Ammonia gas Treatment for Uranium Immobilization at DOE Hanford Site

Silvina Di Pietro

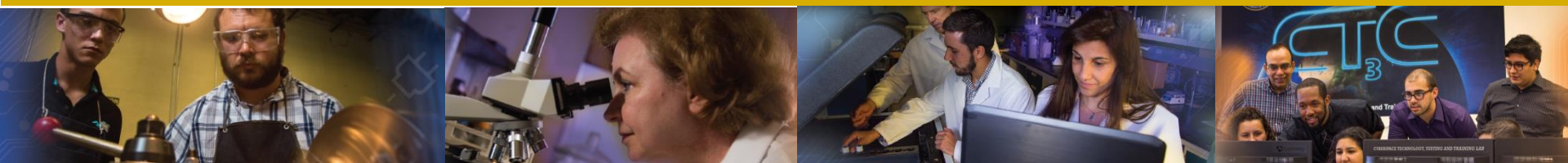
DOE Fellow

DOE-FIU Science and Technology Workforce Development Program

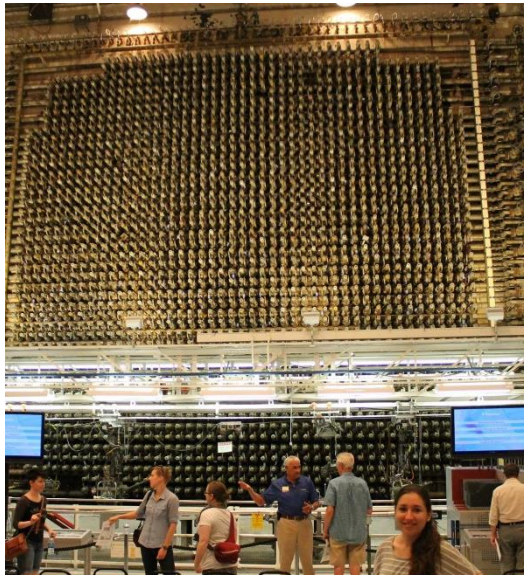
Applied Research Center

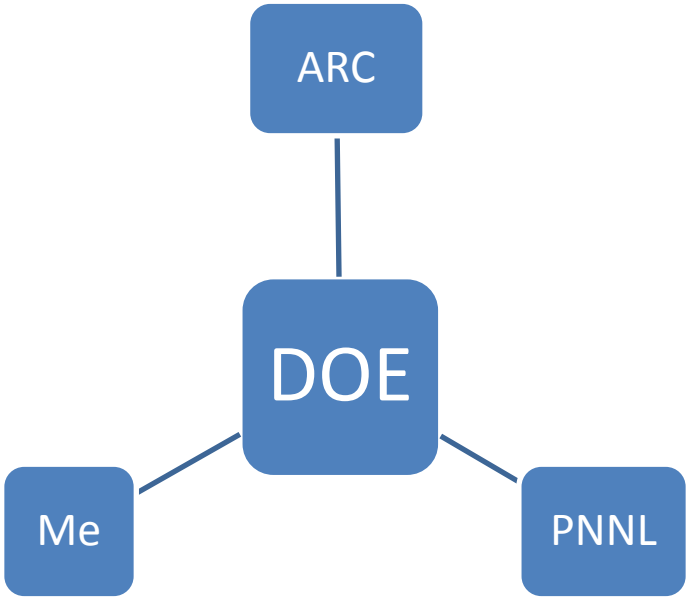
Florida International University

FLORIDA INTERNATIONAL UNIVERSITY



Collaboration
FIU-ARC + PNNL = DOE-EM





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Graduate Student
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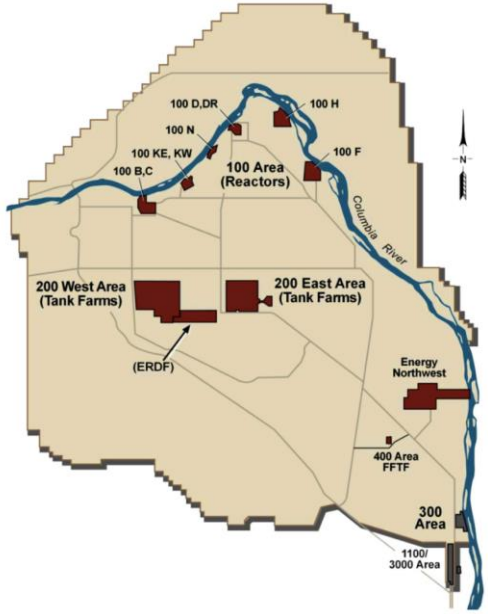
Environmental Track
(photo at *B-reactor* Hanford Site)

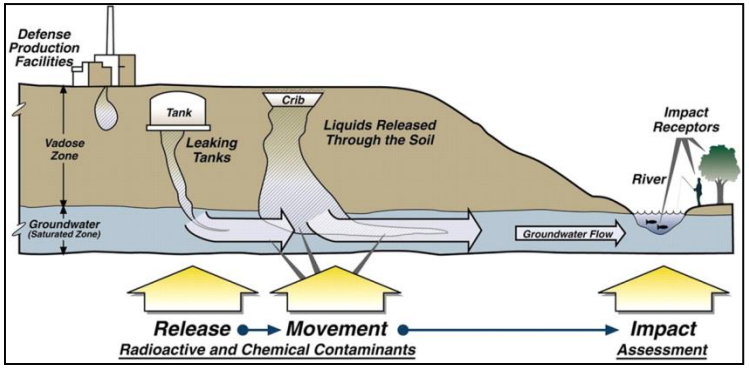
FIU mentors:
Dr. Hilary P. Emerson
Dr. Yelena Katsenovich
PNNL mentors:
Drs. Jim Szecsody
Nik Qafoku

Project Description/Background

- During World War II and the Cold War, the key natural material for the Manhattan project was U
- Used as fuel for the reactors, >200,000 kg of U have been released
- Deep vadose zone (up to 255 ft)
- Contamination measured down to 170 ft
- Oxidizing conditions, pH ~ 8, play a big role



200 Area Hanford Site, Washington State

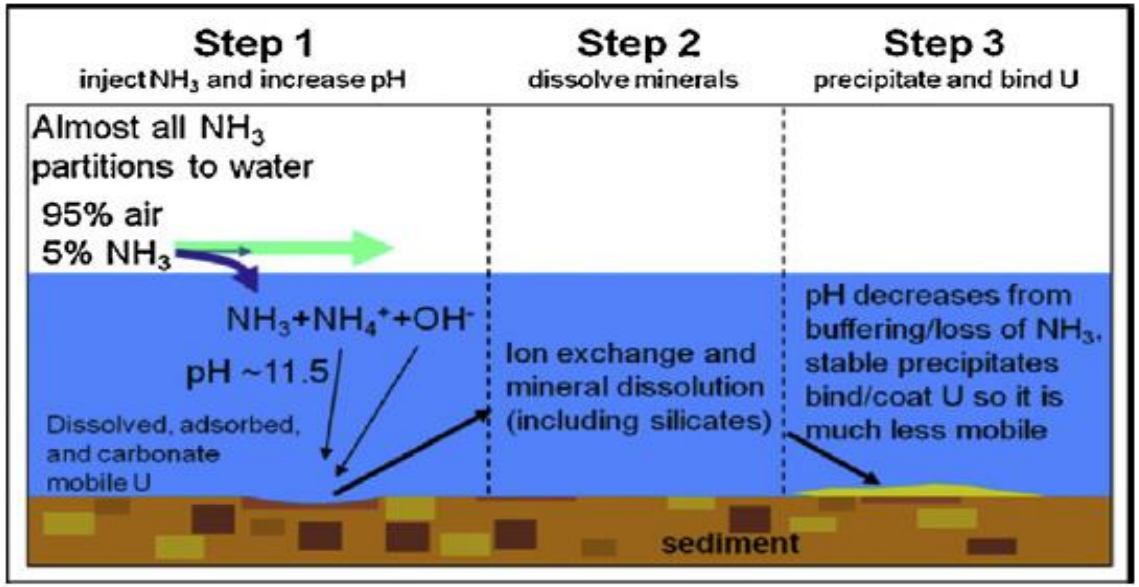


Waste discharges to the Hanford Site vadose zone (Gee *et. al*., 2007)

Remediation Process Summary

- Step 1: gas-liquid equilibrium as NH_3 partitions
- Step 2: alkaline pH allows for aluminosilicate mineral dissolution
- Step 3: precipitation occurs as pH returns to ~ 7 - 8

Two main processes: **adsorption** (complexation with mineral surfaces) and **co-precipitation** (formation of U-containing mineral phases)



(Zhong *et al.*, 2015)

Objective

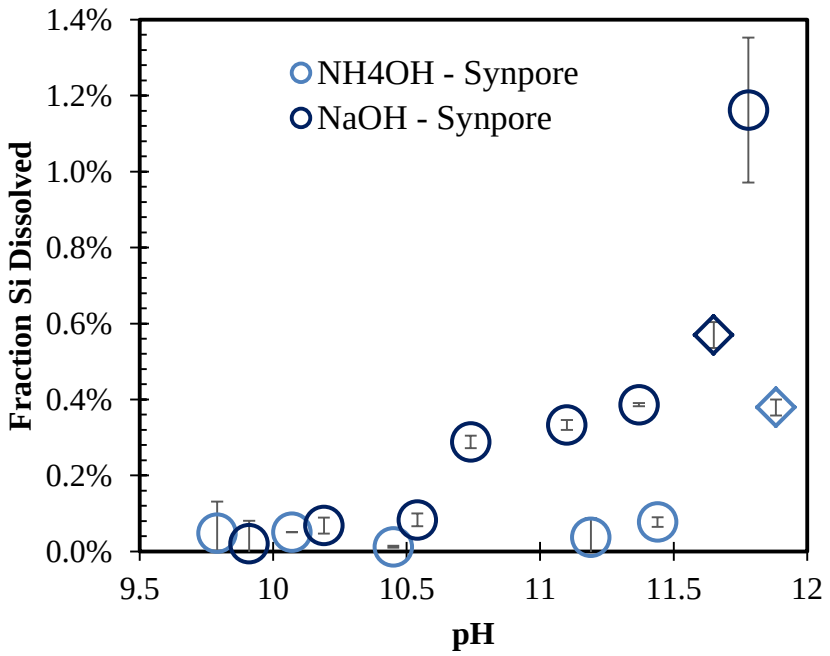
To understand the mechanisms leading
to immobilization of uranium during remediation
(upon injection of NH_3 gas)

Specific aims:

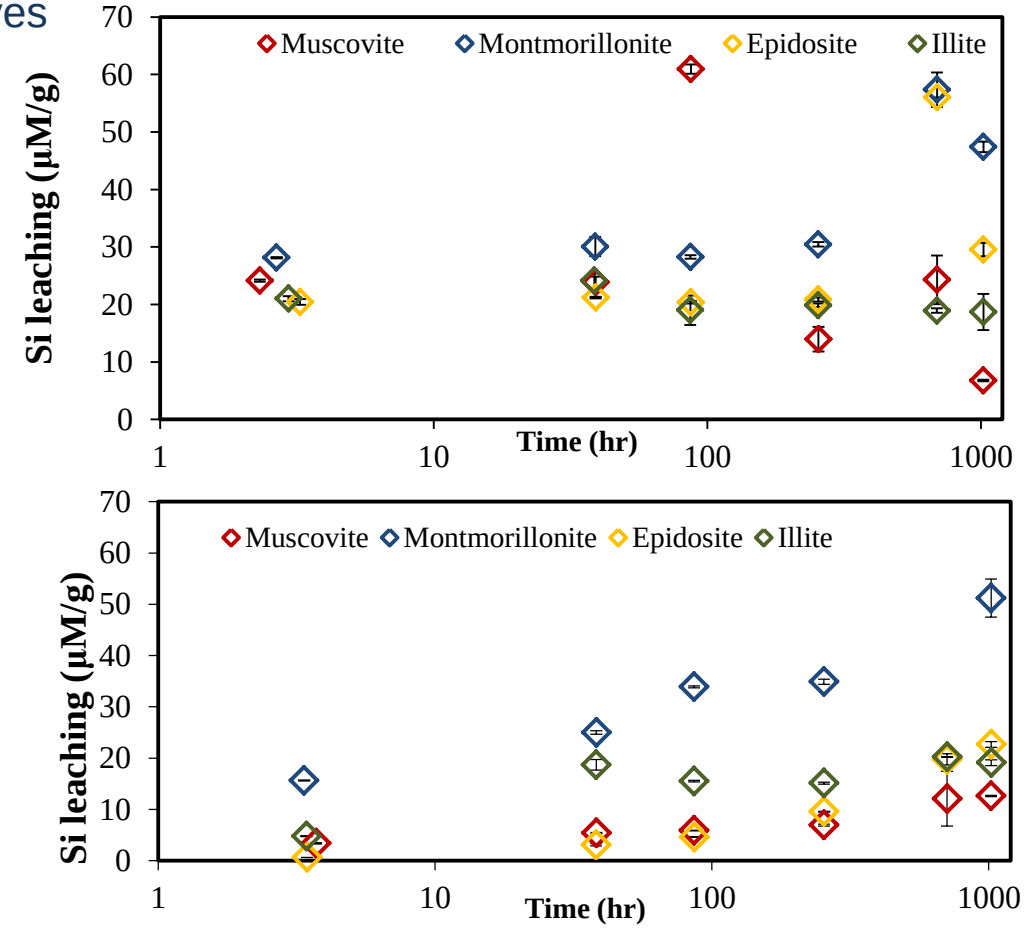
1. Quantify mineral dissolution kinetics
2. Investigate aqueous speciation and U partitioning
3. Characterize solid phases in terms of U speciation and mineralogy changes

Preliminary Results

- Aim 1: pH between 10.5 and 11.0 base treatment differs → amorphous Si dissolves to form soluble silicate



- different mechanisms NaOH vs NH_4OH



Preliminary Results Cont'd

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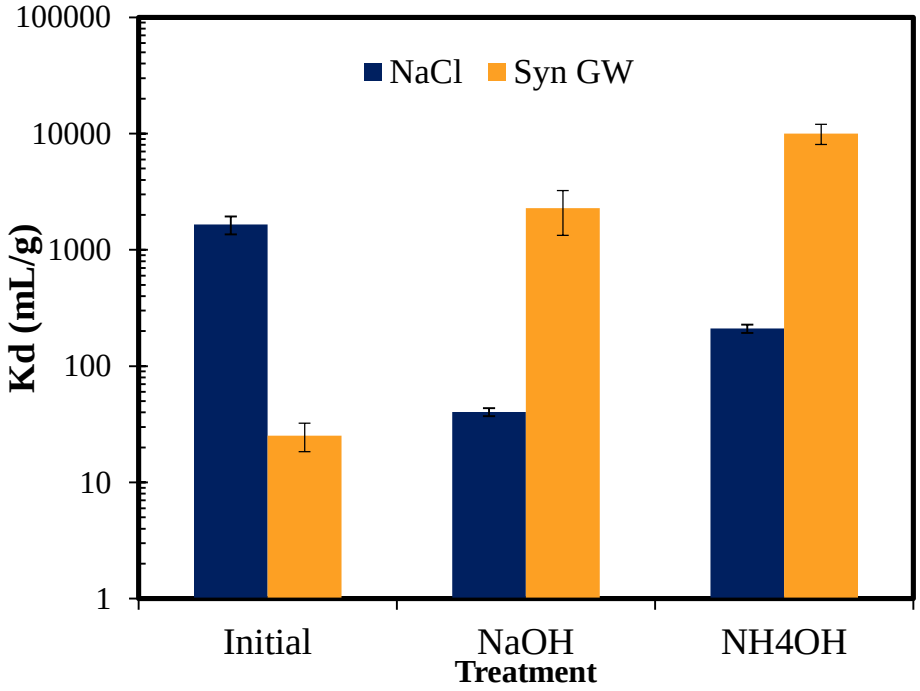
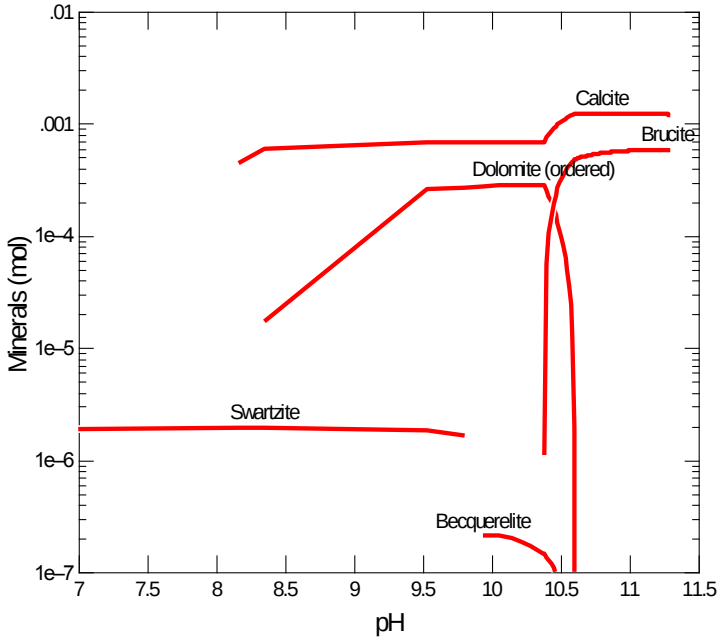
- Aim 2: Removal of U ↑ at elevated pH in synthetic GW → likely due in part to co-precipitation of U with carbonate phases and Becquerelite [$Ca(UO_2)_6O_4(OH)_6$] precipitation





$[SiO_2(aqu)]$ = $1x10^{-4}$ to $2.7x10^{-3}$ M
Note: GWB calculations are for systems in equilibrium

Conclusions

- Aim 1:
  - NaOH and NH_4OH significantly increase mineral dissolution/precipitation
    - » Both in FIU-ARC batch experiments and PNNL internship (different mechanisms: steady-state for NH_4OH, continued leaching for NaOH)
  - Incongruent dissolution (non-stoichiometric ratio) trend
  - Calcium: potential secondary minerals forming
- Aim 2:
  - Significant differences between NaCl and SGW due behavior of U-carbonate complexes
  - Observed point where U precipitation begins in SGW
- Aim 3:
  - Future work

Accomplishments

- **Presentations**
  - "Effects of Ammonia and Variable Redox Conditions on Mineral Dissolution." ***American Chemical Society****, April 1-6, 2017, San Francisco, CA*
  - "Ammonia gas Treatment for Uranium Immobilization at DOE Hanford Site." ***Waste Management Conference****, March 5-9, 2017, Phoenix, AZ*
- **Posters**
  - "Uranium Remediation via Base Treatment" at the ***Life Sciences South Florida @ eMerge Americas Technology Conference****,June 12th, 2017, Miami Beach, FL*
  - "Subsurface Uranium Remediation via Base Treatment." ***March For Science Miami Expo****, April 22, 2017, Miami, FL*
  - "Fate of U and Mineral Dissolution upon Treatment with NaOH or NH_4OH" ***Waste Management Conference****, March 5-9, 2017, Phoenix, AZ*
- **Papers**
  - Emerson, H. P., Di Pietro, S., Katsenovich, Y., and Szecsody, J. (2016). "Effects of Ammonia on Uranium Partitioning and Kaolinite Mineral Dissolution." *Journal of Environmental Radioactivity*, 167, 150-159 (peer-reviewed)
  - Emerson, H.P., Di Pietro, S., Katsenovich, Y., and Lagos, L.E. (2016) "Effects of Ammonia on Uranium Partitioning and Kaolinite Mineral Dissolution." FIU-ARC-2016-800006471-04c-246 (Non peer-reviewed)
  - Di Pietro, S., Emerson, H.P., Katsenovich**,** Y. (2017) "Ammonia Gas Treatment for Uranium Immobilization at US DOE Hanford Site" *Waste Management Conference Proceedings (*Non peer-reviewed)
- **Internship 2016**
  - Completed summer internship at PNNL, currently working on peer-reviewed paper for publication
- **FIU Department of Chemistry *en route* to Ph.D. candidacy**
  - Research Proposal
  - Cumulative Exams
  - Original Proposal
  - Classes (two remaining)

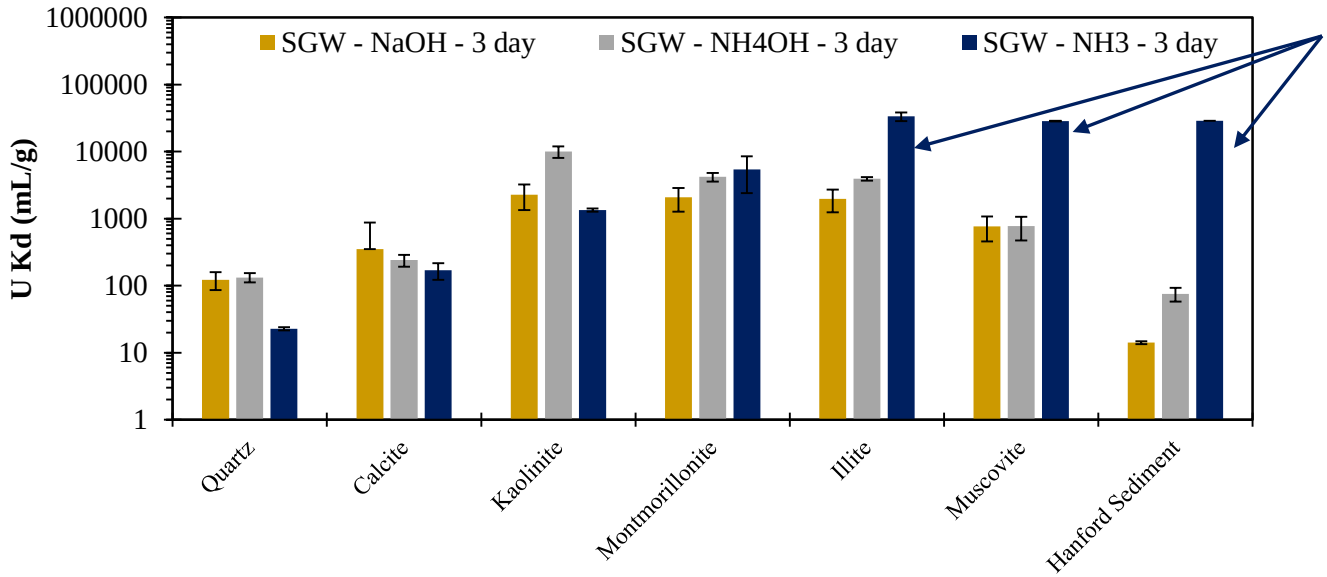
Future Work

To understand impacts of base treatment on:

- Physical and mineralogical changes due to dissolution and precipitation
- Speciation of U in the solid phase due to sorption and co-precipitation

To be accomplished via:

- Characterization of mineralogy via XRD and TEM, Surface area and morphology via BET and SEM, Analysis of U per EMPA, HRTEM, and SEM-EDS
- Predictive Geochemist WorkBench® Speciation modeling



Note: the focus will be on understanding *muscovite* and *illite* behavior with U as they are similar to Hanford sediment in the experiments for NH_3 gas treatment

Acknowledgements

- **FIU ARC Mentors**
  - Dr. Hilary P. Emerson
  - Dr. Yelena Katsenovich

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