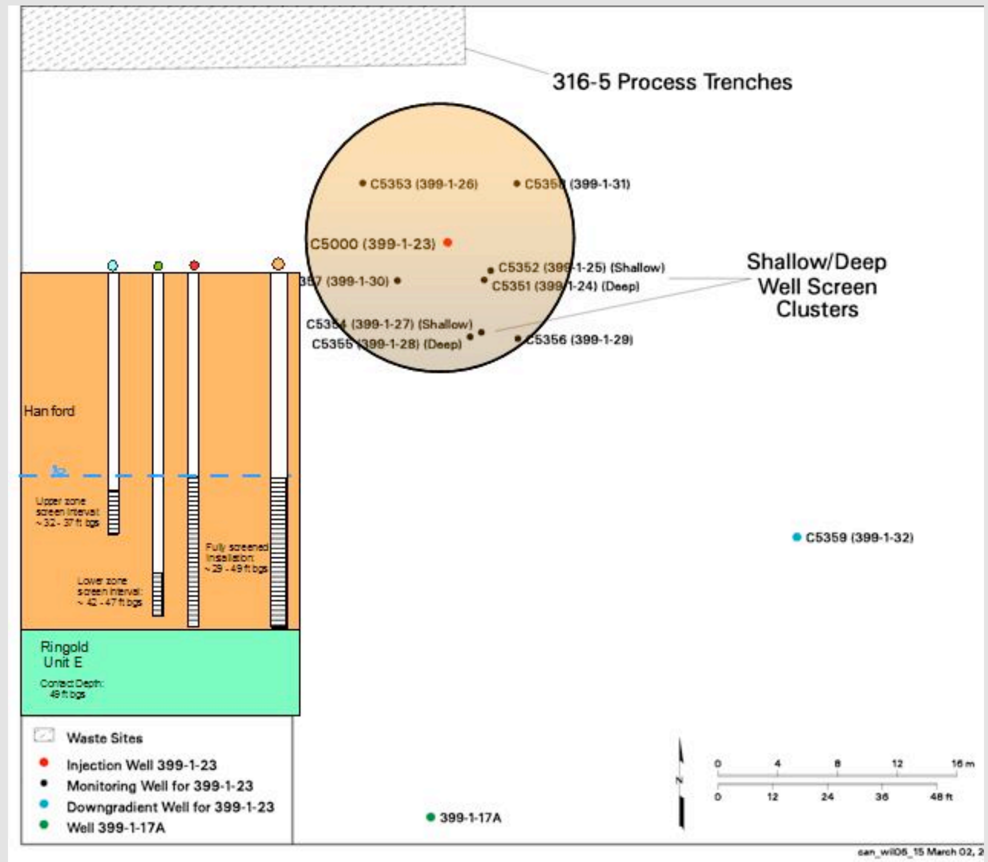
399-1-23, 37.8-38.5 ft

399-1-23, 48.5-49.5 ft
sandy gravel

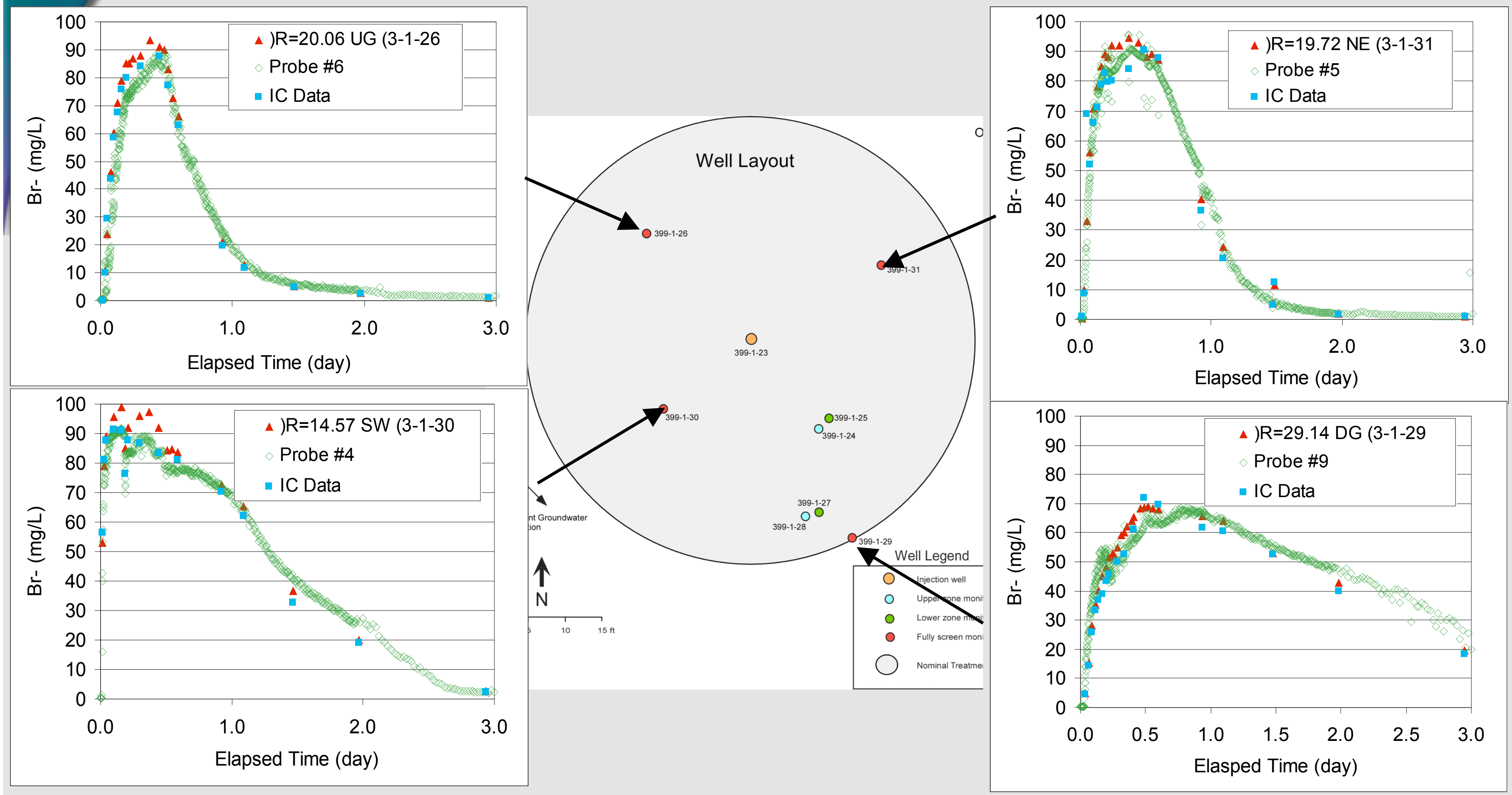
399-3-20, 55-56 ft
gravel

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



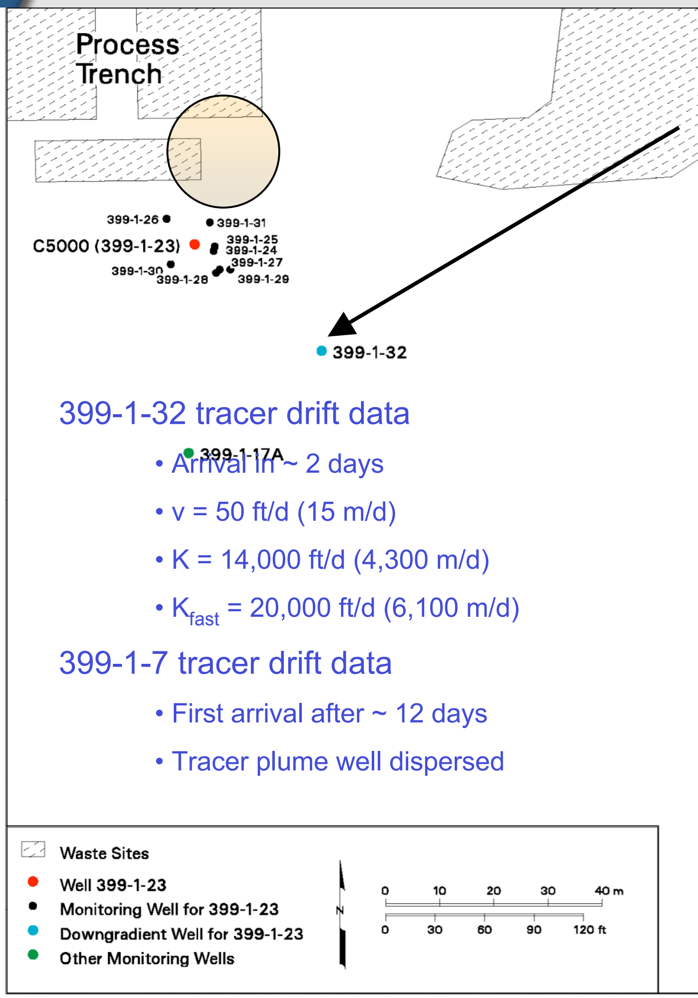
Tracer Test Results within Targeted Treatment Volume



$-\overline{n}_{eff}$ (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

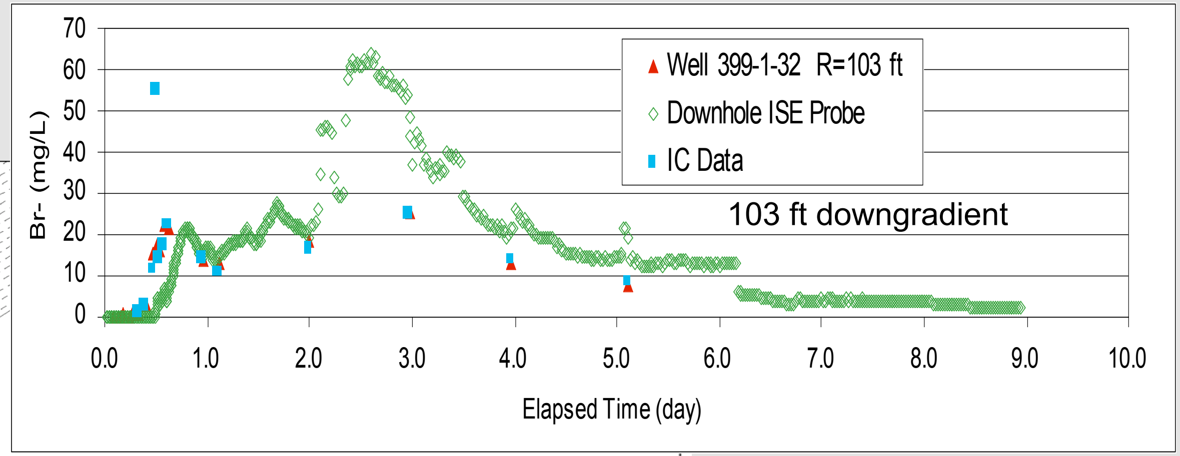


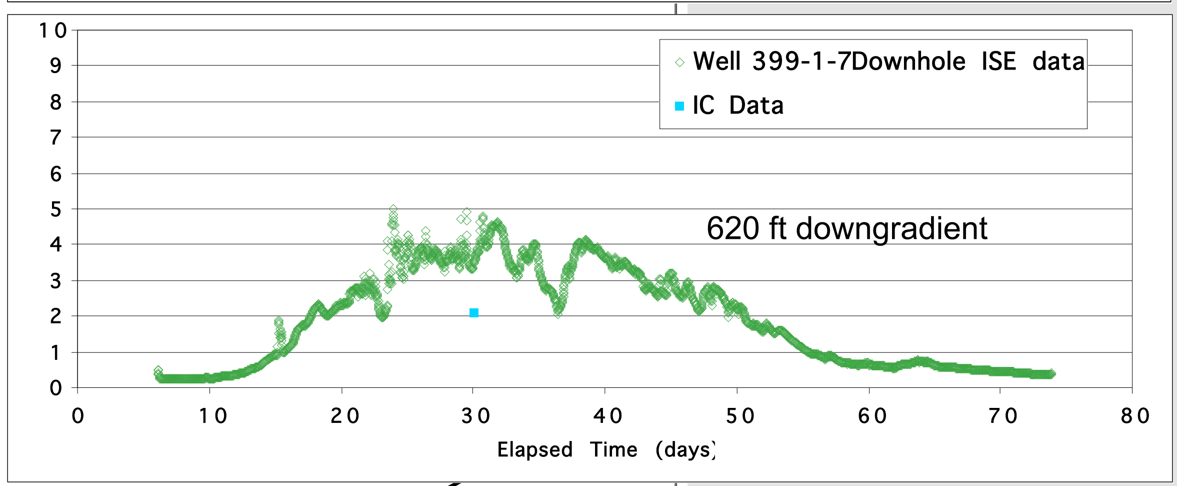
399-1-32 tracer drift data

- Arrival in ~ 2 days
- v = 50 ft/d (15 m/d)
- K = 14,000 ft/d (4,300 m/d)
- K_{fast} = 20,000 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

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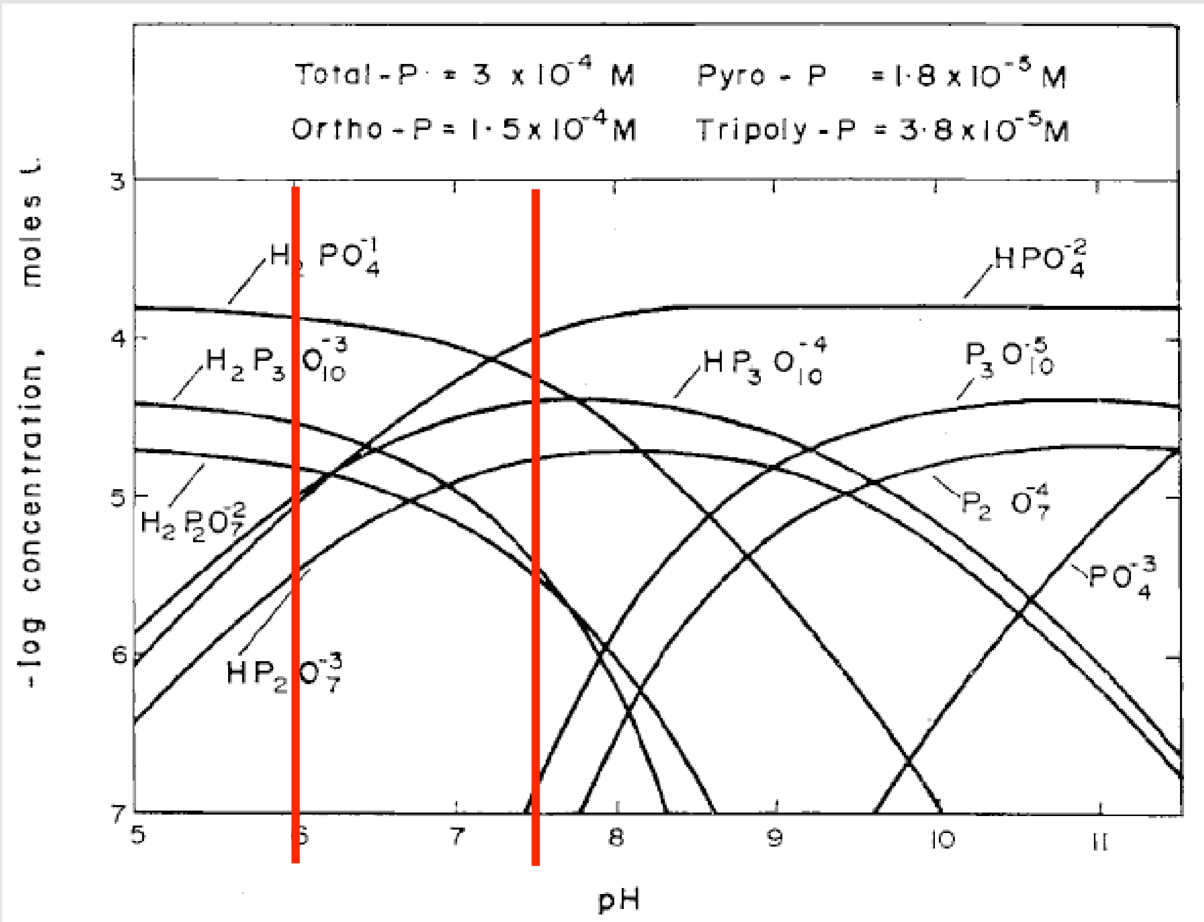
Laboratory Testing Strategy

- ^{31}P 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

Amendment Source	Formula	Solubility, g/L cold H_2O
Sodium Orthophosphate	$Na_3PO_4 \cdot 12H_2O$	40.2
Sodium Pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	54.1
Sodium Tripolyphosphate	$Na_5P_3O_{10}$	145.0
Sodium Trimetaphosphate	$(NaPO_3)_3 \cdot 6H_2O$	Soluble
Sodium Hexametaphosphate	$(NaPO_3)_6 \cdot nH_2O$	Very Soluble
Calcium Dihydrogen Phosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	18
Calcium Hydrogen Phosphate	$CaHPO_4 \cdot 2H_2O$	0.32
Calcium Pyrophosphate	$Ca_2P_2O_7 \cdot 5H_2O$	Slightly Soluble
Calcium Hypophosphite	$Ca(H_2PO_2)_2$	154
Calcium Chloride	$CaCl_2$	745

Site Relevant Speciation



Jenkins et al., 1971

- HPO_4^{-2}
- $H_2PO_4^{-}$
- $H_2P_3O_{10}^{-3}$
- $HP_3O_{10}^{-4}$
- $H_2P_2O_7^{-2}$
- $HP_2O_7^{-3}$

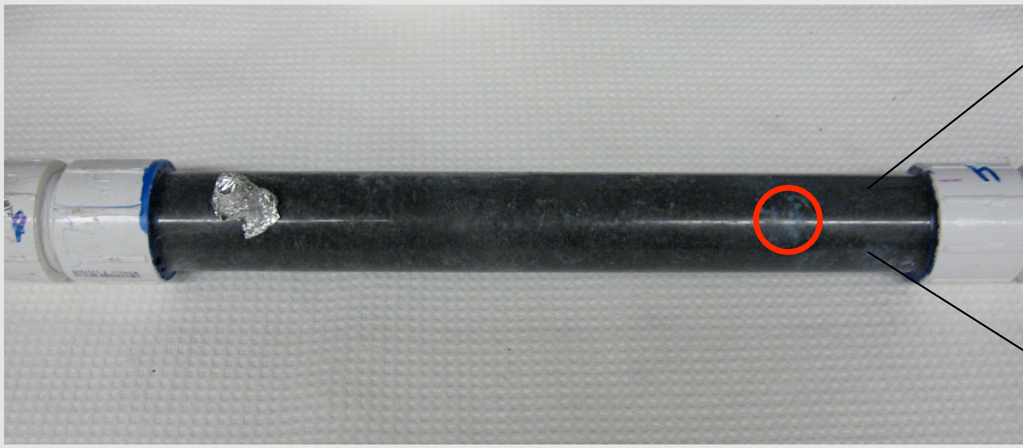
Phosphate Relationships

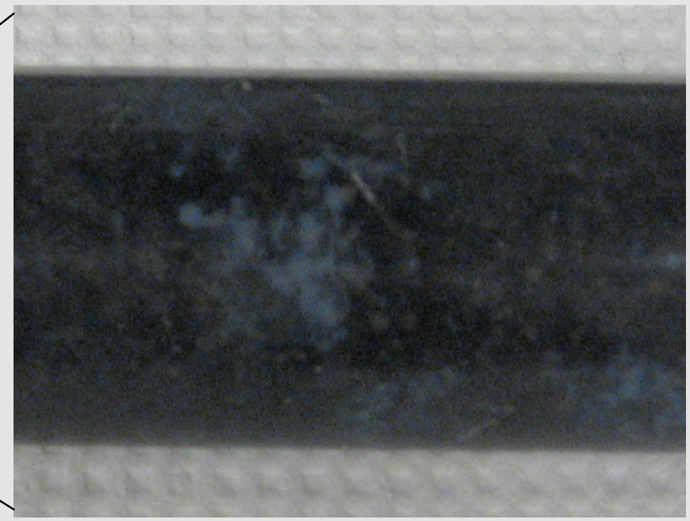
- Phosphate
  - Tripolyphosphate
    - Sorbs to sedimentary material (calcite, Fe and Al oxide, clay)
    - Forms fine ppt. w/ Ca
  - Orthophosphate
    - Sorbs to sediment bound tripolyphosphate complexes increasing rate and degree of precipitation
  - Pyrophosphate
    - Forms heavy, fast settling ppt. w/ Ca
- Calcium

Column Testing

- Test Parameters
  - $[P]_{ortho/pyro/tripoly}$
  - Calcium/phosphorus ratio
  - $[Ca]_{total}$ & $[P]_{total}$
  - pH of amendment solution
- Column Length = 1 ft
- Cross Sectional Area = 0.005 ft^2
- Porosity = 0.25
- Flow Rate = 1.5 L/day
- $[U]_{aq}$ = 1000 μg/L

Uranium Column Testing

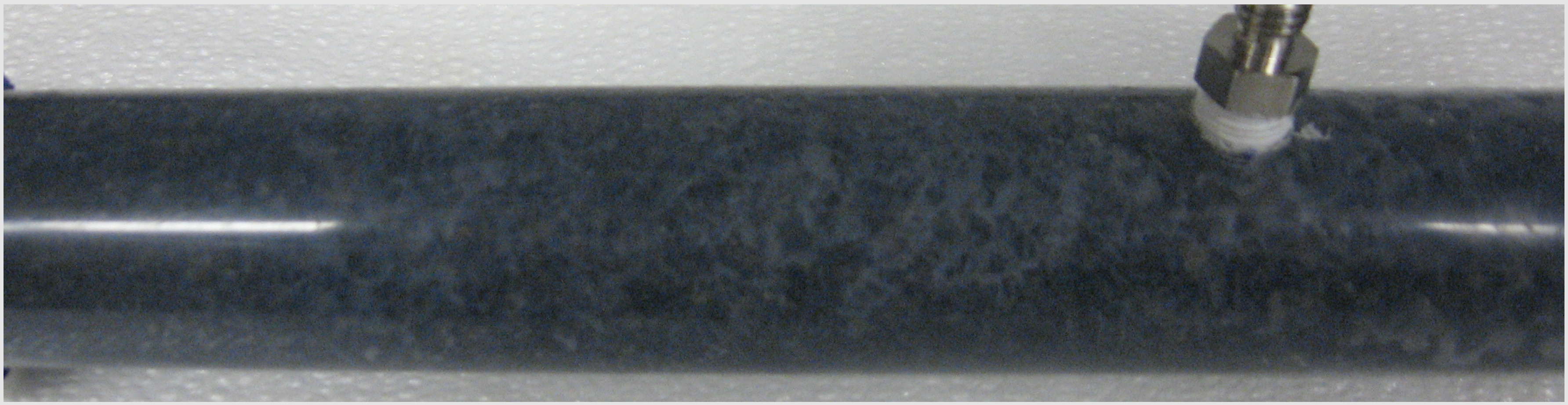




Total $[P]_{aq} = 1.05 \times 10^{-2}$ M
Pyro $[P]_{aq} = 2.63 \times 10^{-3}$ M
$[Ca]_{aq} = 2.32 \times 10^{-2}$ M

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 x 10^{-2} M

Pyro $[P]_{aq}$ = 6.58 x 10^{-3} M

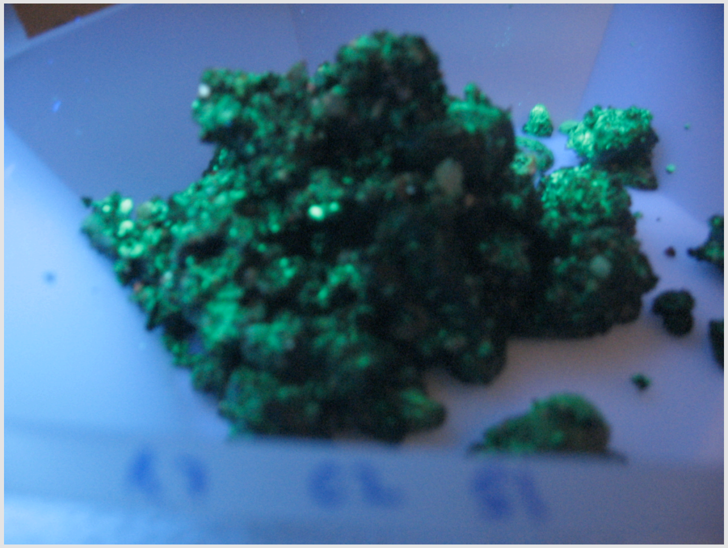
$[Ca]_{aq}$ = 9.98 x 10^{-2} M pH = 7

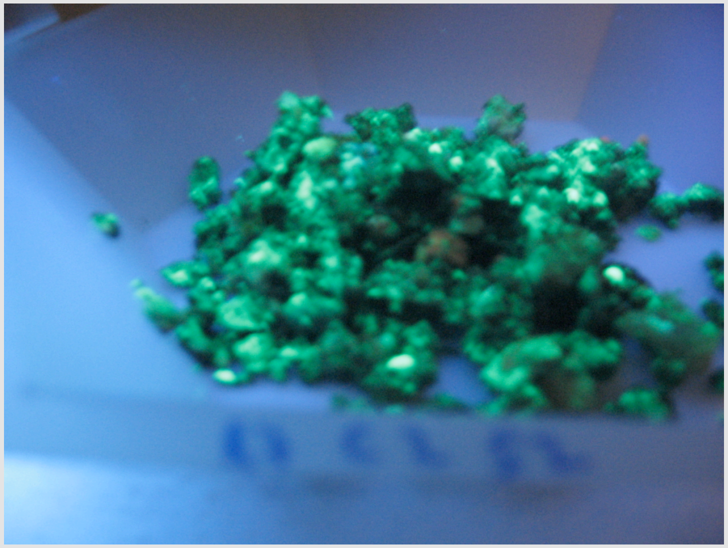
Tripoly $[P]_{aq}$ = 8.77 x 10^{-3} M

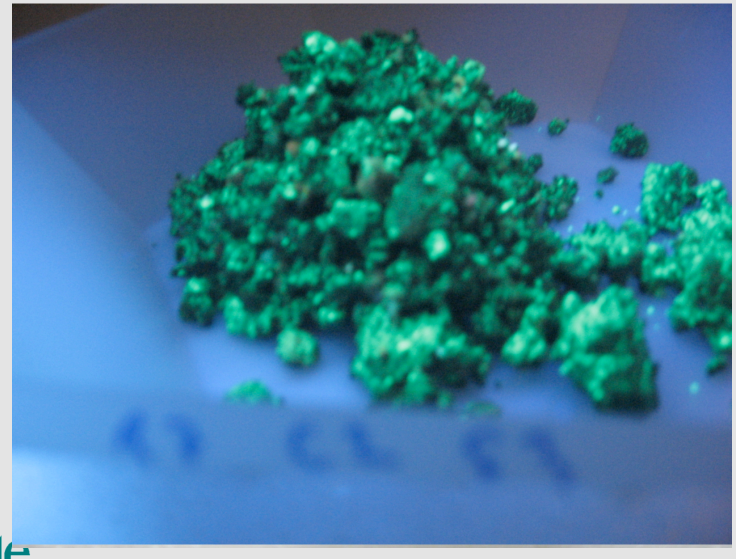
Ortho $[P]_{aq}$ = 1.32 x 10^{-2} M

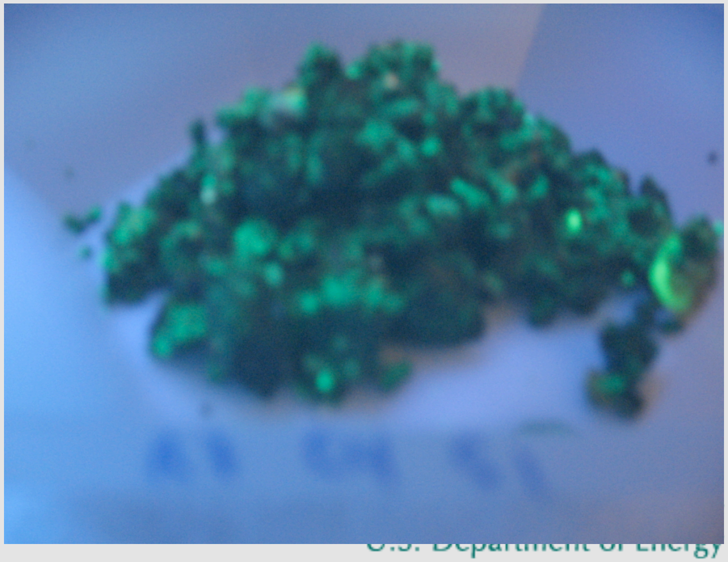
RT = 56 min PV = 52 mL PV = 1 Ca/ 1P

Post-Test Preliminary Analysis

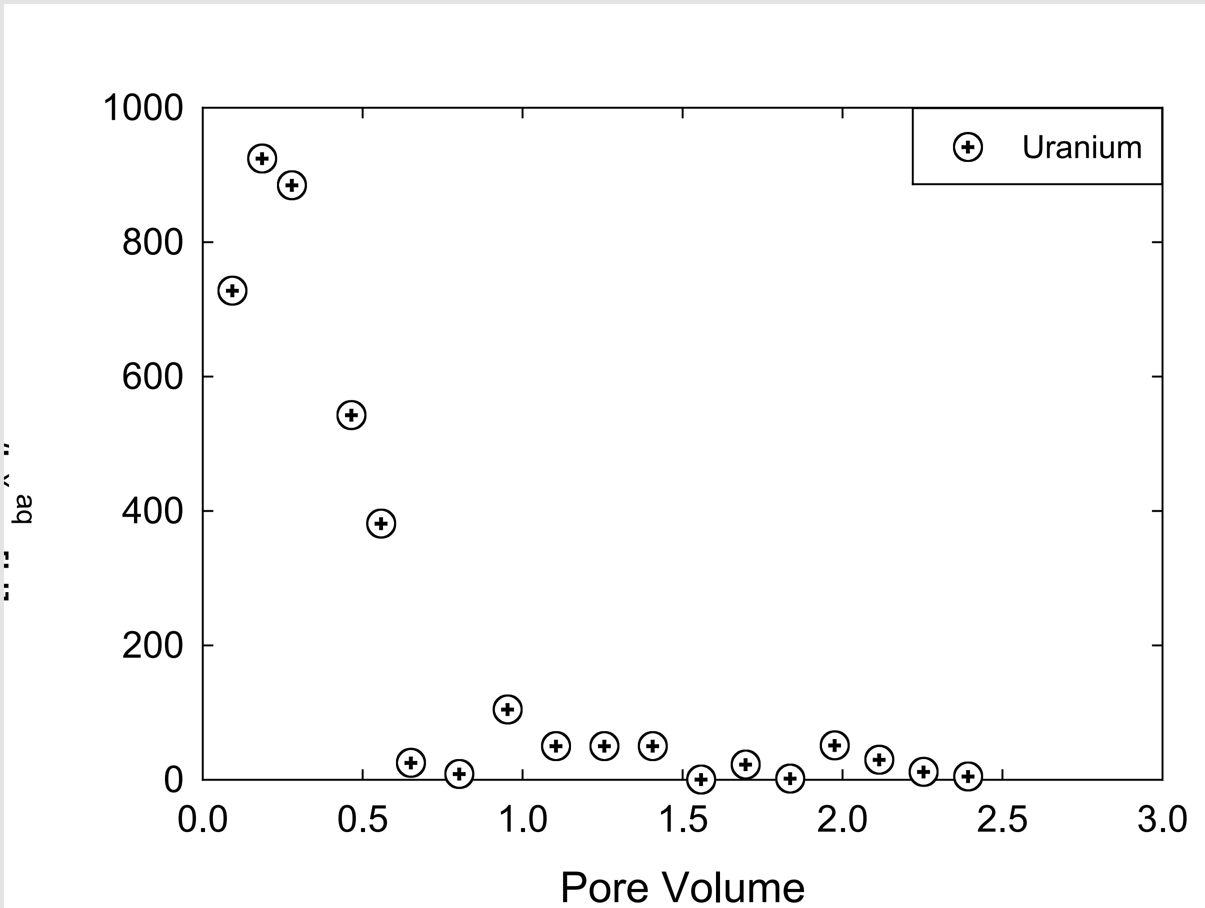




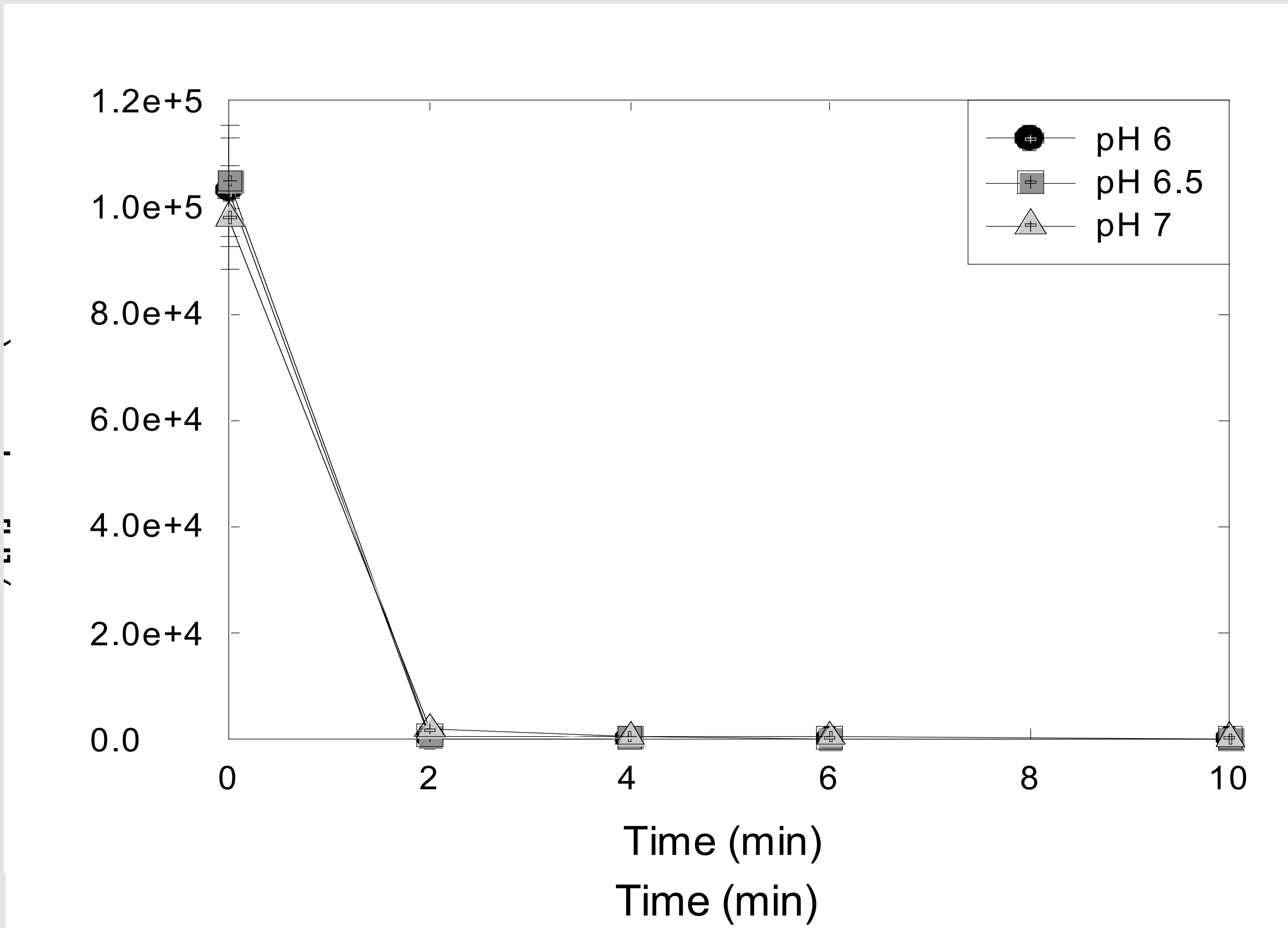




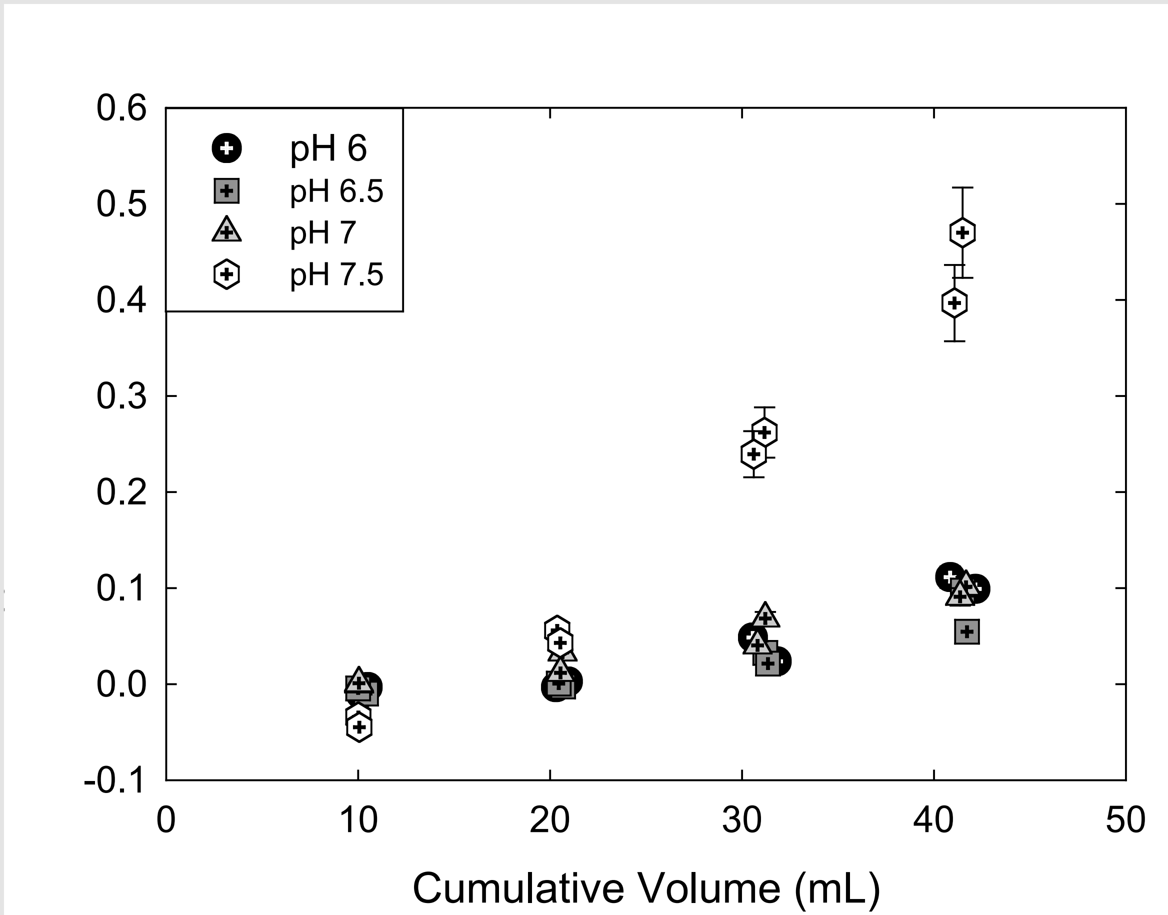
Aqueous Uranium During Treatment



Rate of Uranium Sequestration with Apatite



Stability of Uranium Sequestered with Apatite



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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