Phosphate Barriers for Immobilization of Uranium Plumes

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Uranium Contamination at Hanford

- At least seven distinct uranium plumes have been identified at Hanford.
- Concentrations up to 1,000 X higher than drinking water standard.
- On-going pump-and-treat techniques have not reduced concentration of uranium.
- Cost of pump-and-treat is one million dollars per annum.

Why Use a Phosphate Amendment Strategy?

Many of the proposed remediation strategies utilize Redox changes to immobilize uranium.

- Passive Fe barrier
- Soluble reductive agent
- Biological amendment

Potential negative effects:

- Oxidation "rebound"
  - The reductive capacity of the barrier will become exhausted
  - Re-oxidation of reduced uranium solids
  - Redox front collapses, possibly resulting in rapid release of UO_2^{2+}
- Alteration of flow path, especially in vadose zone environments.

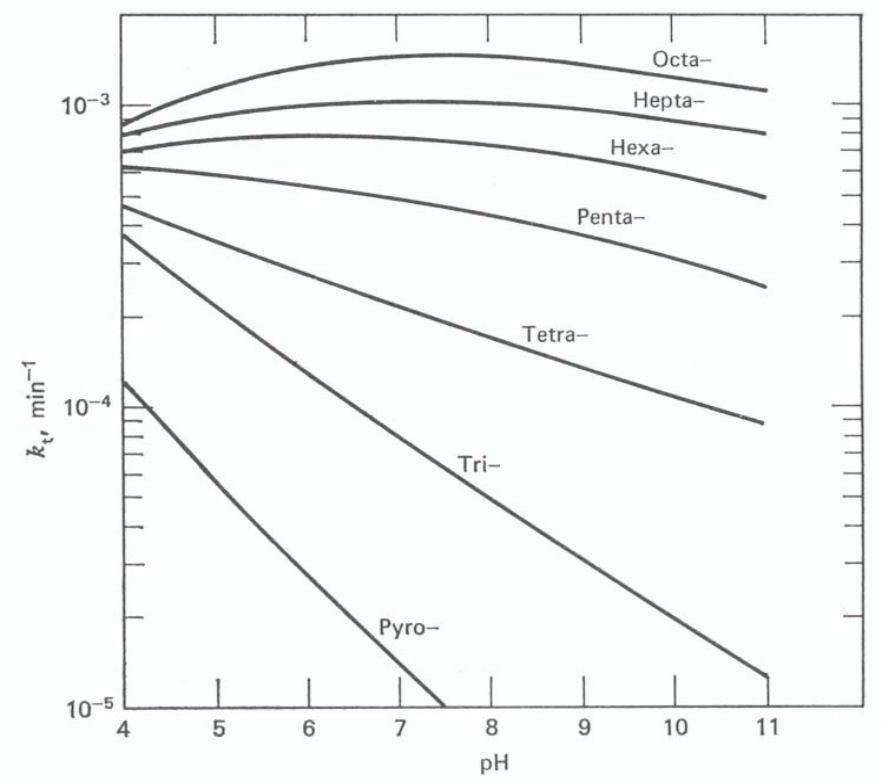
Why Use Phosphate Barriers?

- Precipitation of insoluble uranyl phosphate minerals, *even in solutions containing very small concentrations of uranium* (< 10^6 M U).
- Uranyl phosphate minerals are stable over a wide range of solution compositions.
- Re-oxidation is not a concern.
- Active maintenance not necessary.
- Application does not jeopardize workers.
- Non-toxic and causes no damage to soil.
- Relatively inexpensive.

Information Gaps for Phosphate Barriers

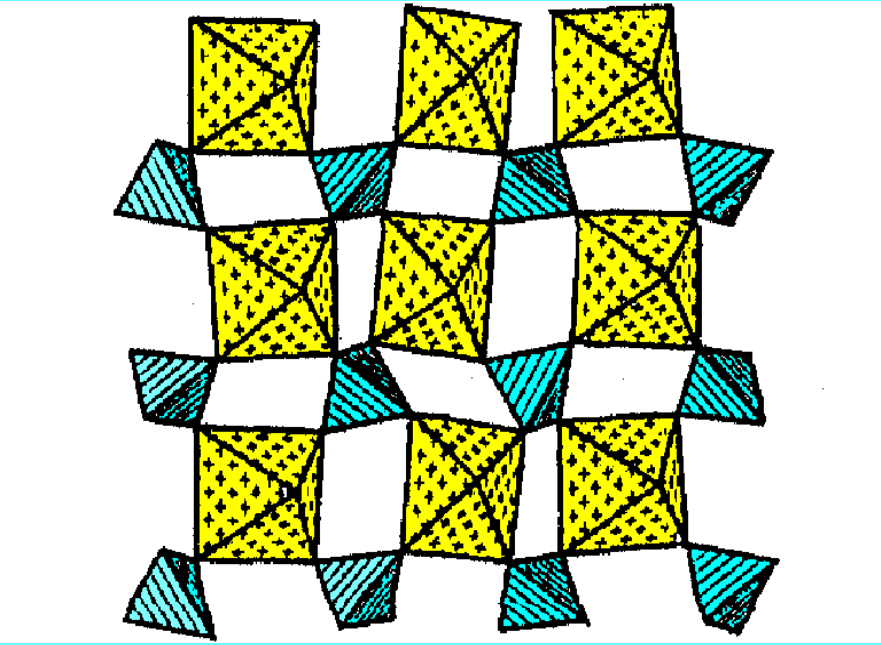
Key Obstacle		Science Solution
▪ Preventing plugging of wells at the point of injection.	→	▪ Hydrolyzation kinetics of soluble phosphate species.
▪ Identity and solubility of uranyl phosphate minerals.	→	▪ Quantifying solubility using well-characterized specimens (single-crystal XRD) under realistic conditions.
▪ Injection of amendment solution without displacing uranium plume.	→	▪ Experiments in unsaturated columns utilizing capillary forces.
▪ Phosphate barrier longevity.	→	▪ Experiments using Pressurized Unsaturated Flow (PUF) apparatus; dissolution kinetics studies.

Hydrolyzation Kinetics of Phosphate Species



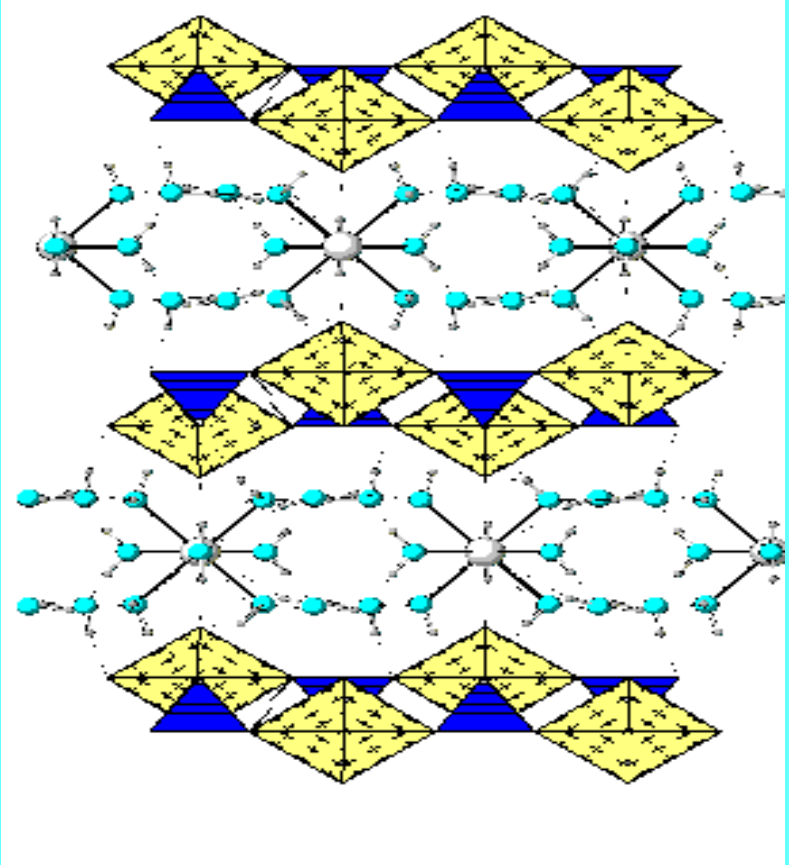
- Speed of hydrolyzation of phosphate chain proportional to precipitation kinetics.
- The longer the chain, the slower the hydrolyzation kinetics.
  - For example, polyphosphate versus pyrophosphate molecule (figure).
- Quantification has been done in beaker tests, but not under conditions relevant to vadose zone hydrology.
- Raman and NMR spectroscopy of hydrolyzation in unsaturated porous media.

Autunite-Group $\{A_{1-2}[(UO_2)(PO_4)]_2(H_2O)_{10-12}\}$ Minerals



- Autunite is the most likely uranyl phosphate to precipitate.
- Flexible chemistry; many substitutions possible.
- Structure is similar to micas with uranyl (yellow) and phosphate (blue) polyhedra forming sheets.
- “A”-site (alkali and alkaline earth) cations and water constitute interlayer sites.

Molecular Structure of Autunite-Group Minerals



- Single-crystal diffraction patterns have recently been published (Locock and Burns, 2002).
- Difficult structure to determine because typically dehydrated.
- Dehydration reactions have profound implications for thermodynamic stability of autunite-group minerals.

Autunite

↓ ↑

Meta-autunite I

↓

Meta-autunite II

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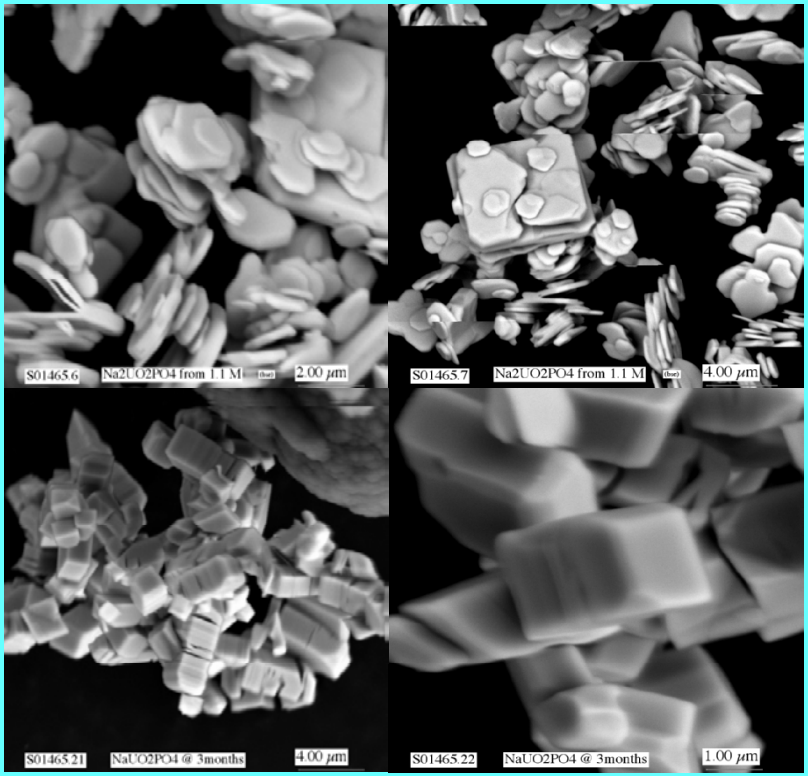
Synthesis of Autunite-Group Minerals



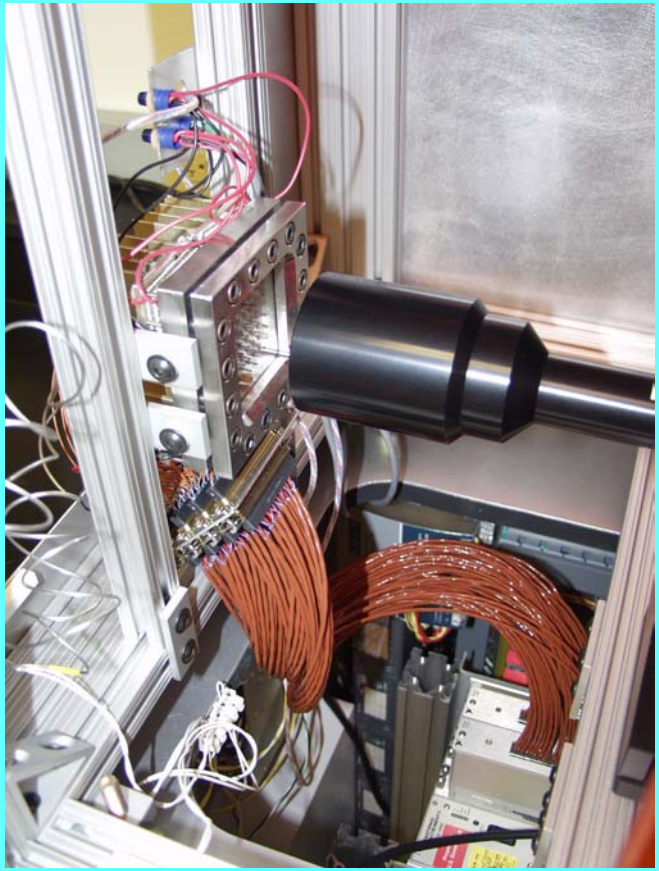
- Past synthesis routes have typically been two-step process.
  - Chernikovite
  - Alkali-exchange
- Difficult to measure thermodynamic stability.
- Identity and relative abundance of dissolved species in equilibrium with autunite has not been accomplished.
- Measurement by combination of isopiestic and NMR methods.

Pressurized Unsaturated Flow (PUF) Test

Picture of PUF System Hardware (Patent #5974859)

- Replicates pore fluid movement in vadose zone environments.
- Partial pressures of important gases (O_2 and CO_2) maintained.
- Solution pH, water content, and ionic conductivity of solution tracked in real time.
- Characterization of solutions and solids performed in real time using micro-Raman techniques.
- Full quantification of dissolution and precipitation rates.

Micro-Raman Spectroscopy System



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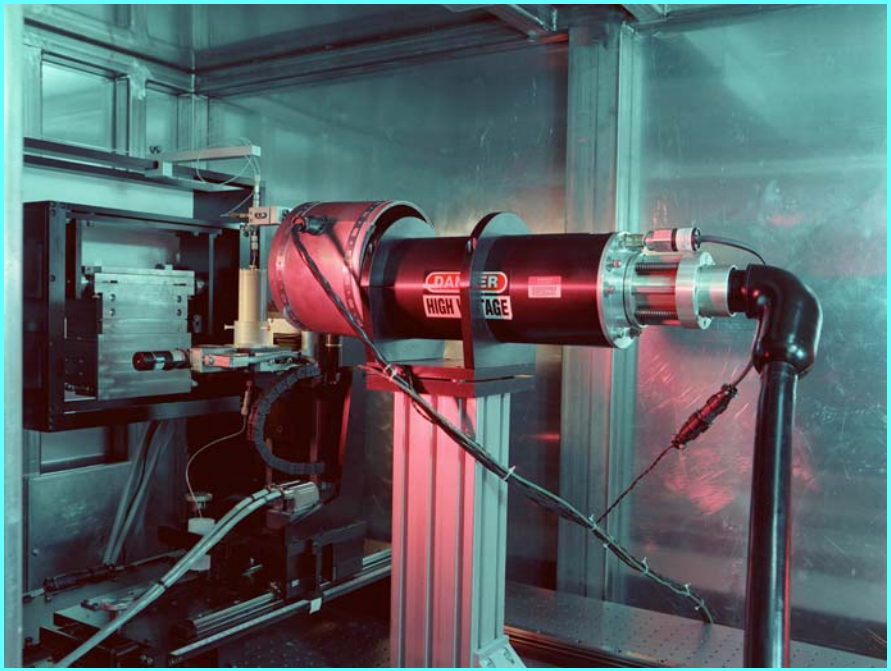
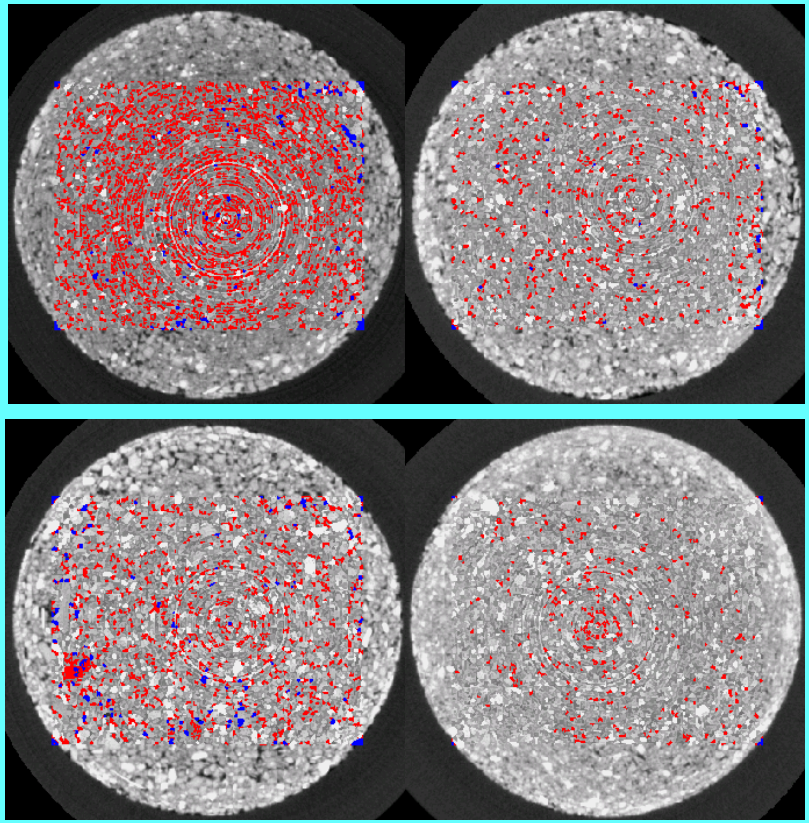
X-Ray Microfocus Tomography (XMT) Laboratory



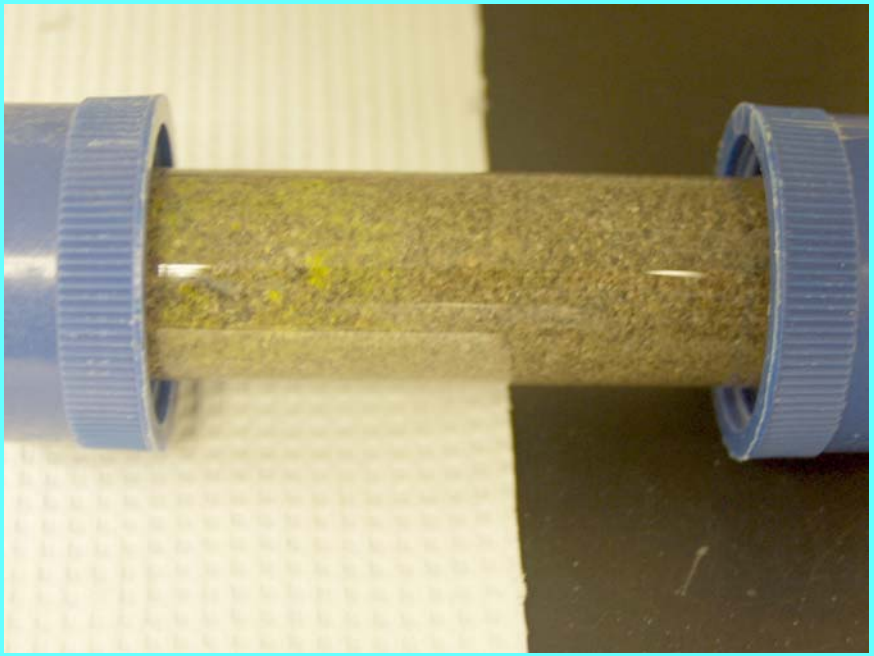
- High energy X-ray device; much like a "CAT-scan", but more powerful and with better resolution.
- A reaction vessel can be analyzed **while the experiment is in progress** to reveal fluid flow and mineral precipitation.
- Reveals changes in pore space volume over the course of the experiment.

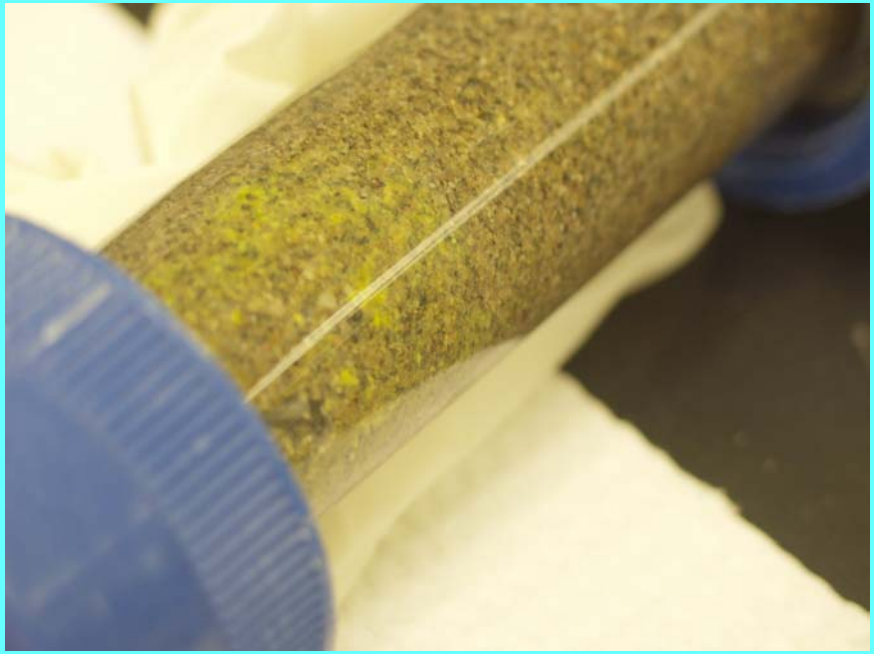
XMT Results—Effects of Pore Volume Changes



- Top two illustrations show pore volume changes before (left) and after (right) $Na_3PO_4(H_2O)_{12}$ is added.
- Bottom two illustrations show pore volume changes before (left) and after (right) phytic acid amendment.
- Both columns show significant reduction in pore volume as precipitation reactions occur.
- Column experiment (not shown) using long chain phosphate (Na poly-phosphate) shows no evidence for pore space reduction.

Column Experiments Doped with Uranium





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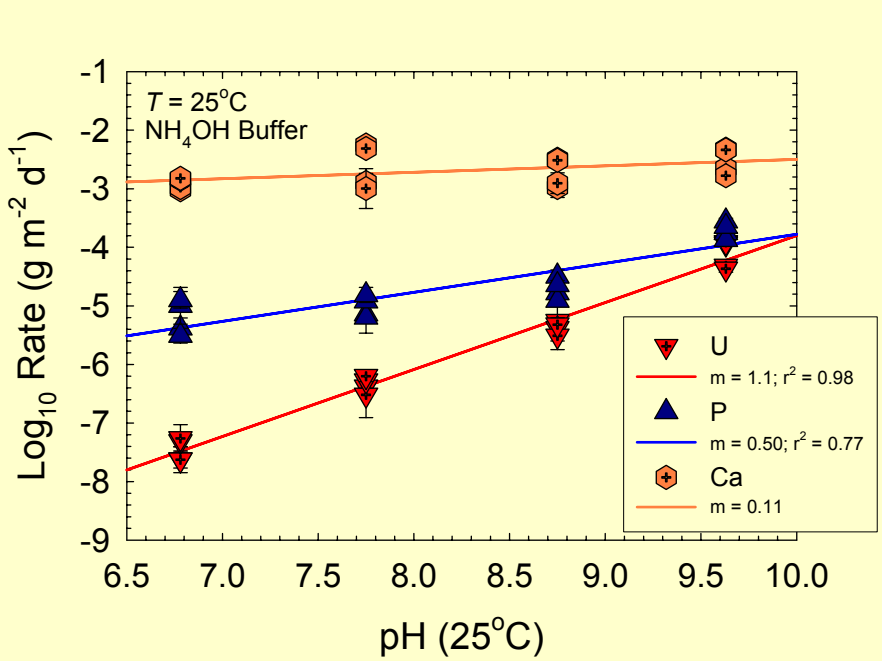
Dissolution Kinetics of Natural Ca-Autunite



- Flow-through experiments with variations in solution pH and temperature.
- Data indicates that U-release is very slow (red line).
- Phosphorous release is faster at neutral pH, identical at alkaline pH.
- Calcium release is fast (10,000X faster at pH = 6.7), likely due to exchange with H_3O^+.

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Summary

- Uranium-contaminated plumes are a significant environmental problem at a number of Defense-related sites across the U.S.
- Barriers that depend on redox reactions will eventually fail.
- Phosphate barriers constitute a robust alternative, but several questions must be addressed:
  - Control of precipitation kinetics of uranyl phosphates upon addition of phosphate amendment.
  - Injection into vadose zone without merely displacing uranium plume.
  - Identity and solubility of the uranyl phosphate.
  - Longevity of the phosphate barrier.
- Dissolution kinetics of autunite minerals show very slow release of uranium.