

## ENVIRONMENTAL REMEDIATION

**PROJECT: Environmental Remediation Science & Technology: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH<sub>3</sub> Gas**

**CLIENT: U.S. Department of Energy**  
**PRINCIPAL INVESTIGATOR: Dr. Leonel Lagos**  
**LOCATION: Hanford Site, WA**

### Description:

*FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of subsurface uranium stabilization through pH manipulation via NH<sub>3</sub> gas injection.*

This work is focused on long-lived uranium contamination, which is one of the key contaminants of concern for the Hanford site. Injection of reactive gases such as NH<sub>3</sub> is an innovative remediation technology shown to decrease uranium mobility in soil and sediments.

Experiments for this task seek to identify and quantify factors controlling these processes, including: biological transformations, ammonia partitioning, and geochemical reactions. This task examines the mechanisms of potential importance using controlled laboratory systems to complement efforts underway at Pacific Northwest National Laboratory (PNNL).

When NH<sub>3</sub> gas is injected into the subsurface, it quickly partitions between aqueous (soil moisture), solid (minerals) and gas phases. In the aqueous phase, NH<sub>4</sub>OH forms and dissociates causing a subsequent increase in pH. This manipulation can significantly alter the pore water chemistry and affect the dissolution of aluminosilicate minerals from sediments.

Furthermore, ammonia losses increase with increased temperature and pH and can be very high in dry neutral or alkaline sediments. Also, sediments rich in carbonate, which is typical for the Hanford Site, require more ammonia gas due to the existing soil

buffering capacity and the formation of ammonia carbonate.

Co-precipitation of U(VI) [as uranyl (UO<sub>2</sub><sup>2+</sup>)] and Si is expected under these high pH conditions. However, the processes leading to co-precipitation and the precipitates forming under these non-equilibrium conditions are still not well understood. Moreover, the stability of possible precipitates requires additional research.

### Technology Benefits:

Ammonia (NH<sub>3</sub>) gas technology offers the potential for radionuclide sequestration through:

- Increased pore water pH
- Precipitation of mineral phases
- Efficient penetration to low permeability unsaturated zones
- Co-precipitation of radionuclides alongside mineral phases

### Objectives:

The major objective of this project is to evaluate the processes occurring during and after ammonia injection into the vadose zone, including ammonia partitioning and effects, uranium fate and mineral dissolution and precipitation.

1. Evaluate the effect of ammonia gas injection on the aqueous phase (i.e. porewater).
  - Evaluate the effect of major porewater constituents on pH change with NH<sub>3</sub> injection (i.e. bicarbonate).
  - Evaluate the role of major porewater constituents on precipitate formation (i.e. Al, Si, Ca, and bicarbonate).
2. Evaluate the effect of ammonia gas injection on solid phases (i.e. mineral components).
  - Examine the deliquescence behavior of solids prepared from synthetic porewater (via isopiestic method).

### ABOUT

*Since 1995, the Applied Research Center at Florida International University has provided critical support to the Department of Energy's Office of Environmental Management mission of accelerated risk reduction and cleanup of the environmental legacy of the nation's nuclear weapons program. ARC's research performed under the DOE-FIU Cooperative Agreement (Contract # DE-EM0000598) can be classified as fundamental/basic, proof of principle, prototyping and laboratory experimentation.*

### Project Contact:

**Dr. Yelena Katsenovich**  
Ph: (305) 348-2338  
Email: katsenov@fiu.edu  
10555 W. Flagler Street, EC 2100  
Miami, FL 33174  
arc.fiu.edu

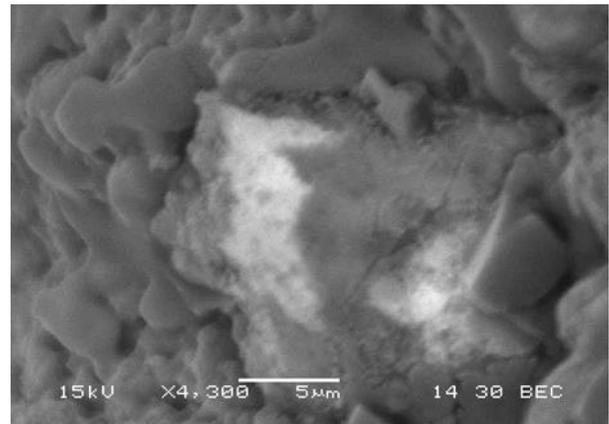
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- Determine osmotic coefficients for samples as a function of water activities.
- 3. Evaluate the fate of uranium during ammonia gas injection.
  - Analyze mineralogical and morphological characteristics of precipitates by XRD and SEM/EDS.
  - Examine the effect of temperature on solubility of U(VI)-bearing precipitates.
  - Evaluate the removal of uranium in the presence and absence of  $\text{NH}_3$  at variable pH using relevant pure minerals and sediments through batch sorption experiments and sequential extraction procedures.

### Accomplishments:

- Potentiometric study of ammonia injection at varying bicarbonate concentrations. Showed that significantly greater  $\text{NH}_3$  gas is required in the presence of bicarbonate.
- Evaluated uranium removal in the presence of pure minerals, synthetic porewaters, and  $\text{NH}_4\text{OH}$  or  $\text{NaOH}$  for pH adjustment. Showed significantly different effects between  $\text{NH}_4^+$  and  $\text{Na}^+$  as well as porewater constituents.
- Evaluated the effect of various silicon, aluminum, calcium and bicarbonate concentrations on the removal of uranium from the supernatant solution. Results show that Si gel formation correlates with removal of U(VI).
- Geochemical modeling software (Geochemist's Workbench & Visual Minteq) predicted the formation of uranyl silicate and uranyl carbonate solid phases under the conditions of the precipitate characterization studies.
- Performed characterization studies of uranium-bearing phases using a range of analytical techniques including x-ray diffraction (XRD), electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and scanning electron microscopy with energy dispersive spectroscopy (SEM w/EDS). Test results revealed matches for cejkaite and grimselite phases and uranium association with Si that correlated with the speciation modeling data.

- Initiated isopiestic measurements to investigate solid-liquid transition of uranium-free, synthetic multicomponent precipitates from major pore water constituents such as  $\text{Na}^+$ ,  $\text{SiO}_3^-$ ,  $\text{Al}^+$ ,  $\text{NO}_3^-$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$ . Results show the deliquescence behavior of precipitates is governed by the solubility of alkali silicate gel and Ca concentration in the sample.



Backscatter SEM images of samples showing U-rich phases

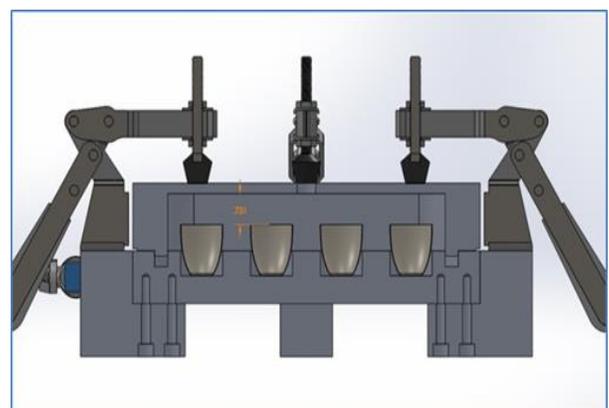


Diagram of isopiestic chamber assembly with aluminum block and nickel crucibles.