DOE-EM Cooperative Agreement
FIU Year 5 Research Review

Presented: March 31 - April 3, 2015
to the U.S. Department of Energy
Dr. Leonel Lagos, PhD, PMP® (Principal Investigator)

FLORIDA INTERNATIONAL UNIVERSITY

FIU-DOE Research Review

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Tues, March 31	Wed, April 1	Thurs, April 2	Fri, April 3
10:00 AM - 12:00 PM *Presentation- Env. Remediation Technologies (FIU Project 3)* Discussion of research area in support of EM	**10:00 AM - 12:00PM** *Presentation- Workforce Development and Training (FIU Project 5)* Discussion of research area in support of EM	**1:00 - 3:00 PM** *Presentation- High Level Waste/Waste Processing Research (FIU Project 1)* Discussion of research area in support of EM	**10:00 AM - 12:00 PM** *Wrap-up - Discussion of DOE-FIU Cooperative Agreement*
1:00 - 3:00 PM *Presentation- Env. Remediation Technologies (FIU Project 2)* Discussion of research area in support of EM	**1:00 - 3:00 PM** *Presentation- D&D and Env. Mgmt IT Research (FIU Project 4)* Discussion of research area in support of EM		

Project 2: Rapid Deployment of Engineered Solutions to Environmental Problems

Presenters: Dr. Yelena Katsenovich, Research Scientist
Dr. Ravi Gudavalli, Post Doctorate Fellow
Dr. Vasileios Anagnostopoulos, Post Doctorate Fellow

Florida International University

Project Staff and Students

FIU Applied Research Center

Project Manager:	**Leonel Lagos, Ph.D., PMP®**
Faculty/Staff:	**Dr. Yelena Katsenovich** **Dr. Ravi Gudavalli** **Dr. Vasileios Anagnostopoulos**
Students/DOE Fellows:	**Claudia Cardona** **Hansell Gonzalez** **Robert Lapierre** **Sandra Herrera** **Aref Shehadeh** **Christian Pino** **Christine Wipfli** **Kiara Pazan**

Project Clients and Collaborators

PNNL Collaborators:	Dr. Dawn Wellman Dr. Jim Szecsody Dr. Nik Qafoku Dr. Hope Lee, Brady Lee, Sabrina Saurey
SRS Collaborators:	Dr. Miles Denham Dr. Brian Looney

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Project Description

Project supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of the uranium stabilization process through pH manipulation using NH_3 gas injection and the U.S. Department of Energy's Savannah River Site in remediating uranium in F/H area seepage basins.

Project Description

- Task 1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH3 Gas
  - **Subtask 1.1**: *Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH3 Gas*
    - **Carryover scope**: Testing different standards such as calcium chloride and lithium chloride to get better deliquescence predictions on U-free samples at low water activities values.
    - Evaluate the stability of the U-bearing precipitates created in the soil as a result of ammonia gas remedial actions. This information would help to accurately predict the mobility of U(VI) in the post-treated vadose zone soil.

Project Description

- **Subtask 1.2**: *Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions*
  - Investigate bacteria-U(VI) interactions under anaerobic conditions and study the potential role of bicarbonate to influence U(VI) biorelease by *Shewanella oneidensis* MR-1 from autunite minerals.
- **Task 2**: Remediation Research and Technical Support for Savannah River Site
  - **Carryover scope**: Explore the effect of the higher HA concentrations up to 50 ppm and study if there are any synergistic interactions between U(VI) ions, humic acid and silica on the U(VI) removal.

Project Description

- **Subtask 2.1**: *FIU's support for groundwater remediation at SRS F/H Area*
  - Investigate whether a base solution of dissolved sodium silicate can replace the carbonate base to restore the pH of the treatment zone;
- Subtask 2.2: *Monitoring of U(VI) bioreduction after ARCADIS demonstration at F-Area*
  - Determine whether forms of reduced iron such as siderite and pyrite would arise in the reducing zone after molasses and sulfate addition and if any mineralogical changes occurred in sediments.
- Subtask 2.3: *The sorption properties of the humate injected into the subsurface system.*
  - Conduct batch sorption experiments to understand the HA sorption versus pH to correlate results with HA injection tests

Project Description

- Task 3: Evaluation of ammonia fate and biological contributions during and after ammonia injection for uranium treatment
  - Subtask 3.1: *Investigation on NH3 partitioning in bicarbonate-bearing media.*
    - Investigate NH_3 partitioning in the bicarbonate-bearing solutions at different pH and temperature conditions
  - Subtask 3.2: *Bacteria community transformations before and after NH3 additions.*
    - Investigate the bacteria community transformation in soil before and after ammonia addition.

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Project 2
Accomplishments

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Project-Wide Major Accomplishments

- Waste Management Symposium 2015
  - **5 DOE Fellows and 1 Grad student** prepared posters based on the research conducted under this project for the WM student poster competition
  - **Christine Wipfli (DOE Fellow)** won first prize for student poster
  - DOE Fellow **Hansell Gonzalez**, a PhD student, gave an oral presentation titled, “The Influence of Humic Acid and Colloidal Silica on the Sorption of U(VI) onto SRS Sediments Collected from the F/H Area”
  - **Robert Lapierre** (M.S. Chemistry) DOE Fellow student, was awarded with the Roy G. Post Foundation Scholarship

Project-Wide Major Accomplishments

- Two manuscripts were accepted for publications in the peer-review journals
  - Sepulveda-Medina P , Katsenovich Y, Wellman D, Lagos L. *The Effect of Bicarbonate on the Microbial Dissolution of Autunite Mineral in the Presence of Gram-Positive Bacteria*- Environmental Radioactivity Journal (*in press*)
  - Sepulveda-Medina P, Katsenovich Y, Musaramthota V , Lee M , Lee B, Dua R, Lagos L. *The Effect of Uranium on the Bacterial Viability and Cell Surface Morphology Using Atomic Force Microscopy in the Presence of Bicarbonate Ions* - Research in Microbiology (*in press*)

Project-Wide Major Accomplishments

Milestone No.	Milestone Description	Completion Criteria	Due Date
2014-P2-M1	Completion of solubility measurements of U(VI)-free samples; and Completion of solubility measurements using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope).	E-mail notification to DOE	1/30/15
2014-P2-M2	Completion of literature review on physical mechanisms associated with the fate of ammonia after injections into subsurface	E-mail notification to DOE	10/31/14
2014-P2-M3	Completion of samples preparation using the reduced amount of silica (50mM)	E-mail notification to DOE	11/7/2014
2014-P2-M4	Complete preparation of a draft manuscript on the removal of uranium via ammonia gas injection method.	E-mail notification to DOE	12/15/2014
2014-P2-M5	Obtain anaerobic facultative microorganisms, Shewanella sp., from PNNL and complete preparations to set up autunite leaching experiments.	E-mail notification to DOE	10/3/2014
2014-P2-M6	Complete preparations for the microcosm experiments prepared with SRS sediments using sulfate additions.	E-mail notification to DOE	9/12/2014

Project-Wide
Major Accomplishments

Client Deliverables	Responsibility	Acceptance Criteria	Due Date
Draft Project Technical Plan	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	6/18/2014- Completed
Subtask 1.1 Prepare a progress report on the solubility measurements via isopiestic method.	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	2/16/2015- Completed
Subtask 2.1.Progress report on batch experiments prepared with SRS sediments, colloidal Si and higher HA concentration up to 50ppm (carryover scope).	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	3/30/2015
Subtask 2.2 Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	1/30/2015- Completed
Monthly Progress Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Monthly
Quarterly Progress Reports	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Quarterly
Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Mid-Year Review)	Project Manager	Presentation to DOE HQ and Site POCs	3/31/2015

Subtask 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH3 Gas

Solubility Measurements of Multicomponent Solids via Isopiestic Method

Claudia Cardona, DOE Fellow
Civil and Environmental Engineer, Ph.D. Candidate

Florida International University

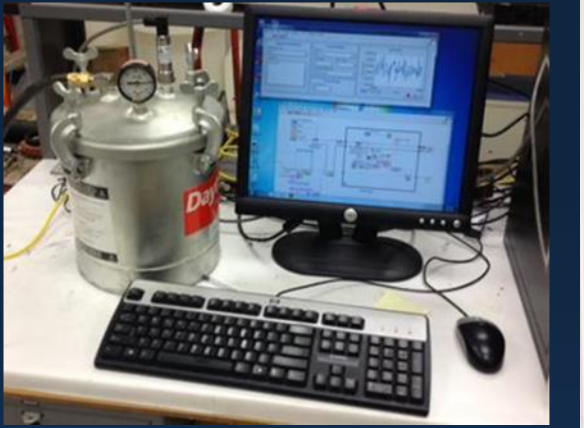
Project Description

- Evaluate the solubility of uranium-bearing precipitates using the isopiestic method.
- Investigate deliquescence behavior of synthetic multicomponent precipitates combined from major pore water constituents after NH_3 injection in the VZ.

Experimental Procedures

- Standards and samples were dried at 40ºC for at least for 24 hours and weighed using high precision balance ($1*10^{-5}$ g).
- Samples were placed in the isopiestic chamber and equilibrated with a standard solution at 25ºC.
- Lithium Chlorine (LiCl) and calcium chlorine ($CaCl_2$) were used as standards.
- Equilibrium was determined by reweighing samples at intervals until a constant a_w obtained.

Isopiestic Method



Isopiestic Vapor-Chamber connected to the acquisition system

Aluminum block with holes for the nickel crucibles

Experiment Calculations

- The osmotic coefficient, Ø, is calculated using molality according to the equation proposed by Guo(2012).
- The Ø and water activities, a_w, for the multicomponent precipitate samples are calculated as follows:

$$\varnothing = \frac{(v * m * \varnothing)standard}{\sum v_i m_i}$$

$$\ln a_w = -v \ * m_i {}^{*}\varnothing_i$$

Where: v is the stoichiometric coefficient m is the molality.

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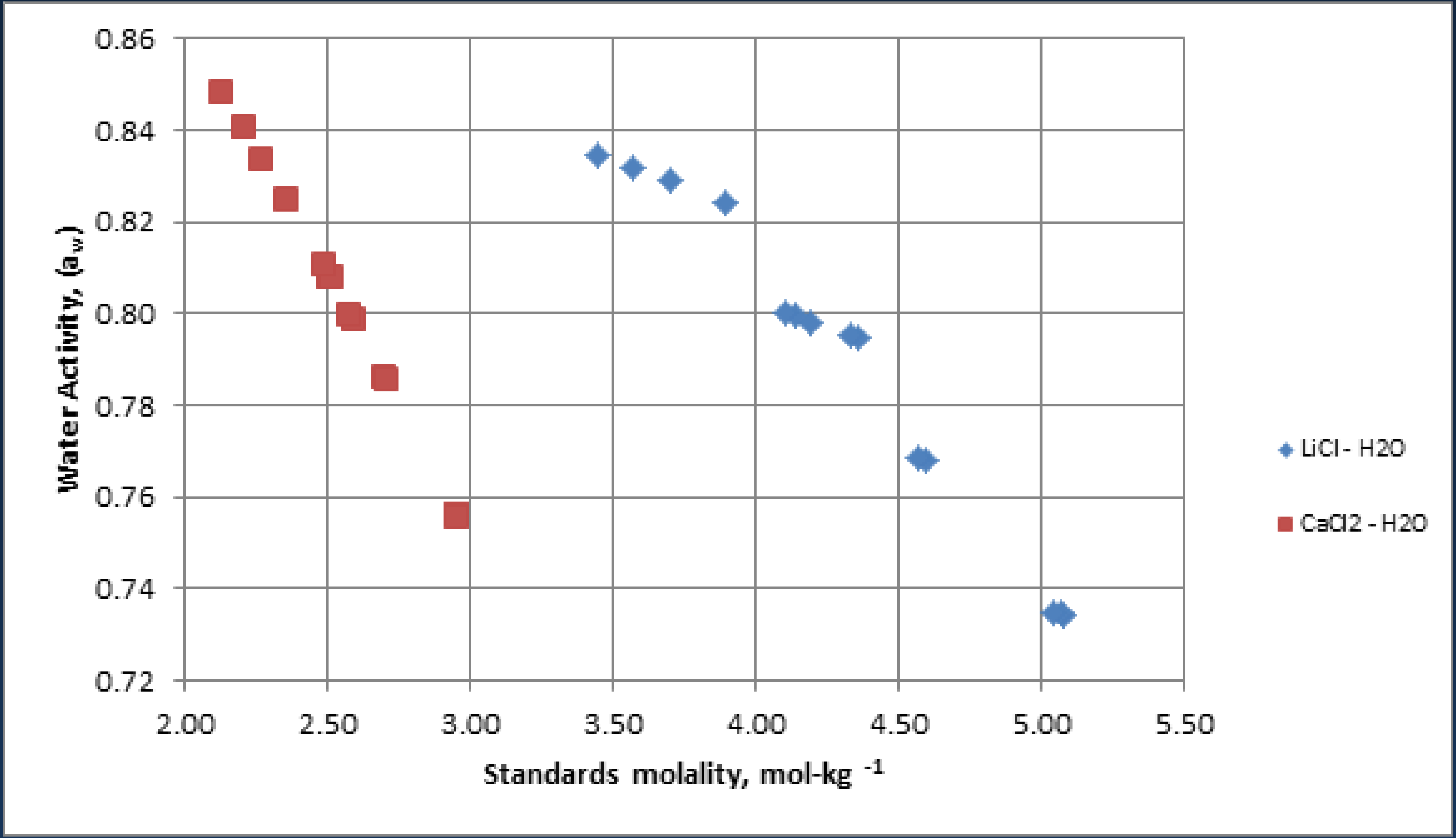
Multicomponent Preparation

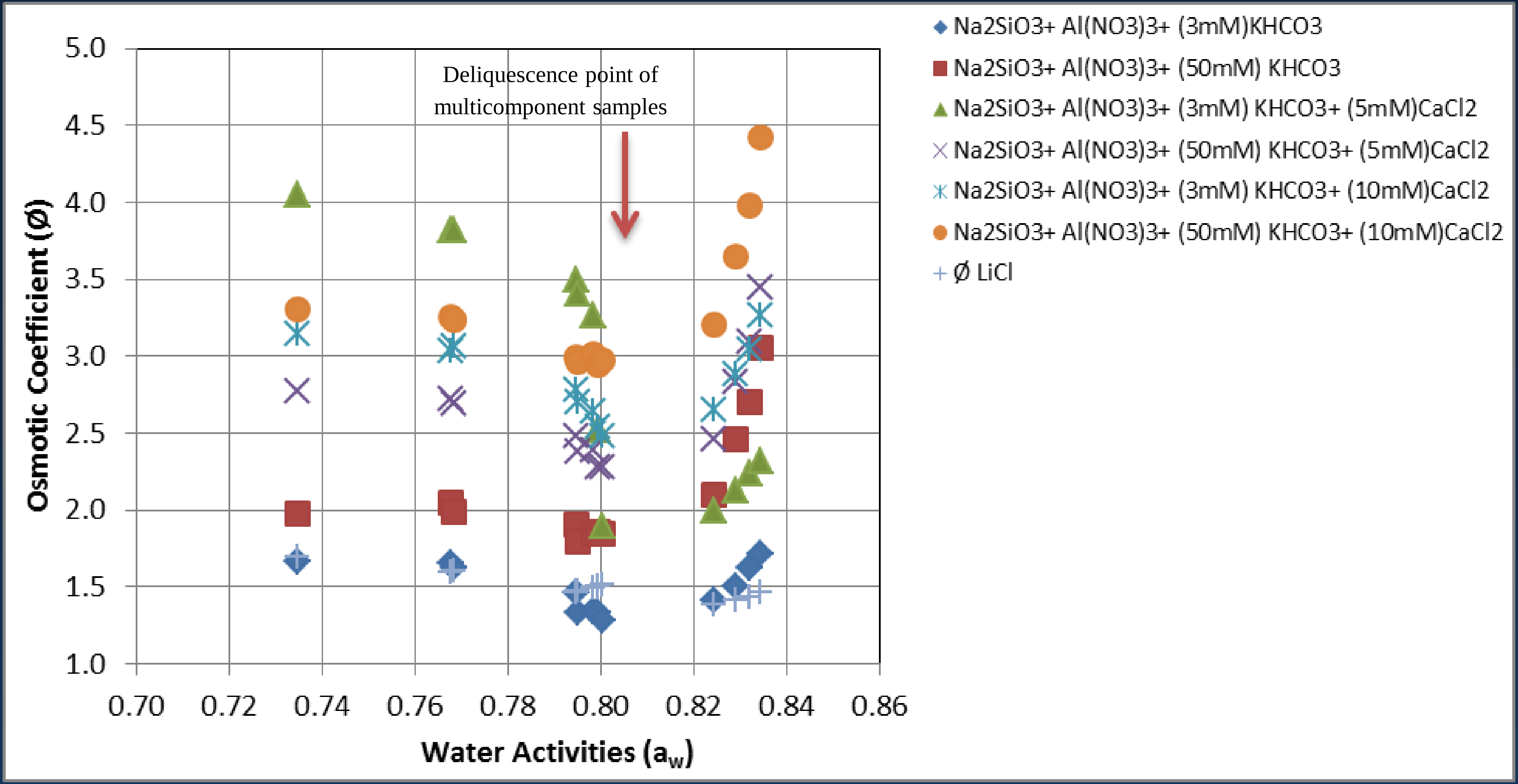
- Multicomponent precipitate samples were combined from Na+, SiO_3^-, Al^+, NO_3^-, K^+, HCO_3^-, Ca^{2+}, and Cl^- ions.
  - Si and Al concentrations of 100 mM and 5 mM, (Si/Al=50)
  - HCO_3^- of 3 mM and 50 mM
  - Ca of 5 mM and 10 mM
  - Uranium (VI) was not included in these samples

Amount of Stock Solution and DIW (uL)				
$Na_2SiO_3 \cdot 9H_2O$ = 2368 and $Al(NO_3)_3 \cdot 9H_2O$ = 1000				
Crucible	**Sample**	**$KHCO_3$**	**$CaCl_2 \cdot 2H_2O$**	**DIW**
7	3 mM $KHCO_3$, no Calcium	75	0	6657
8	50 mM $KHCO_3$, no Calcium	1250	0	5382
9	3 mM $KHCO_3$, 5 mM Calcium	75	20	6537
10	50 mM $KHCO_3$, 5 mM Calcium	1250	20	5362
11	3 mM $KHCO_3$, 10 mM Calcium	75	20	6537
12	50 mM $KHCO_3$, 10 mM Calcium	1250	20	5362

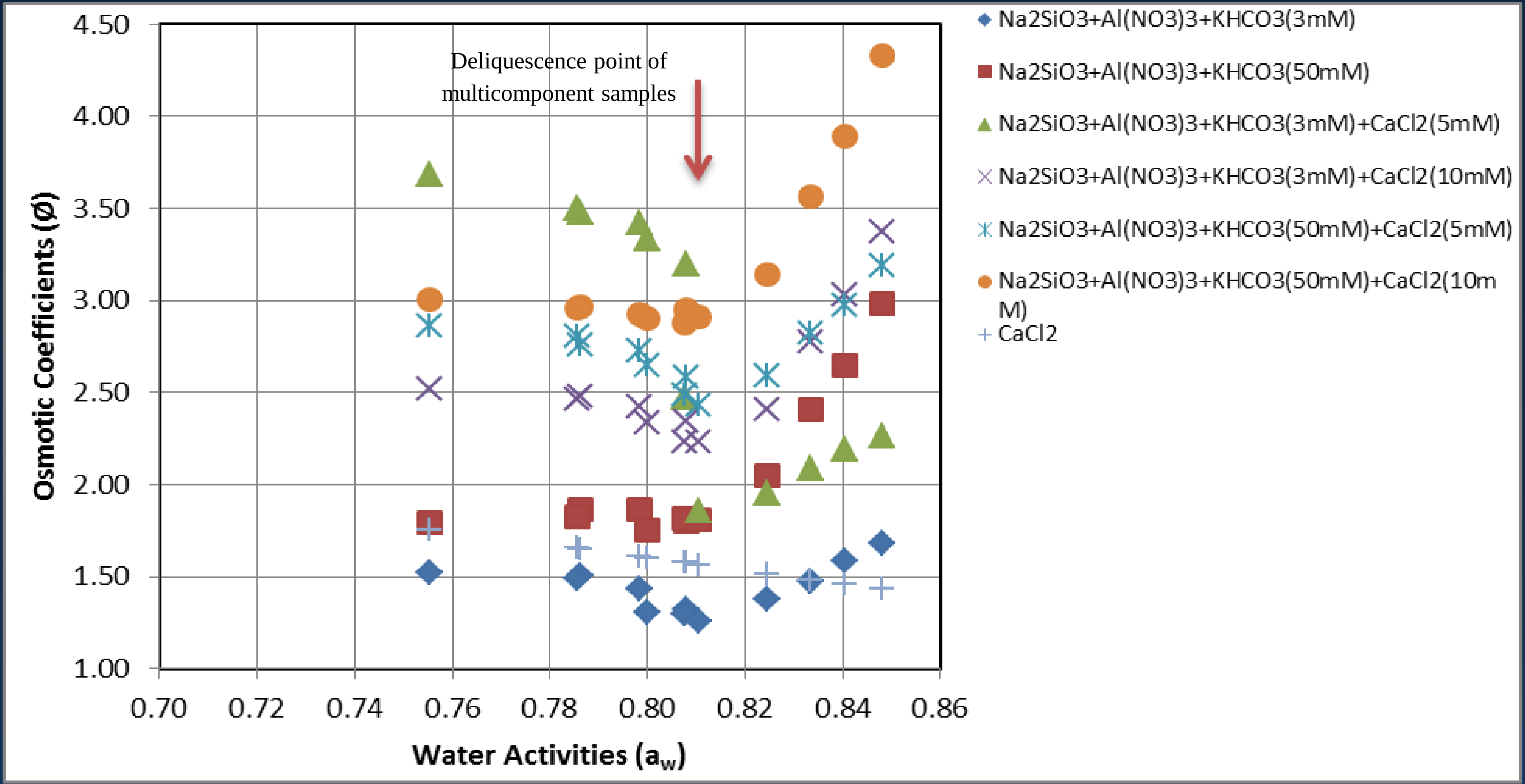
Changes of a_w vs. molality for LiCl and $CaCl_2$ standards



Osmotic coefficient, Ø, for multicomponent samples as a function of a_w using LiCl

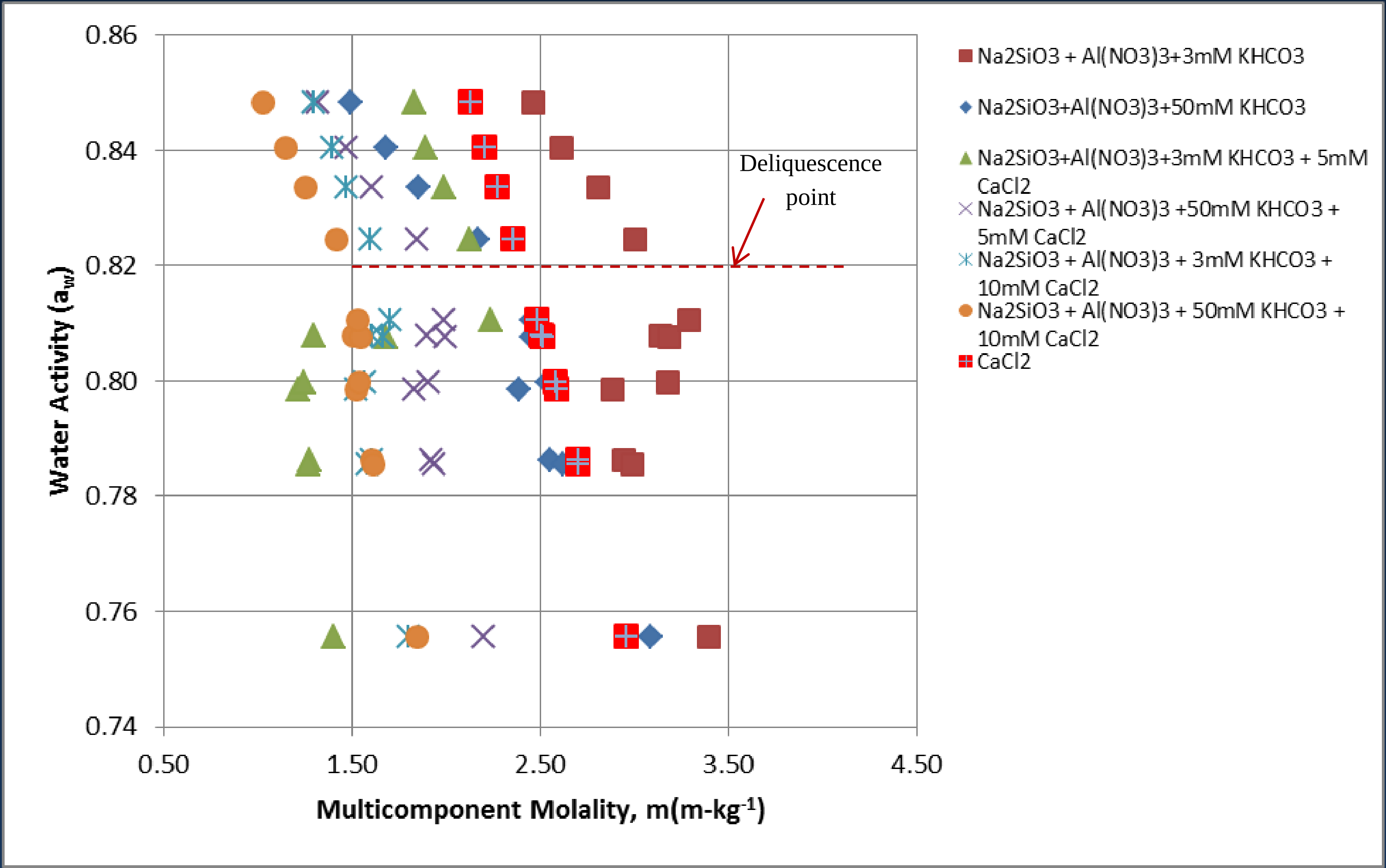


Osmotic coefficient, ø, for multicomponent samples as a function of aw, using $CaCl_2$

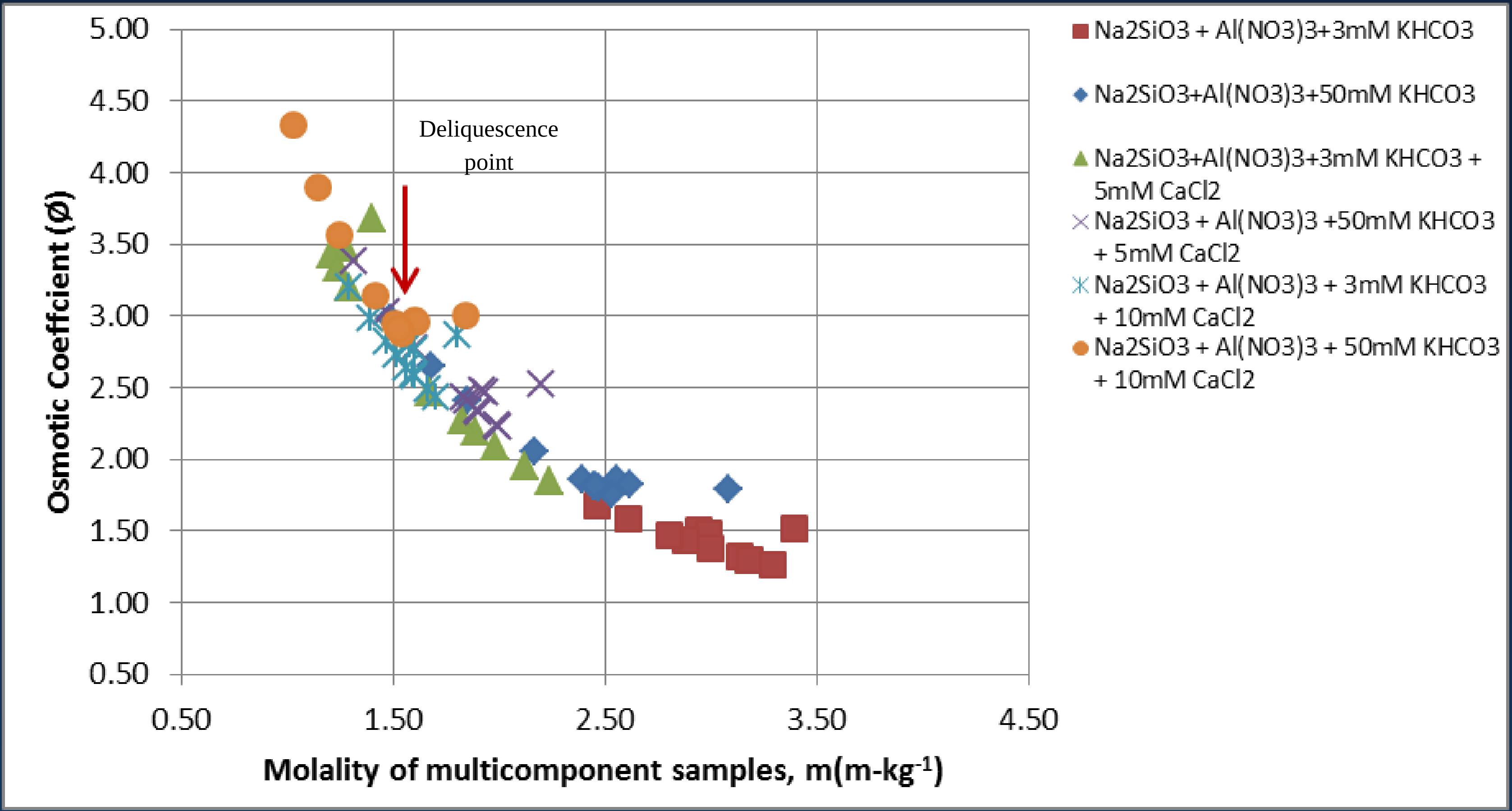


Deliquescence point of multicomponent samples

a_w against molalities for the multicomponent samples using $CaCl_2$

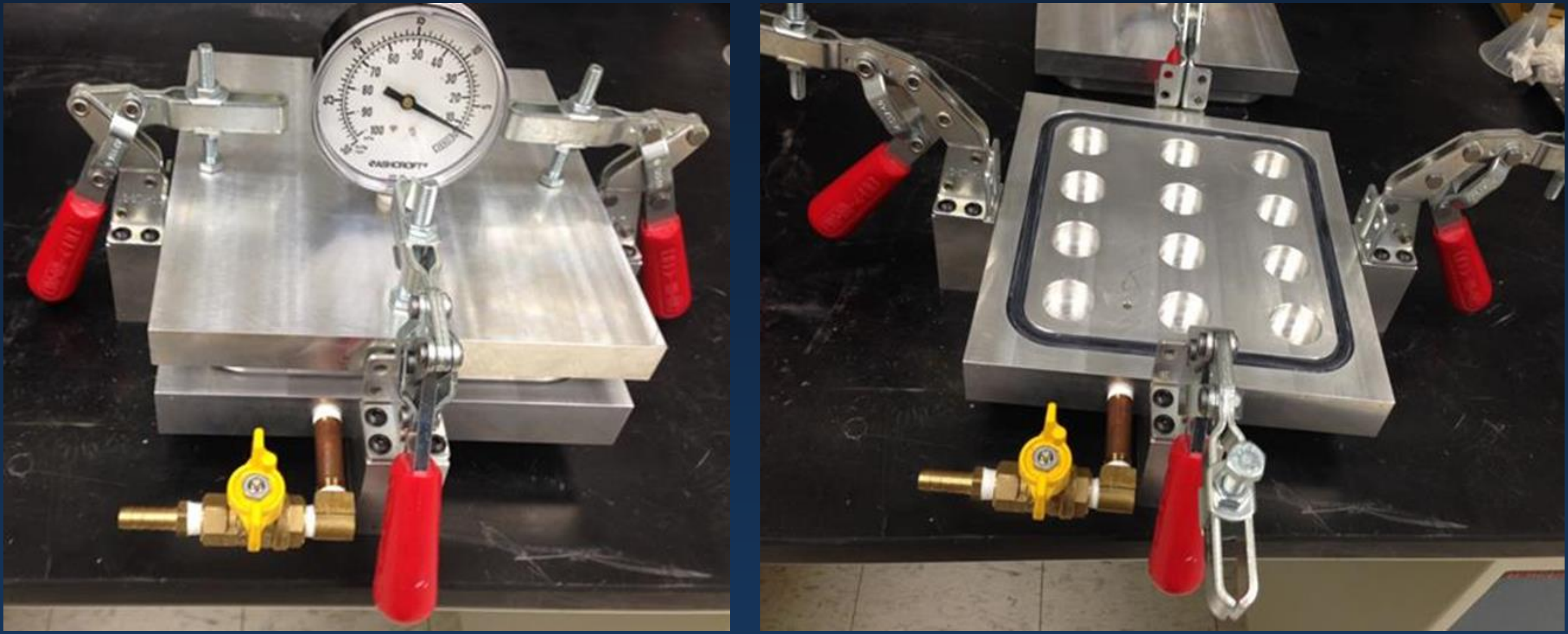


Osmotic coefficient vs. molalities for the multicomponent samples using $CaCl_2$



Future Work

- New set of dry precipitates, composed of Si-Al-Ca-HCO_3 and U(VI)



Task 1.1 Characterization of the Uranium-Bearing Solid Phases Produced by the NH_3 Injection Remediation Method for the Hanford 200 Area Vadose Zone

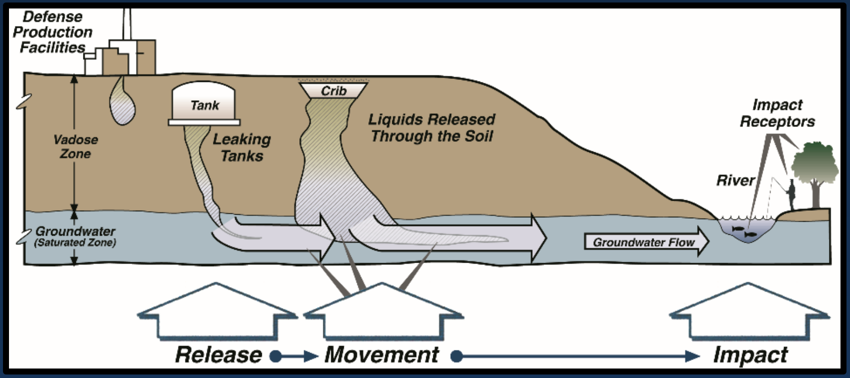
Robert Lapierre
B.S. Chemistry, DOE Fellow
M.S. Chemistry Candidate

Florida International University

Project Description

To sequester the flow of mobile radiological contaminants in the Hanford vadose zone, gas injected remediation amendments have been under investigation

- The NH_3 injection method functions by changing the subsurface porewater chemistry to limit the mobility of uranium species



Research Objectives

- The laboratory scale application of the remediation method using a synthetic porewater system
- The characterization of the uranium-bearing solid phases form using this method
- The evaluation of the roles of major system components in the uranium speciation

Experimental Approach

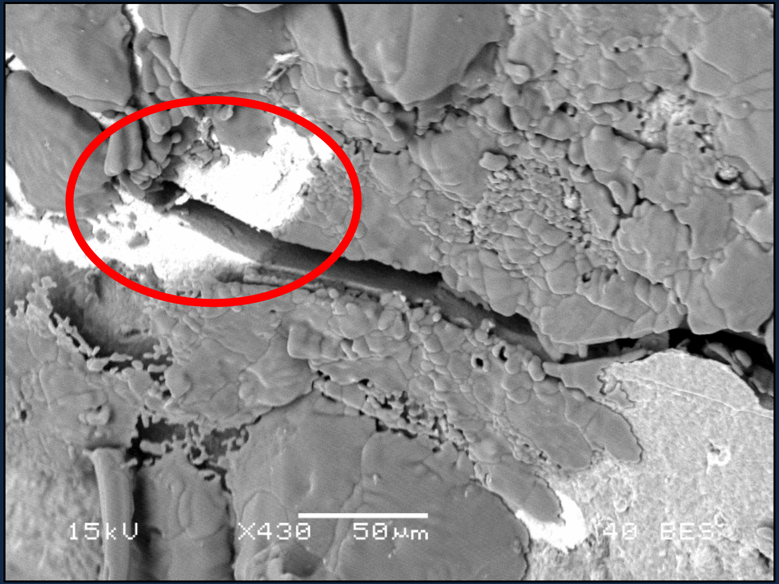
- Samples analyzed using a range of techniques to characterize and identify the solid uranium-bearing phases produced

Analytical Technique	Data
Kinetic Phosphorescence Analyzer (KPA)	• Pre and post-treatment analysis of the supernatant solution for uranium content
Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM w/ EDS)	• Sample morphology • Differentiation of the uranium-rich region (by BEC) • Confirmation of elemental presence by EDS
X-Ray Powder Diffraction (pXRD)	• Solid phase ID by comparison of the diffraction pattern to a library of standards • Confirmation of crystallinity • Interpretation of the molecular structure
Transmission Electron Microscopy (TEM)	• Selective Area Electron Diffraction (SAED) - Diffraction information for selected point rather than bulk sample (as in pXRD)

Experimental Approach

- Geochemical modeling software has been employed to support experimental investigations into the roles of various porewater components
  - Visual Minteq and Geochemist's Workbench equilibrium models

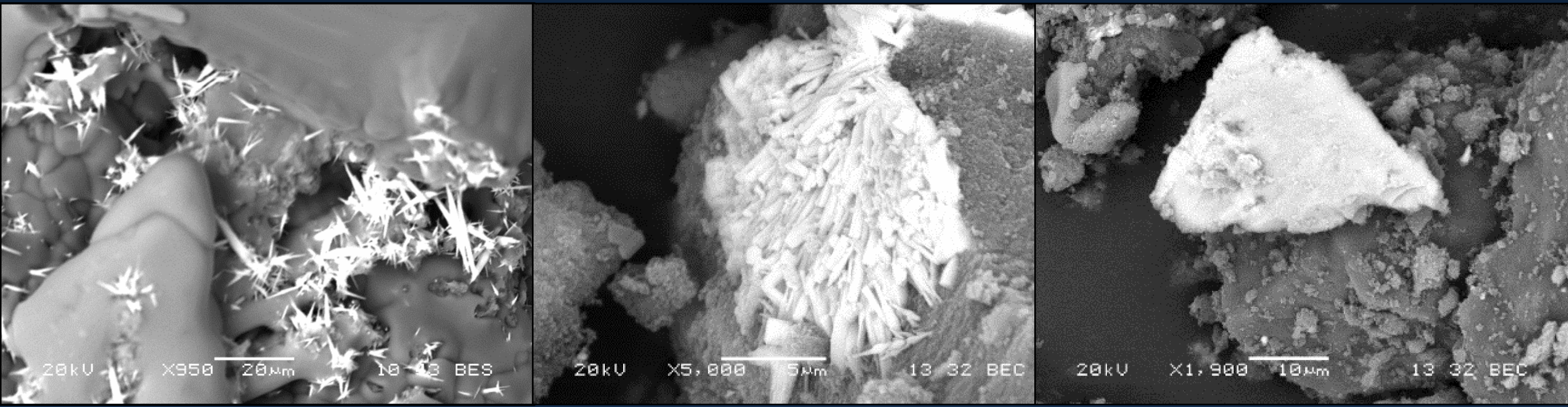
Results - SEM/EDS



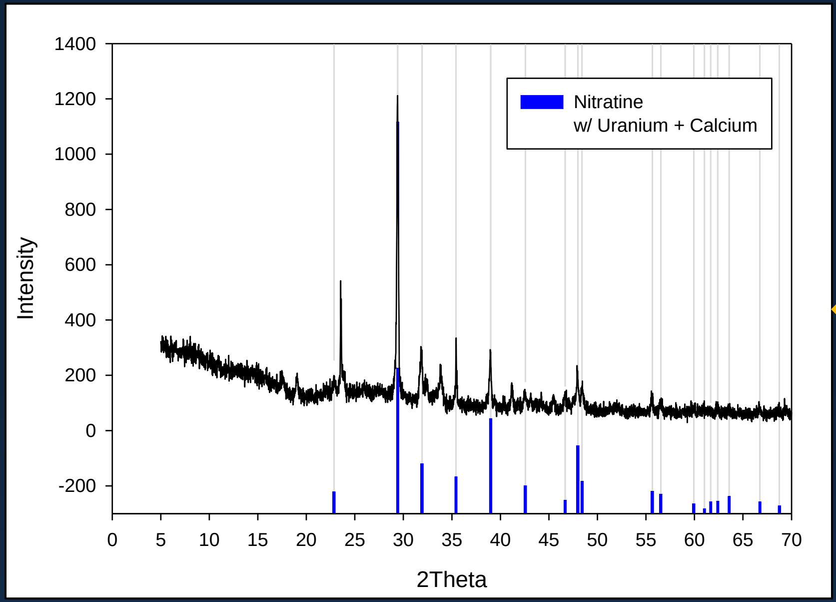
- SEM imaging for early samples showed two regular morphologies for uranium-rich regions
  - Ongoing studies focused primarily on the crystal-like phases (right)

Results - X-ray Diffraction

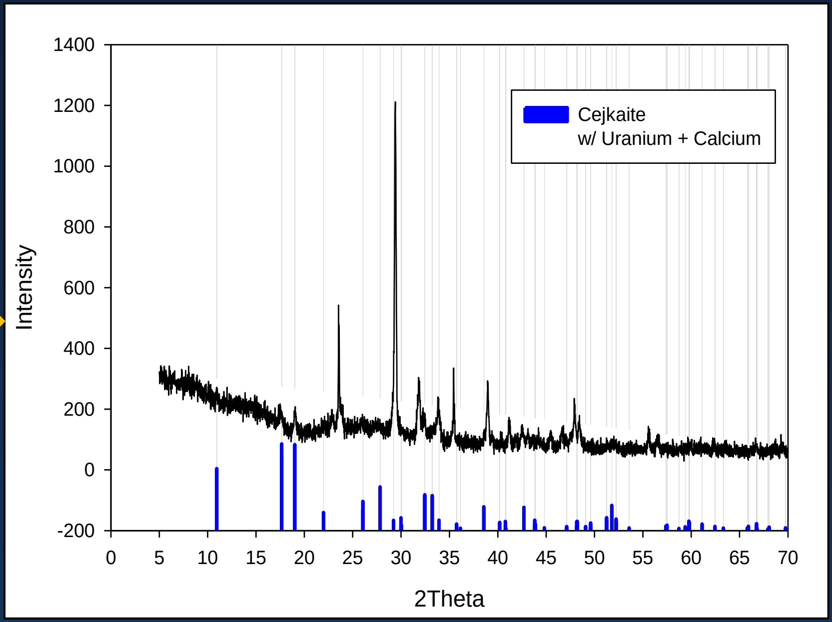
- Select samples were pulverized for XRD analysis
  - Compared to a library of patterns for various minerals



Results - XRD Data

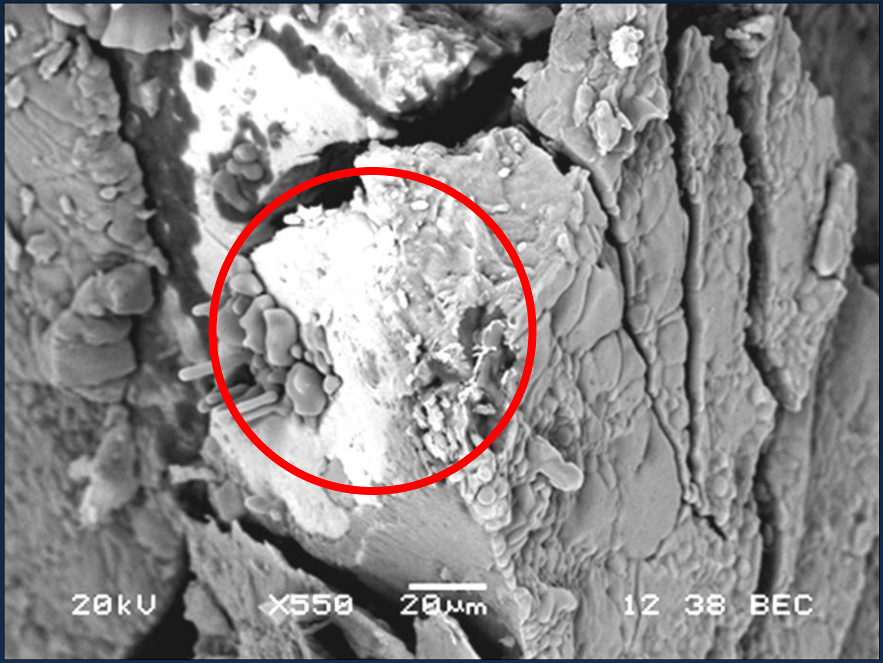


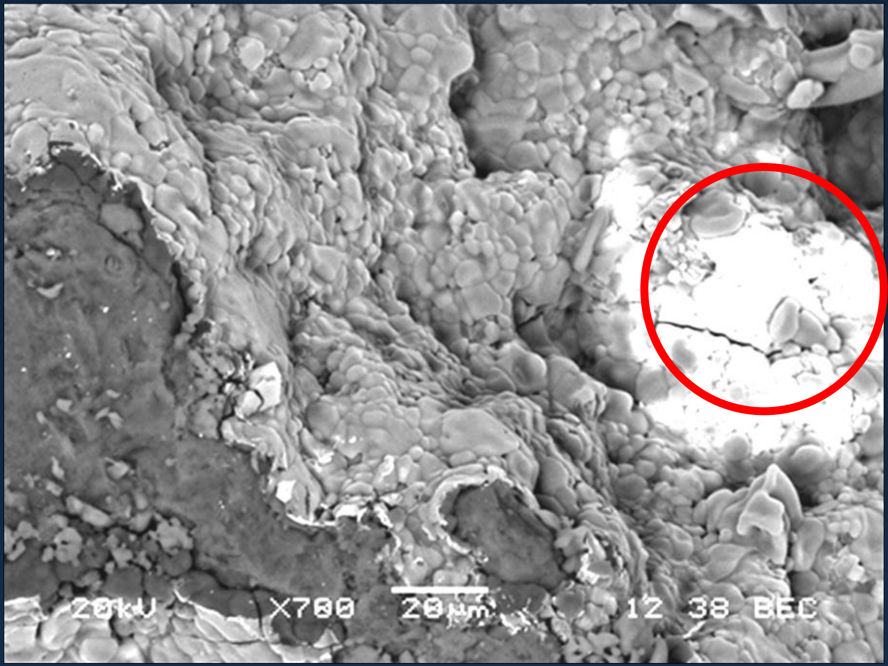
Comparison of XRD patterns for uranium-containing sample (^{w}/ Ca) to the pattern for nitratine ($NaNO_3$)



Comparison of XRD patterns of uranium-containing sample (^{w}/ Ca) to the pattern for cejkaite ($Na_4(UO_2)(CO_3)_3$)

Results – Elevated Uranium Content





- SEM imaging after a drastic increase in uranium content
  - No needle-like crystalline structures seen in prior samples
  - Minimal XRD analysis data

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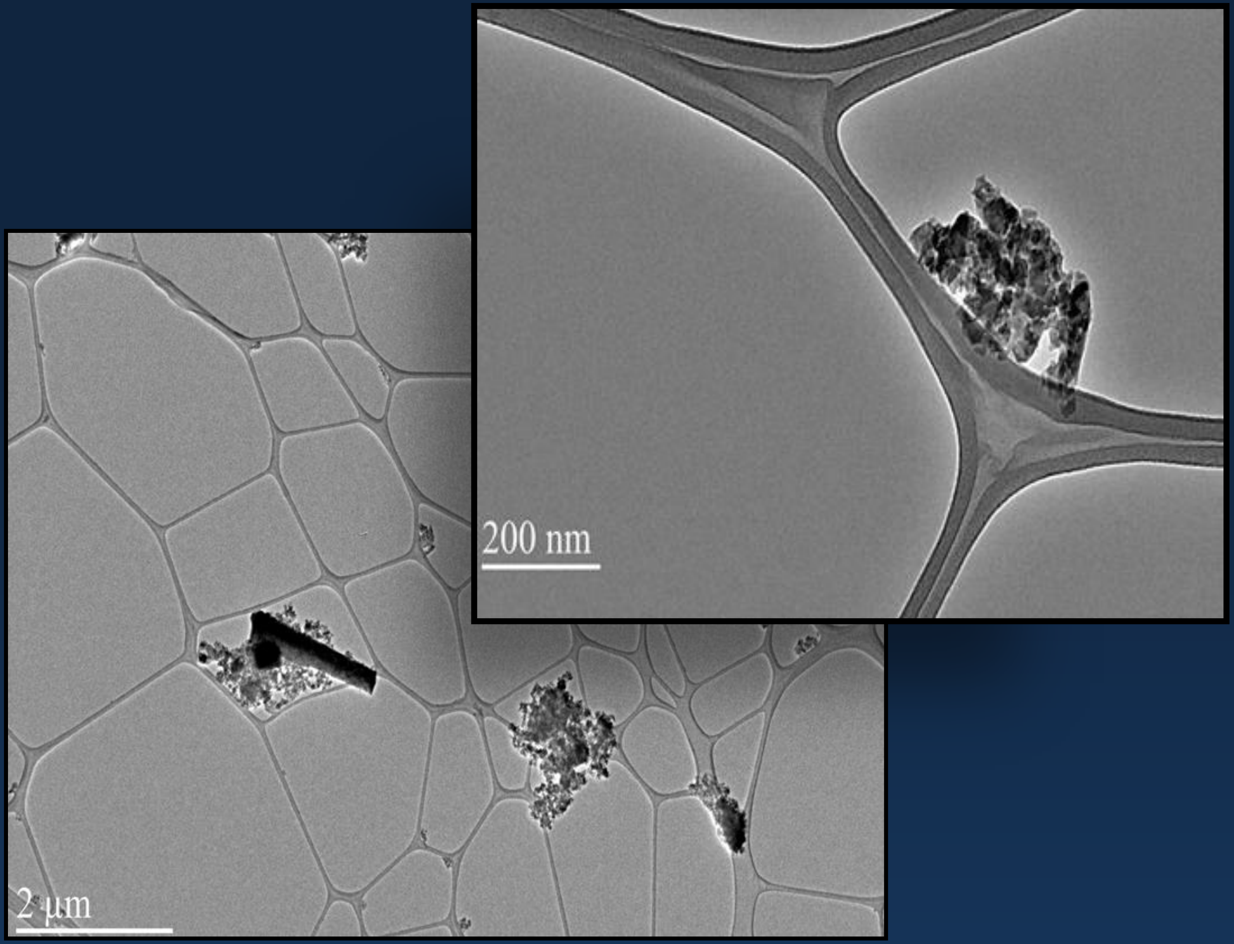
Results - TEM Analysis

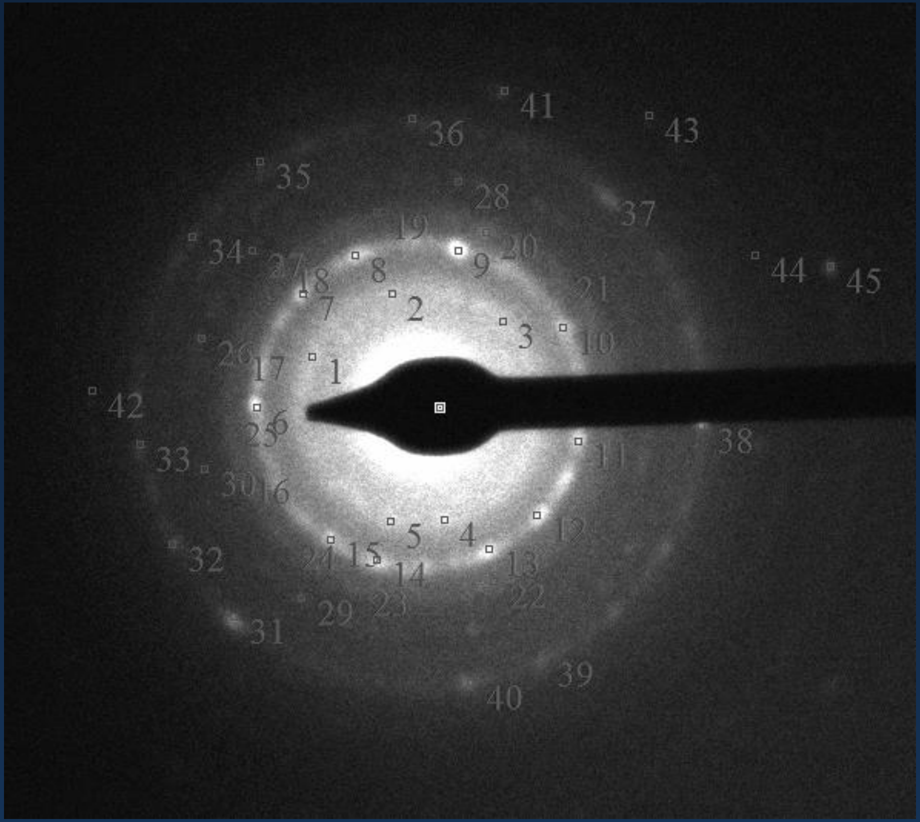
- The 200 ppm U samples with plentiful needle-like structures was selected for TEM
- A short study was performed to determine the best solution for preparing a sample suspension
  - 2 minute extractions
  - KPA analysis
- Suspensions prepared in ethanol

Results - TEM Analysis



Transmission Electron Microscope (TEM) image

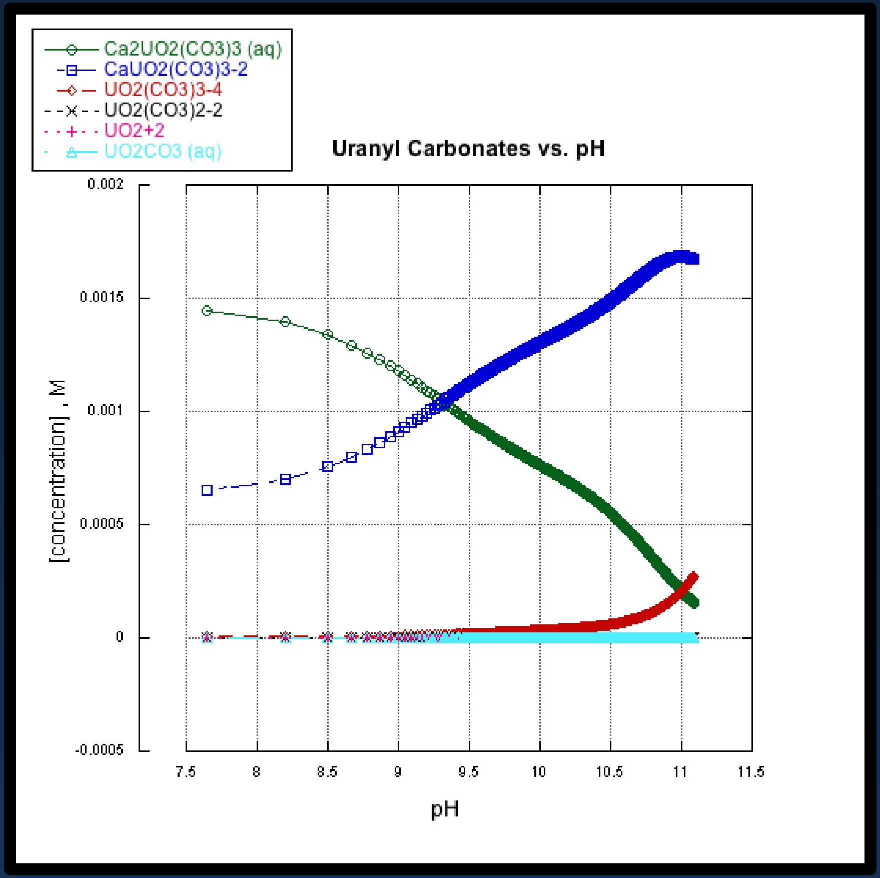
Results - TEM Analysis



TEM diffraction pattern

- Analysis is ongoing
  - Preliminary findings show a clearly polycrystalline pattern
  - Average d-spacings are being compared to those of proposed minerals a diffraction database

Results - Geochemical Modeling



- The understanding of geochemical modeling software is still limited
  - Working to effectively add this capability to support the experimental data

Future Work

- Complete an ongoing optimization study for new sample preparation methods
- Continued sample preparation and analysis with a focus on alternative uranium phases
  - Bicarbonate study
- Expanded geochemical modeling predictions for the system
  - Waiting on updated database
- Proposal for analysis at PNNL's EMSL facility
  - To expand instruments available for analysis chemicals containing radiological components
    - FIB, **TEM w/ EDS**, Scanning TEM, EMPA

Task 1.2

Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions

Sandra Herrera, DOE Fellow
Civil and Environmental Engineer, M.S. Candidate

Florida International University

Task 1.2 - Background

- Remediation of uranium at Hanford Site 300 area via tripolyphosphate injections could sequester uranium (VI) in an insoluble form, creating different types of uranium phosphate minerals like autunite.
- Formed autunite, as a phosphorus-containing mineral, can attract bacteria to liberate phosphorus, meeting their nutrient requirements and causing uranium release back into the environment.
- Factors that influence the dissolution of such minerals come into question.
- Bacteria can play a significant role in the dissolution of minerals and the formation of secondary minerals.

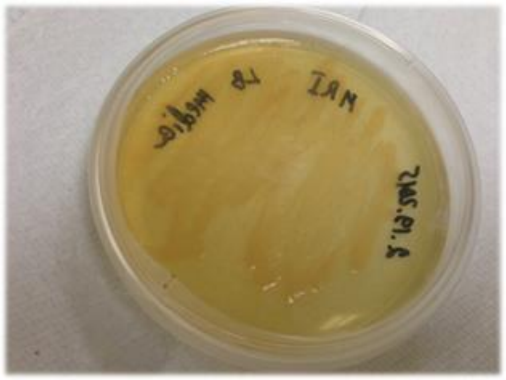
Objectives

- Evaluate bacterial interactions with uranium (VI) by focusing on facultative anaerobic bacteria, *Shewanella Oneidensis MR1*.
- Study the effect of bacteria on the dissolution of the uranyl phosphate solid phases created as a result of sodium tripolyphosphate injections into the subsurface at the Hanford 300 Area.
- Evaluate the role of anaerobic bacteria as one of the factors affecting the outcome of environmental remediation.

Experimental procedures

- 16 crimp-sealed bottles were prepared with 50 ml of media solution and 90 mg (4.4 mM of uranium VI) Ca-autunite mineral obtained from Hanford site.
- Bottles were inoculated with Shewanella Oneidensis MR1 strains when autunite was equilibrated with the media solutions.
- Bacteria was obtained from Pacific Northwest National Laboratory (PNNL).

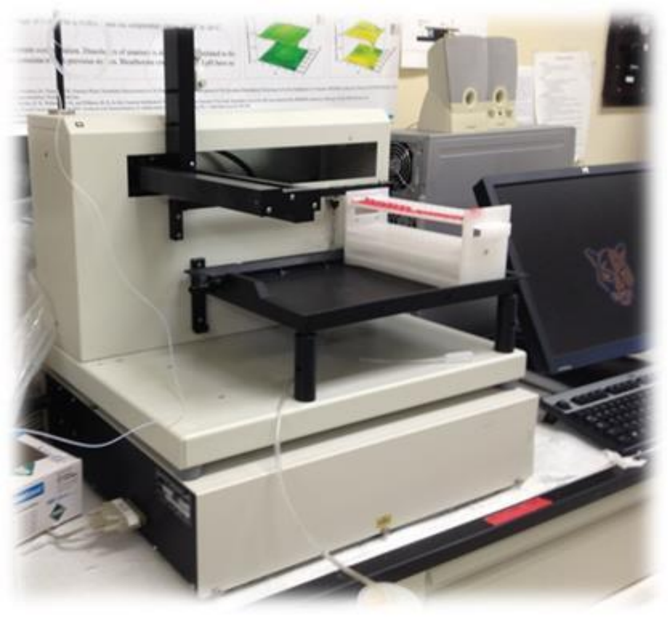
Experimental bottles



Shewanella Oneidensis MR1 growth on LB media

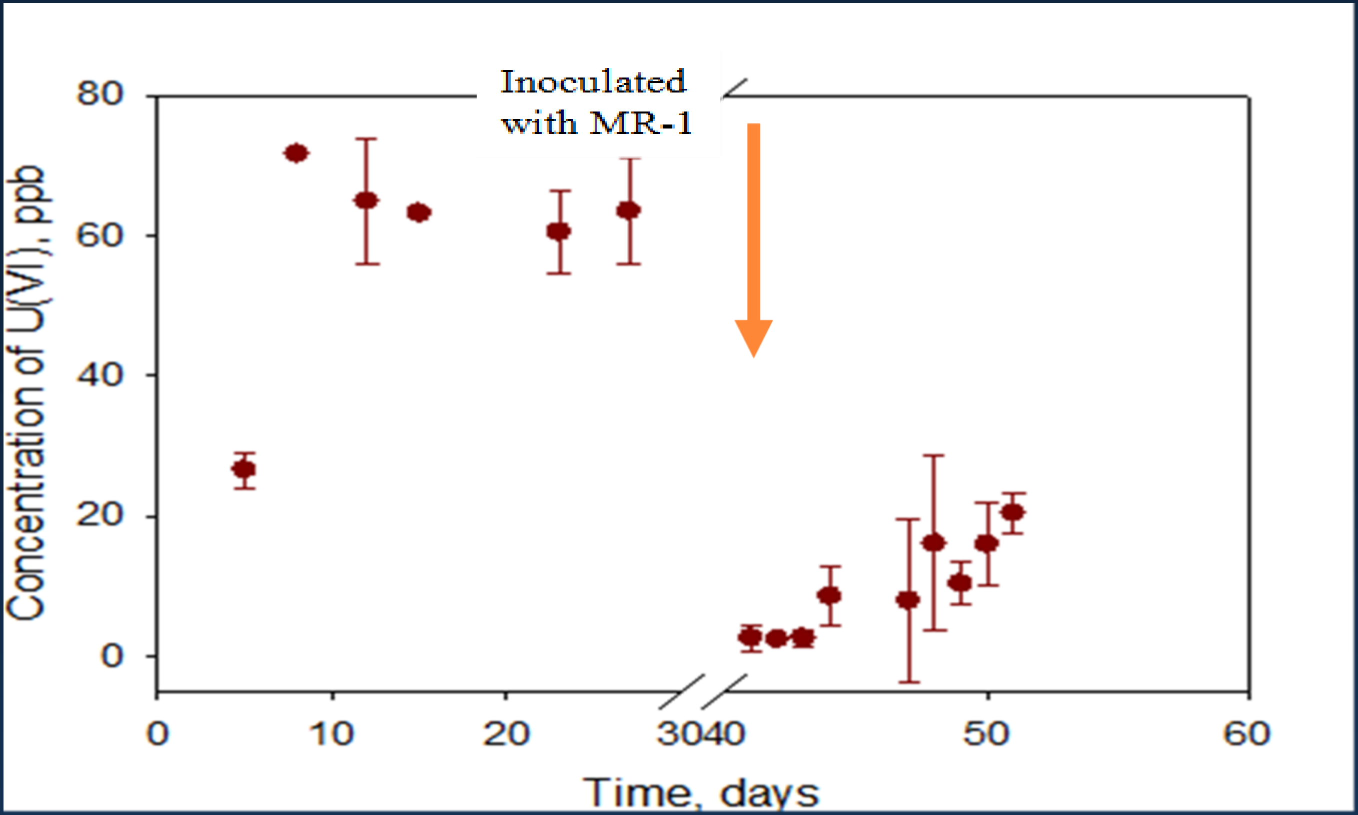
Experimental approach

- Solution media preparation
  - 20 mM Na-Hepes buffer
  - pH 7
  - 10 mM Lactate
  - Bicarbonate: 0, 3, 5 and 10
  - bacteria-free control
- Samples were taken from the supernatant solutions of the experimental and control bottles
- Wet and dry digestion was performed until a white solid residue was acquired
  - Dilution was made for KPA analysis to determine concentration of U (VI)



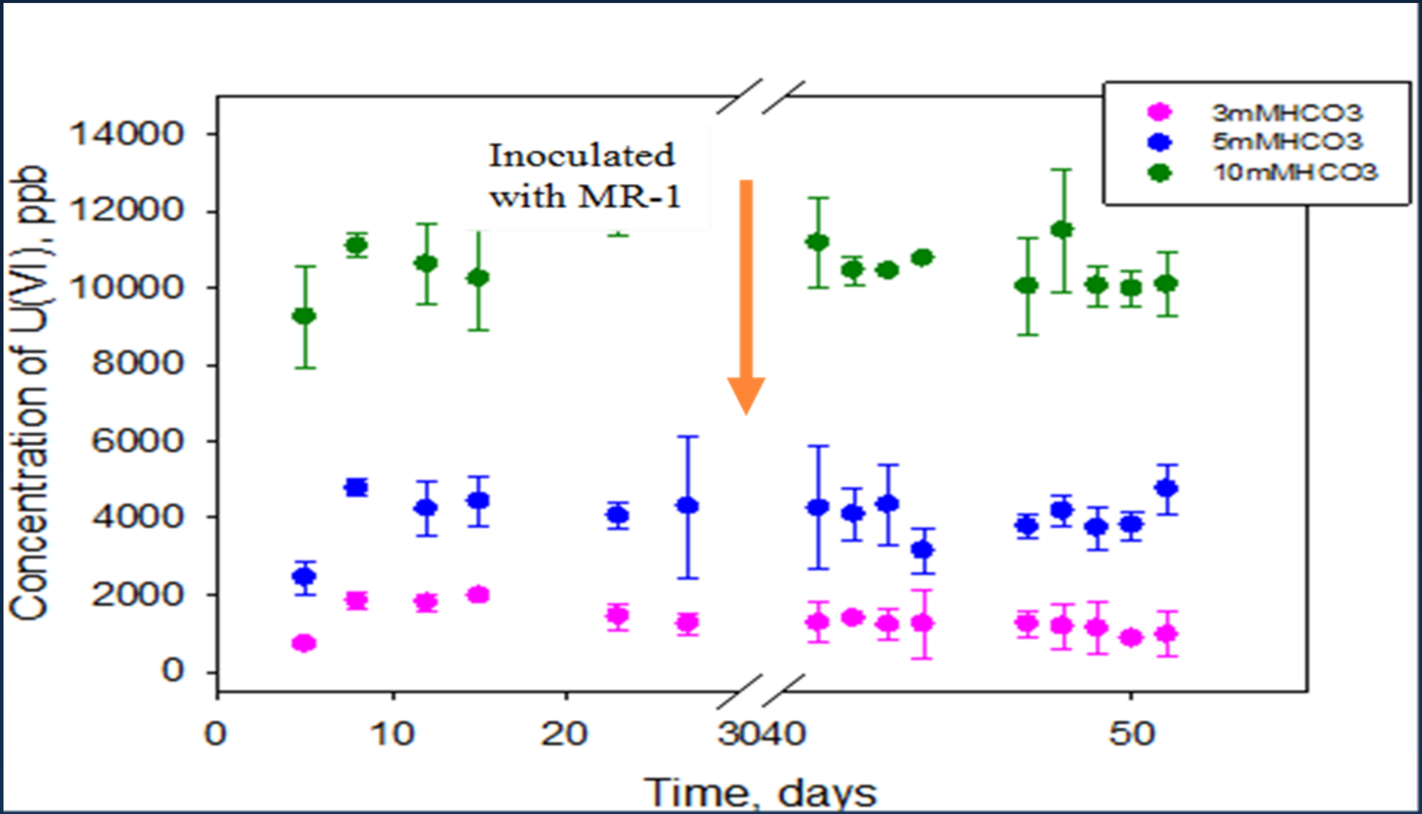
KPA instrument

Preliminary Results



Uranium concentration released into the aqueous phase as a function of time with no bicarbonate addition.

Preliminary Results - Cont.



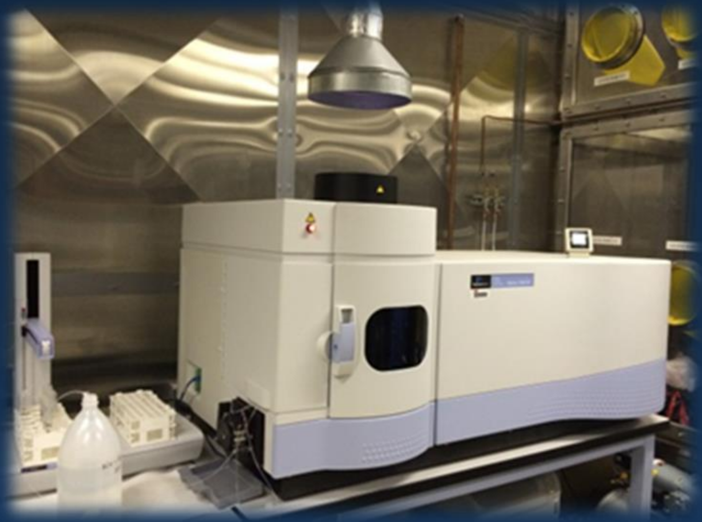
Uranium concentration released in the aqueous phase as function of time using three different bicarbonate concentrations: 3,5 and 10 mM.

Conclusions

- Higher bicarbonate concentrations might interfere with uranium (VI) reduction by anaerobic bacteria.
- Reduce time of sampling before the inoculation and prolong sampling time after inoculation.
- It might be necessary to increase concentration of lactate or do periodical lactate additions to sustain microbial process.

Future Work

- Repeat experiment in strictly anaerobic conditions in the glove box and evaluate if further reduction of uranium (VI) is obtained in the presence of carbonates (HCO_3^-).
- Finalize analysis of calcium and phosphorous via ICP instrument.



Task 2.1- FIU’s support for groundwater remediation at SRS F/H Area

Christian Pino, DOE Fellow, Chemistry

Florida International University

Task 2.1 (Carryover)

- Carryover scope: Explore the effect of higher HA concentrations up to 50 ppm and study if there are any synergistic interactions between U(VI) ions, humic acid and silica on the U(VI) removal.
- Objective: Investigate synergistic interactions between U(VI) ions, HA and Si:
  - Study the influence of humic acid (HA) and Si on the sorption of U(VI) onto F/H Area sediments.
- Study the effects of environmental variables such as pH, concentrations of HA and Si on the removal behavior of U(VI) in the multi-component batch systems.

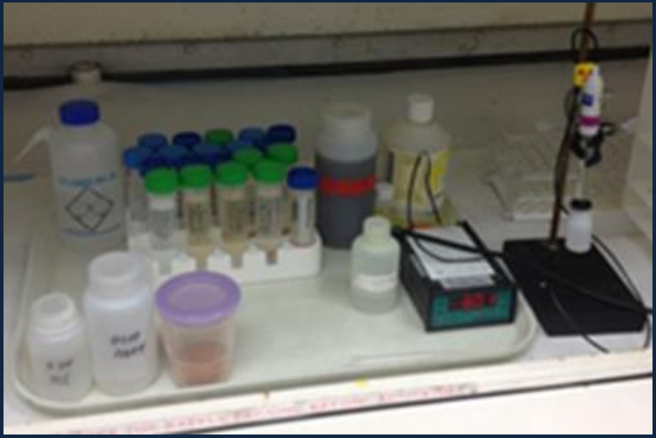
Task 2.1 (Carryover) - Progress

- Previous experimentation was completed with **10 ppm** humic acid concentrations
  - **Batch 1:** Si (3.5 mM) +U(VI) (0.5 ppm)
  - **Batch 2:** Si (3.5 mM) +U(VI) (0.5 ppm) + HA (10 ppm)
  - **Batch 3:** U(VI) (0.5 ppm) + HA (10 ppm)
  - **Batch 4:** Sediments + Si (3.5 mM) +U(VI) (0.5 ppm)
  - **Batch 5:** Sediments + Si (3.5mM) +U(VI) (0.5ppm) + HA 10ppm)
  - **Batch 6:** Sediments + U(VI) (0.5 ppm) + HA
  - **Batch 7:** Sediments + U(VI) (0.5 ppm) (10 ppm)

Task 2.1 (Carryover) - Progress

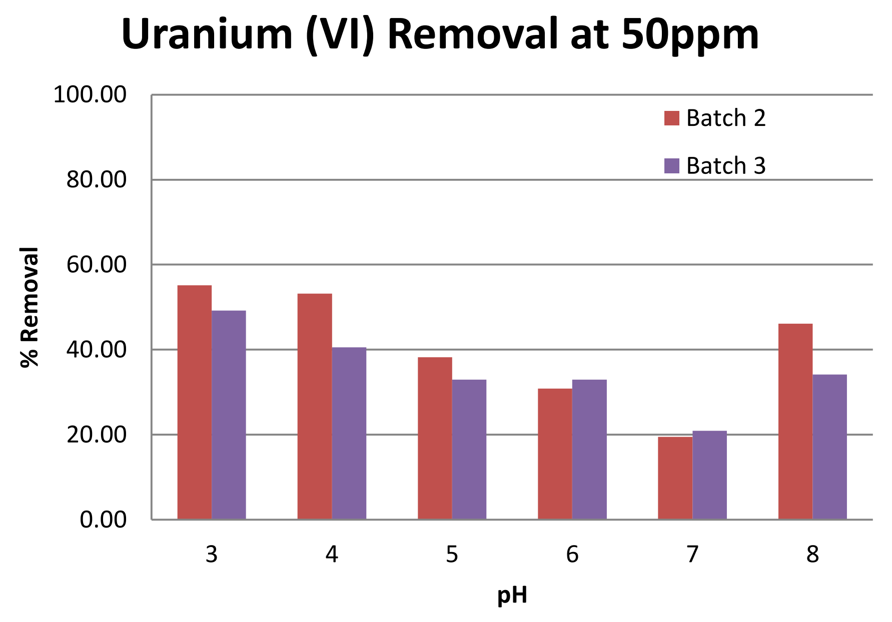
- Prepared batches 2, 3, 5 and 6 with 50 ppm HA in triplicates
- Soil collected from FAW1 at a depth of 70-90’
  - Sieved through <2 mm
- Uranium was added prior to adjusting pH
- Samples were placed on shaker for 3 days, followed by centrifugation
- Samples were filtered through 0.45 µm syringes
- Measured uranium concentration via KPA and Fe, Si via ICP-OES
- Compared results to those of 10ppm humic acid previously analyzed

Task 2.1 (Carryover) - Experimental Set Up



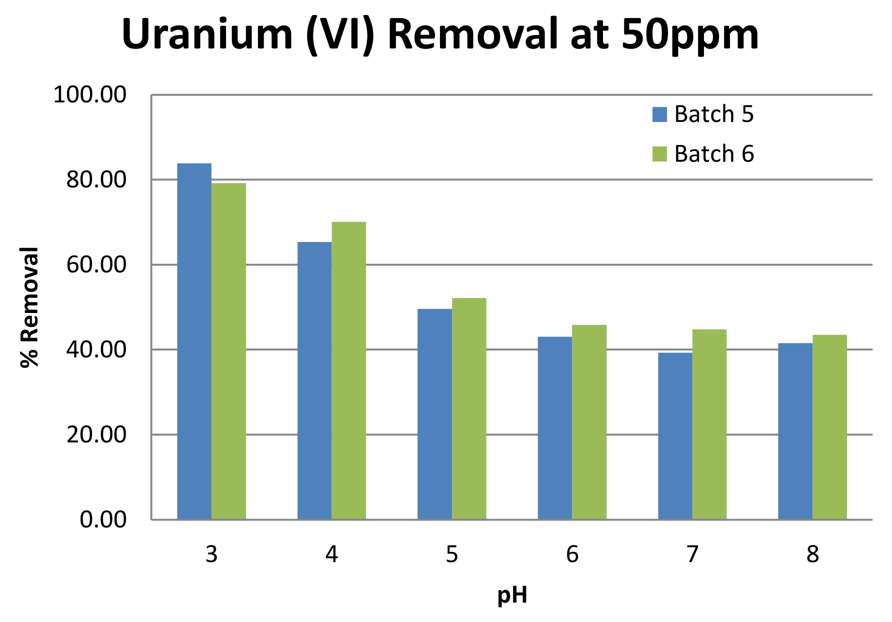
Task 2.1 (Carryover)- Results Batch 2 and 3

- Maximum U(VI) removal was seen at pH 3 with 55.17 and 49.22
- Least amount of removal occurred at pH 7 with 19.51and 20.89
- Samples containing silica showed slightly higher removal compared to samples with no silica
- Humic acid is very insoluble at low pH values unlike uranium which is very soluble
  - Possible coagulation may have caused the highest removal at low pH

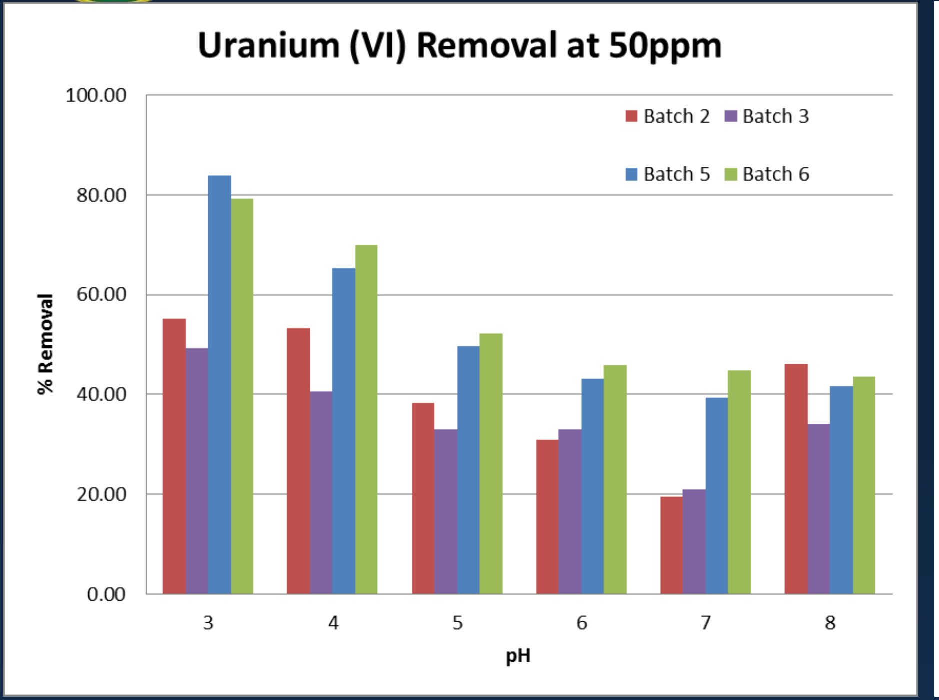


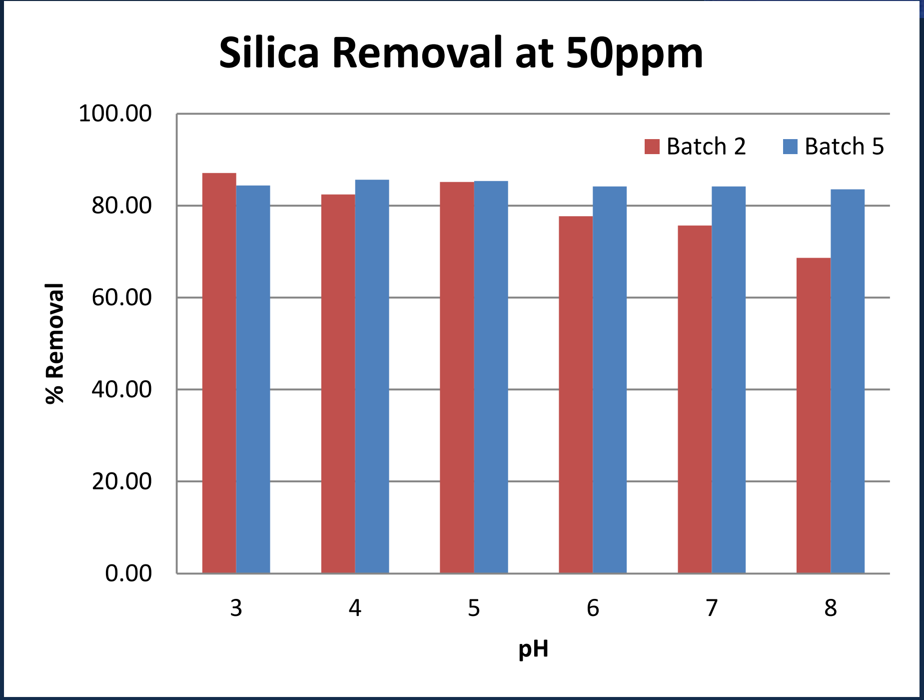
Task 2.1 (Carryover)- Results Batch 5 and 6

- Maximum U(VI) removal was seen at pH 3 with 83.93 and 79.16
- Between pH 5 to 8, removal was between 40-53%
- Batch 5 and 6 unlike 2 and 3 contains sediment, which yield a much higher removal rate
  - More binding sites present with sediment



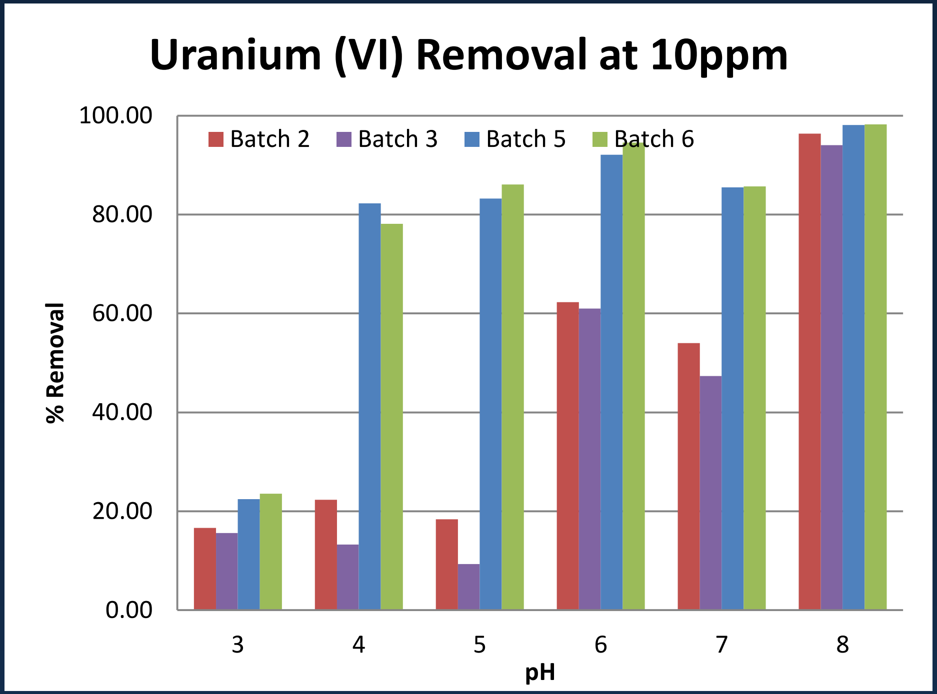
Task 2.1 (Carryover)- Results

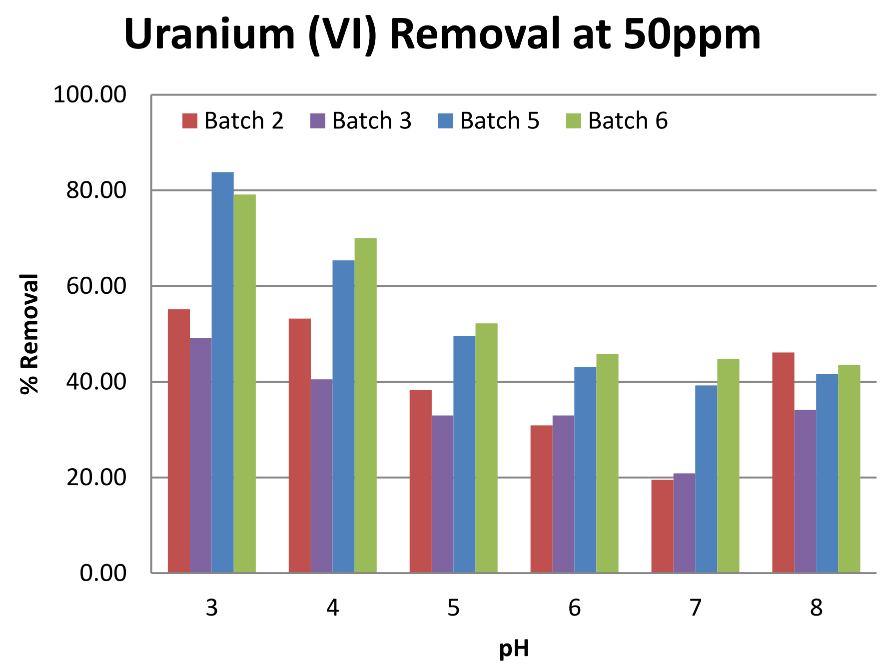




- For all batches colloidal silica does not seem to have a significant effect in U(VI) removal
- Silica percent removal slightly decreased for batch 2 as pH increased though batch 5 remained at 83-85% removal at all pH values

Task 2.1 (Carryover)- Comparing 10 and 50ppm





- 10 ppm samples showed the highest removal occurring at higher pH values 6-8; significant increase in removal with soil up to pH 8
  - Unlike 50 ppm which show the highest removal at acidic pH
  - Sediment inclusion shows increased removal at both concentrations

Task 2.1 (Carryover)- Conclusions

- Colloidal silica does not seem to have a significant effect in removal compared to sediment
- Inclusion of sediment showed a higher overall removal
- At acidic pH the humic acid and uranium aggregate together due to their opposite charges
  - aggregation in conjunction with soil creates more binding sites seem to allow for a high removal rate
  - With increase in pH, less aggregation will occur due to less solubility of humic acid thus reducing the possibility for interaction

Task 2.1 (Carryover) - Future Work

- Analyze unfiltered samples with 50 ppm HA to be able to make direct comparison with 10 ppm HA data
- Repeat experiments with 30 ppm HA to see if any trend in U removal using intermediate HA concentration

Task 2.1

Sodium Silicate Treatment for Uranium (VI) Bearing Groundwater Systems at F/H Area at Savannah River Site

Christine Wipfli, DOE Fellow,
Undergraduate Student, Env Engineering

FLORIDA INTERNATIONAL UNIVERSITY

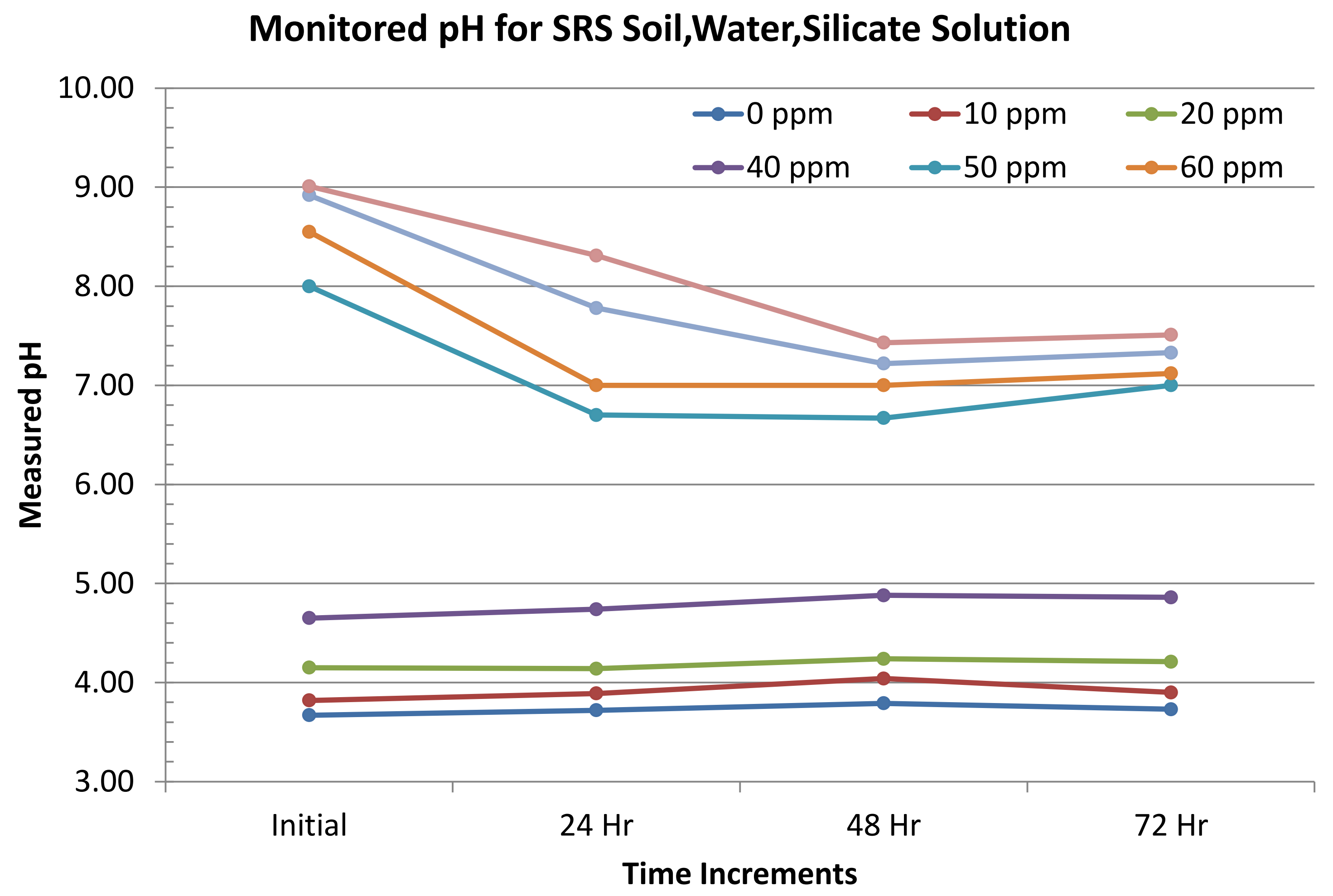
Project 2.1 - Description

- Objective: To evaluate whether a base solution of dissolved silica can be used to replace a carbonate base previously used to increase the pH of the treatment zone.
- To investigate the addition of sodium silicate to increase the pH of the treatment zone in order to achieve uranium precipitation, therefore immobilizing the contaminant.
- Conduct a series of experiments to identify the optimal concentration of sodium silicate required to achieve uranium precipitation.

Project 2.1 - Procedure Part 1

- An experiment was conducted in order to determine the effect of sodium silicate on the pH of a solution containing SRS soil and synthetic groundwater.
- Each sample was spiked with the appropriate volume from the sodium silicate stock solution in order to achieve final desired sodium silicate concentrations of 10, 20, 40, 50, 60, 70, and 80 ppm.
- The samples were placed on a platform shaker for three days during which pH readings were collected in regular intervals to determine which silicate concentration produced a pH in the neutral range.

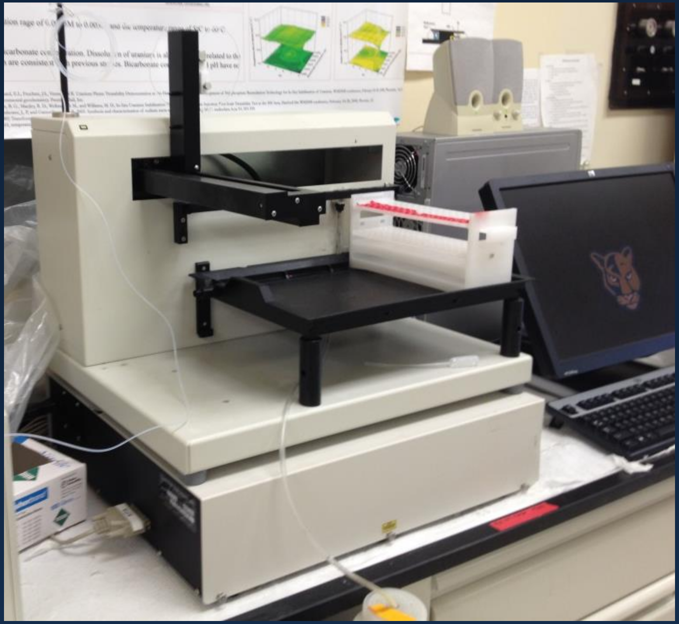
Project 2.1 - Results Part 1

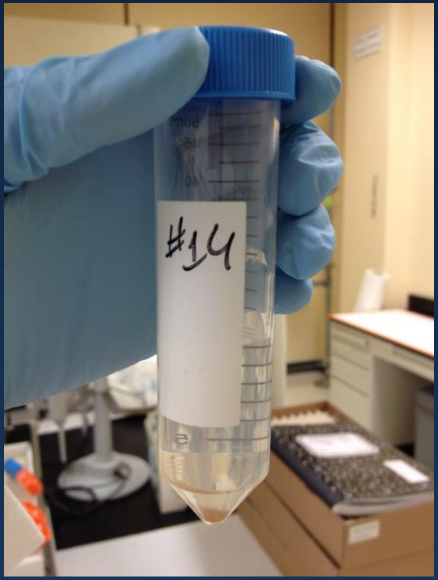


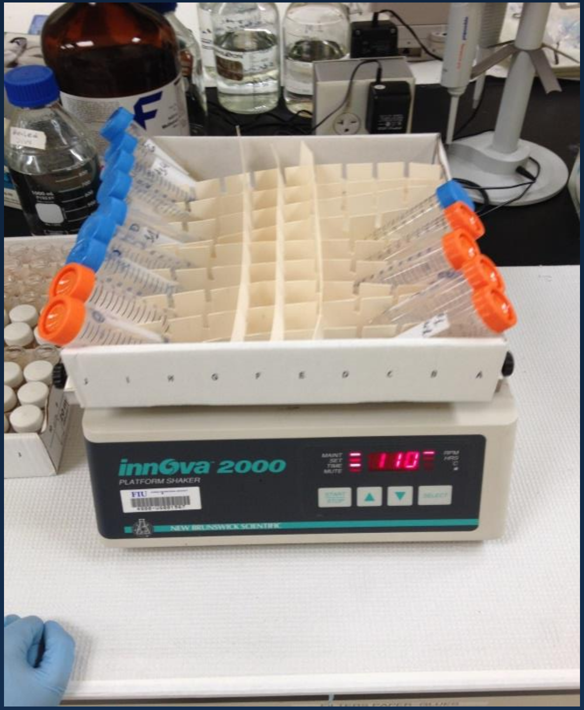
Project 2.1 - Procedure Part 2

- A sequential experiment was conducted specifically using 40 and 50 ppm of sodium silicate with SRS soil, synthetic groundwater, and 0.5 ppm of uranium (VI), in order to investigate the removal of uranium in the aqueous phase via precipitation.
- Each sample was analyzed using the Kinetic Phosphorescence Analyzer (KPA) in order to measure uranium concentrations in the supernatant.
- By measuring the concentration of uranium in the supernatant the percent removal is obtained revealing the amount of uranium precipitation that occurred for each silicate concentration.

Project 2.1 - Experimental Setup







Project 2.1 - Results Part 2

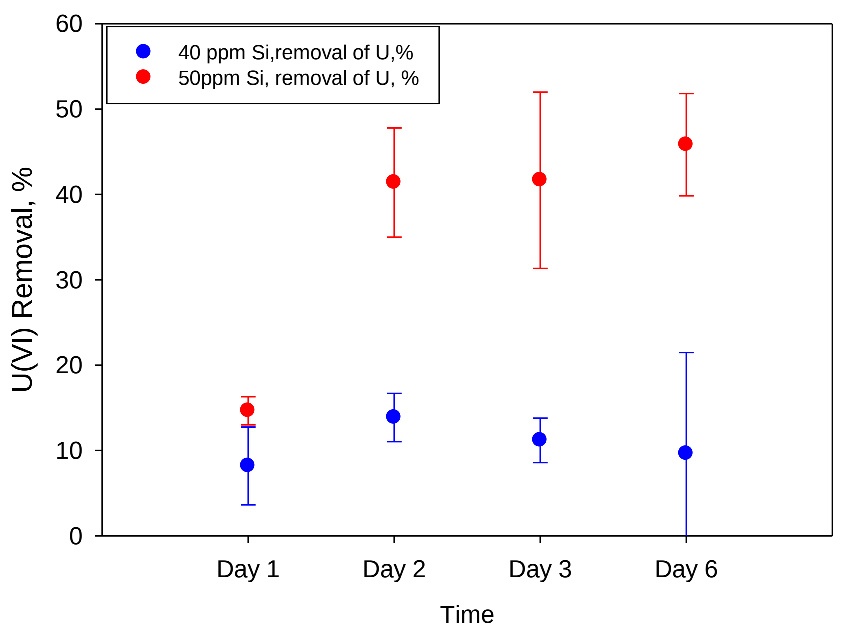


Figure 1. U(VI) % removal as a function of time for non-filtered samples for 40 and 50 ppm of sodium silicate.

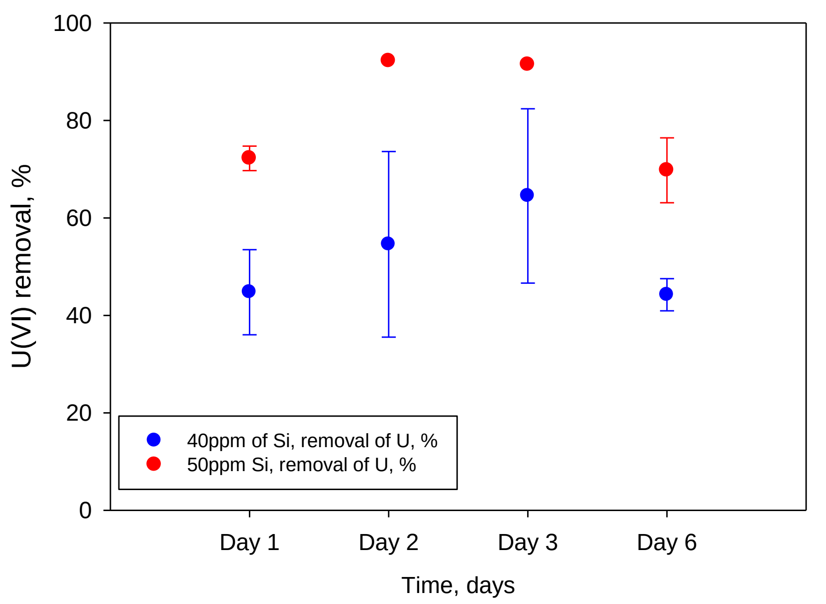


Figure 2. U(VI) % removal as a function of time for filtered samples for 40 and 50 ppm of sodium silicate.

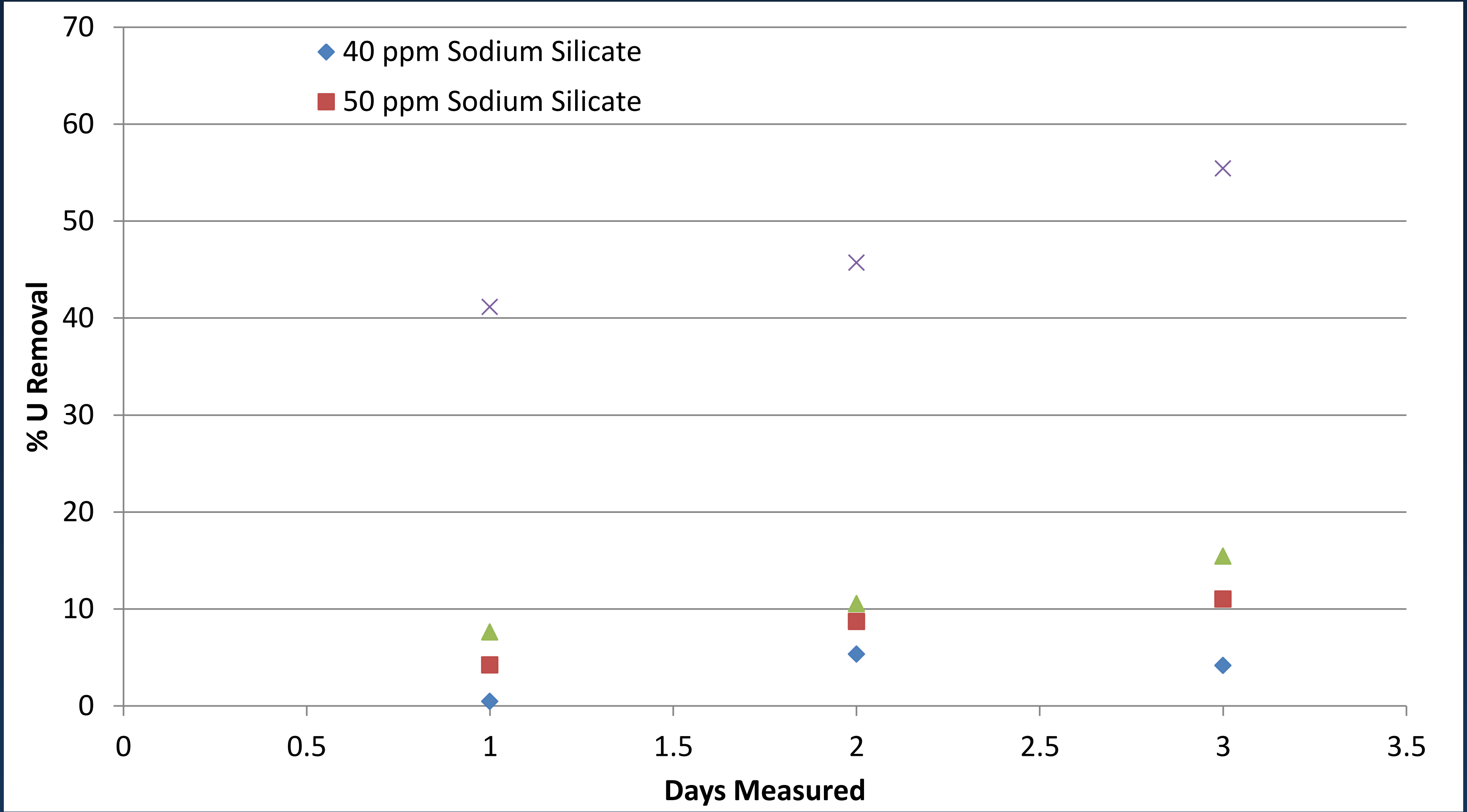
Project 2.1 - Results Part 2 Cont.

- 50 ppm achieved the larger percent of uranium precipitation with a range of 15-45% removal for the non-filtered samples and between 60-95% removal for the filtered samples.
- A large difference between the removal of filtered and non-filtered samples from the same day was observed for both sodium silicate concentrations tested, indicating that there is a considerable amount of uranium species retained in the filter.
- The addition of sodium silicate proved effective in the removal of uranium from the aqueous phase via precipitation.

Project 2.1 - Procedure Part 3

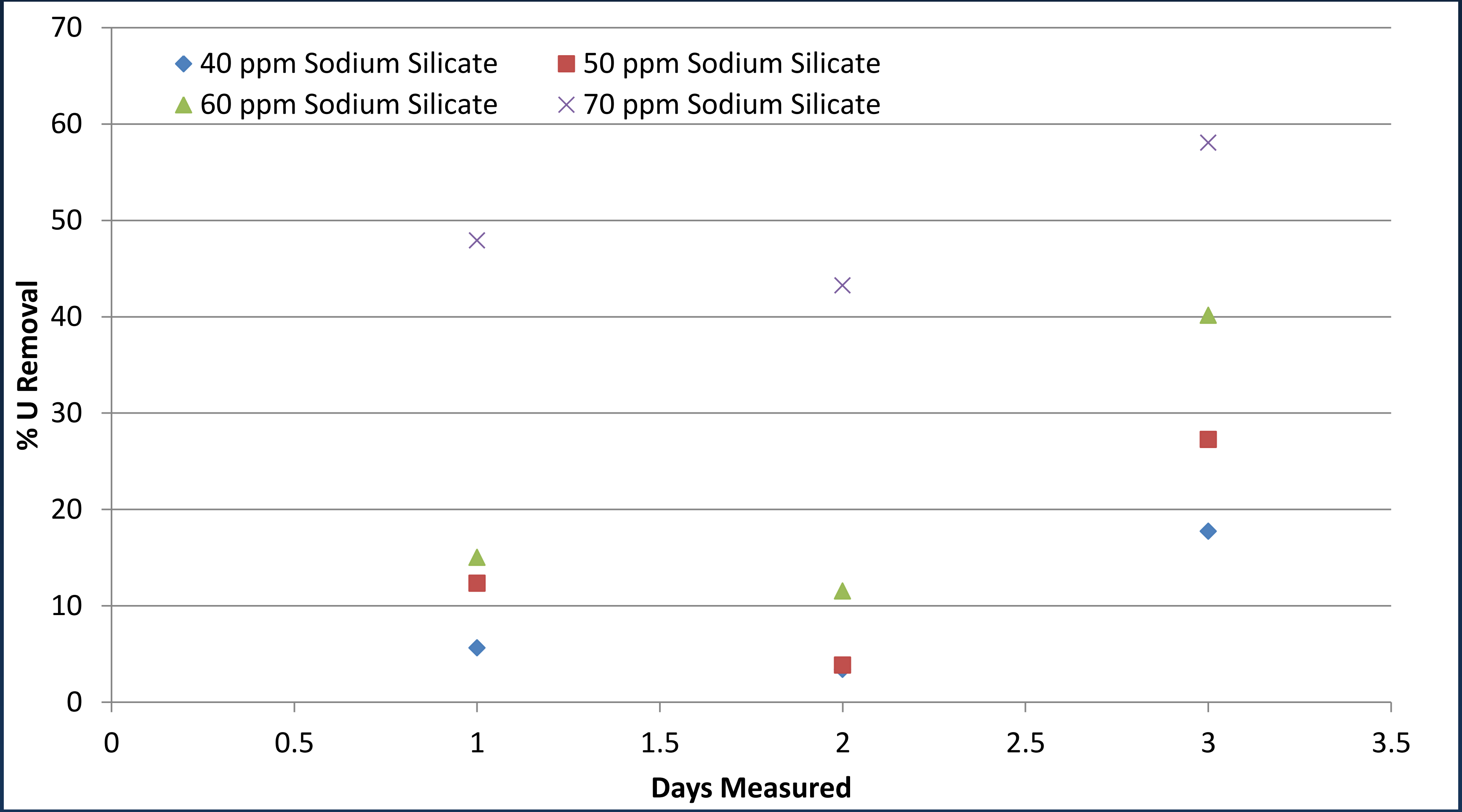
- An additional experiment was conducted using 40, 50, 60, and 70 ppm concentration of sodium silicate.
- As uranium precipitation was achieved, the precipitate was removed via filtration.
- A small amount of supernatant was extracted from each sample to analyze via a KPA.
- The percent of uranium removed via precipitation is observed in the graphs.

Project 2.1 - Results Part 3A



Uranium removed (%) for non-filtered samples for 40, 50, 60, and 70 ppm of sodium silicate.

Project 2.1 - Results Part 3B



Uranium removed (%) for filtered samples for 40, 50, 60, and 70 ppm of sodium silicate.

Project 2.1 - Results 3

- The amount of uranium precipitation was directly influenced by the concentration of sodium silicate present in each sample.
- In the filtered samples, less precipitate was present in the supernatant due to the filtration process so the percent of uranium removed was higher.
- Overall, 70 ppm appeared to have the highest percent of uranium removal via precipitation.

Project 2.1 - Future Work

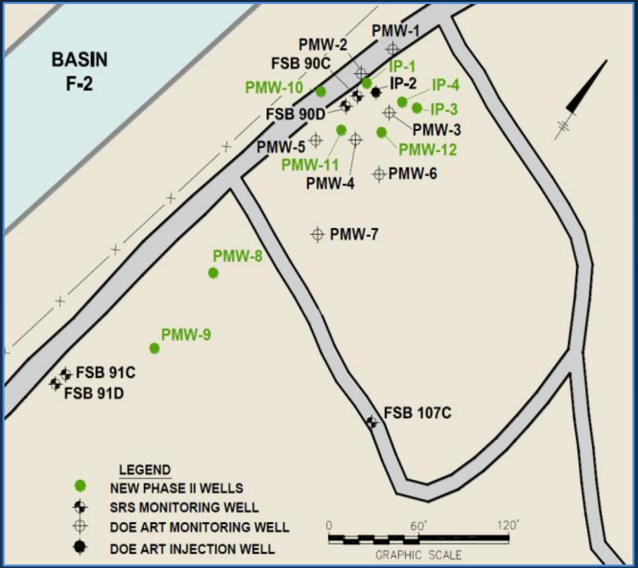
- Examine the conditions under which uranium precipitate experiences resolubilization.
- Examine mineralogy and surface morphology of dried uranium precipitate using XRD and SEM/EDS.

Task 2.2 - Monitoring of U(VI) bioreduction after ARCADIS demonstration at F-Area

Aref Shehadeh- DOE Fellow,
Undergraduate Student, Env Engineering

FLORIDA INTERNATIONAL UNIVERSITY

Task 2.2 - Monitoring of U(VI) bioreduction after ARCADIS demonstration at F-Area



- The F/H Area Seepage Basins received approximately 1.8 billion gallons of acidic waste solutions.
- The acidic nature of the basin waste solutions triggered the mobilization of soluble uranium (VI).
- In 2010, ARCADIS implemented *in-situ* injections of a molasses substrate as part of the *Enhanced Anaerobic Reductive Precipitation* (EARP) process.
- This was done to produce anaerobic conditions conducive to the reductive precipitation of uranium.

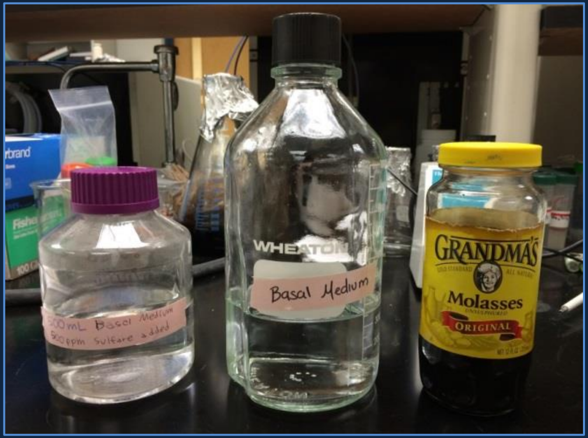
Task 2.2 - Objectives

$UO_2{}^{2+}{}_{(aq)} + 2e^- = UO_{2(c)}$

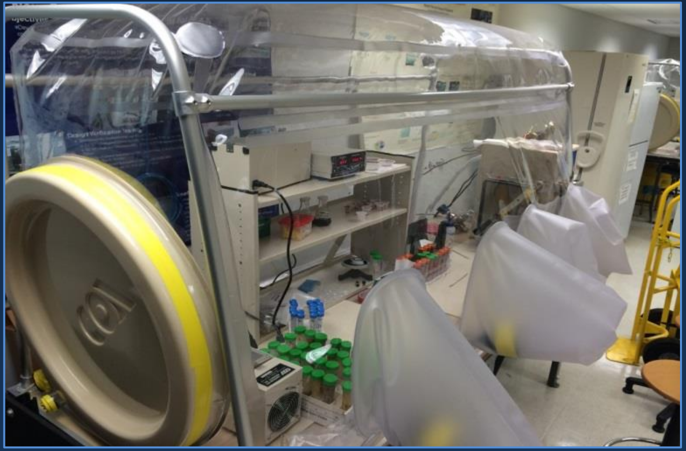
- Determine the mineral composition of SRS fine clay fractions and identify all iron-oxide phases.
- Investigate if phases of reduced iron (ferrous carbonate and ferrous sulfide) would arise in the reduced zone after the bioreduction process has occurred.
- Determine the types of reactions that might occur in the anaerobic aquifer.
  - Evaluate soil samples for re-oxidation.

Task 2.2 - Methodology

Batch 1 and 2 Composition				
Set #	**Set #1**	**Set #2**	**Set #3**	**Set #4**
Soil (mL)	20	20	20	20
Basal Medium (mL)	12	12	12	12
Sulfate (ppm)	500	500	-	-
Molasses (Wt %)	5-10	5-10	5-10	5-10
Anaerobic Bacteria	0.5	-	-	0.5



- Batch 1 and 2 had the same composition
  - Batch 1 had four sets of triplicate samples
  - Batch 2 had four individual samples
- Batch 2 was pH-adjusted to a neutral level before introducing SRS sediments
- Samples were placed into an airlock chamber to ensure anaerobic conditions



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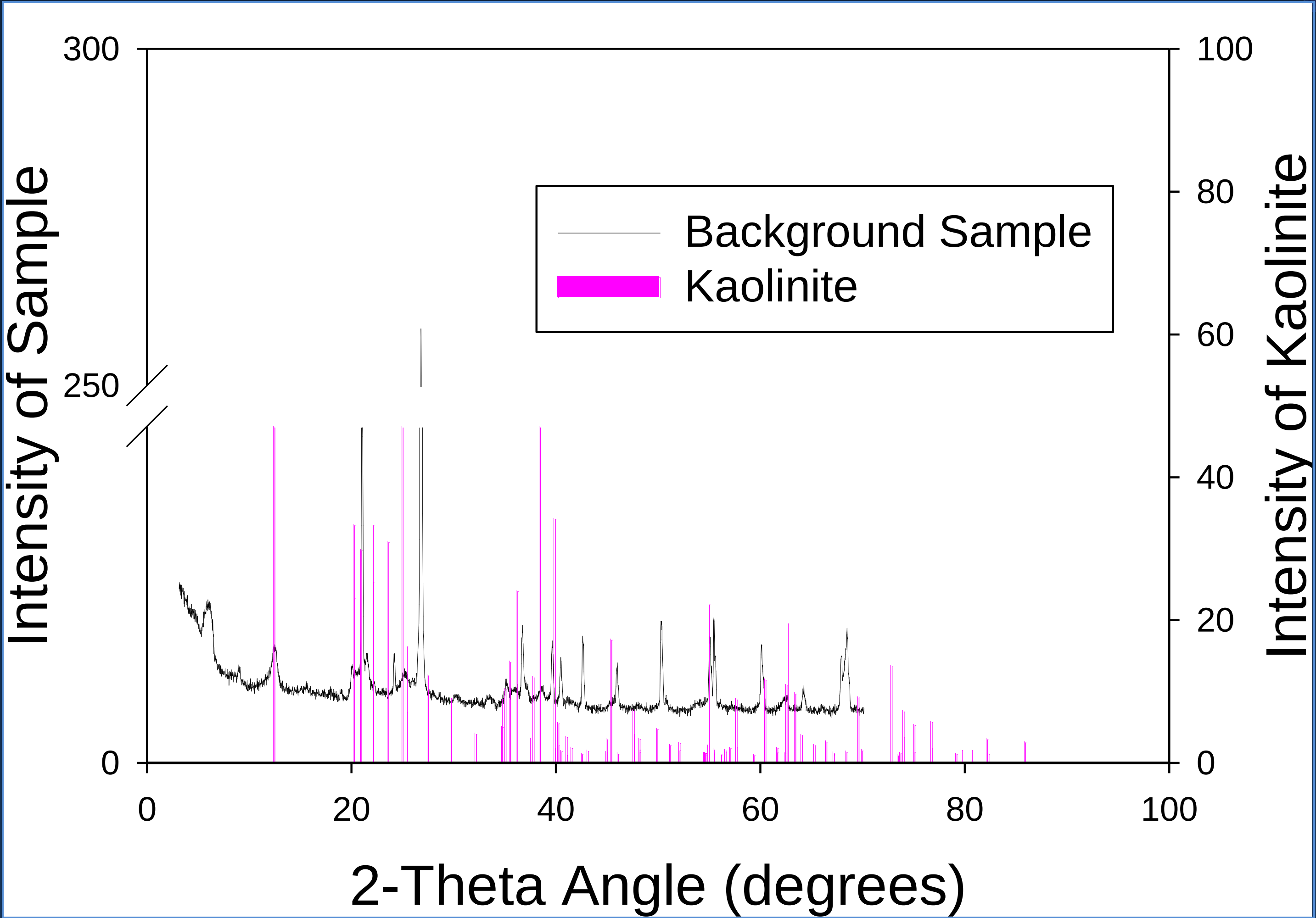
Task 2.2 - Methodology

- A pH evolution study was conducted to find the type of pH changes that occurred in the samples

- X-ray Diffraction analysis was conducted to identify mineralogical changes
  - patterns were compared against known XRD patterns for siderite and pyrite

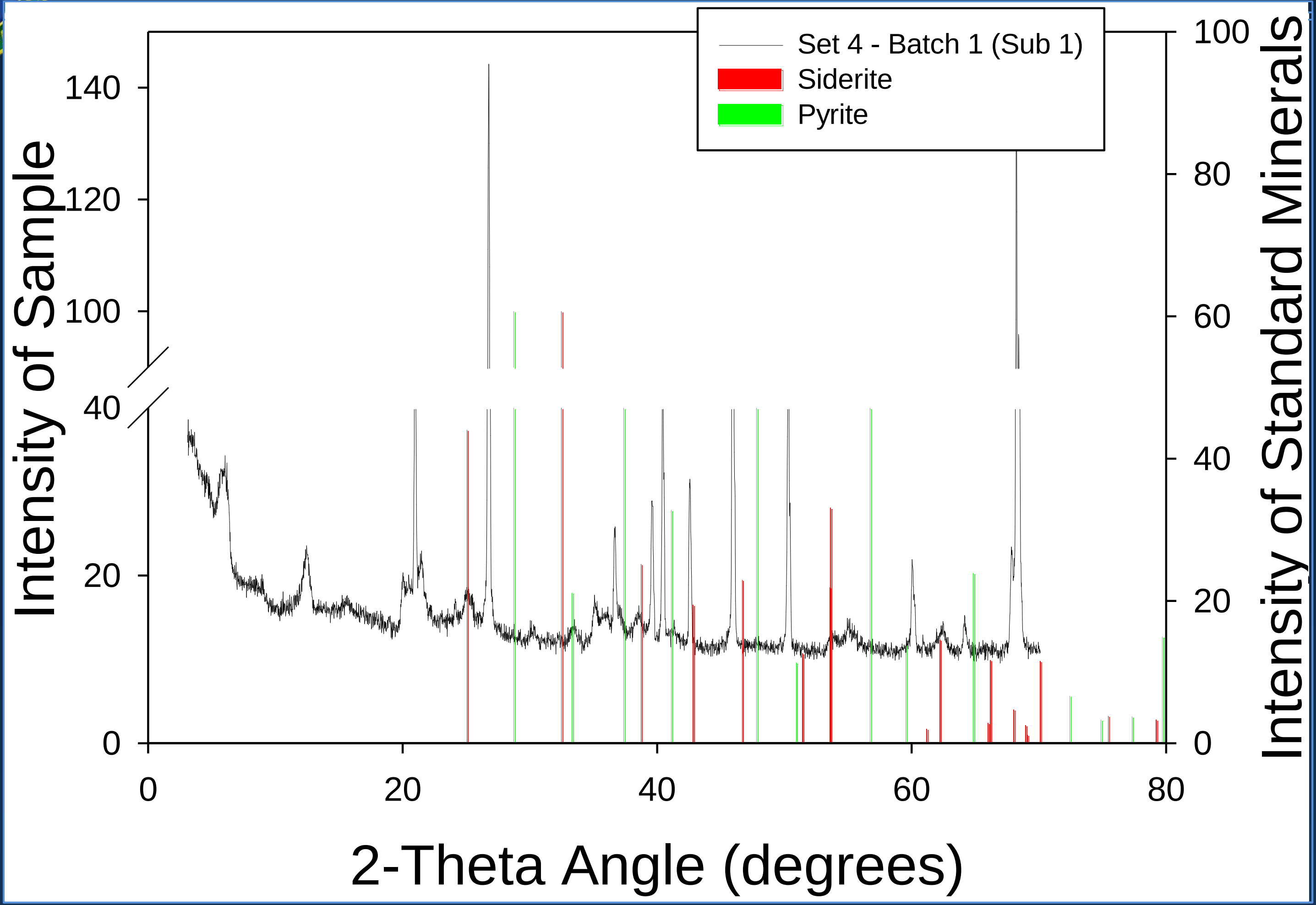
- ICP-OES analysis was conducted on supernatants after being filtered through 0.45 mm filters and diluted by a factor of 200 in nitric acid (1%).

Task 2.2 Results - Background XRD



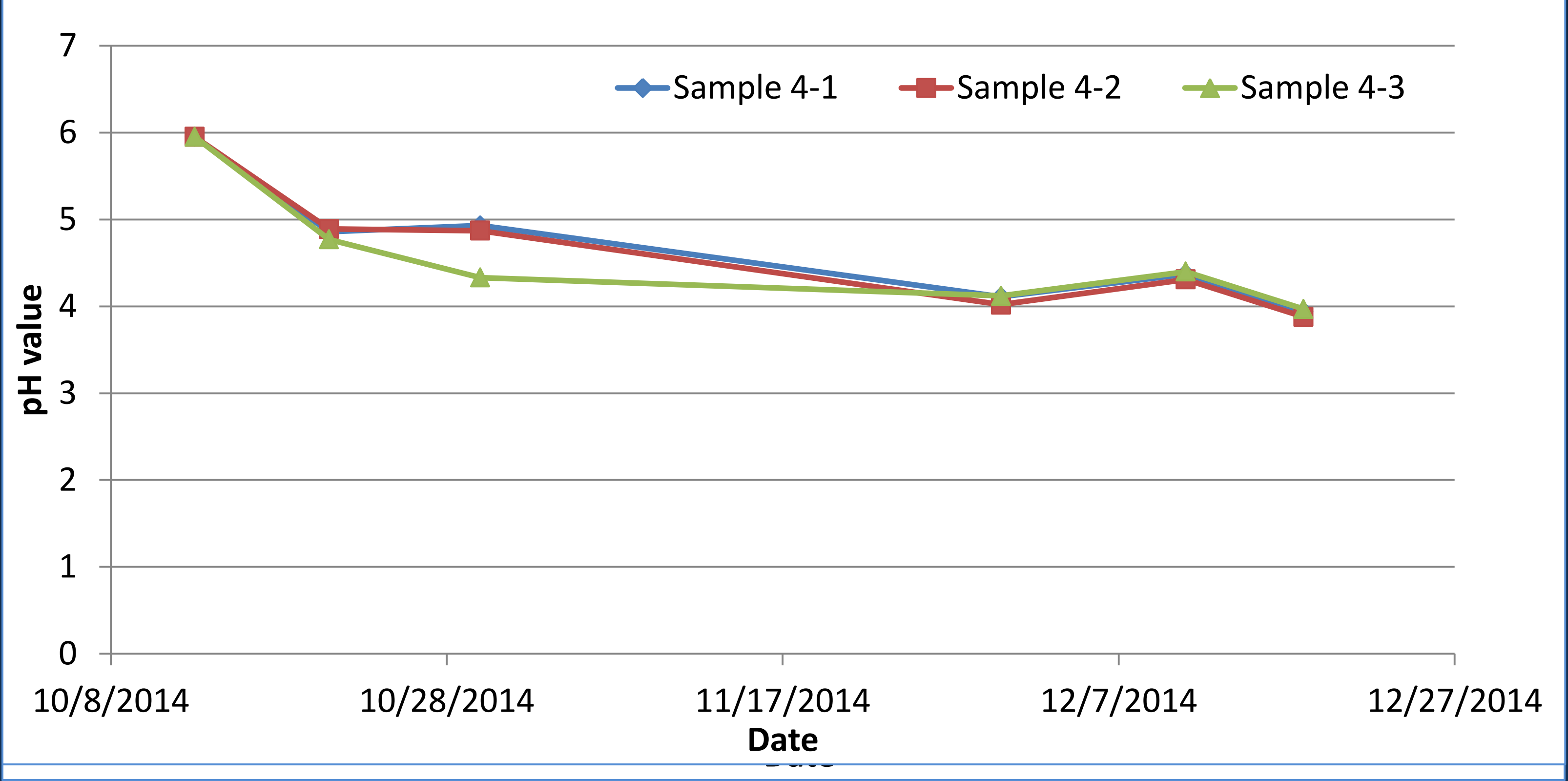
XRD analysis on background samples matched with: quartz, goethite, montmorillonite, and kaolinite

Task 2.2 Results - Batch 1: XRD



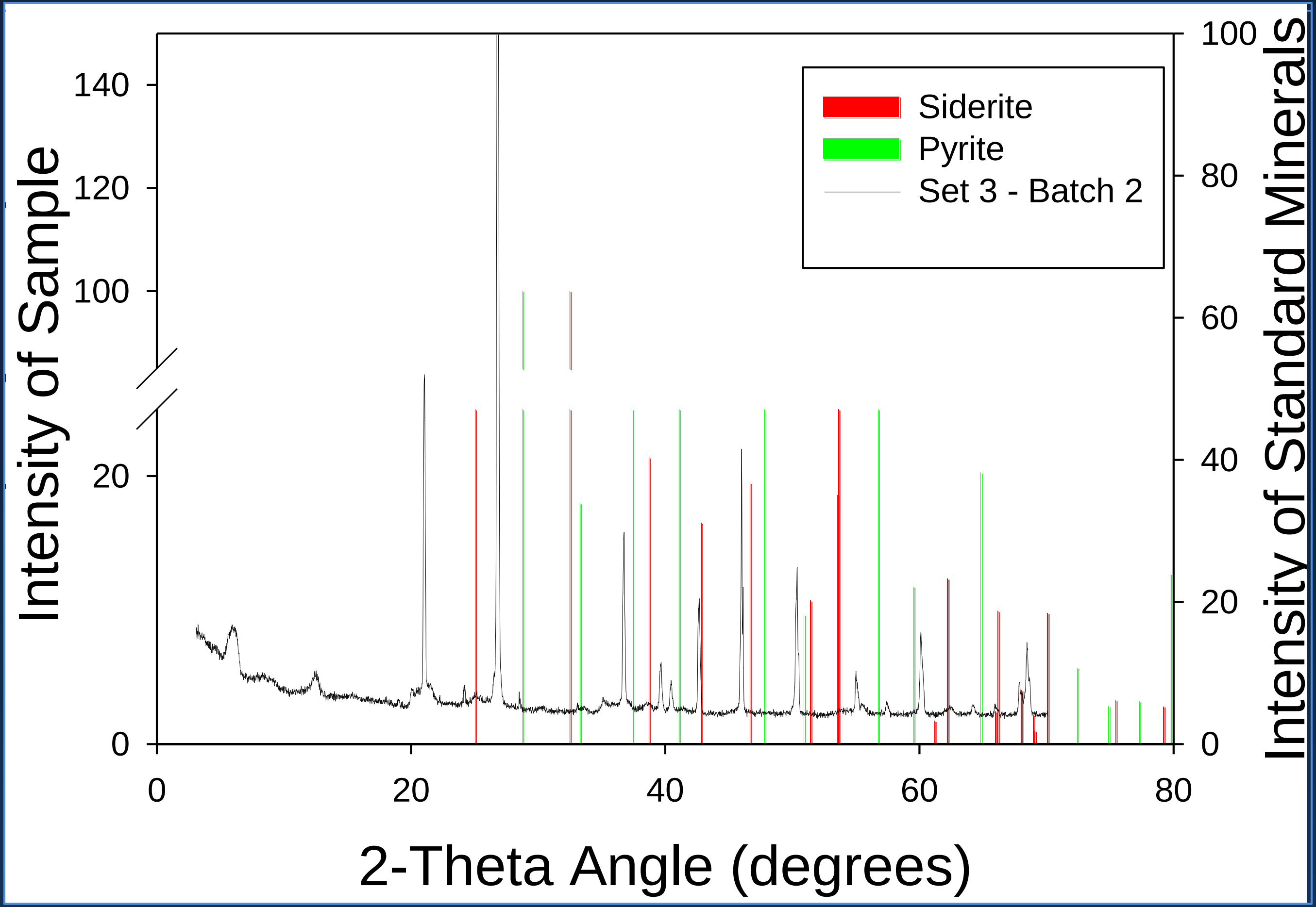
XRD analysis on Batch 1 sub-samples revealed no matches with siderite or pyrite
A second set of sub-samples taken later also revealed no matches

Task 2.2 Results - Batch 1 pH change



- A decline in pH values was observed across all Batch 1 samples
- The decline can be attributed to the the fermentation process of molasses and the natural acidity of SRS sediments

Task 2.2 Results - Batch 2 XRD



- XRD analysis on Batch 2 sub-samples revealed no matches with siderite or pyrite
- A second set of sub-samples taken later also revealed no matches

Task 2.2 Results - Batch 2 pH Change

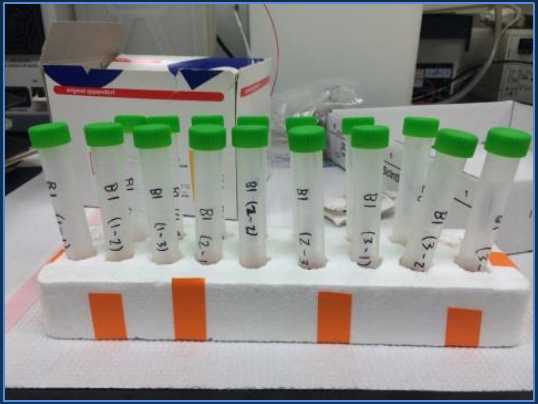
Date	**Measured pH values**			
	Sample 1: Basal medium, 500 ppm sulfate, molasses, bacteria	Sample 2: Basal medium, 500 ppm sulfate, molasses	Sample 3: Basal medium, molasses	Sample 4: Basal medium, molasses, bacteria
11/24/2014	7	7.02	7	6.99
11/30/2014	4.98	4.92	4.98	5.14
12/11/2014	5.28	5.13	5.23	5.41
12/18/2014	4.71	4.62	4.63	4.74

- Although Batch 2 was first pH-adjusted to a neutral pH, the pH followed the same declining trend as observed in Batch 1.
- It was concluded that this was the natural condition within the microcosm and that the acidic state was inevitable.

Task 2.2 Results - ICP

- High ferrous iron concentrations in most of the samples suggesting that anaerobic conditions were established.
  - The highest was 13312.80 ppb in Batch 1/ Set 1-2.
  - The lowest was amounts were found in Batch 2/ Set 2 through 4 where the iron concentration was low enough to be outside of the calibration curve.
- Batch 1 samples containing the anaerobic bacteria (Sets 1 and 4) had the highest average iron concentrations.
  - Iron-reducing bacteria may have biodegraded molasses using ferric iron as a terminal electron acceptor which would explain the higher soluble ferrous iron concentrations.

Description	Fe Concentration, ppb
Batch 1	7808.57
Batch 2	5092.99
Batch 3	5141.05
Batch 4	6403.53



Task 2.2 Future Work

- Repeat ICP on Batch 2 Samples 2 through 4 with a lower calibration curve.
- Repeat XRD analysis on Batch 2 Samples 2 through 4 under different parameters to observe any small peaks that may have been missed.
- Conduct a mass balance analysis on Batch 2 Samples 2 through 4 for iron analysis.
- Determine the reactions that will occur once the samples are returned to aerobic conditions.

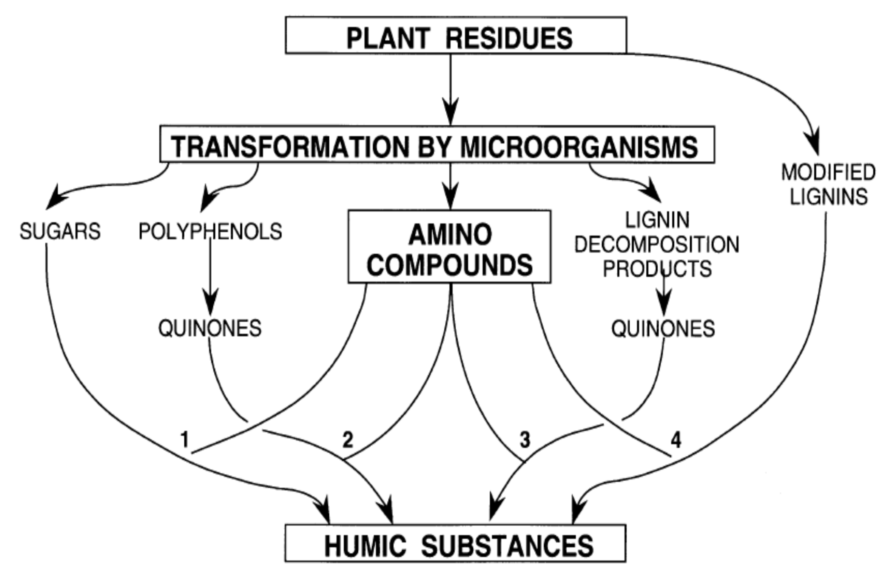
Task 2.3 The sorption properties of the humate injected into the subsurface system

Hansell Gonzalez Raymat
DOE Fellow
Graduate Student, Ph.D. in Chemistry

Florida International University

Task 2.3 Humic Substances

- Humic substances are ubiquitous in the environment, occurring in all soils, waters, and sediments of the ecosphere.
- Humic substances arise from the decomposition of plant and animal tissues.

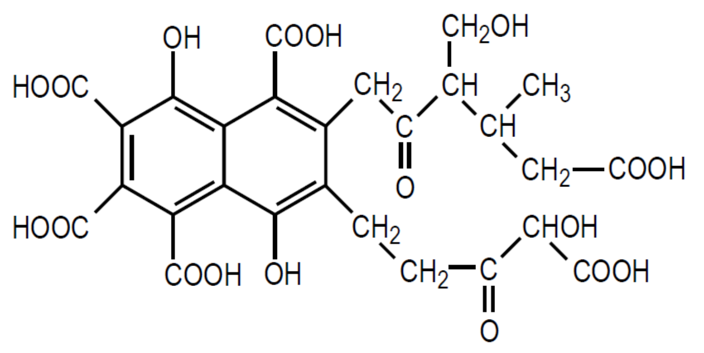


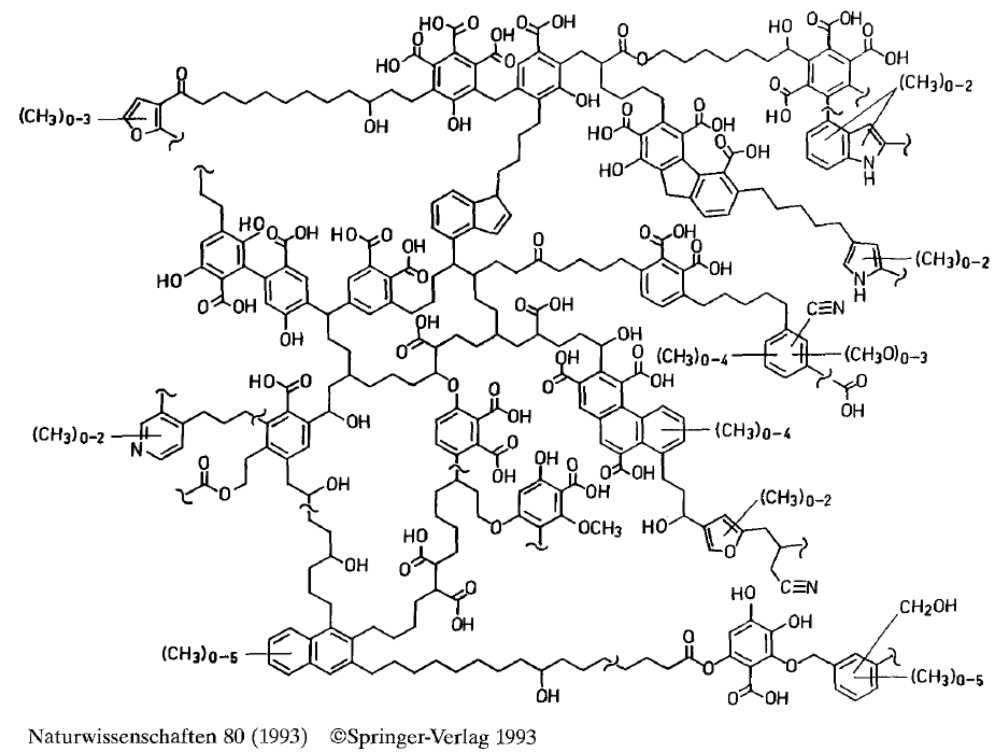
Environmental Soil Chemistry 2nd Edition

Compound	pH
Fulvic Acid	All pH values
Humic Acid	Insoluble at pH < 2
Humin	Insoluble at all pH values

Task 2.3 Fulvic and Humic Acid Model Structure

Buffle (1977)





Naturwissenschaften 80 (1993) ©Springer-Verlag 1993

Schulten and Schnitzer (1993)

Task 2.3 Huma-K

- Huma-K is an organic fertilizer that comes from the alkaline extraction of leonardite (a low-rank coal).
- Huma-K has a high content of humic substances.

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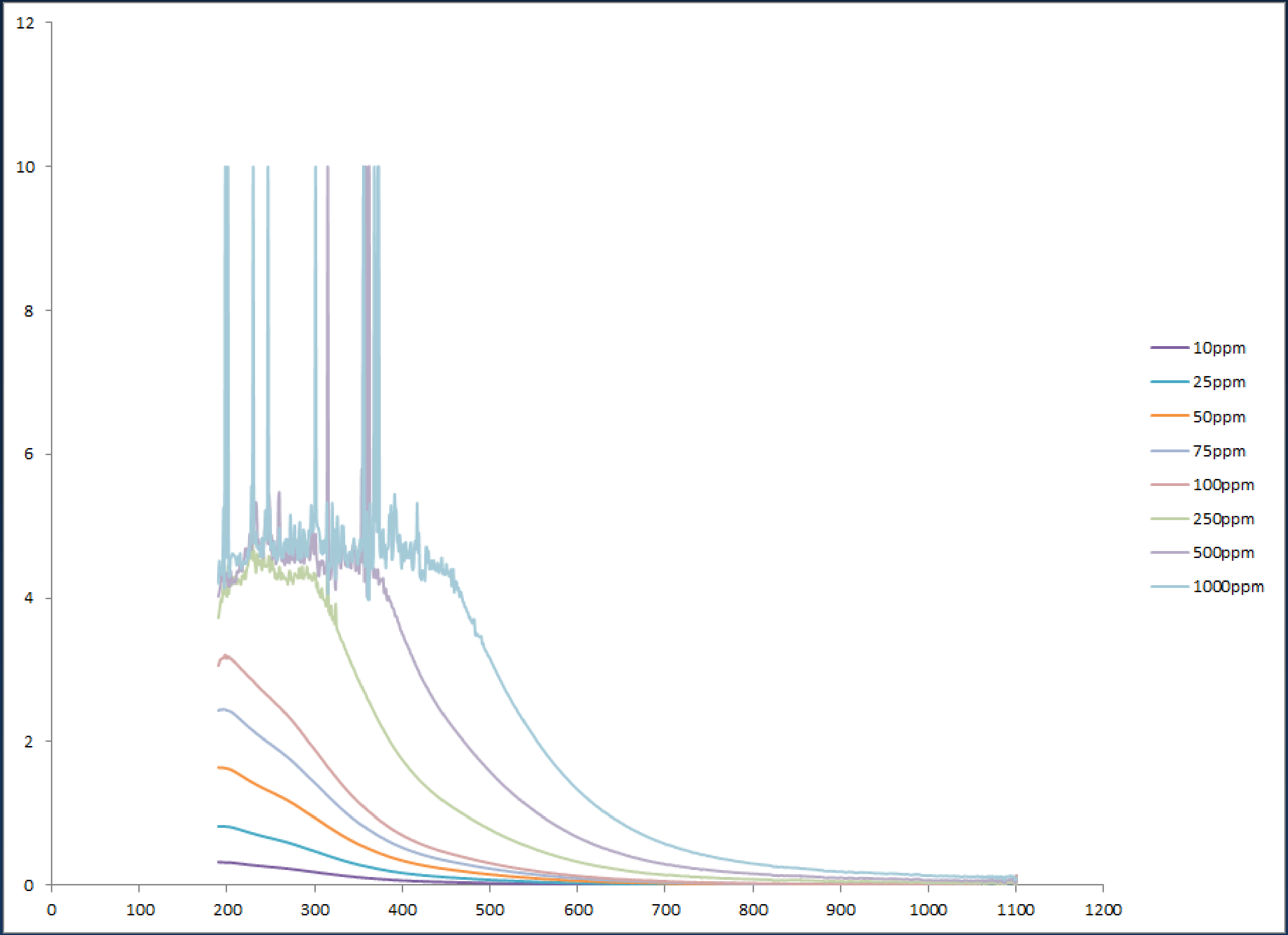
Task 2.3 Objective

- To know how Huma-K sorbs to aquifer sediments when injected.
  - Understanding of sorption behavior
  - Maximum sorption loading capacity of humate on sediments
- Study the effects of different environmental variables.
  - pH and concentrations of humate
- Assist in evaluating whether Huma-K can be used as an in situ amendment for the remediation of groundwater contaminated with uranium.

Task 2.3 Spectrum of Standards



Task 2.3 - Experimental Approach

- Sediments from Savannah River Site (FAW1 70’-90’) were disaggregated and sieved to a particle size of ≤ 2 mm.
- For the sorption experiment, the following concentrations (ppm) were used: 10, 25, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500.

Centrifuge tube with sediment and humate solution

Samples in shaker table for 24 hours (100rpm)

Centrifuge at 2700rpm (30min)

2.3 Experimental Approach

Liquid phase was analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer.

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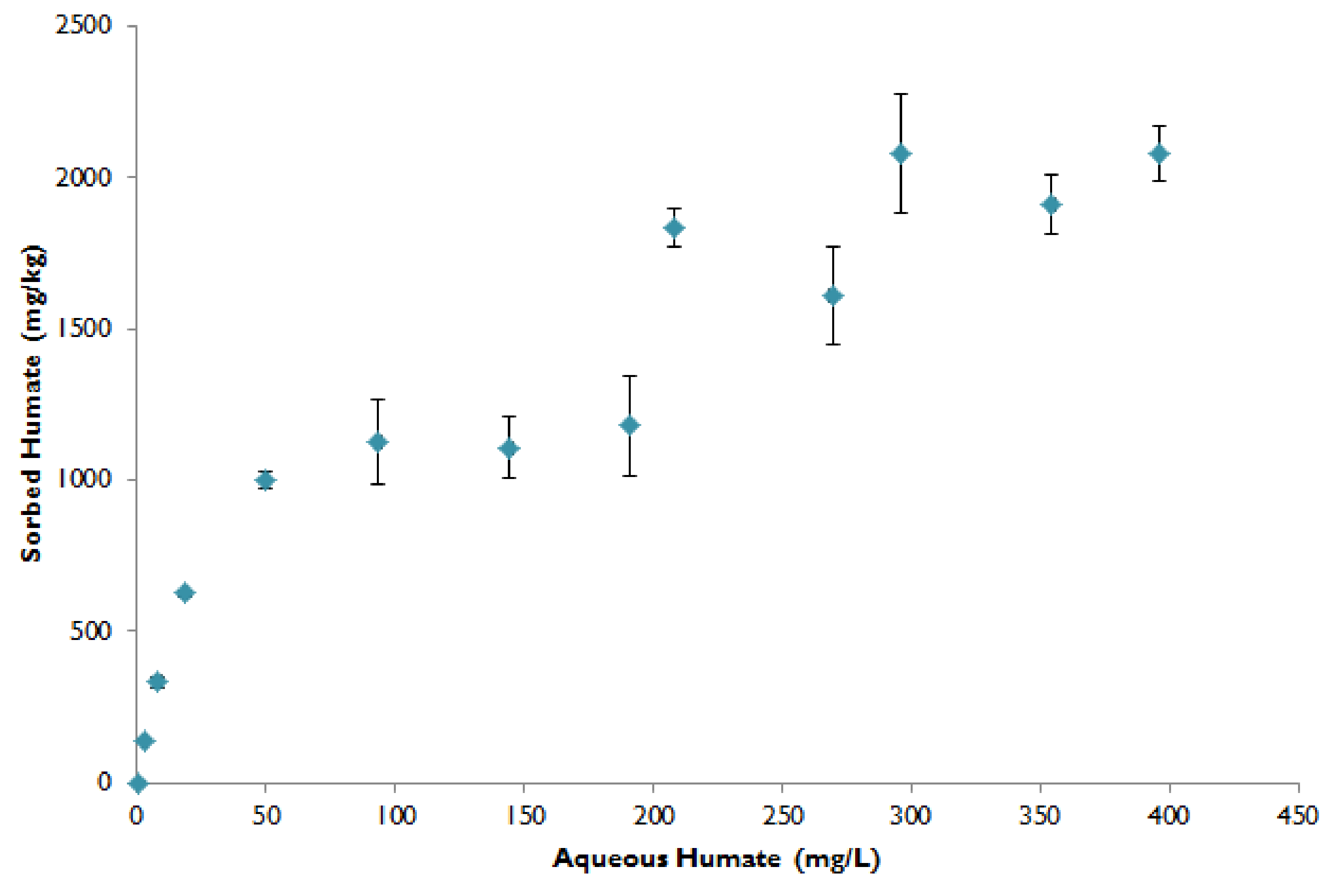
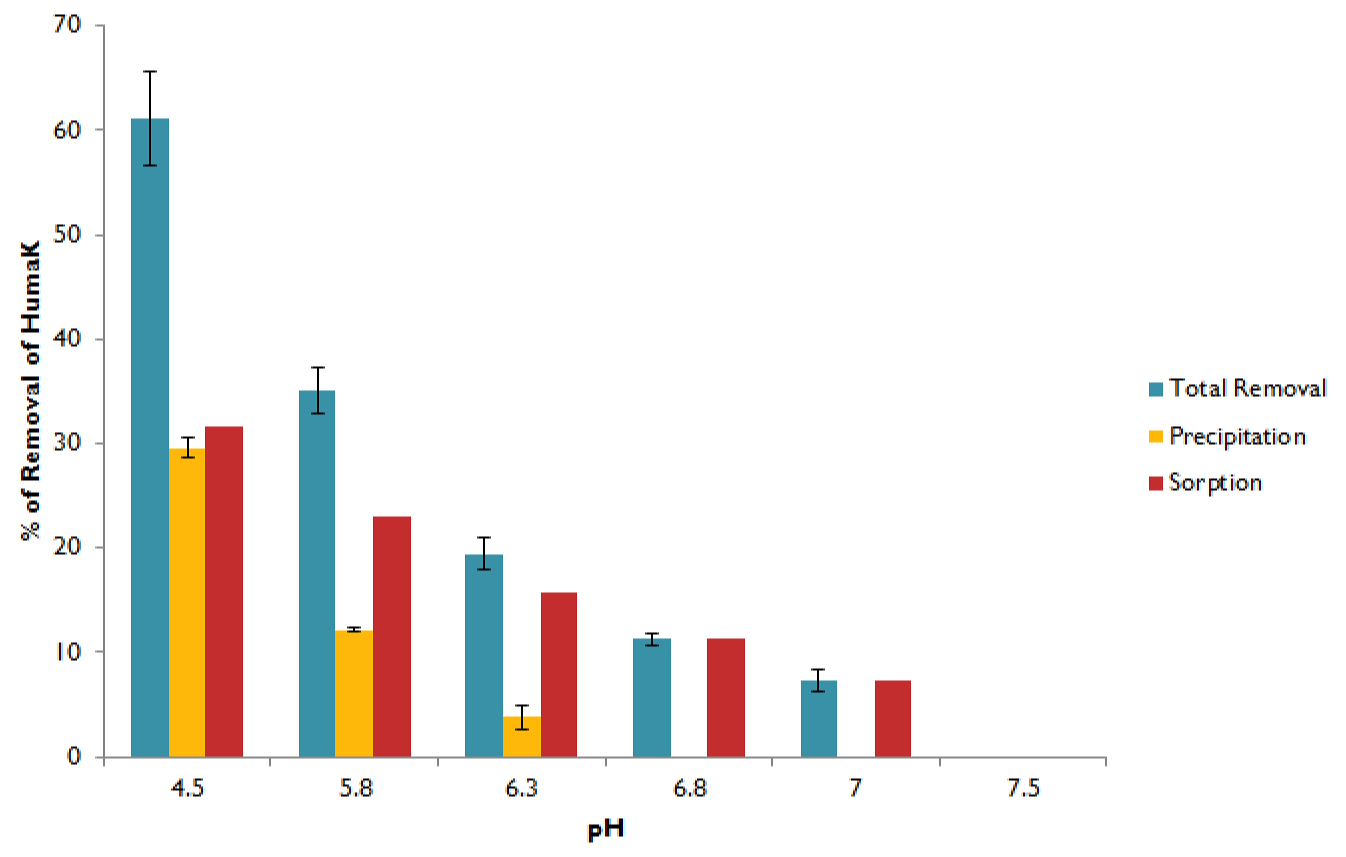
Task 2.3 Results - Sorption at pH 4



Task 2.3 Results - Sorption and Precipitation



Task 2.3 Conclusions

- Sorption of Huma-k on Savannah River Site sediments follows a Langmuir adsorption up to a concentration 250 ppm.
- After all the binding sites have been occupied in the sediments, there is probably another mechanism of sorption of Huma-K.
- In the sorption study at different pH values, it was seen that sorption and precipitation is decreased with increasing pH.

Task 2.3 Future Work

- Kinetic experiment for sorption and desorption of Huma-K.
- Kinetic experiment for sorption of Uranium on Savannah River Site sediments with and without Huma-K.

Task 3: Evaluation of ammonia fate and biological contributions during and after ammonia injection for uranium treatment

Christian Pino, DOE Fellow, Chemistry,
Kiara Pazan, DOE Fellow, Env. Eng.

FLORIDA INTERNATIONAL UNIVERSITY

Task 3 - Introduction

- Contamination to the vadose zone at Hanford resulted from leaks of radioactive waste from high-level storage tanks into the ground during production of atomic weapons.
  - Key contaminant: Uranium(VI)
- Ammonia (NH_3) gas technology offers the potential and feasibility of radionuclide sequestration.
  - Increase pH in pore water
  - Precipitation of mineral phases
  - Penetration to low permeable zones

Task 3- Background

- The amount of NH_3 required to increase soil pH depends on the soil cation exchange capacity.
- NH_3 gas dissolves in soil moisture and reacts to form NH^{4+} and OH^- ions.
- Carbonate rich soils, like in Hanford, require more ammonia due to soil buffering capacity and ammonia carbonate formation.
- Expected processes:
  - Biological transformation
  - Partitioning and vapor transport
  - Geochemical reactions

Task 3 - Purpose

- Study the potential biological and physical mechanisms associated with the fate of ammonia after injection into unsaturated subsurface.
  - Understand the partitioning of NH_3 in bicarbonate-bearing solutions at different pH, and temperature.
  - Predict potential results during and after NH_3 gas injection into Hanford's vadose zone.

Task 3 - Experimental Approach

- Investigate factors that affect ammonia gas partitioning
  - Soil characteristics
  - Pore water composition
  - Bicarbonate ions (buffer capacity increase)
  - Temperature

Task 3 - Experiments

- Injection of 100% concentration ammonia gas in solutions with varying parameters over time
  - pH: 6 to 11
  - Temperature
  - Bicarbonate concentration: 3 mM - 100 mM

Task 3- Experimental Setup

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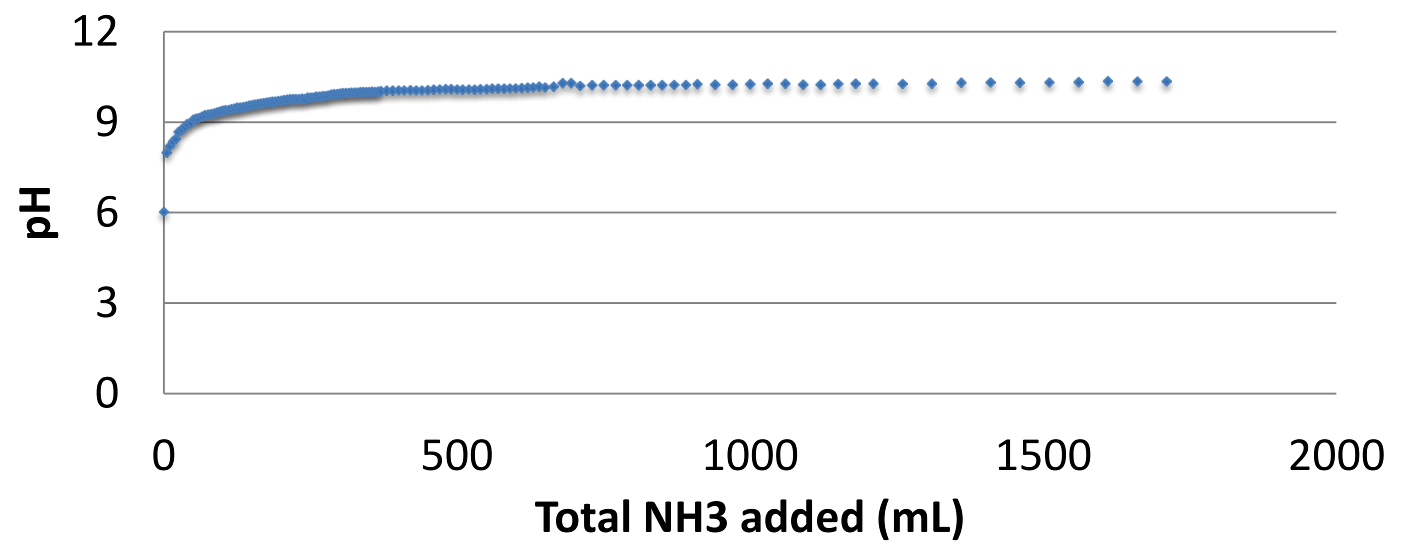
- 100% NH_3 gas will be extracted from a Tedler bag via syringe pump to transfer to a specific volume of liquid.
- A meter with attached pH/temperature module, conductivity module, and ammonia ion-selective electrode is used to collect data.
- Preliminary experiments used lower NH_3 concentrations to improve developed methods.

Florida International University

Task 3 - Preliminary Experiment

- The same experiment was performed with stirrer on to observe if there was a better distribution of ammonia.
- A greater amount of NH3 was added, in increments of 5 - 50 ml, yet pH did not reach 11.



Task 3 - Future work

- Perform experiments using bicarbonate solutions at different temperature
- Investigate the bacteria community transformations in soil before and after NH3 additions

Masters & PhDs

- PhD students: Claudia Cardona and Hansell Gonzalez
  - Claudia passed the qualifying exam, her expected graduation is summer 2016
  - Hansell passed two exams out of three required by the Chemistry Department. His expected graduation is Fall 2017.
- Robert Lapierre and Sandra Herrera are working on MS degree
  - Expected graduation is Fall 2015

Internships

- Hansell Gonzalez - Savannah River National Laboratory, Aiken, SC
  - Summer Site Mentor: Dr. Miles Denham
- Robert Lapierre - Pacific Northwest National Laboratory, Richland, WA
  - Summer Site Mentor: Dr. Jim Szecsody
- Christian Pino - Pacific Northwest National Laboratory, Richland, WA
  - Summer Site Mentor: Amoret Burnn

Conferences & Presentations

Oral presentation on WM-2015 (Session107):

- **Hansell Gonzalez**, Yelena Katsenovich, Miles Denham, Ravi Gudavalli, Leonel Lagos, "**The Influence of Humic Acid and Colloidal Silica on the Sorption of U(VI) onto SRS Sediments Collected from the F/H Area**".

Students posters displayed on WM-2015:

- **Aref Shehadeh** (DOE Fellow), "**Monitoring of U(VI) Bioreduction After ARCADIS Demonstration at Savannah River Site F-Area**"
- **Christine Wipfli** (DOE Fellow), "**Sodium Silicate Treatment for Uranium (VI) Bearing Groundwater Systems at F/H Area at Savannah River Site**"
- **Christian Pino** (DOE Fellow), "**Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit**"
- **Hansell Gonzalez Raymat** (DOE Fellow), "**Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination**".
- **Robert Lapierre** (DOE Fellow), "**Characterization of the Uranium-Bearing Products of the Ammonia Injection Remediation Method**".
- **Sandra Herrera Landaez** (Graduate assistant), "**A Study of Autunite Dissolution in the Presence of Shewanella Oneidensis MR1 and Different Bicarbonate Concentrations**".

Future Work

As part of the renewal work scope for the new Cooperative Agreement (2015-2020) FIU will:

- Task 1. Remediation Research and Technical Support for the Hanford Site
  - Investigate the deliquescence behavior of uranium-bearing multicomponent precipitates at different temperatures and compositions.
  - Investigate the dissolution of autunite and apatite in the presence of facultative (e.g., Shewanella) and anaerobic microorganisms in bicarbonate-amended media.
  - Investigate potential biological and physical mechanisms associated with ammonia (NH3) gas injections; (New) investigate via column experiments for the bacterial community response associated with the degree of saturation.

Future Work - Task 1

- (New) Evaluate ammonia adsorption onto the Hanford soil in the presence of bicarbonate.
- (New) Study transformations of the bacteria community before and after NH3 injections.
- (New) Investigate the influence and corresponding electrical geophysical response of microbial activity on vadose zone uranium sequestration using gas phase ammonia injections.

Future Work

- Task 2. Remediation Research and Technical Support for Savannah River Site
  - Investigate synergetic interactions between humate and silica.
  - Conduct humate batch sorption/ desorption studies in the presence of U(VI) to control uranium behavior.
  - Conduct column studies to investigate the effect of HA on uranium mobility through porous media.