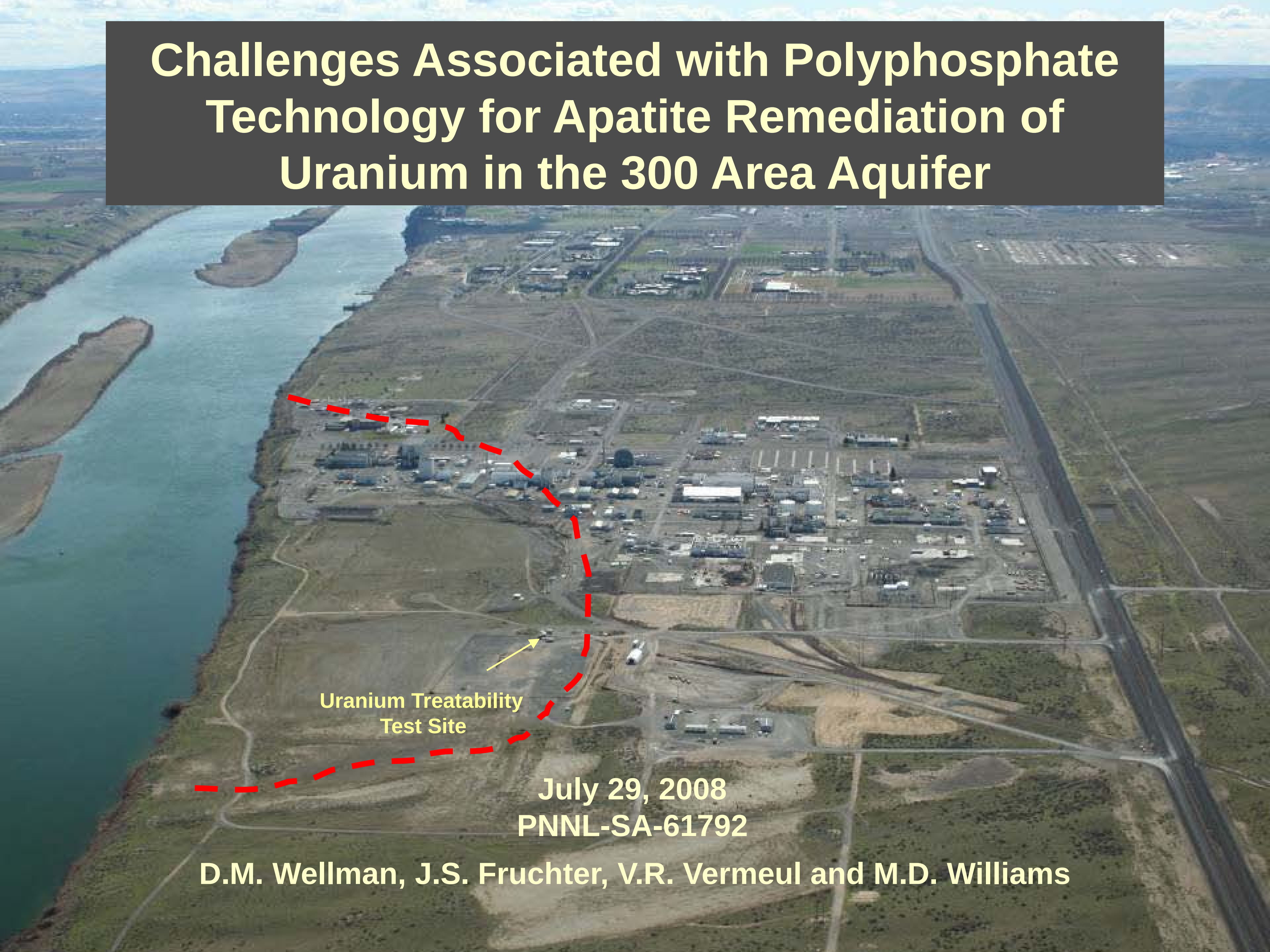
Challenges Associated with Polyphosphate Technology for Apatite Remediation of Uranium in the 300 Area Aquifer



July 29, 2008

PNNL-SA-61792

D.M. Wellman, J.S. Fruchter, V.R. Vermeul and M.D. Williams

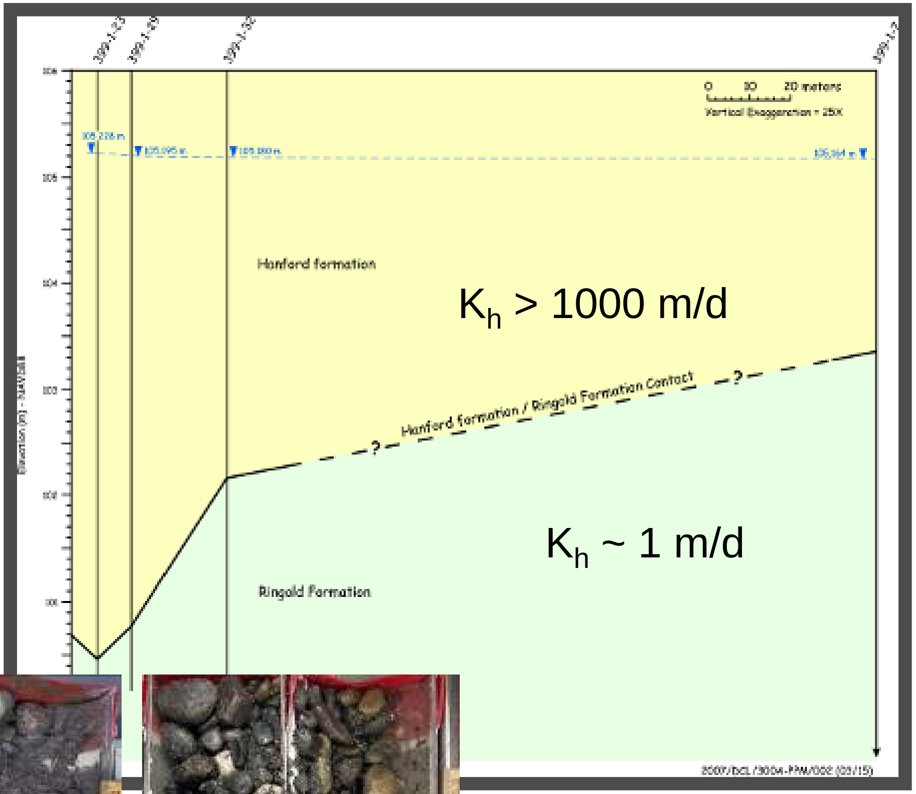
Polyphosphate Remediation Approach

Injection	Amendment	Formula	Conc., (g/L)	Conc., M
1	Sodium Orthophosphate	NaH_2PO_4	0.5925	4.94×10^{-3}
	Sodium Pyrophosphate	$Na_4P_2O_7$	0.657	2.47×10^{-3}
	Sodium Tripolyphosphate	$Na_5P_3O_{10}$	1.209	3.29×10^{-3}
	Sodium Bromide	NaBr	0.103	1.00×10^{-3}
2	Calcium Chloride	$CaCl_2$	3.405	3.07×10^{-2}
3	Sodium Orthophosphate	NaH_2PO_4	0.5925	4.94×10^{-3}
	Sodium Pyrophosphate	$Na_4P_2O_7$	0.657	2.47×10^{-3}
	Sodium Tripolyphosphate	$Na_5P_3O_{10}$	1.209	3.29×10^{-3}
	Sodium Bromide	NaBr	0.103	1.00×10^{-3}

- Initial polyphosphate amendment injection
  - precipitate aqueous uranium within the treatment zone as autunite
  - prevent formation of soluble calcium-uranate phases, which may redissolve releasing a pulse of uranium into the groundwater upon injection of the soluble polyphosphate
- Calcium-chloride ($CaCl_2$)
  - calcium source for apatite formation
- Final polyphosphate injection
  - additional time-released phosphorus for lateral precipitation of calcium-phosphate as the remedy migrates downfield

300 Area Hydrodynamic and Geochemical Conditions

- Open framework geology
  - Hanford formation at this site ranges from silty sandy gravel to open framework gravels
  - Heterogeneities
- High Flow Velocities
  - Porosity = 18%
  - Groundwater velocity ~15 m/day
  - Hydraulic conductivity ~4,300 m/day
- Geochemical:
  - pH 7-8
  - $[CO_3^{2-}]$ = ~1.13 x 10^{-3} mol/L



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

399-3-20, 55-56 ft
gravel

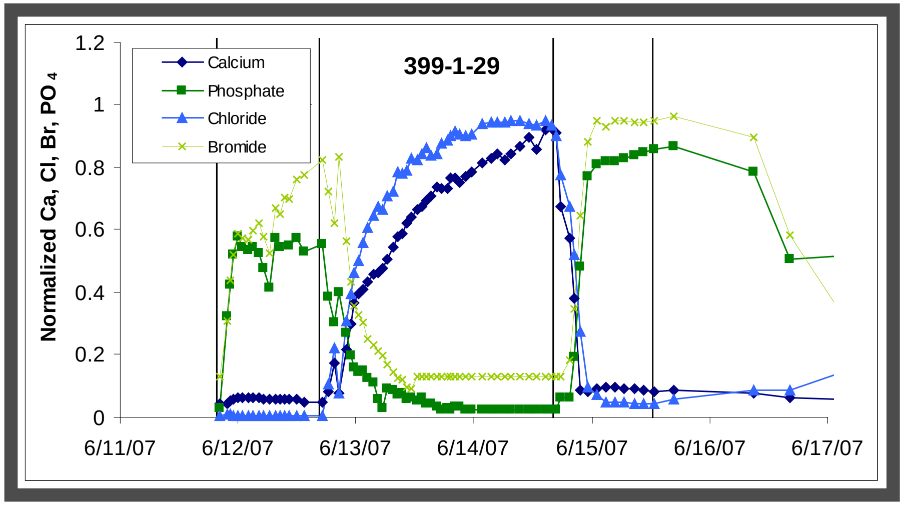
Pacific Northwest
NATIONAL LABORATORY

300 Area Implementation Challenges

- Hydrodynamic
  - High groundwater velocities
  - Lack of surface area related to the large size of the clasts in the aquifer
    - Limited degree of mixing and extent of precipitation of apatite
  - Open framework geology
    - Inhibited retention of apatite
- Geochemical
  - High solution-to-apatite ratios
    - Limitations on the amount of apatite-forming reagents that could be introduced to the subsurface
    - Rapid dispersal of the reagents
  - pH & Carbonate
    - Aqueous speciation of uranium
    - Apatite surface speciation
    - Mechanism of retention

High Flow Velocity and Low Surface Area

- Limited mixing of Ca and P injection phases
  - Remedy injection rate = 756 L/min
  - Open framework sedimentary matrix
    - large clasts and minimal fine-textured particles afford limited surface area
  - Low effective retardation values, coupled with rapid dispersal of the reagents within the 300 Area subsurface, resulted in high solution-to-apatite ratios for indirect, long-term treatment



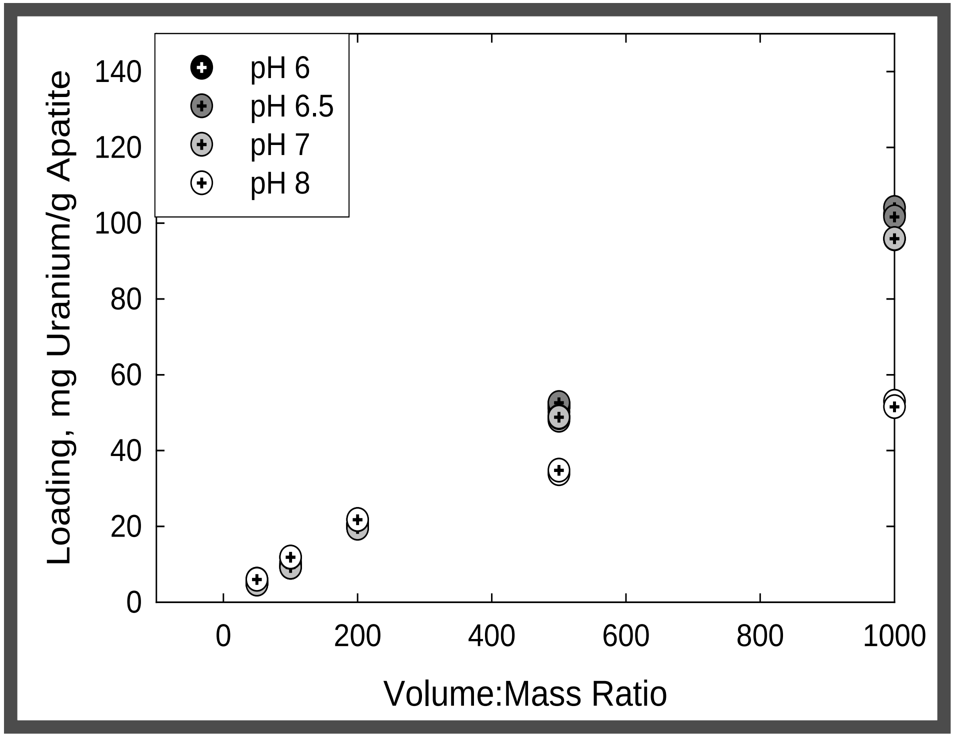
Normalized BTC for Calcium, Phosphorus, Chloride, and Bromide at Down-Gradient Well 399-1-29. Characteristic results with limited mixing of the calcium and phosphorus injections during the pilot-scale field test

Injection	Laboratory R_{ef}	Field R_{ef}
Polyphosphate	2.41	0.80
Calcium	4.76	1.14

Pacific Northwest NATIONAL LABORATORY

High Solution-to-Apatite Ratio

- Aquifer Conditions
  - η = 18%
  - ρ_b = 2.21 g/cm^3
  - Sediment-to-water ratio = 12.28 g/cm^3
- Remedial Target Solution to Apatite Ratio = 100 - 325 mL/g apatite (0.1% - 0.025 wt%)
- $[U]_{aq}$ = 1 mg/L
- Invariant as a function of pH under the range of 6 to 7 and increases linearly over the solution-to-solid ratio of 0 to 1,000
  - 100 mg U/g apatite
- pH 7 - 8, the mass of uranium removed from solution displays a gradual increase from ~30 mg U/ g apatite to a maximum of ~50 mg U/ g apatite
- Potential efficiency for sequestration of uranium is within the range spanning the upper bounds between pH 7 and 8

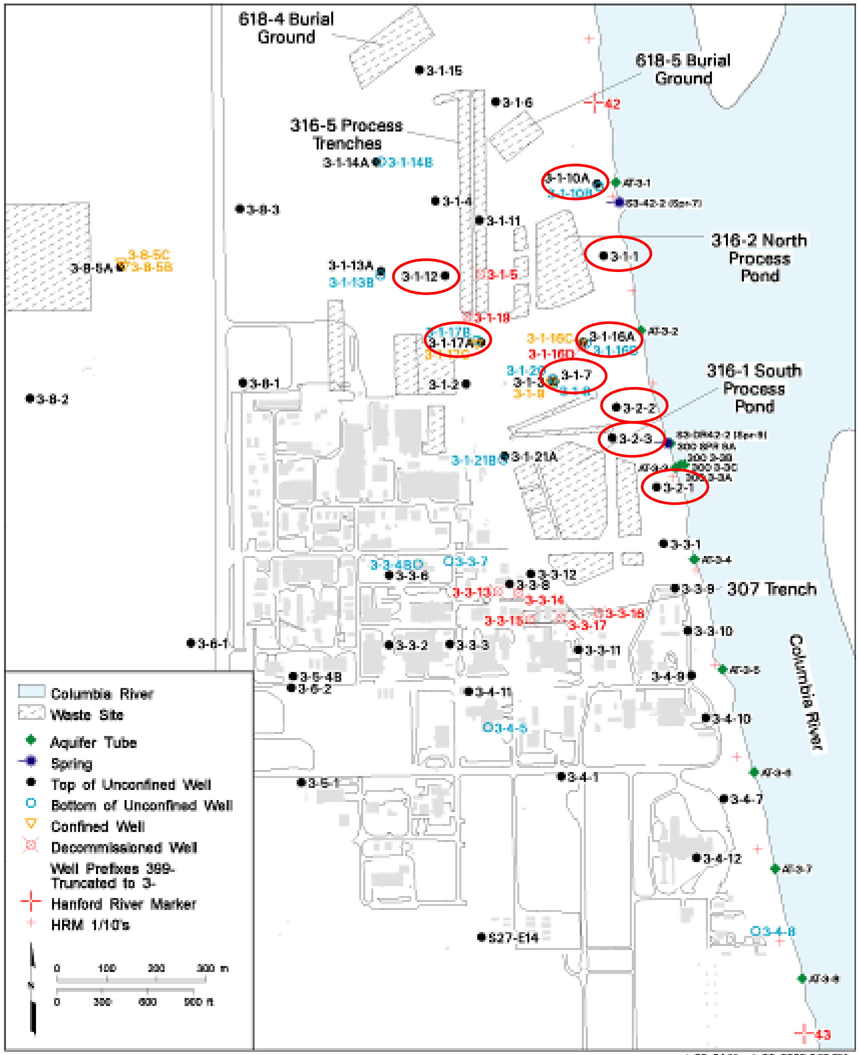


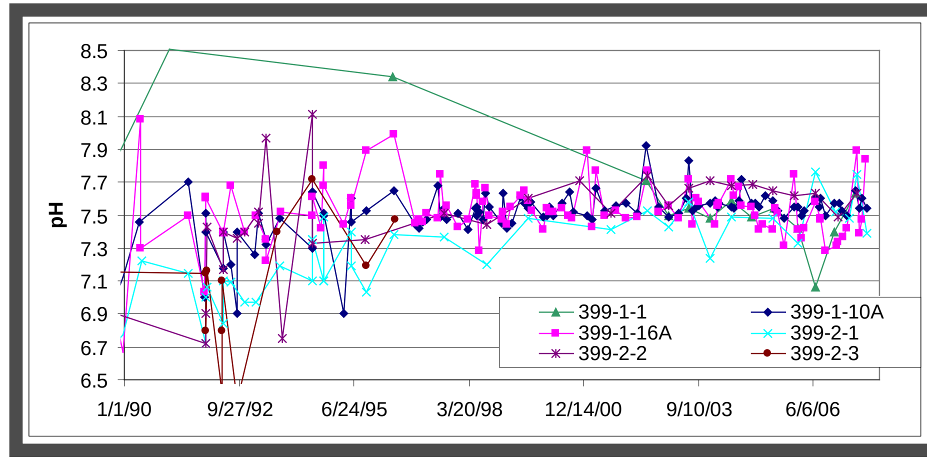
Pacific Northwest NATIONAL LABORATORY

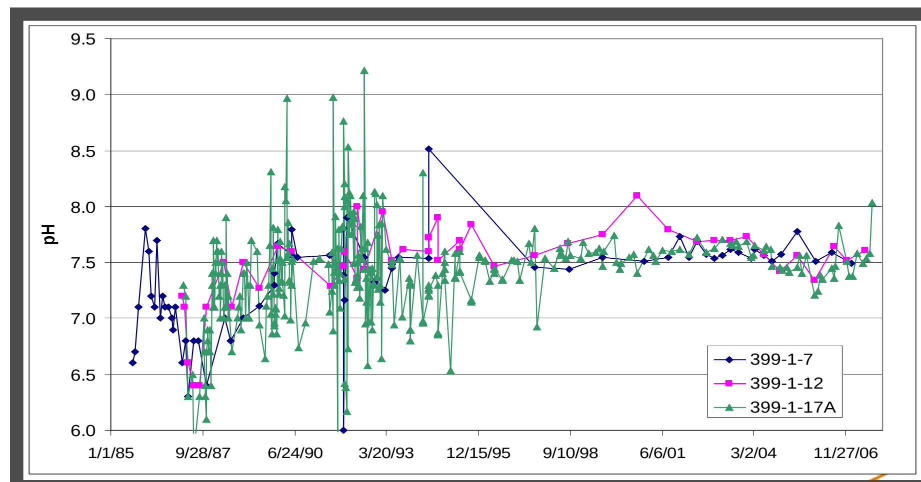
Potential Strategies to Address Hydrodynamic Issues

- Significantly shorter injection durations for alternating pulses of calcium and polyphosphate
- Lower injection rate
- Revised amendment formulation containing a higher content of ortho- and pyrophosphate which would increase reaction rates
- Possible inclusion of tripolyphosphate, or longer chains, within the calcium injection phase

Historical pH values for select near-river and inland wells near the 300 Area polyphosphate pilot test site

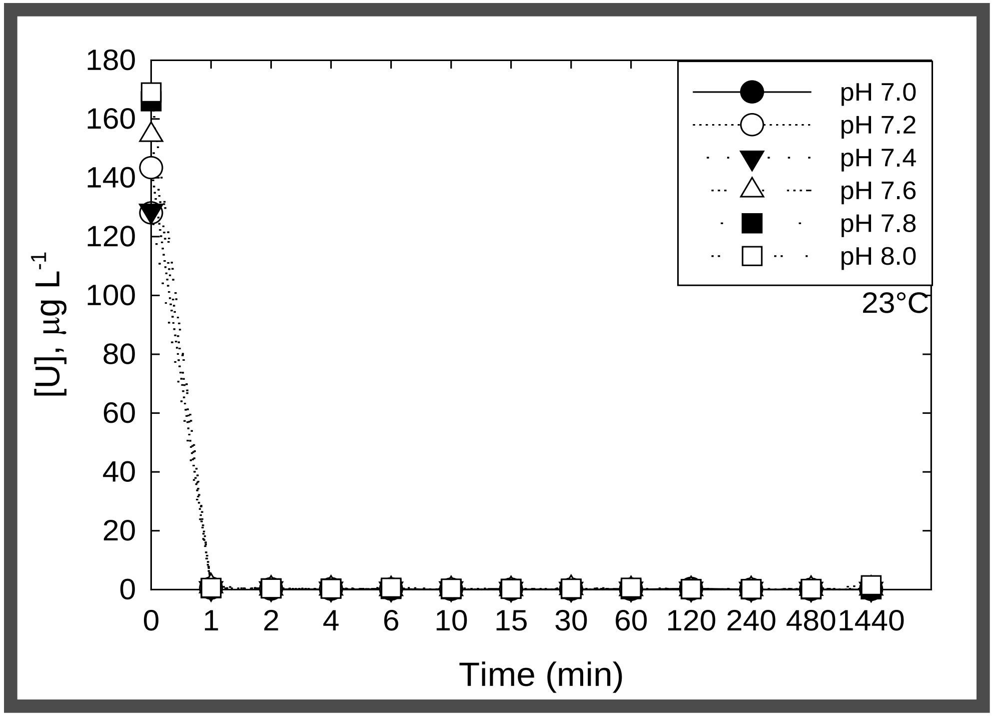






Initial Remedial Conditions - pH Dependence of Uranium Sorption on Apatite

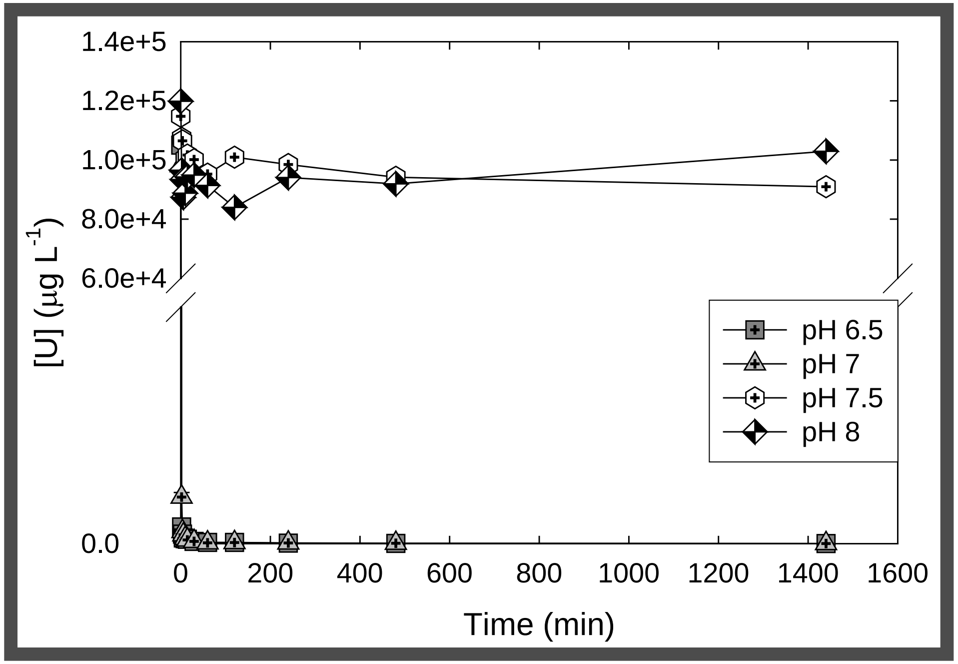
- Quantitative precipitation of apatite during pilot-scale field test = 0.025 wt% of hydroxyapatite
  - η = 18%
  - ρ_b = 2.21 g/cm^3
  - Sediment-to-water ratio = 12.28 g/cm^3
  - Solution-to-apatite ratio = 325 mL/g apatite
- $[U]_{aq}$ = 120 μg/L
- Number of available surface sites exceeds the concentration of uranium
- Results do not show any apparent limitations to uranium removal



Pacific Northwest NATIONAL LABORATORY

Extended Treatment Conditions - pH Dependence of Uranium Sorption on Apatite

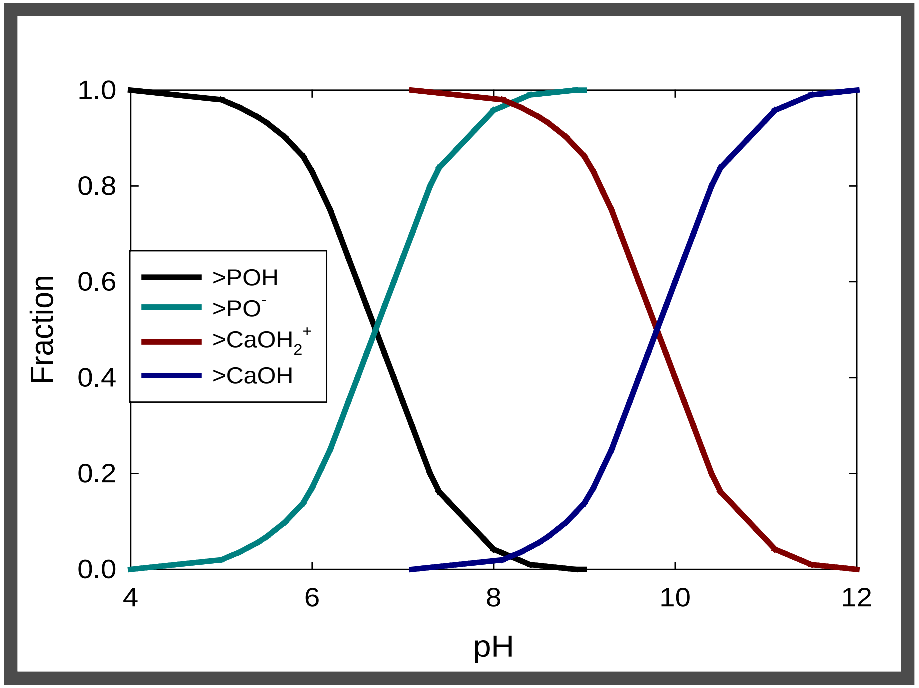
- Target hydroxyapatite = 0.1 wt%
  - η = 18%
  - ρ_b = 2.21 g/cm^3
  - Sediment-to-water ratio = 12.28 g/cm^3
  - Solution-to-apatite ratio = 100 mL/g apatite
- $[U]_{aq}$ = 100 mg/L
- Concentration of uranium exceeds the number of available surface sites
- Dependence on pH increases as more uranium is sequestered on the apatite surface
- Decreased performance at pH values ≥7.5
  - Only ~15% of the aqueous uranium was removed



Pacific Northwest NATIONAL LABORATORY

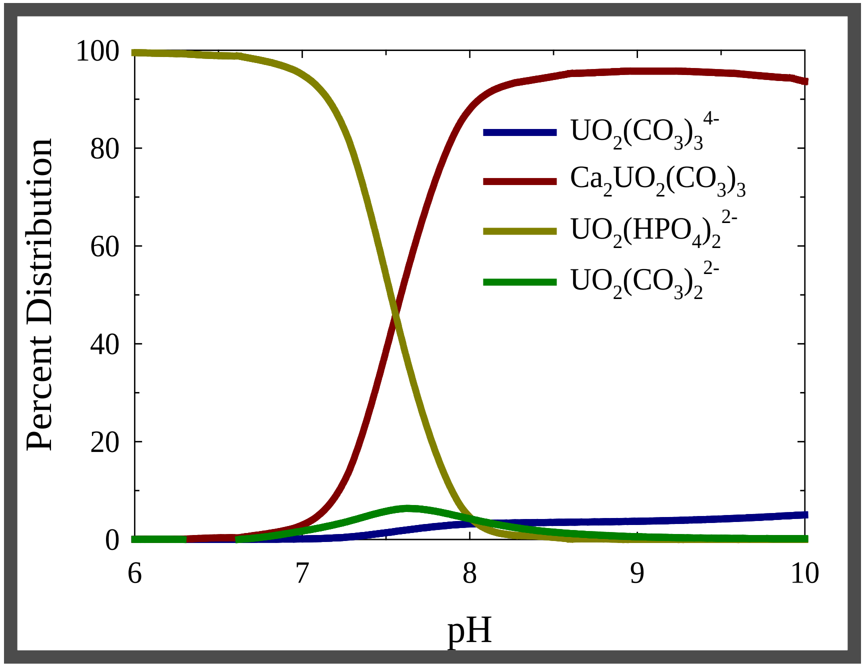
Apatite Surface Speciation

- ≡$CaOH_2^+$ and ≡POH, affording a pH_{pzc} of 7.13 upon exposure to atmospheric CO_2
- Above pH 4 the ≡POH sites begin to deprotonate affording a fraction of ≡POH and ≡PO^- sites
- Near pH ≅ 6.6 the surface speciation is predicted to be approximately 50% ≡POH and 50% ≡PO^-.
- At a pH of ~7, ≡$CaOH_2^+$ surface sites begin to deprotonate
- pH ≅ 9.7 affords approximately 50% ≡Ca-OH_2^+ and 50% ≡CaOH



Effect of Speciation on Uranium Sequestration

- $UO_2(HPO_4)_2^{2-}$ is the dominant aqueous species predicted below pH 7.5.
- The dominant aqueous species for pH > 7.5 is the ternary species $Ca_2UO_2(CO_3)_3$.
- Dominance of cationic surface sites and anionic aqueous uranium species at pH < 7 results in greater sequestration of uranium with apatite.
- Increasing proportion of anionic surface sites and neutral aqueous species at pH values > 7 reduces the affinity of the aqueous uranium species for the apatite surface

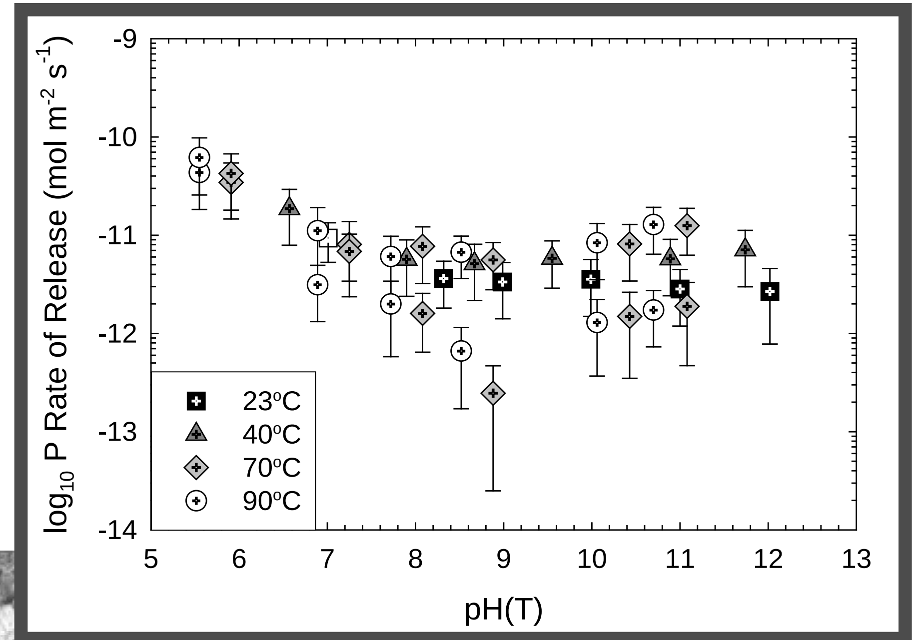


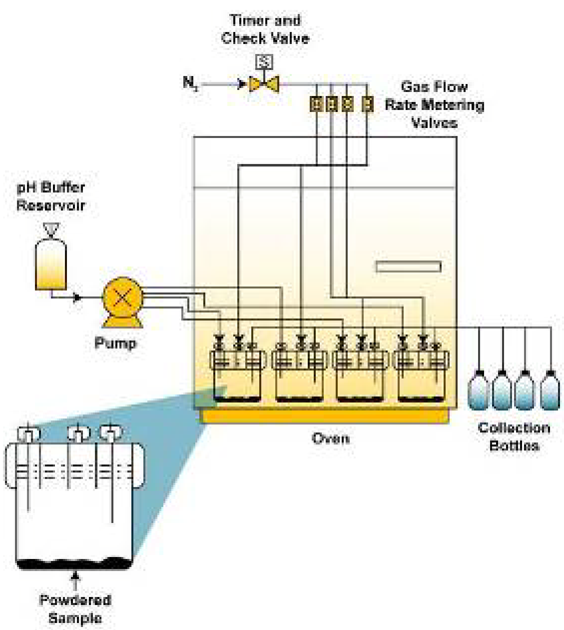
Apatite-based Retention of Uranium under Advective Conditions

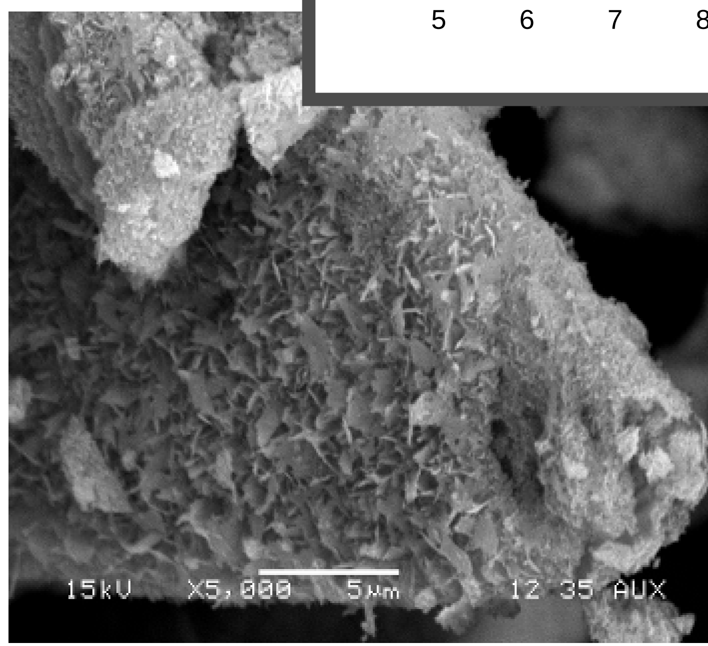
- Sorption and/or surface complexation of uranium could occur until all surface sites have been depleted
- Long-term stability of uranium sequestered via apatite is dependent on the mechanism of retention
- Efficacy of uranium retention of apatite will be governed by
  - Dissolution of apatite providing a source of aqueous phosphate coupled with precipitation of autunite
  - Rate of uranium desorption
  - Rate of transformation

Rate of Apatite Dissolution

- Dissolution is invariant over the pH range of 6 to 8
- Dissolution is invariant with temperature
- Increased surface area of apatite crystals serve as nucleating surface for rapid precipitation



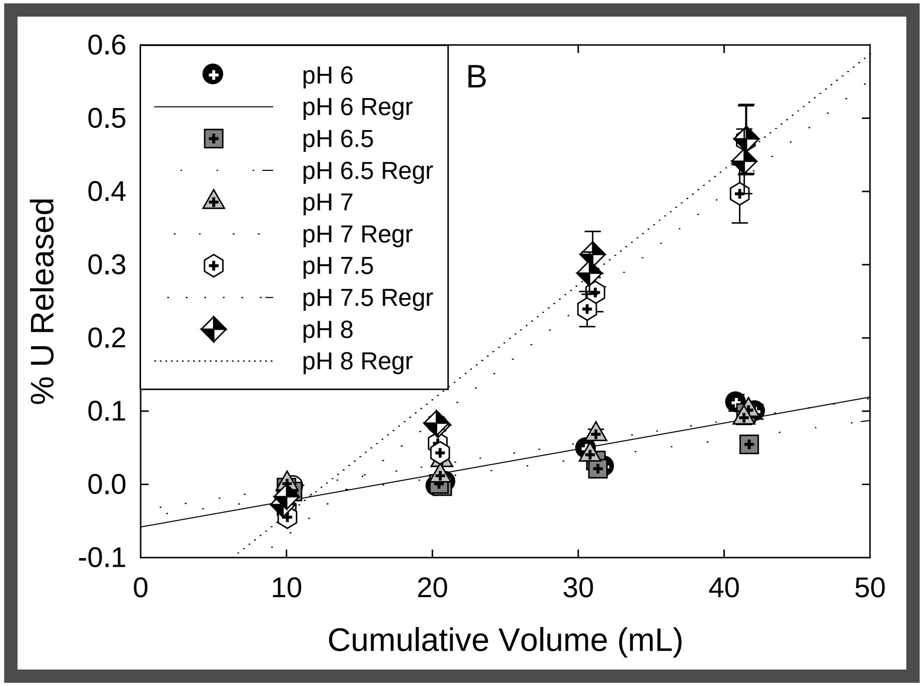




Pacific Northwest
NATIONAL LABORATORY

Uranium Desorption

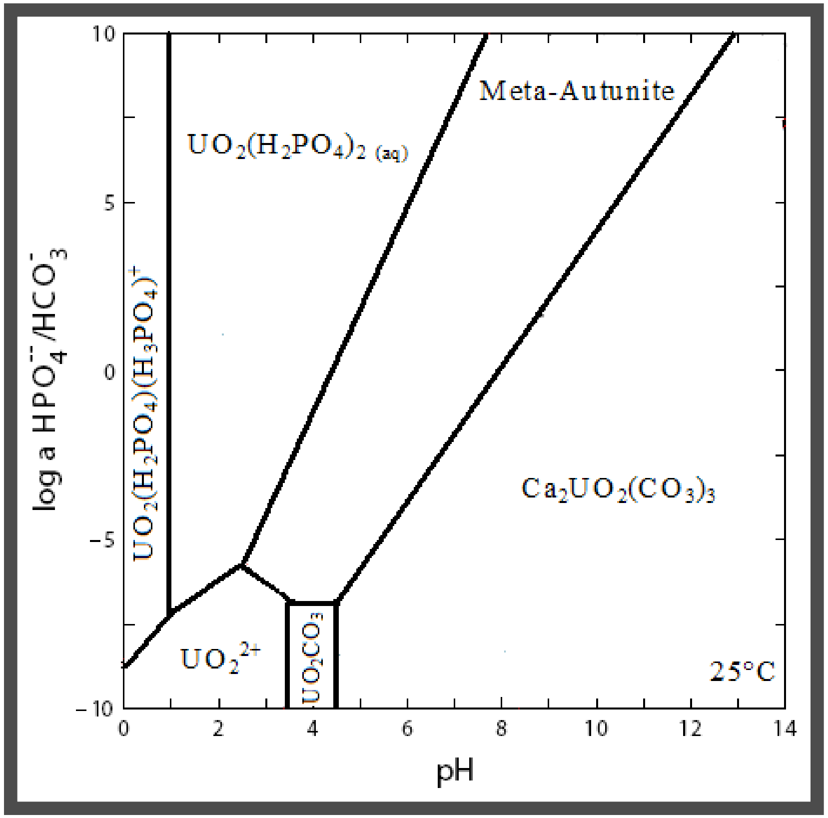
- ~4000 pore volume of groundwater
  - Solution to apatite ratio = 100 mL/g apatite
  - Target hydroxyapatite = 0.1 wt%
    - η = 18%
    - ρ_b 2.21 g/cm³
    - Sediment to water ratio = 12.28 g/cm³
- Uranium is tightly retained with apatite under pH range 6 to 7
- Decreased performance at pH values ≥7.5
- Concentration of uranium released increased linearly with fresh groundwater



Pacific Northwest
NATIONAL LABORATORY

Apatite Sequestration of Uranium

- Absence of carbonate
  - Sorbed uranium concentrations > 5500 mg U(VI)/g resulted in precipitation of chernikovite (H-autunite)
- Presence of carbonate
  - Chernikovite formation was not observed, even with uranium loadings up to 12,300 µg U(VI)/g
- High calcium and carbonate concentrations and flow rates in the 300 Area may act to inhibit the transformation of sorbed uranium to autunite group minerals prior to desorption and complexation



Fuller et al. (2002)

300 Area Implementation Challenges

- Formation and emplacement of apatite via polyphosphate technology
  - Degree of mixing and extent of precipitation of apatite
  - Geologic framework for retention and accessibility of apatite
- Efficacy of uranium sequestration by apatite assumes that the adsorbed uranium would subsequently convert to uranyl-phosphate (autunite-group) minerals
  - Highly susceptible to dynamic geochemical conditions
  - Long-term stability of uranium sequestered via apatite is dependent on the mechanism of retention
  - High carbonate concentrations in the 300 Area may act to inhibit the transformation of sorbed uranium to autunite group minerals

Advances in Polyphosphate Technology for Uranium Remediation

- Transport of Polyphosphate Compounds under Saturated Conditions
- Quantified the Hydrolysis of Polyphosphate - Balance between polyphosphate degradation rate and groundwater flow rate for controlled autunite/apatite precipitation
- Nucleation and Precipitation of Apatite from Polyphosphate – Interaction of polymeric phosphate species, significance of bicarbonate
- In Situ Formation of Autunite and Apatite via Polyphosphates – Optimized sources of calcium and phosphorus based on solubility, flow rate, hydrolysis rate, and precipitation kinetics
- Quantified the Rate and Extent of Uranium Sequestration with Apatite
- Quantified the Longevity of Apatite Barrier under 300 Area Conditions
- Conducted first field-scale demonstration of polyphosphate technology