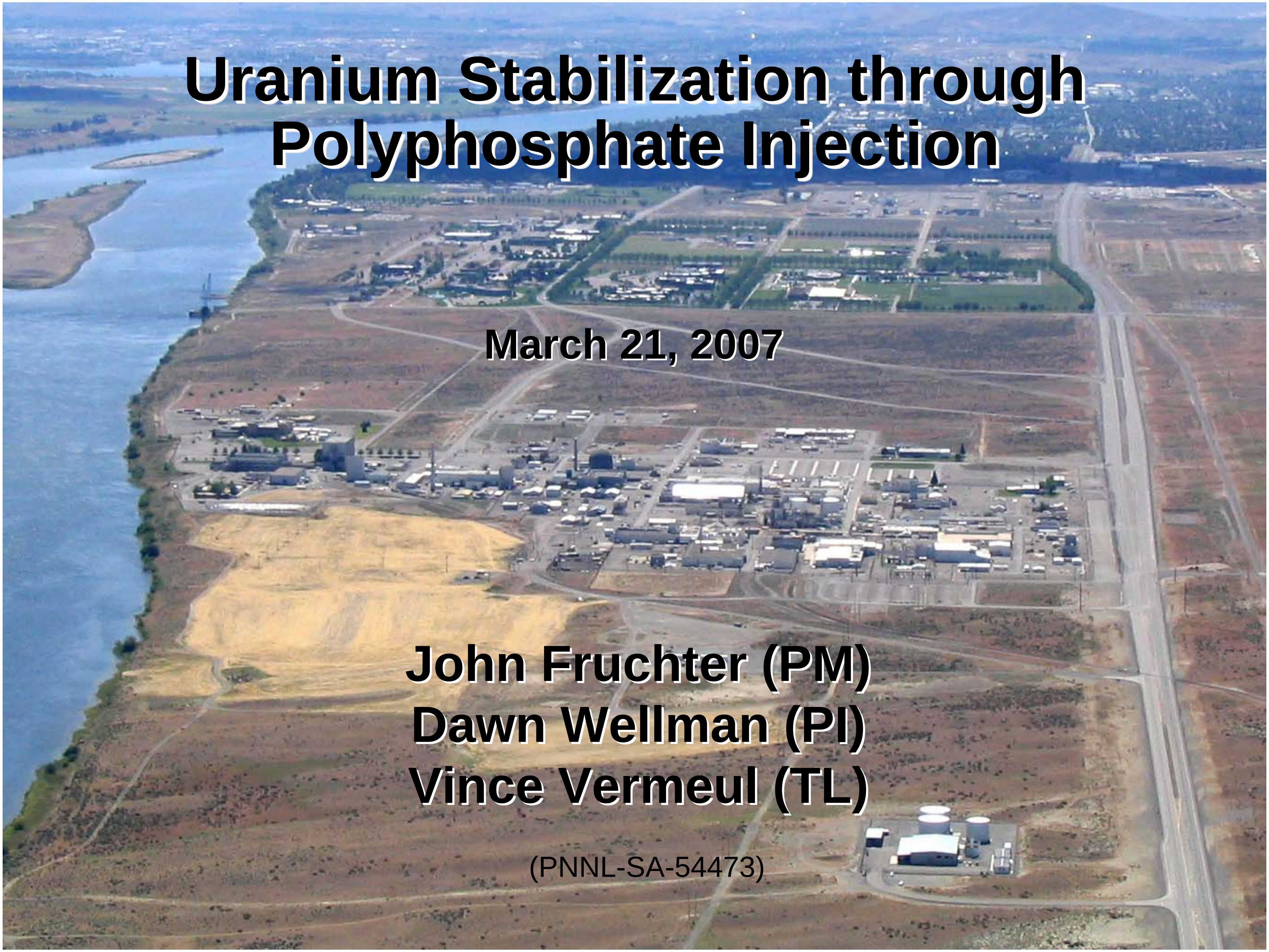

Uranium Stabilization through Polyphosphate Injection

March 21, 2007

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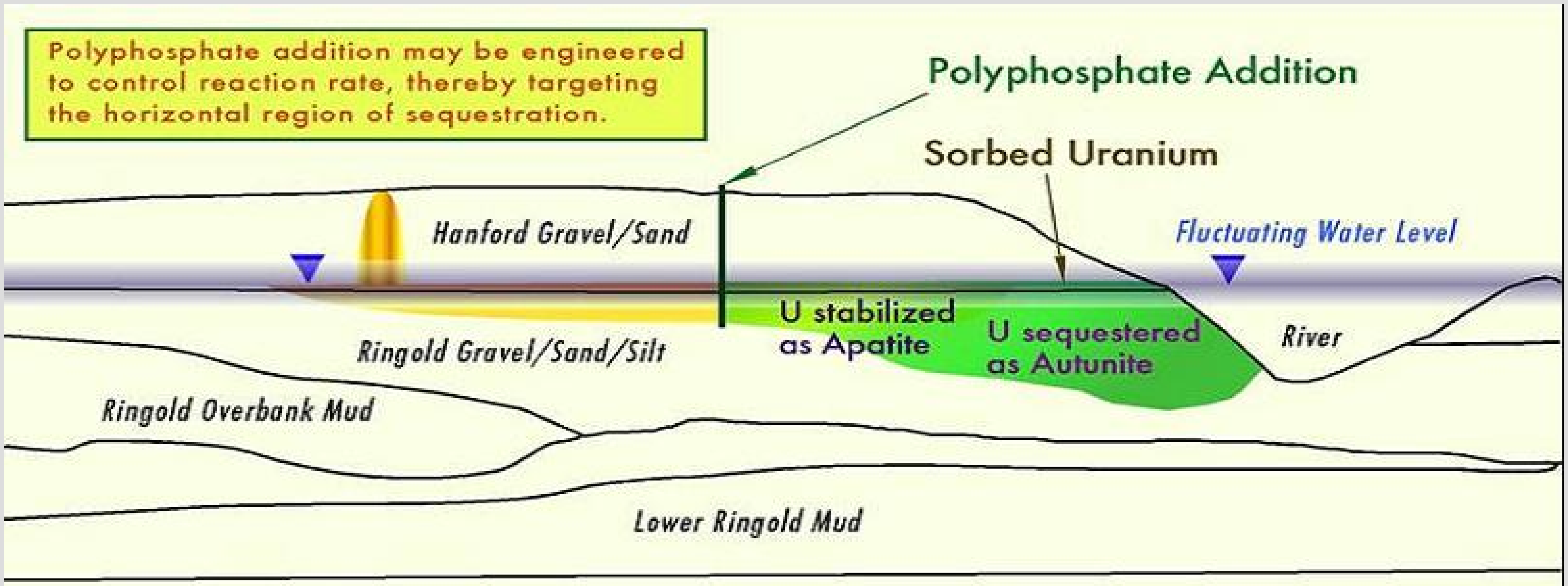
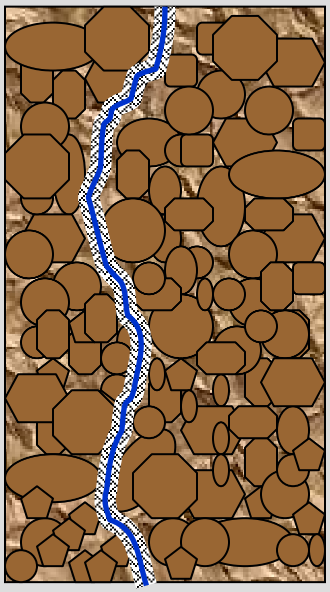
(PNNL-SA-54473)

Deployment of Phosphate Amendment for In-Situ Immobilization of Uranium

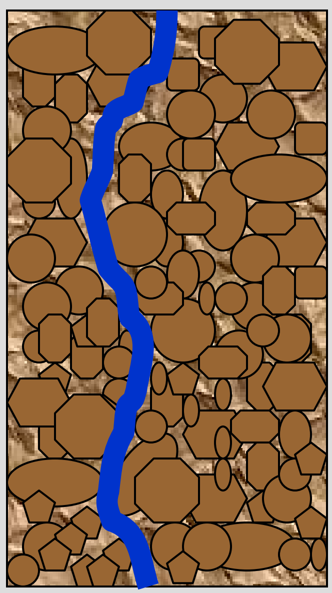


- Injection of soluble polyphosphate
- Lateral plume treatment
- Uranyl phosphate mineral (autunite) formation
  - Immediate sequestration
- Apatite formation
  - Sorbent for uranium
  - Conversion to autunite
- Enhancement of MNA

Challenges to Phosphate Amendments: Rapid Precipitation Kinetics



- Injection of short-chain phosphate molecules results in rapid flocculation and precipitation of phosphate phases
- Decrease hydraulic conductivity



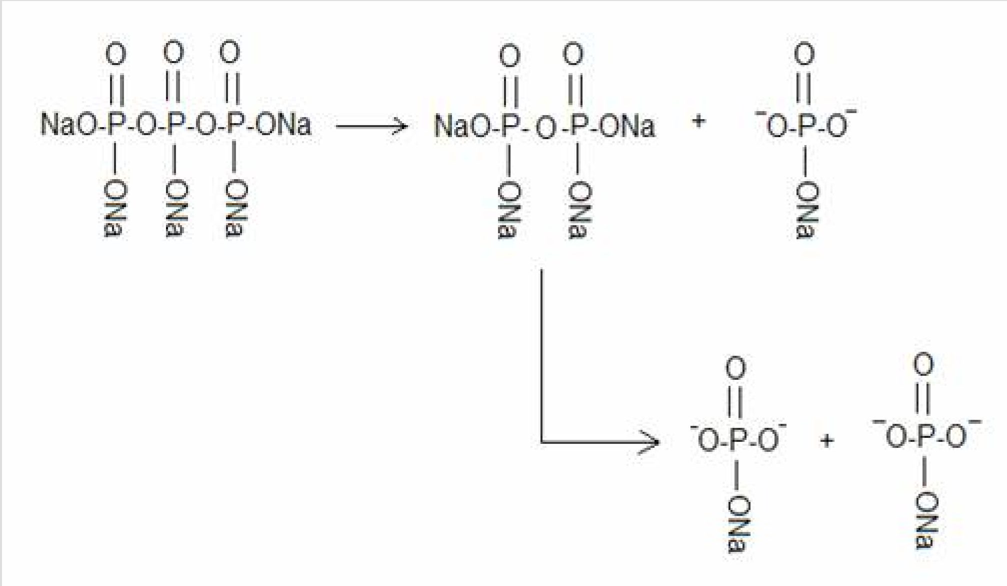
- Polyphosphate precludes rapid precipitation
- No measurable change in hydraulic conductivity

Effect of Phosphate on Hydraulic Conductivity

	Monophosphate	Na Polyphosphate
	$Na_3(PO_4)(H_2O)_{12}$	$[Na_3(PO_4)]_3$
ΔH for Constant Head Test (cm)	24.90	24.90
Average Hydraulic Conductivity (before phosphate treatment)	0.61	0.28
Average Hydraulic Conductivity (after phosphate treatment)	0.45	0.29
% Difference:	-26.23 (±5)	+3.57 (±5)

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

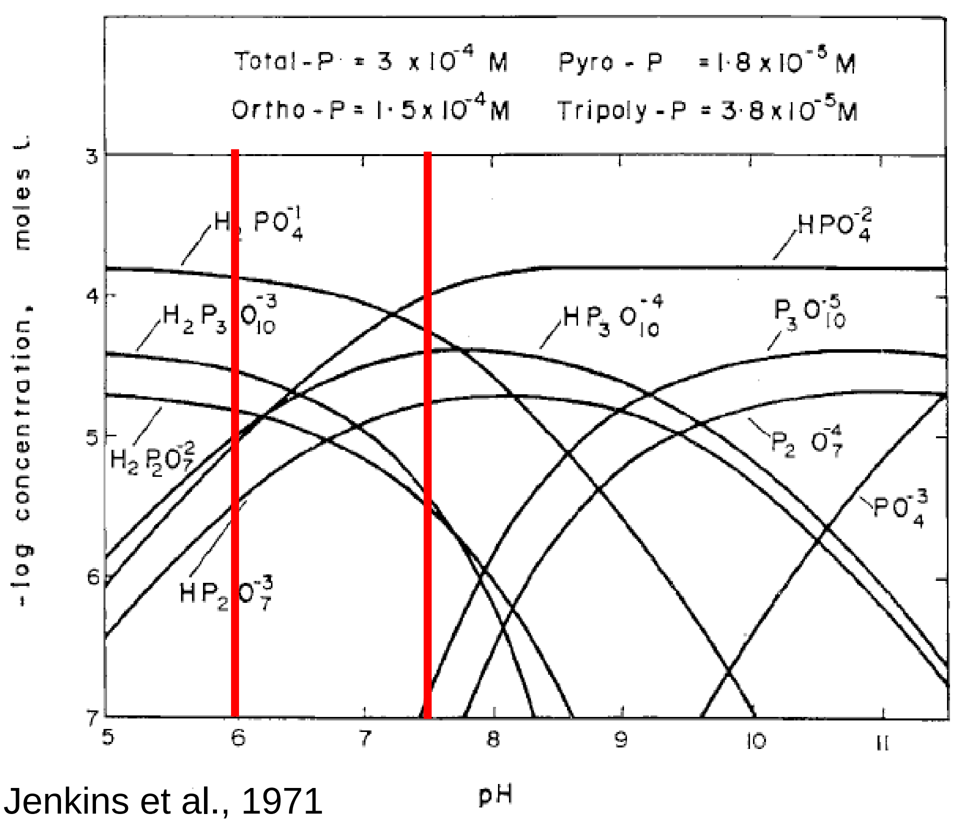


Polyphosphate amendment can be tailored to delay formation of autunite and apatite.

Laboratory Testing Strategy

- 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
- ^{31}P NMR Hydrolysis Experiments
  - Quantified the degradation of tripolyphosphate 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
- Column Tests
  - Emplacement Efficiency
    - Amendment Transport
    - Autunite/Apatite Formation
- Single Pass Flow Through Dissolution Tests
  - Rate of autunite and apatite dissolution

Site Relevant Speciation



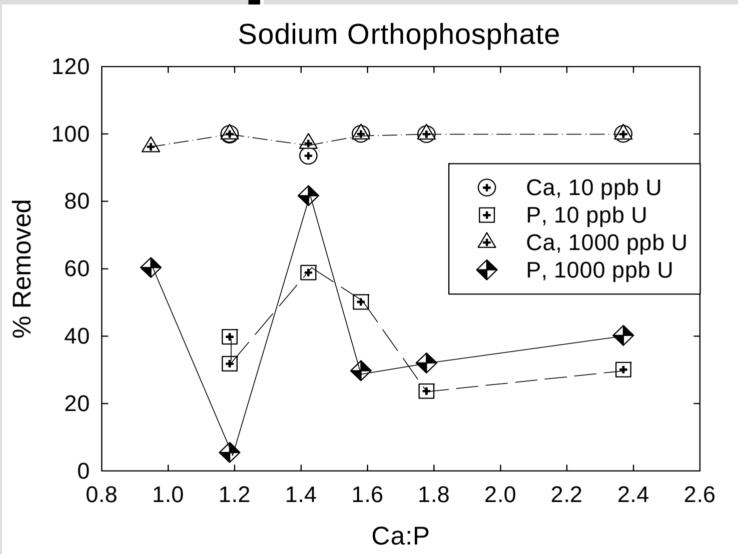
Jenkins et al., 1971

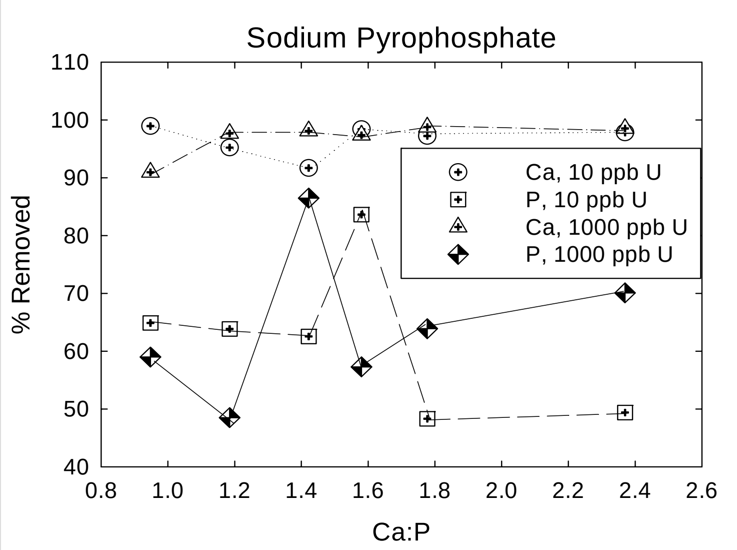
- HPO_4^{-2}
- $H_2PO_4^{-}$
- $H_2P_3O_{10}^{-3}$
- $HP_3O_{10}^{-4}$
- $H_2P_2O_7^{-2}$
- $HP_2O_7^{-3}$

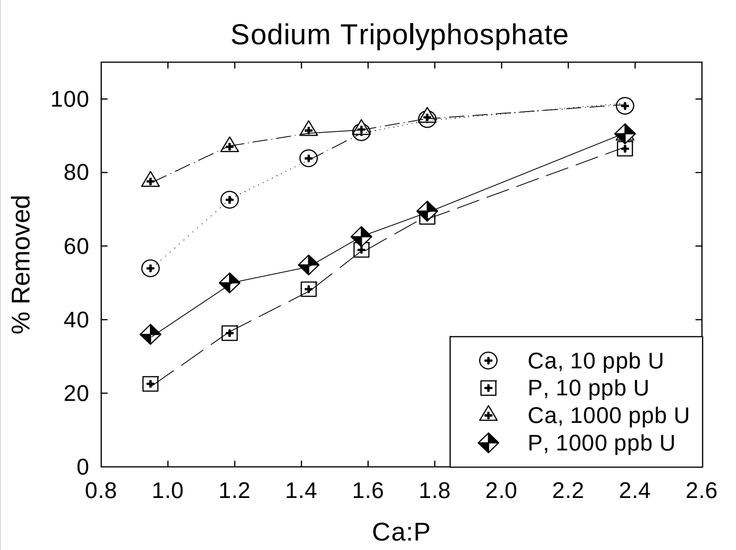
Calcium-Phosphate Relationships

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

Calcium – Phosphate Ratio Batch Tests





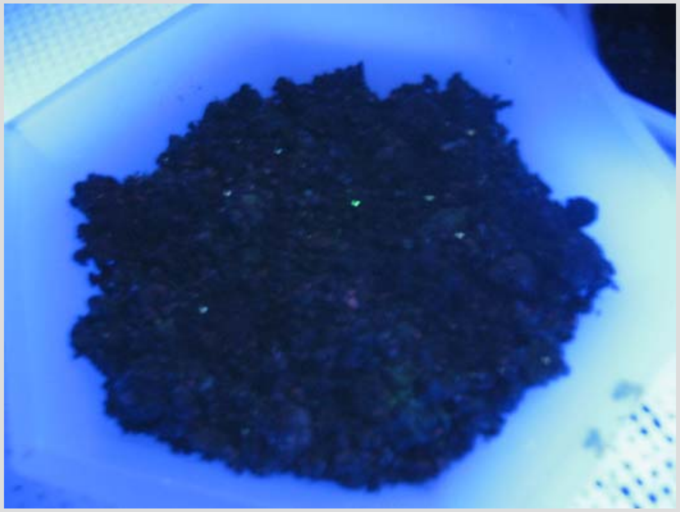


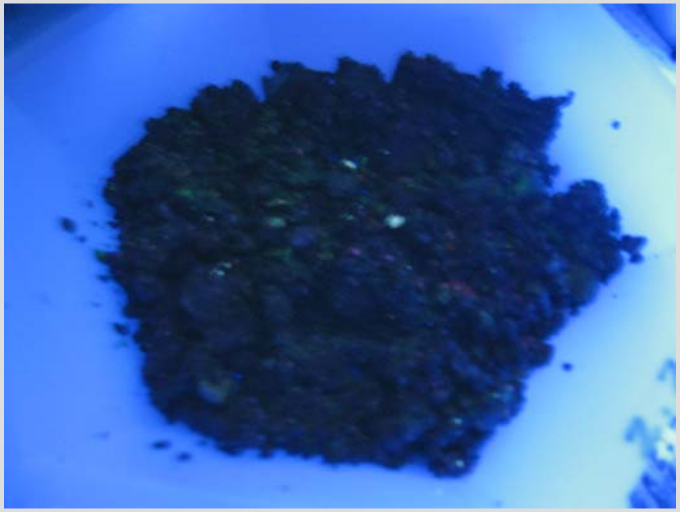
Column Testing

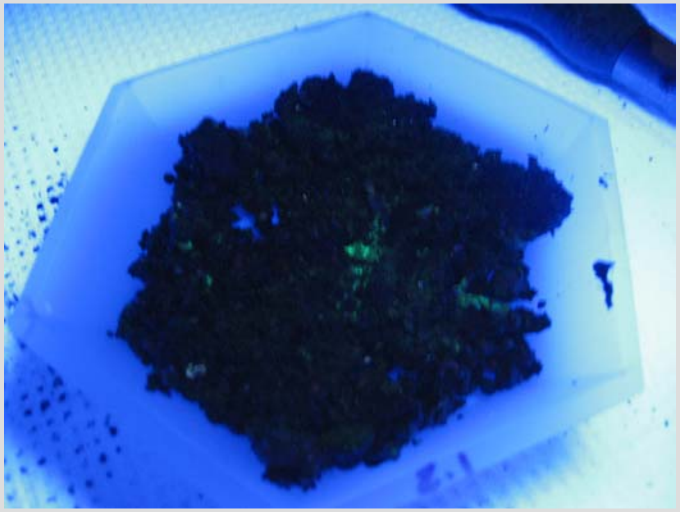
- Test Parameters
  - $[P]_{ortho/pyro/tripoly}$
  - Calcium/phosphorus ratio
  - $[Ca]_{total}$ & $[P]_{total}$
  - pH of amendment solution
- Column Length = 1 ft
- Cross Sectional Area = 0.005 ft^2
- Porosity = 0.25
- Flow Rate = 1.5 L/day
- $[U]_{aq}$ = 1000 μg/L

Control Column

Assessment of Post-Test Preliminary Analysis





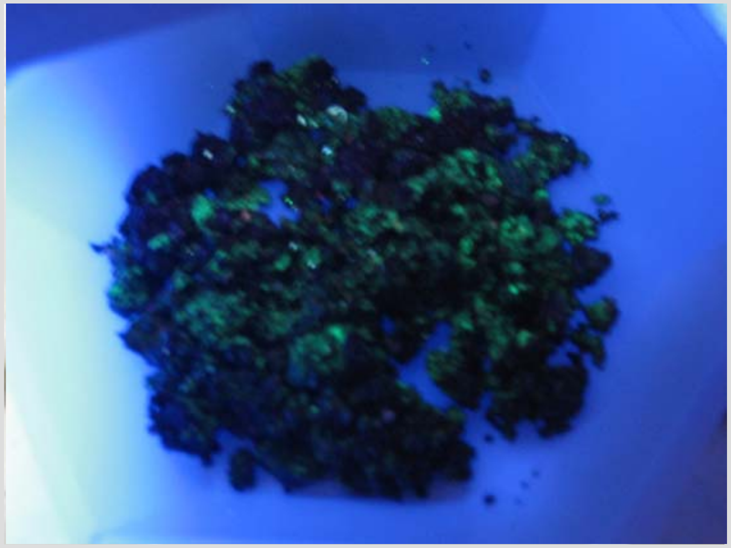


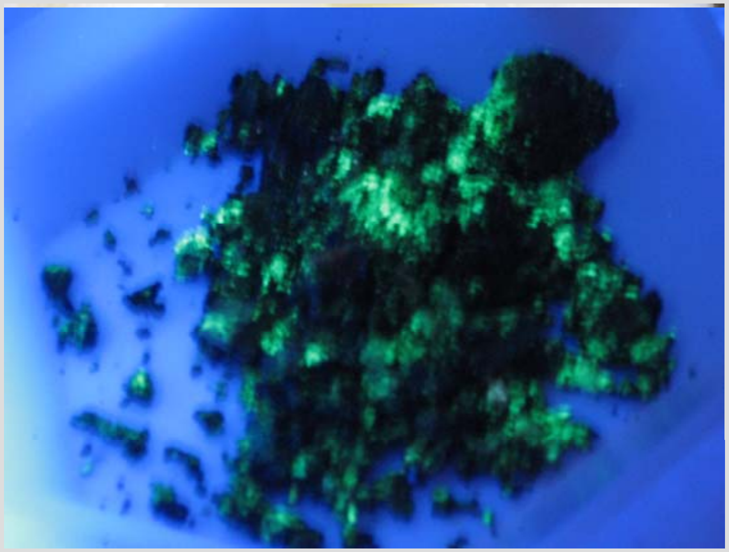
Uranium Column Testing

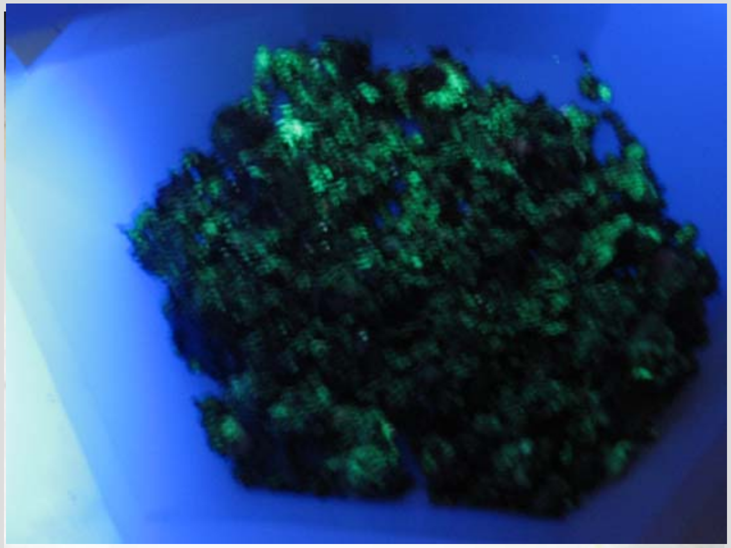
Total $[P]_{aq}$ = 5.20 x 10^{-3} M
Pyro $[P]_{aq}$ = 1.30 x 10^{-3} M
$[Ca]_{aq}$ = 1.15 x 10^{-2} M

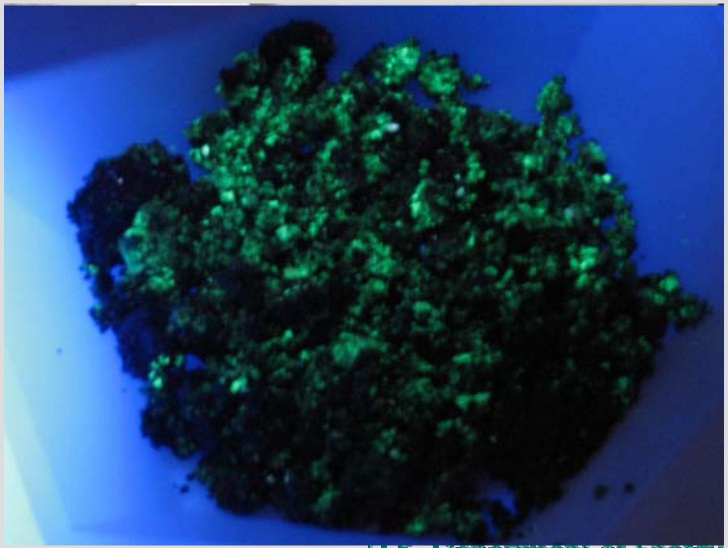
Tripoly $[P]_{aq}$ = 2.60 x 10^{-3} M
Ortho $[P]_{aq}$ = 1.30 x 10^{-3} M
pH adj. to 7

Post-Test Preliminary Analysis

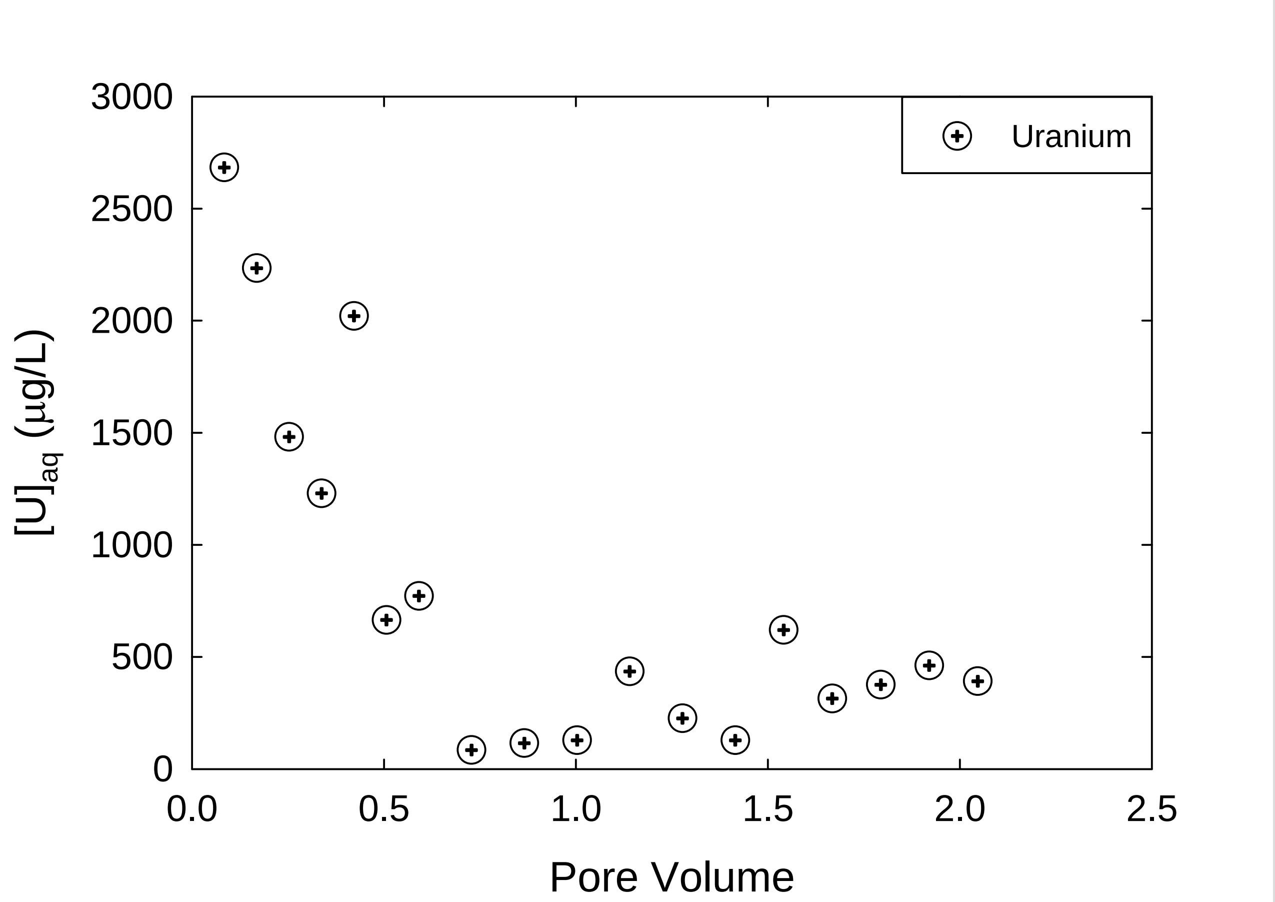








Uranium Immobilization



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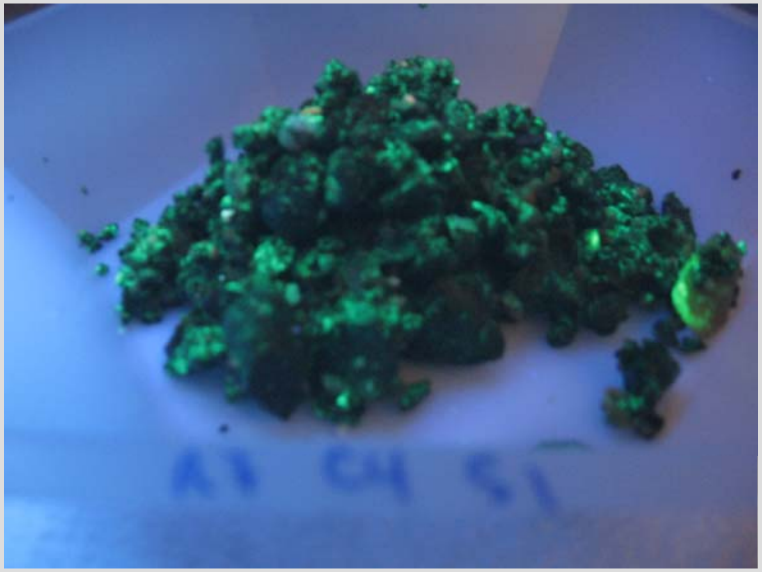
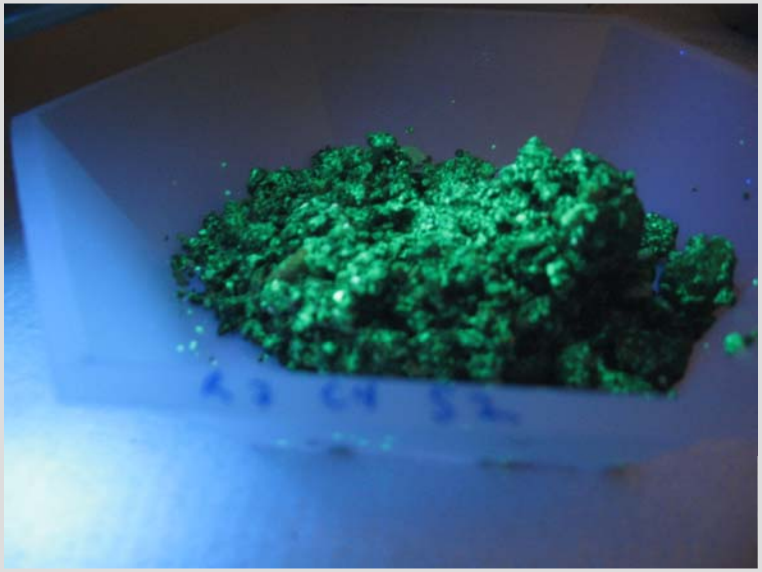
Uranium Column Testing

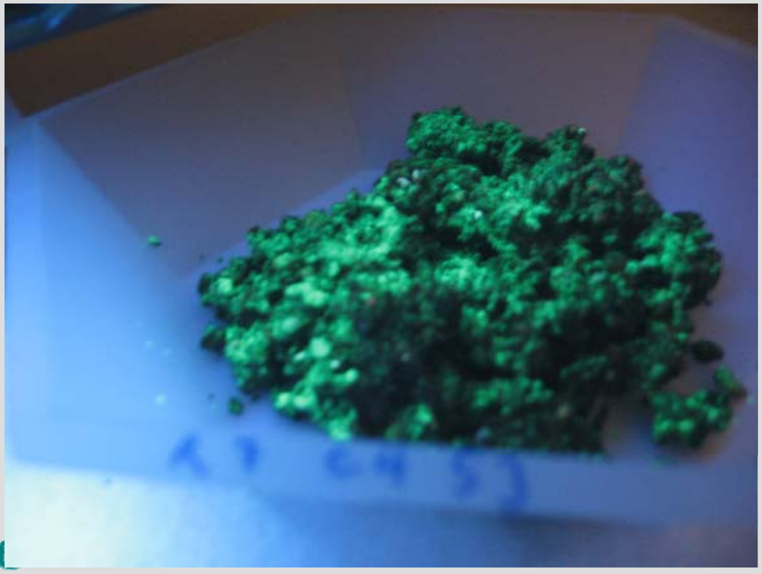
Total $[P]_{aq} = 5.26 \times 10^{-2}$ M
Pyro $[P]_{aq} = 1.32 \times 10^{-2}$ M
$[Ca]_{aq} = 1.16 \times 10^{-1}$ M pH = 7

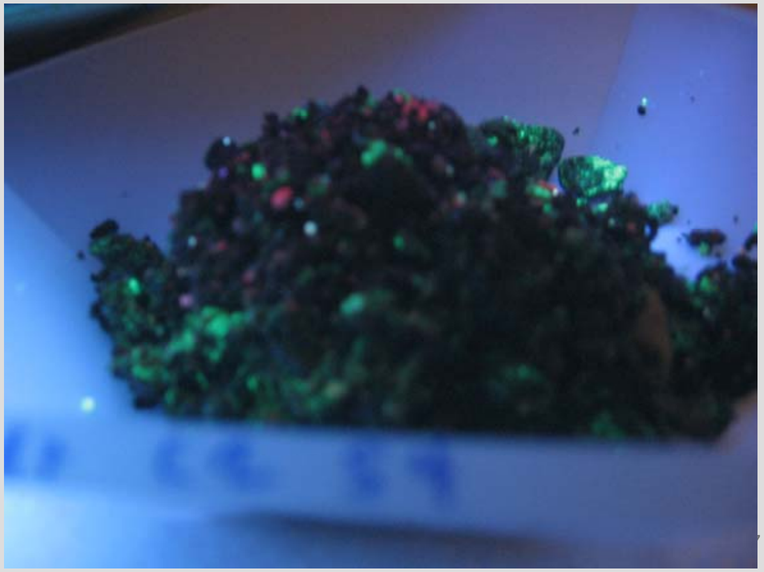
Tripoly $[P]_{aq} = 2.63 \times 10^{-2}$ M
Ortho $[P]_{aq} = 1.32 \times 10^{-2}$ M
RT = 56 min PV = 52 mL PV = 1 Ca/ 1P

Post-Test Preliminary Analysis

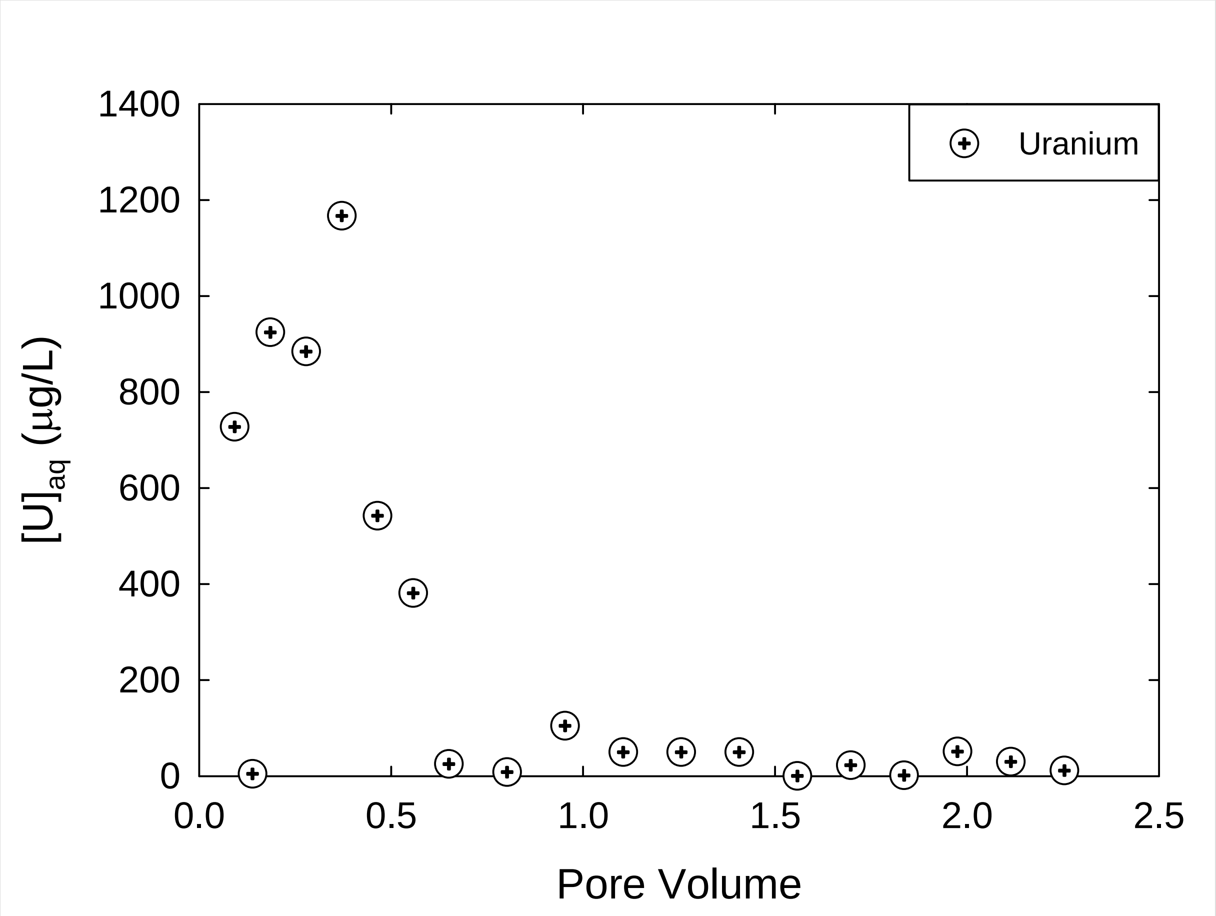




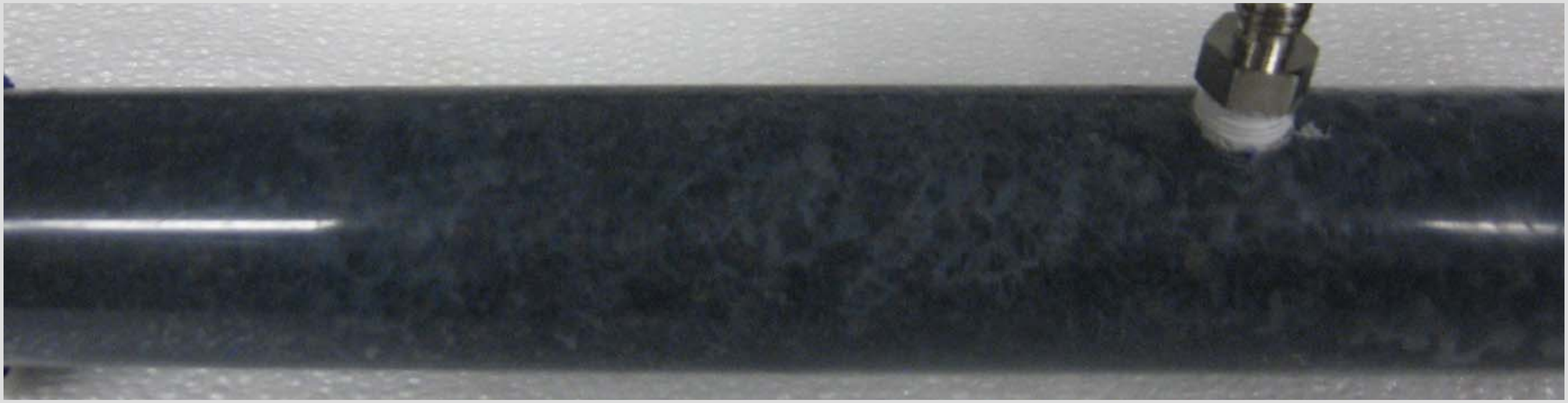




Uranium Immobilization



Uranium Column Testing



Total $[P]_{aq}$ = 5.26 x 10-^{2} M

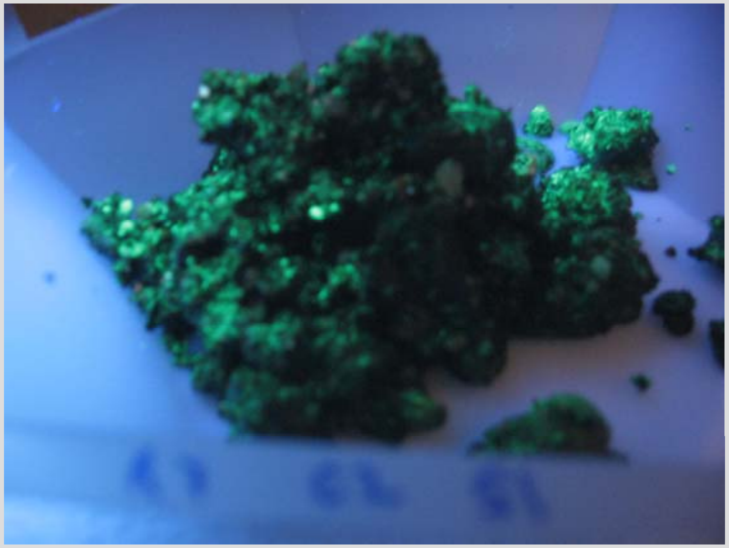
Tripoly $[P]_{aq}$ = 2.63 x 10^{-2} M

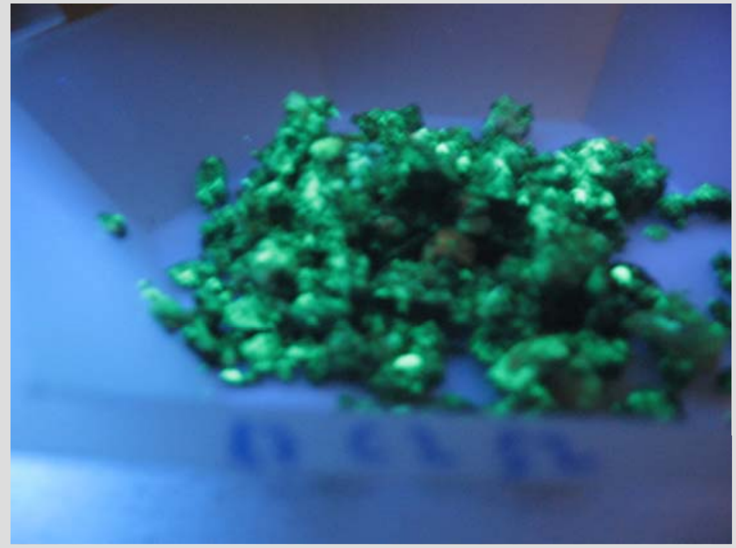
Pyro $[P]_{aq}$ = 1.32 x 10^{-2} M

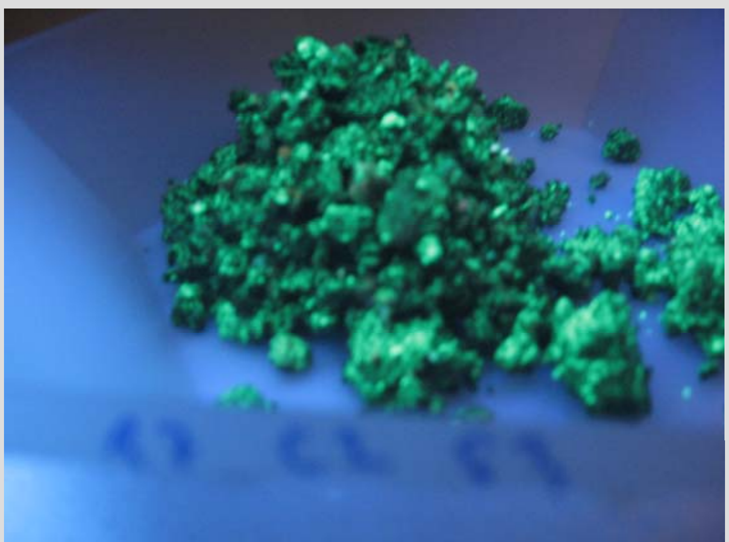
Ortho $[P]_{aq}$ = 1.32 x 10^{-2} M

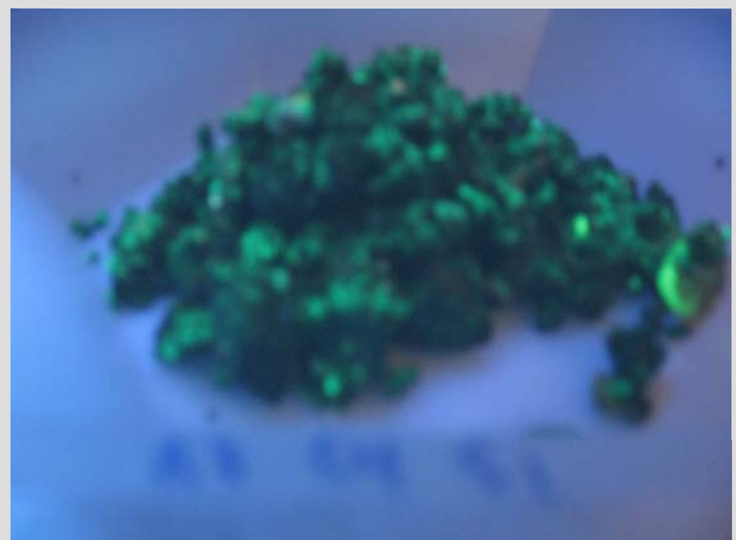
$[Ca]_{aq}$ = 9.98 x 10^{-2} M   pH = 7   RT = 56 min   PV = 1 Ca/ 1P

Post-Test Preliminary Analysis

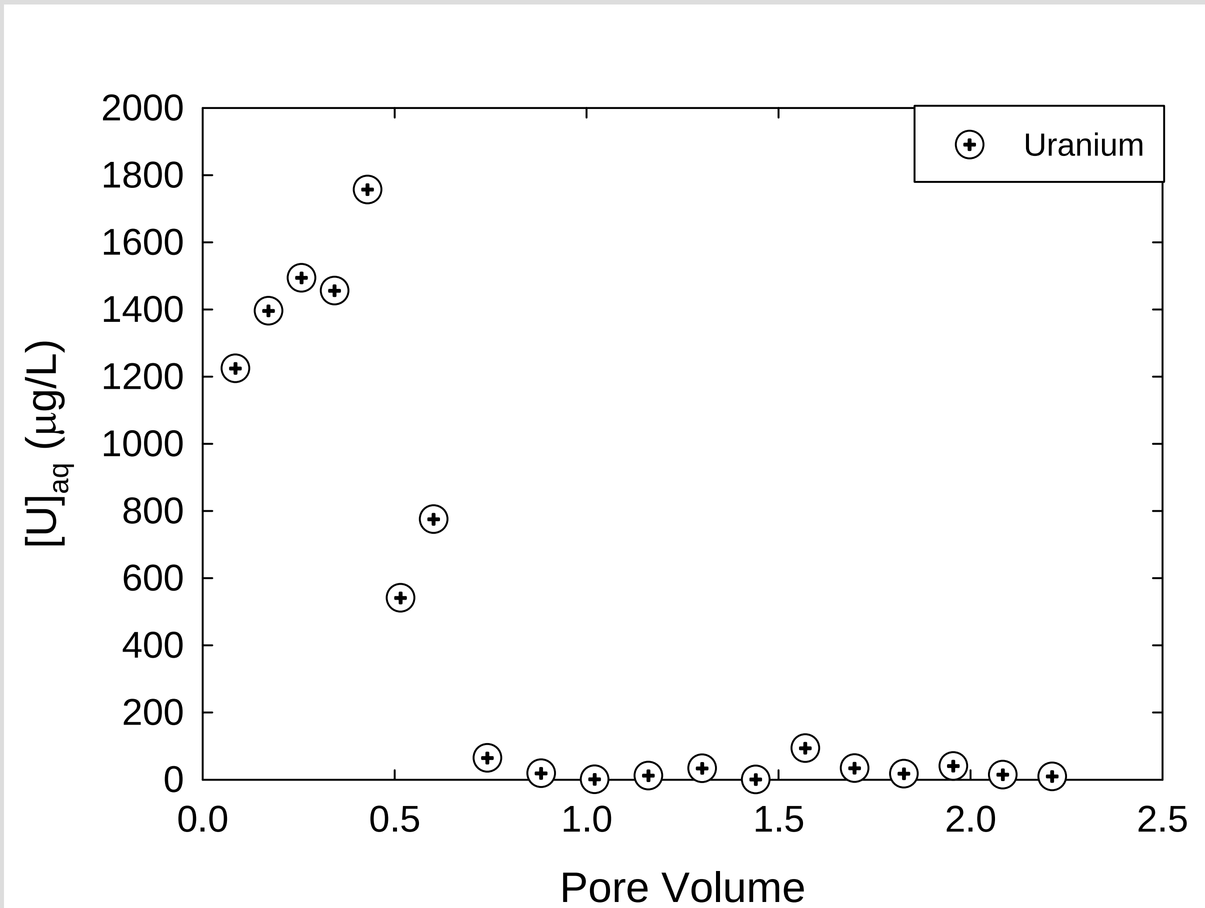








Uranium Immobilization



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  - Kent Parker
  - Elsa Rodriguez
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Uranium Stabilization through Polyphosphate Injection: Field Studies

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Pacific Northwest National Laboratory
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