Uranium Fate and Mineral Transformations upon Remediation with Ammonia Gas

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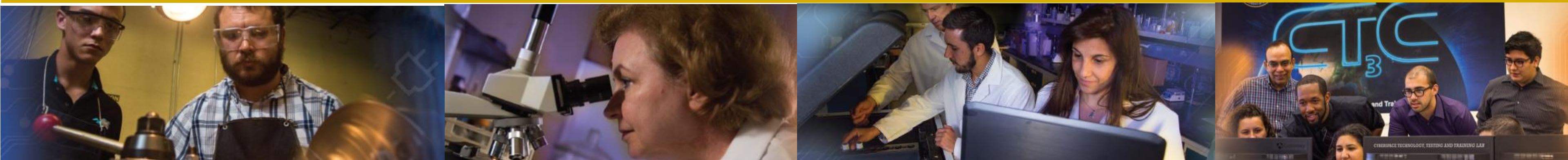


Background

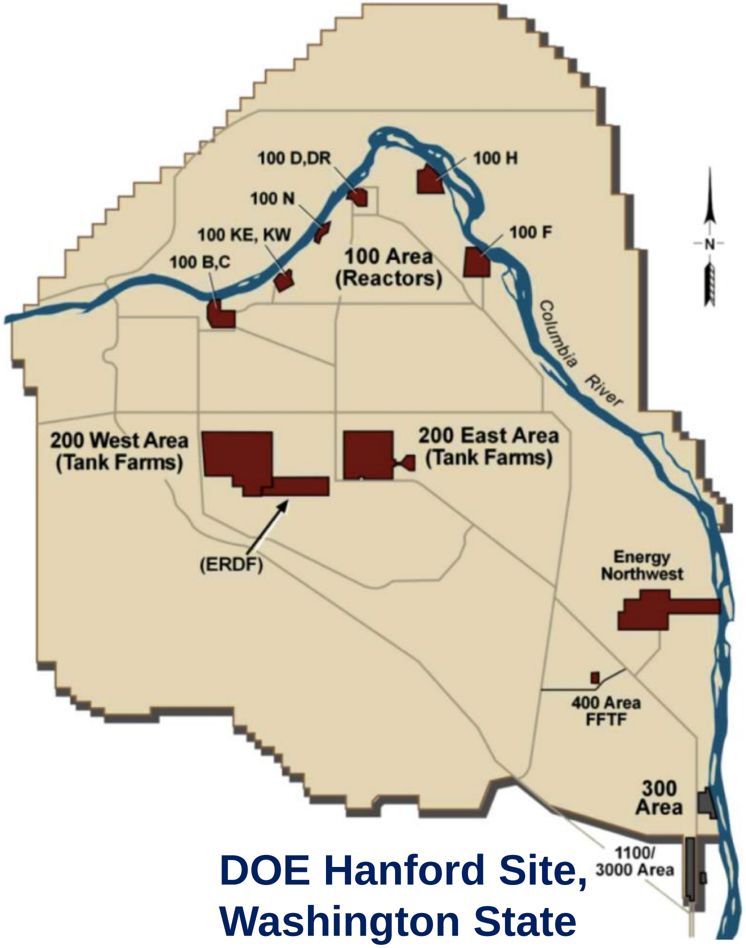
Hanford Site U Contamination

Uranium Fate at Hanford:

- **> 200,000 kg of U have been released (Zachara *et al*., 2007)**
- **Oxidizing conditions → play a big role!**
  - High mobility due to the presence of U-carbonate complexes
  - U(VI) → most soluble and stable uranyl ion (UO_2^{2+})
  - U(IV) → most insoluble and least mobile

Why NH_3 Gas Injection for Remediation?

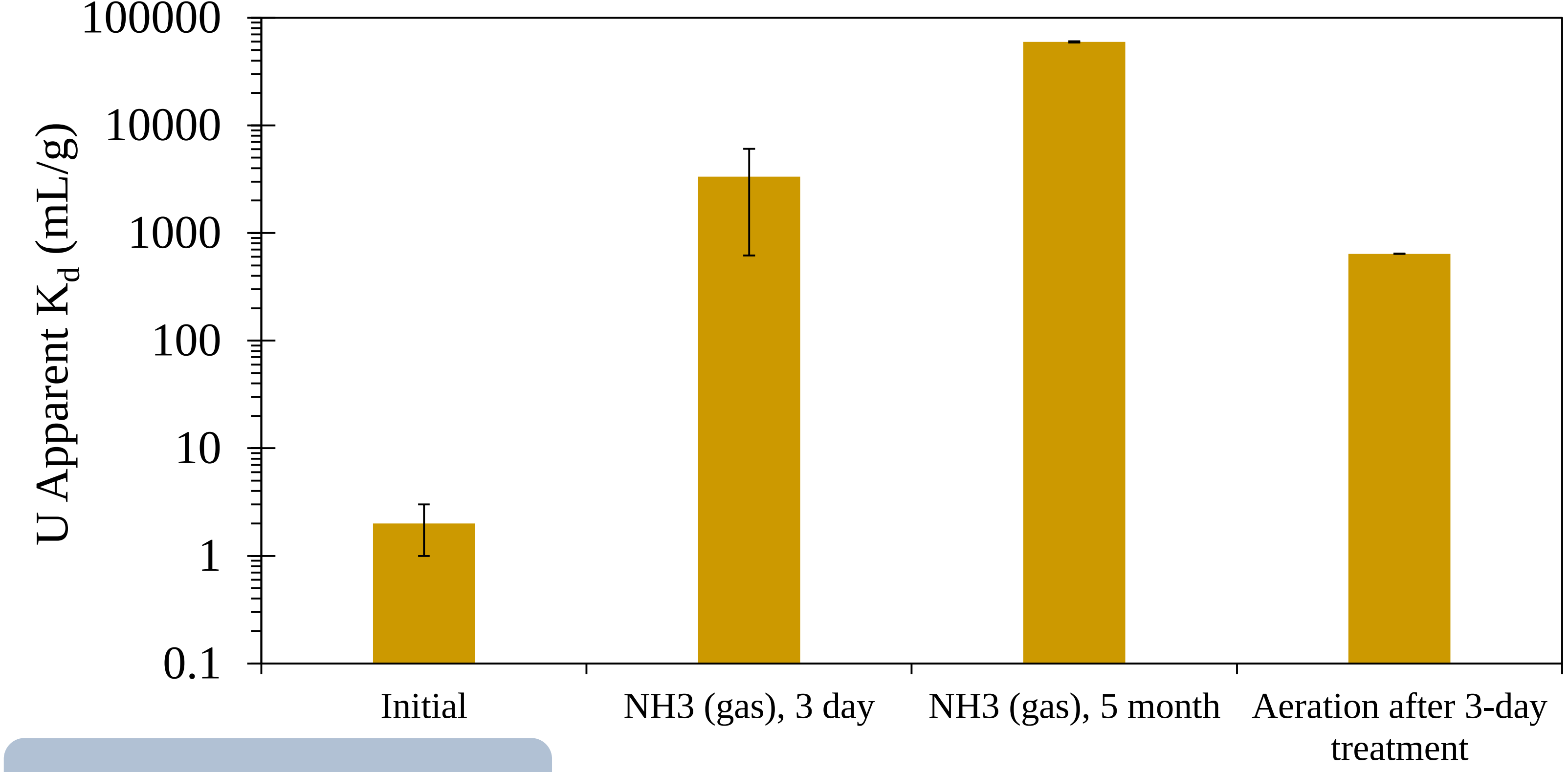
Alkaline pH induced mineral dissolution and as NH_3 dissipates, U co-precipitates with low solubility minerals



DOE Hanford Site, Washington State

Background

U Removal with NH_3 gas Treatment

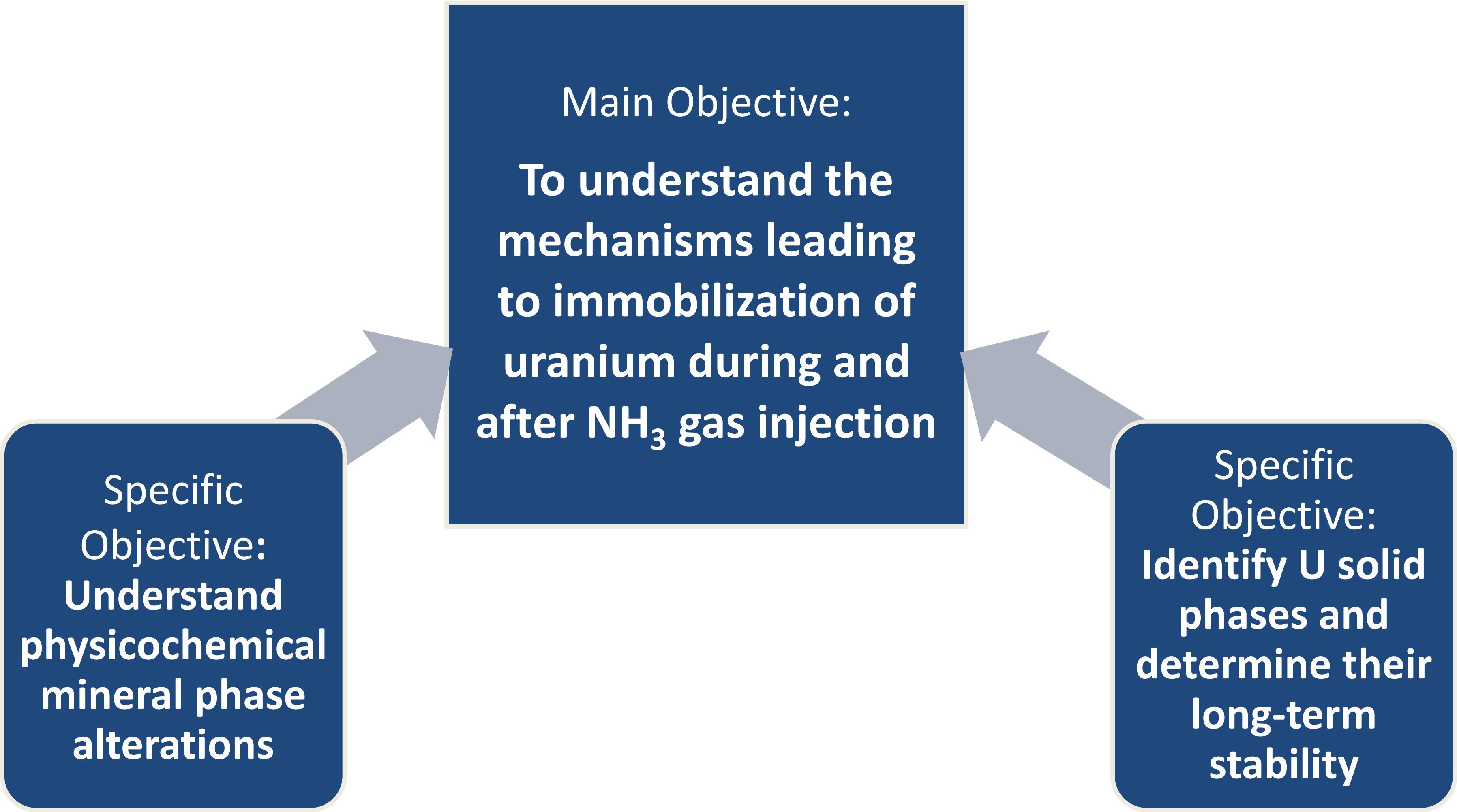


$$K_d = \frac{[U]_{solid}}{[U]_{aqueous}}$$

>2 orders of magnitude increase in K_d!

However, we don’t understand what U is associated with or if it is stable long term

Objectives



Main Objective:

To understand the mechanisms leading to immobilization of uranium during and after NH_3 gas injection

Specific Objective:
Understand physicochemical mineral phase alterations

Specific Objective:
Identify U solid phases and determine their long-term stability

Experimental Methodology

The Process

Phyllosilicate minerals in experiments:

- Present at the Site
- Significant mineral dissolution under the basic conditions
- Feldspar weathering:

  muscovite → montmorillonite → illite

Solutions in experiment:

7.2 mM Synthetic Groundwater (SGW): solution containing ions (i.e., Na^+, Ca^{2+}, HCO_3^-, etc.) replicating Hanford Site's porewater

Uranium
- SGW solution spiked with U(VI) exposed to minerals and sediments

Treatment
- Ammonia Gas

Time
- Reaction time up to 5 months

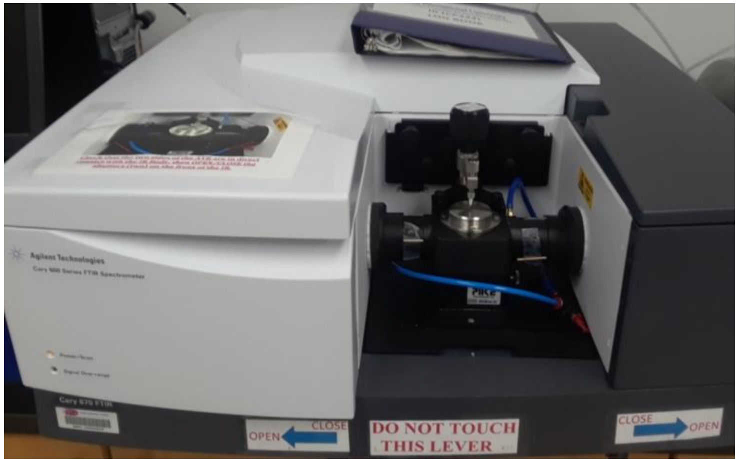
Aeration
- Ammonia gas dissipation/neutralization

Goal
- Understand U adsorption, co-precipitation and redox processes influencing removal

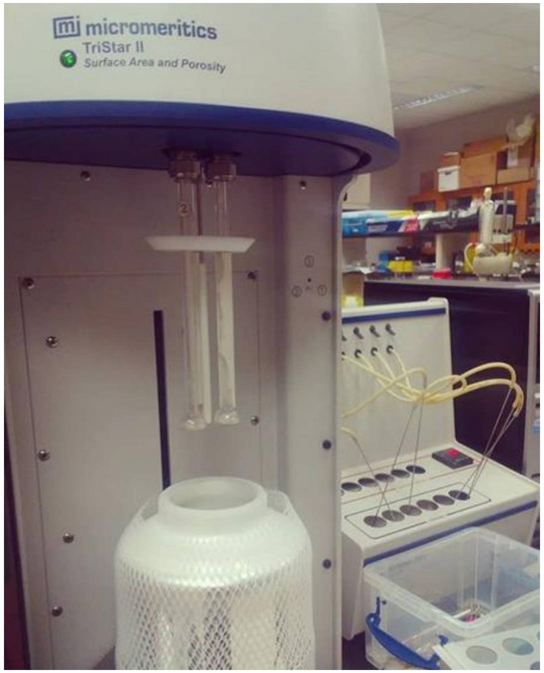
Experimental Methodology

Analytical Instrumentation

Instrumentation to identify alterations in mineral phases, both surface and bulk fractions

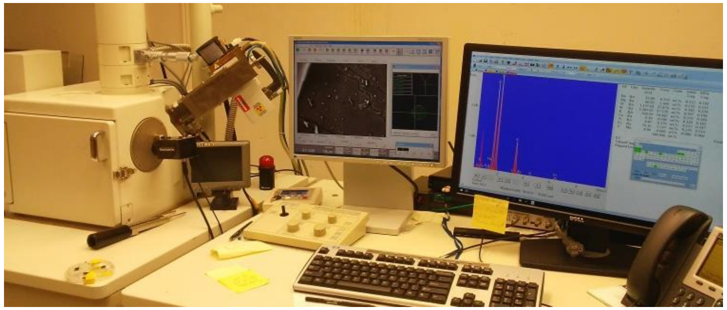


Fourier-Transform Infrared Spectroscopy (FTIR) → surface analysis of molecular absorbance



Branauer-Emmett-Teller (BET) → surface area

X-ray Diffraction (XRD) → bulk analysis



Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS) → elemental composition

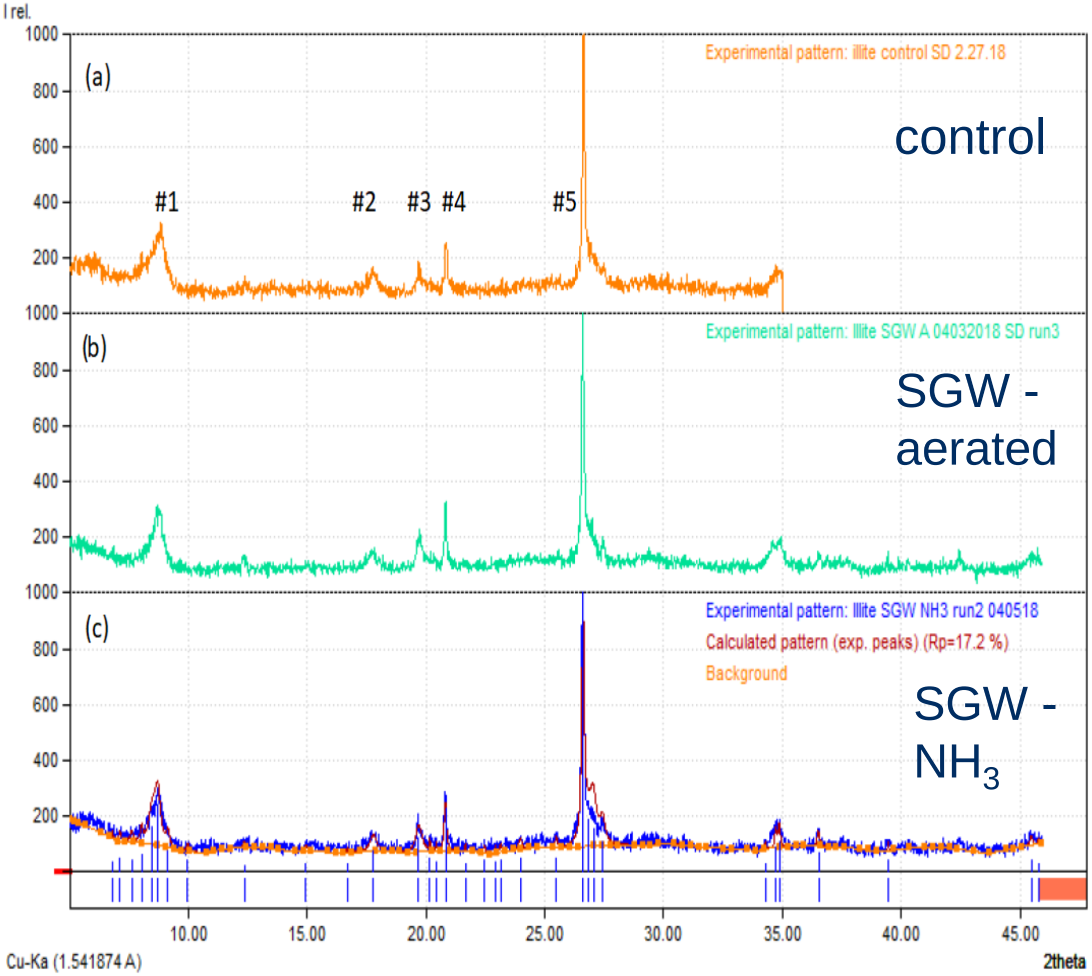
Solid Phase Characterization

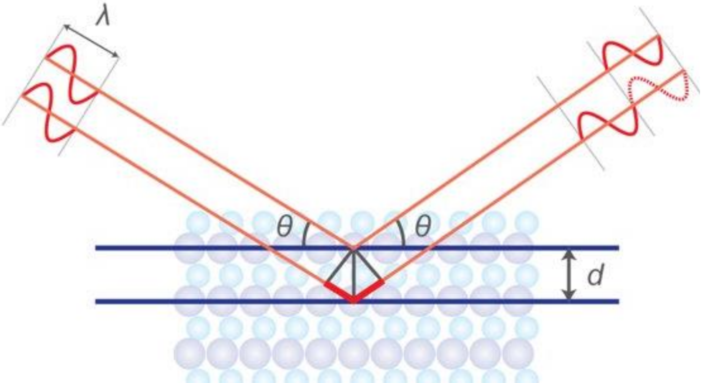
XRD of Illite

- X-ray diffraction (**XRD**) = non-destructive tool to identify bulk crystalline phases
- Goal: identify mineral alterations pre and post treatment NH_3 gas
- Overall: not a significant change among peaks

Illite:

$K_{0.7}Al_2[Al_{0.7}Si_{3.4}O_{10}](OH)_2$



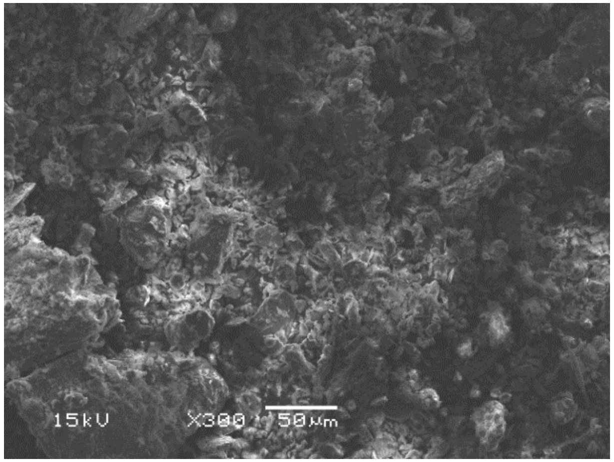


(https://www.rigaku.com/en/techniques/xrd)

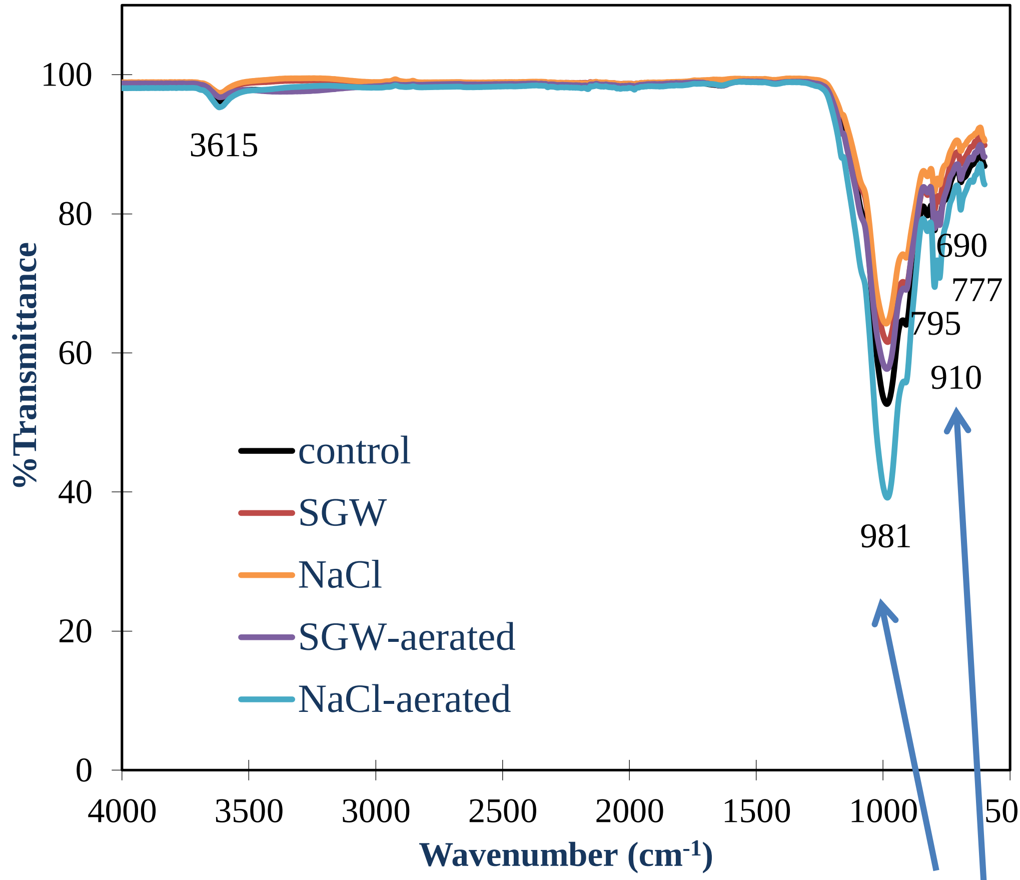
Solid Phase Characterization

FTIR of Illite

- Fourier-transform infrared spectroscopy (**FTIR**) = molecule absorbs radiation when the frequency is same as incident radiation
- Goal: understanding surface mineralogy differences in absorbance pre and post treatment NH_3 gas
- Overall trend: aerated>control>NH_3 treated



SEM image of Illite sample that underwent treatment and aeration



Si-O-Si band

Al-Al-OH bending

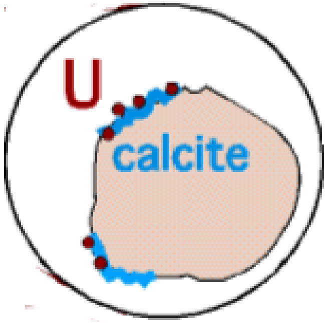
Solid phase characterization

XANES of Illite

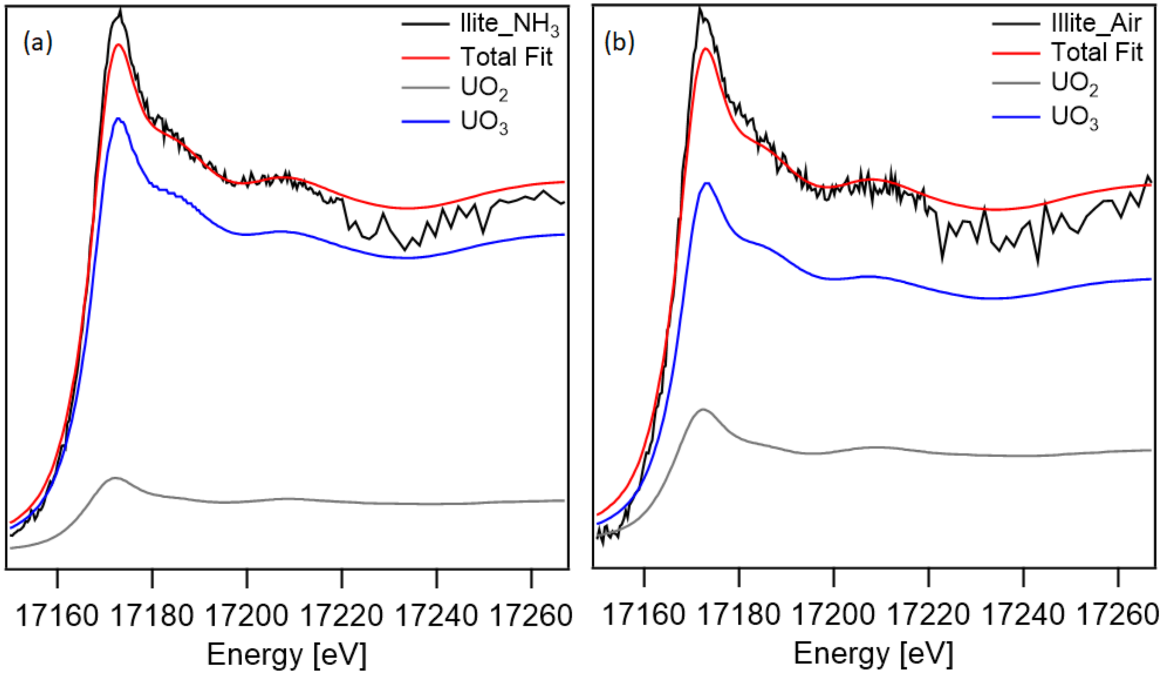
Valence State	Illite NH_3	Illite Aerated
U(IV)	15±8%	26±11%
U(VI)	91±8%	74±11%

Analysis:

- X-ray Absorption Near Edge Spectroscopy (**XANES**) = determine the oxidation state of a metal complex
- Goal: determine the oxidation state of the U in the solid phase
- Finding: small fraction (26±11%) remained reduced



(Szecsody *et al*., 2010)



Analysis conducted by Dr. Sarah Saslow (PNNL) at Argonne Advanced Photon Source

Conclusions

1. Mineral phase changes are difficult to identify in the ‘bulk’, (i.e. XRD does not show significant shifts)
2. Evidence of some changes via surface but more data will be gathered during internship (i.e. FTIR)
3. Reduced U in the solid phase (XANES analysis) following a 3-day treatment period – Not expected!

Future Work

- **On-going Experiments**
  - **Goal:** Expose minerals (illite, muscovite and montmorillonite) to NH_3 gas and then characterize solids (both with and without aeration)
    1. Long term: minerals + U exposed to NH_3 gas for ~6 months
    2. Short term: minerals + U exposed to NH_3 gas for 3-7 days

Mineral*	µg U/gram of solid
Illite	1710
Muscovite	1710
Hanford Sediments	1660

- **PNNL internship #2**: June 4th-August 10th, 2018 with Dr. Szecsody
  1. Solid phase characterization of clean minerals exposed to NH_3 gas
  2. Solid phase characterization of solids exposed to U and NH_3 gas
  3. Incorporation of iodine into apatite minerals

Accomplishments

2017-2018

PhD Candidate as of April, 24th 2018!

Honors and Awards

- DOE-NE *Innovations in Nuclear R&D* Award based on 2017 Waste Management Proceedings Paper ($1500, April 2018)
- 2nd Place Student Poster (Waste Management Conference, March 2017)

Peer-reviewed Publications

- Emerson, H. P., Di Pietro, S., Katsenovich, Y., and Szecsody, J. (2018). “Uranium Immobilization in the Presence of Minerals Following Remediation via Base Treatment with Ammonia Gas” *Journal of Environmental Management*. Under review.
- Di Pietro, S., Emerson, H.P., Katsenovich, Y., and Szecsody, J. (2018) “Mineral Dissolution following basic treatments.” *Environmental Science and Technology*. In Preparation.

Non Peer-reviewed Publications

- Emerson, H.P., Di Pietro, S., Katsenovich, Y., and Szecsody, J. (2018) “Base treatment for uranium immobilization at DOE’s Hanford site” *Waste Management Symposia Proceedings.*
- Di Pietro, S., Emerson, H.P., Katsenovich, Y. (2017) “Ammonia Gas Treatment for Uranium Immobilization at US DOE Hanford Site” *Waste Management Symposia Proceedings.*

Conference Presentations

- Di Pietro, S., Emerson, H.P., Katsenovich, Y., “Potential Impacts to Local Mineralogy from Remediation with Ammonia Gas.” *American Chemical Society*, *August 19-24, 2018, Boston, MA*
- Di Pietro, S., Emerson, H.P., Katsenovich, Y., “Effects of Alkaline Treatment on Mineral Dissolution for Hanford Sediments.” *Waste Management Conference, March 18-22, 2018, Phoenix, AZ*
- Di Pietro, S., Emerson, H.P., Katsenovich, Y., “Effects of Alkaline Treatment on Mineral Dissolution for Hanford Sediments” *DOE Fellows Poster Competition - Applied Research Center, Florida International University November 7th, 2017, Miami, FL*

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