



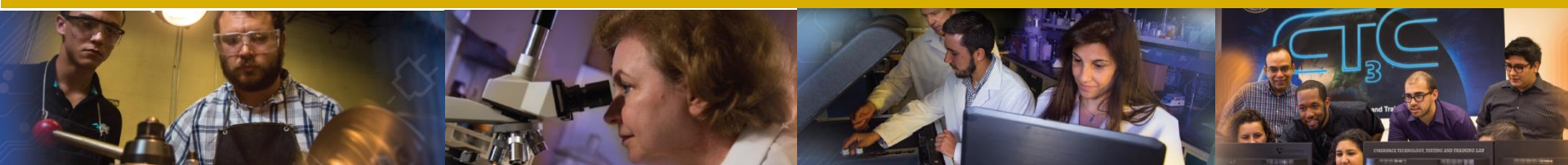
FIU
Applied Research
Center

solution driven

FIU PROJECT 2: YELENA KATSENOVICH

ENVIRONMENTAL REMEDiation SCIENCE & TECHNOLOGY

FLORIDA INTERNATIONAL UNIVERSITY





FIU Personnel and Collaborators



Principal Investigator: Leonel Lagos

Project Manager: Yelena Katsenovich

Faculty/Staff: Angelique Lawrence, Ravi Gudavalli, Hilary Emerson

Postdoctoral Fellows: Mehrnoosh Mahmoudi

DOE Fellows/Students: Mohammed Albassam, Silvina Di Pietro, Alejandro Garcia, Hansell Gonzalez Raymat, Ron Hariprashad, Alejandro Hernandez, Juan Morales, Ripley Raubenolt, Alexis Smoot, Christine Wipfli, Frances Zengotita, Silvia Garcia, Katherine Delarosa, Ximena Lugo

DOE-EM: Genia McKinley, Kurt Gerdes, Paul Beam, Skip Chamberlain, Mathew Zenkowich, Jeff McMillan

DOE-SRS: Jeff Crenshaw, Nixon Peralta

SRNL: Brian Looney, Carol Eddy-Dilek, John Dickson, Elizabeth Hoffman, Hope Lee, Luke Reid, Daniel Kaplan.

SREL: John Seaman

PNNL: Nik Qafoku, Jim Szecsody, Timothy Johnson, Vicky Freedman

LANL: Don Reed

DOE-CBFO: Russ Patterson, Anderson Ward



Project Tasks and Scope

Task 1: Remediation Research and Technical Support for the Hanford Site

- Laboratory-scale experiments to study impacts of potential *in situ* remediation techniques on the subsurface at Hanford.
- Investigate geophysical techniques for tracking remediation progress

Task 2: Remediation Research and Technical Support for Savannah River Site

- Laboratory-scale experiments to study contaminant fate and the impacts of potential *in situ* remediation techniques on the subsurface at SRS.

Task 3: Surface Water Modeling of Tims Branch

- Development of an integrated hydrology model to simulate flow characteristics and contaminant fate and transport under various hydrological conditions in Tims Branch watershed at SRS.

Task 5: Research and Technical Support for WIPP

- Laboratory-scale experiments to study the fate of actinides and lanthanides at the WIPP site.



Task 1: Remediation Research and Technical Support for the Hanford Site

Task 1.1 – Remediation Research with Ammonia Gas for Uranium



Site Needs:

DOE-EM has a critical need to understand the biogeochemical processes influencing the fate of U(VI) following release of >200,000 kg of U during WWII and the Cold War. Remediation of U in the deep vadose zone may be accomplished by injection of NH₃ gas. Manipulation of pH via ammonia gas is a potential remediation technology that can lead to incorporation of U(VI) into the sediments. Pilot scale injection is planned for 2018-2019 to test the viability of this remediation technology on a field scale.

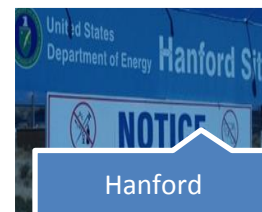
Objectives for FIU FY8:

The objective is to identify the physicochemical mechanisms controlling immobilization of U via NH₃(g) injection in the Hanford vadose zone.

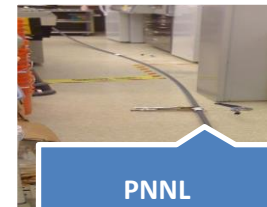
- Measure removal of U from the aqueous phase following NH₃(g) injection.
- Characterize physicochemical changes in minerals.
- Determine the long-term stability of U-solid phases after NH₃(g) injection.



FIU ARC
Laboratory
Batch-scale



Hanford DOE-EM
Field Remediation
for U



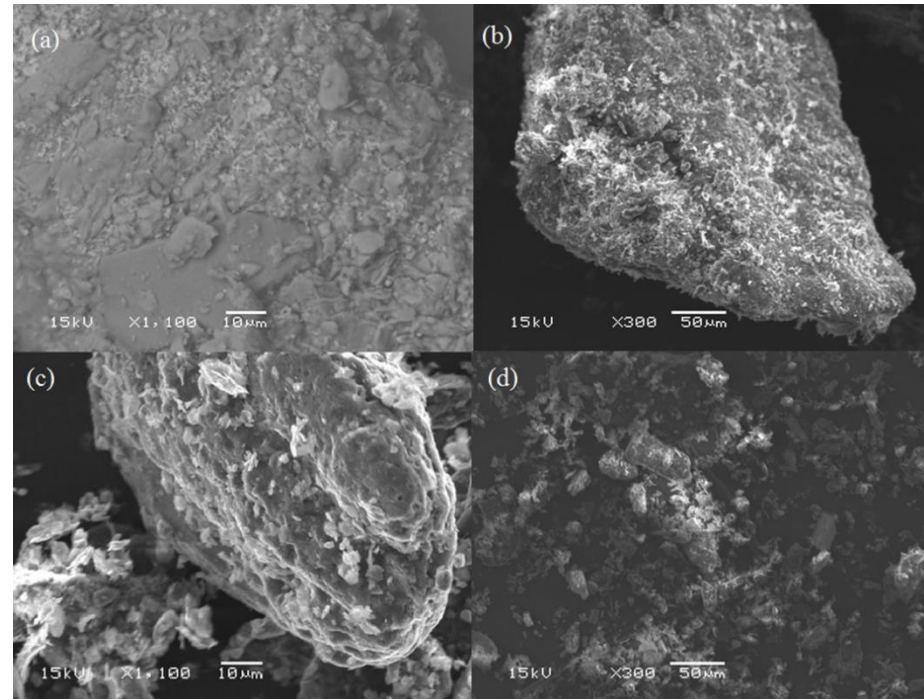
PNNL
Pilot-scale and
Column*



Task 1.1 – Remediation Research with Ammonia Gas for Uranium FY8 Research Highlights



- *Ongoing* – Characterizing solid phases (with and without U) to identify dominant mineral phases controlling U behavior.
- Finalized results measuring U partitioning and mineral dissolution following base treatments (NaOH, NH₄OH, and NH₃ gas).
- Showed that co-precipitation of U with Ca-carbonate is significant in controls.
- Clay minerals remove more U than Hanford sediments and calcite.
- Quartz removes the most U when mineral surface area is accounted for.



SEM imaging of illite minerals following treatment with NH₃ gas and aeration.

Note: Al:Si ratios measured on the surface vary from 0.28-0.55

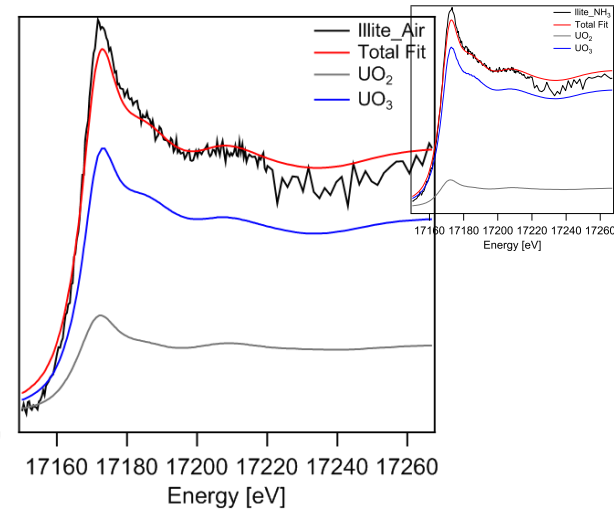
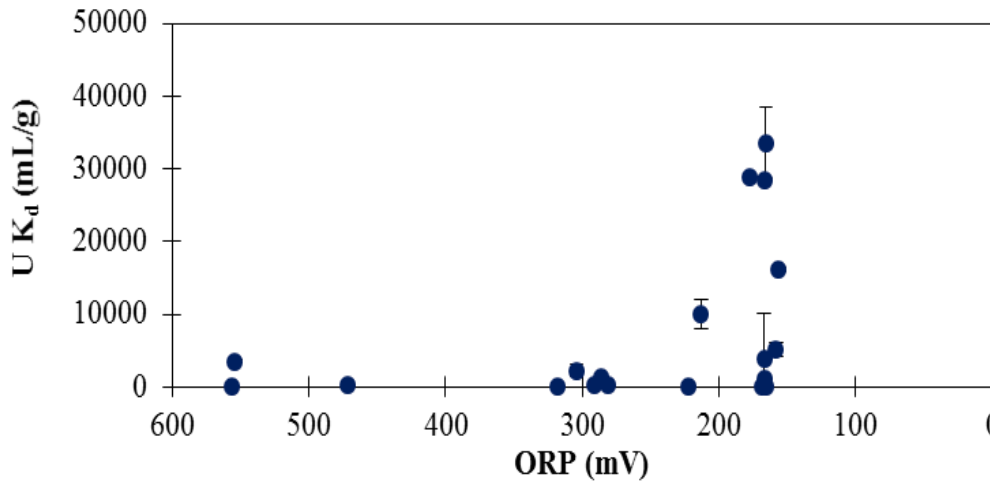


Task 1.1 – Remediation Research with Ammonia Gas for Uranium

FY8 Research Highlights



- Showed significant changes in redox conditions and identified stable U(IV) in solid phases via XANES analysis conducted at Argonne’s synchrotron.



Valence State	Illite + NH ₃	Illite + NH ₃ + Aerated
U(IV)	15±8%	26±11%
U(VI)	91±8%	74±11%



Task 1.1 – Remediation Research with Ammonia Gas for Uranium FY8 Accomplishments



- DOE-NE *Innovations in Nuclear R&D Award* based on 2017 Waste Management Proceedings Paper (Di Pietro, \$1500).
- Publication in *Applied Geochemistry* "Assessment of Calcium Addition on the Removal of U(VI) in the Alkaline Conditions Created by NH₃ Gas".
- Publication in *Journal of Environmental Management* under review "U immobilization in the presence of minerals following remediation via base treatment with ammonia gas".
- 2018 Waste Management Conference Proceedings Paper "Base treatment for U immobilization at DOE's Hanford site".
- Presentations at Fall ACS Meeting in Boston and Goldschmidt (August 2018) and Waste Management Symposia (March 2018).



Task 1.1 – Remediation Research with Ammonia Gas for Uranium FY9 Objectives

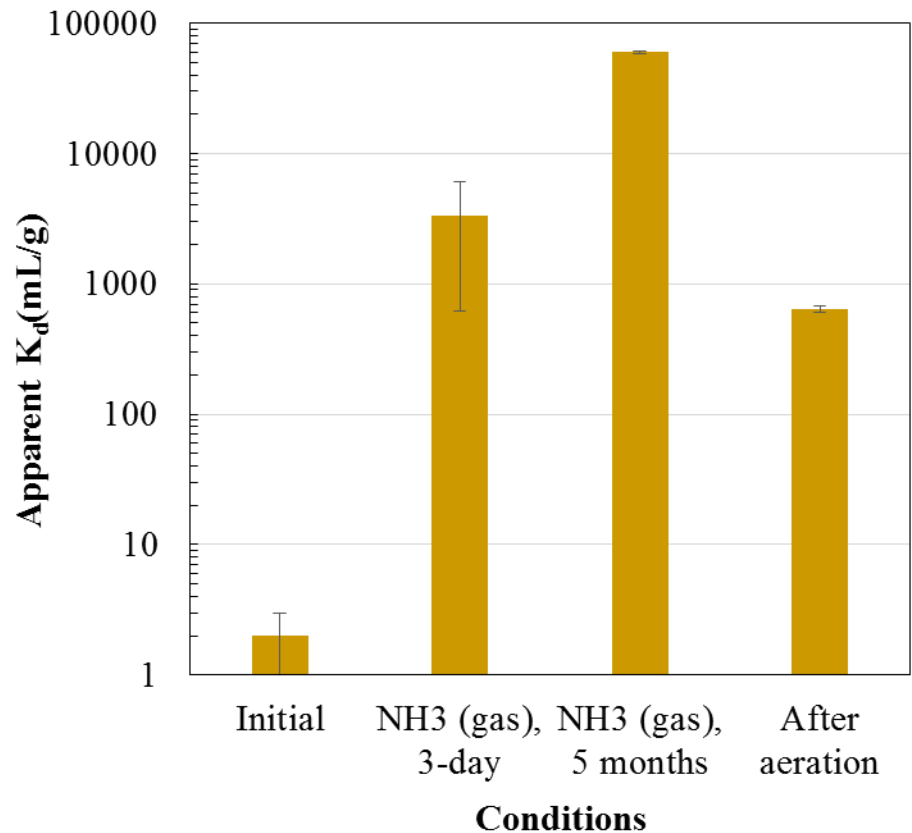


To understand impacts of base treatment on long-term fate of U:

- Physical and mineralogical changes due to dissolution and precipitation of muscovite, illite, and Hanford sediments*
- Speciation of U in the solid phase due to sorption and co-precipitation
- Stability of solid U phases

To be accomplished via:

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



*Due to similar removal during ammonia gas treatment, we hypothesize that these may be the controlling minerals or at least exhibit similar removal processes.



Task 1: Remediation Research and Technical Support for the Hanford Site

Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments



Site Needs: Research on environmental remediation requires knowledge on subsurface contaminant distributions, which may be accomplished using geophysical techniques. FIU is conducting column studies to test the feasibility of corresponding electrical geophysical response to measure microbial activity spurred by ongoing remediation efforts for uranium.

Objectives for FIU FY8:

Investigate the influence and corresponding electrical geophysical response of microbial activity on geochemical changes in simplified column experiments.

- Conduct column experiments under strictly controlled conditions to get a better understanding of the microbial-driven changes within the subsurface.
- SIP measurements in soil-free columns with only autoclaved SG.
- Measure SIP of autoclaved Hanford soil saturated with oxygen-free SGW.
- Add heat deactivated microbial cells of *Shewanella Oneidensis* to measure an impact in the SIP signature of the media.
- Add active microbial cells of *Shewanella Oneidensis* to measure live cells distinct SIP signals.
- Compare results of the SIP measurements between experimental steps.



Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments

FY8 Research Highlights



- Constructed a new sediment filled column.
- Measured both heat deactivated microbes and live microbes for possible surface polarization effects.
- Continuous monitoring of microbial growth. Carbon source is 200 mg/L glucose.
- Effluent samples are taken 5 days a week.
- SIP measurements are taken every 10 mins with occasional interruptions in order to charge 12V battery.
- Further analysis of existing data for prior experiments.

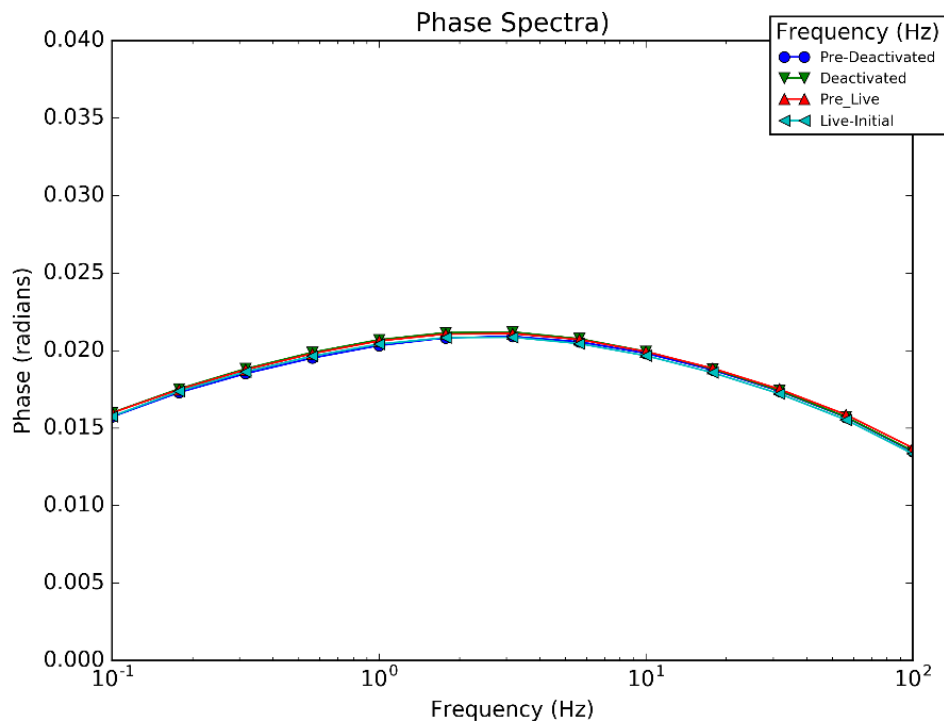


New column for basic experiments



Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments

FY8 Research Highlights



- No difference in the measured phase between abiotic Hanford fine sand, heat deactivated microbes and immediately after injection of live microbes.
 - Not much changes just on the presence of microbes itself.
- Higher concentrations of deactivated microbes may provide measureable difference.
- Higher frequency range equipment may also be able to detect difference.
- Ongoing- column's monitoring after injection of live *Shewanella* cells.

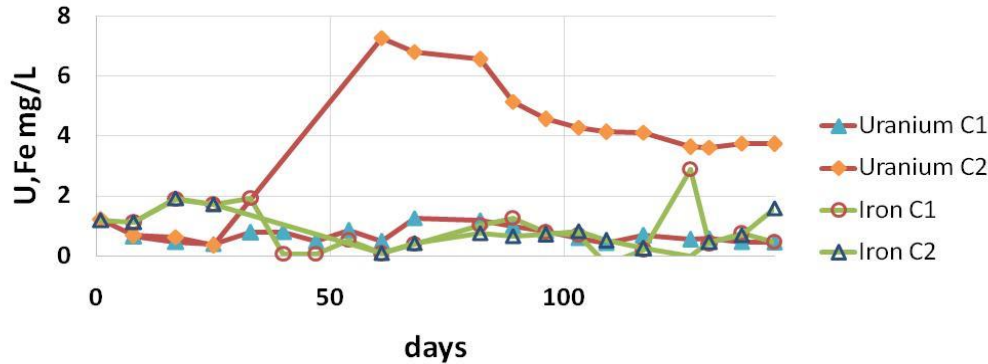


Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments

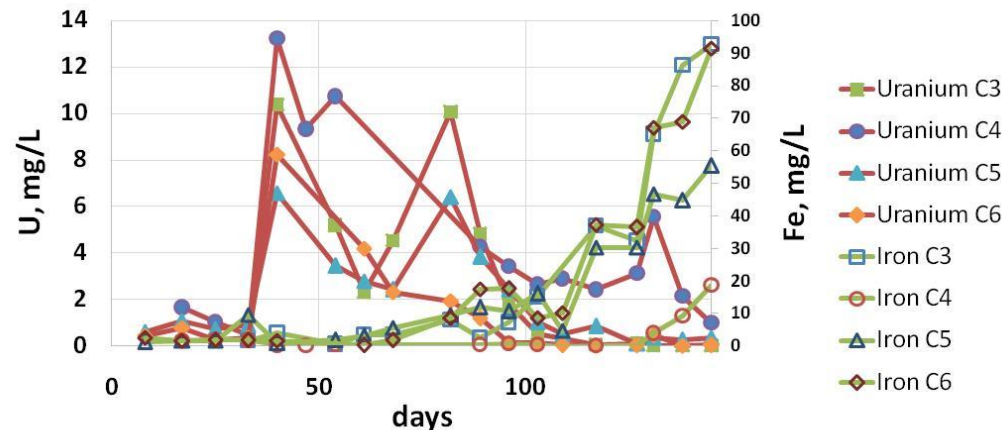
FY8 Research Highlights



Dissolved Iron, Uranium Fall 2016



Dissolved Iron, Uranium Fall 2016

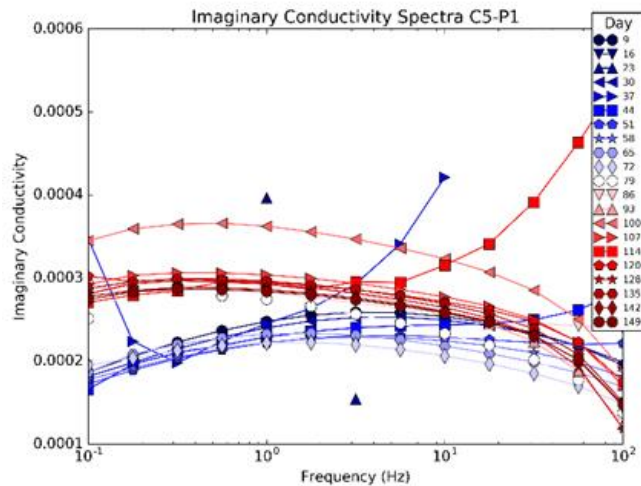
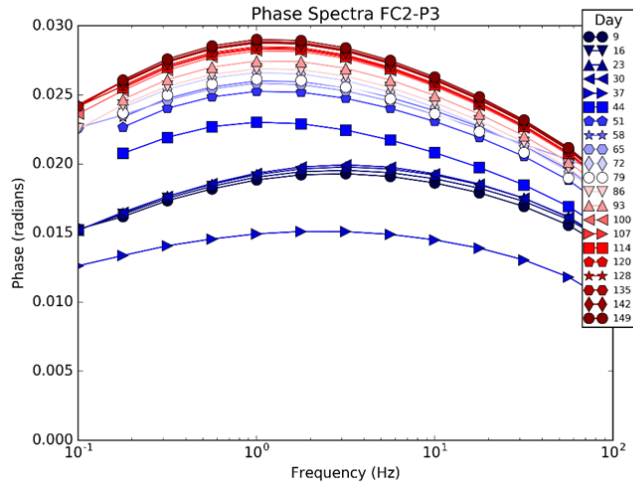


- Completion of iron and uranium analysis for Fall 2016 and Spring 2017 experiments.
- Increases in U(VI) concentrations tied to the presence of HCO_3 due to the formation of mobile uranyl carbonate complexes.
- Injection of microbes cause sudden increase in U(VI) concentrations, possibly due to bio dissolution of autunite particles.
- Sudden drop in concentrations in columns without HCO_3 followed by 2nd peak could be due to shift from oxic to anoxic conditions suggested by increase of ferrous iron concentrations.



Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments

FY8 Research Highlights

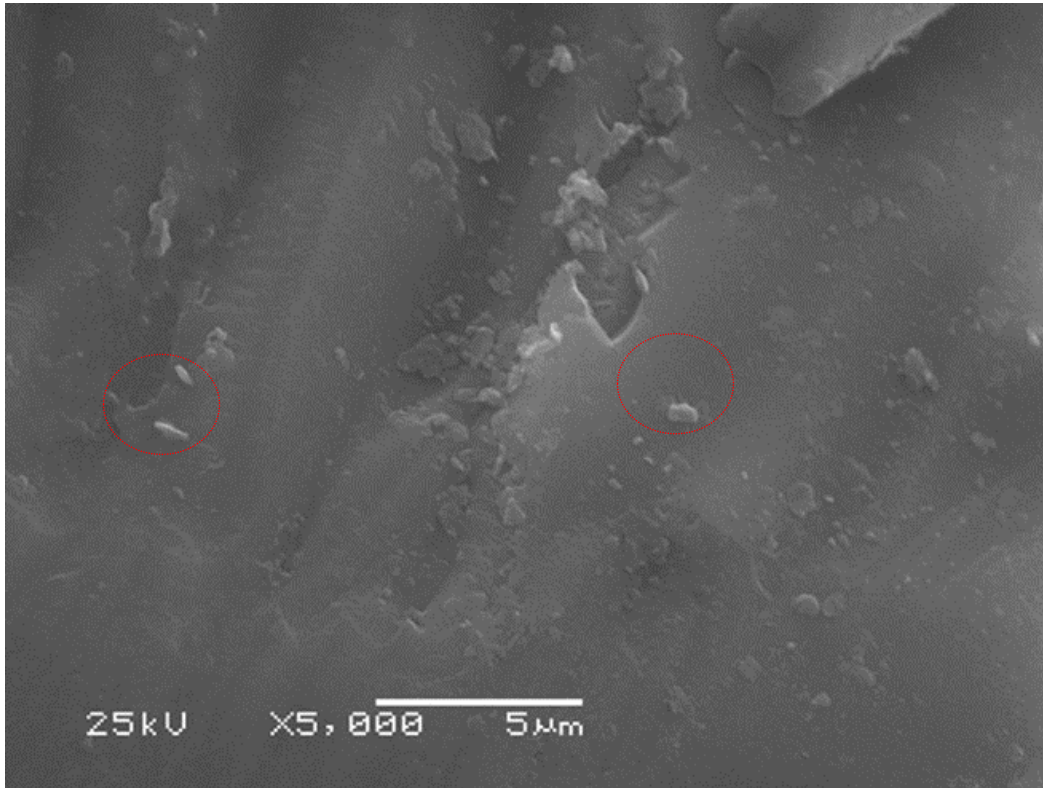


- Increases in phase and imaginary conductivity seen in control column with bicarbonate, which is likely due to solid phase precipitation (calcite).
- Microbial columns show flattening of spectra as well as increase in imaginary conductivity at low frequencies (<10Hz).
 - Imaginary conductivity is consistent in microbes -inoculated columns.



Task 1.3 – Investigation of Electrical Geophysical Response to Microbial Activity in Saturated Environments

FY8 Accomplishments



- Results presented as a poster at AGU 2017 and as a poster and oral presentation at WM 2018 as well as in conference proceedings.
- Thesis due for completion in summer 2018.

**This task will be completed
in FIU Year 8**

Image shows there is no formation of microbial biofilm on the sediment surface, only single cells attached to the surface



Task 1: Remediation Research and Technical Support for the Hanford Site

Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

Site needs:

DOE-EM has a critical need to address challenges associated with Tc-99 remediation of the contaminant plumes in deep vadose zones. It requires understanding on the fate of Tc in conditions related to the Hanford Site and explore the effect of bicarbonates on redox transformations of Tc-99 to facilitate identification of promising Tc-99 remediation technologies.

Objectives for FIU FY8:

The objective is to study the reduction of Tc-99 in the presence of bicarbonates under reducing conditions in Hanford soil and pure mineral magnetite.

- Measure effect of pH on TcO_4^- reduction under anaerobic conditions.
- Investigate the effect of specific surface area on Tc reduction.
- Study the effect of ferrous iron area on Tc reduction.
- Investigate if Tc(VII) precipitates as TcO_2 or form soluble Tc(IV)- carbonate complexes under circumneutral reducing conditions in the presence of bicarbonate.
- Determine the role of ferrous-bearing mineral phases, such as magnetite, in the sequestration/immobilization of Tc.



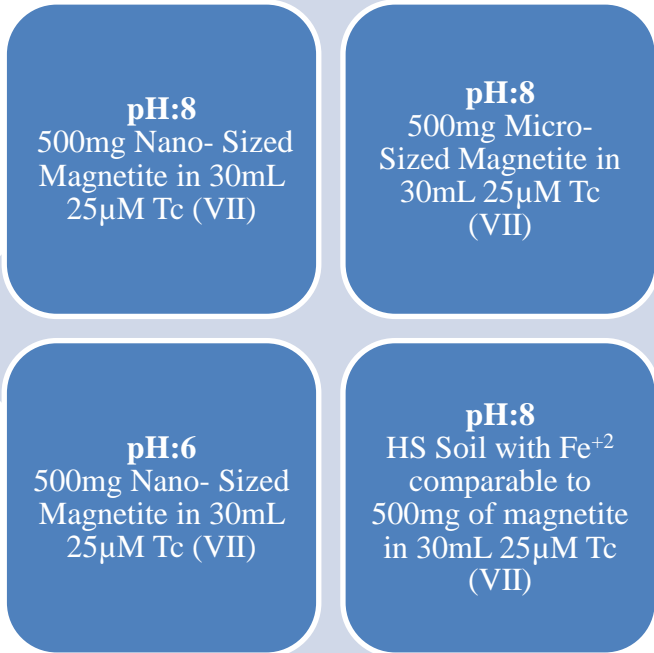
Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

Methodology



Specific Surface Area Effect

pH Effect



Bicarbonate / Bicarbonate Free

Mineral Phase Effect



Sample rotor



Liquid scintillation counter

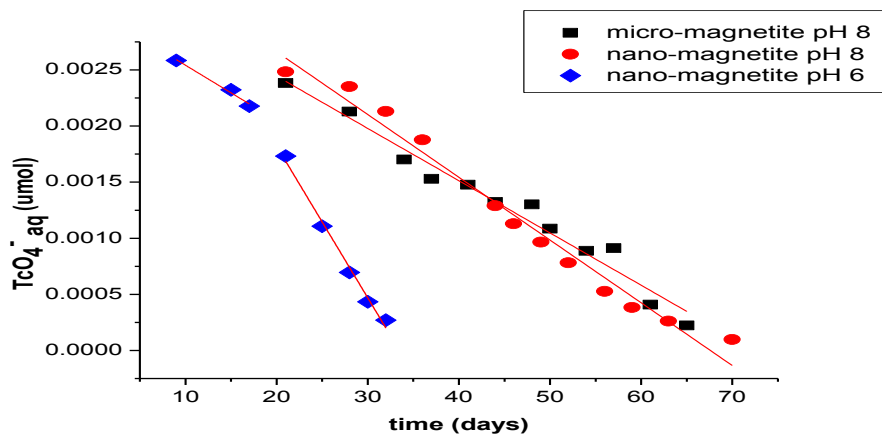


Anaerobic glovebox

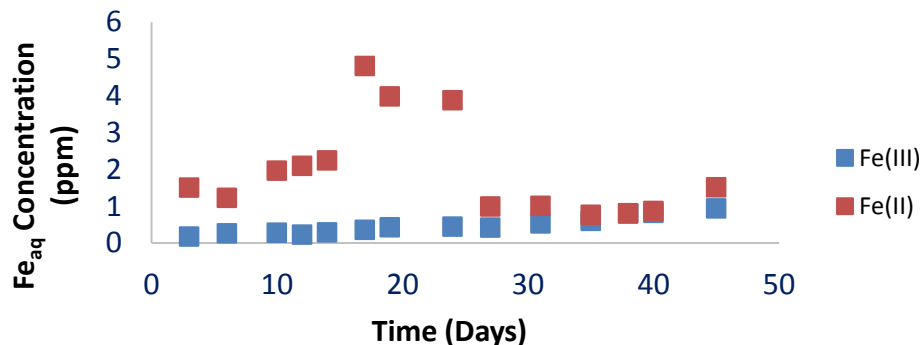


Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

FY8 Research Highlights



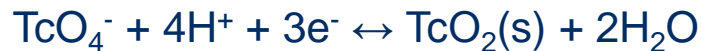
Linear regression (least squares method) for Tc-99 reduction by nano-magnetite at pH 6 and nano- and micro- magnetite at pH 8.



Fe(II) and Fe(III) concentrations as a function of time during Tc-99 sequestration by nano-magnetite at pH 6.

Mineral phase	pH	k (nmol d ⁻¹)	R ²
Micro - magnetite	8	0.046 ± 0.002	0.97
Nano - magnetite	8	0.058 ± 0.003	0.98
Nano - magnetite	6	0.049 ± 0.003 ^a	0.97
		0.15 ± 0.004 ^b	0.99

- No significant reduction of Tc-99 was observed in the Hanford soil
- Pertchnetate reduction is significantly enhanced at lower pH values



- No Fe(III)_{aq} detected at pH 8 (blue dots)
- Same pattern for ferric iron for micro- and nano-magnetite, as well as Hanford soil - Gradual increase and sharp decrease due to saturation



Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

FY8 Research Highlights



Fe(II), Fe(III) and Total Iron in Micro- and Nano-Magnetite and HS Soil

	Fe (II) *	Fe (III)*	Fe(II) in solid	Fe(III)/Fe(II)
Nano-magnetite	10 ±0.3	23±2	20±0.7	2.3
Micro-magnetite	3.4 ±0.05	26±4	7±0.1	8
HS Soil (d<300)	0.06±0.02	1.6± 0.4	0.14±0.03	29

*(mg in 50 mg of solid)

Saturated species at pH 6 and 8 (nitrogen atmosphere) as predicted by Visual Minteq

pH 6	pH 8
Fe ₂ O ₃ (maghemite, lepidocrocite and ferrihydrite)	Fe ₂ O ₃ (maghemite, lepidocrocite and ferrihydrite)
FeO(OH) (goethite and lepidocrocite)	FeO(OH) (goethite and lepidocrocite)
Fe ₃ O ₄ (magnetite)	

- Pertechnetate reduction rate at pH 6 accelerates when precipitation of ferric oxides takes place, whereas at pH 8, Tc-99 reduction rate is constant despite ferric oxide precipitation (absence of Fe(II)_{aq})
- Presence of Fe(II)_{aq} in the system and its potential sorption on the newly formed phases is probably the reason behind pertechnetate reduction acceleration

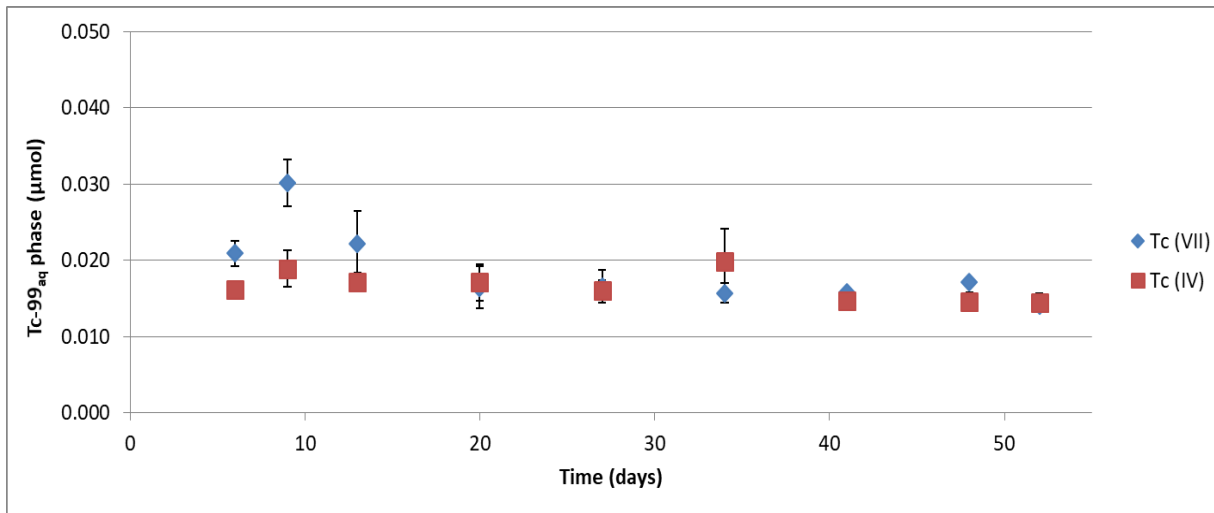


Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

FY8 Research Highlights



Tc(VII)aq and Tc(IV)aq concentrations as a function of time



- Data indicate that there is no change in the dissolution rates over time.

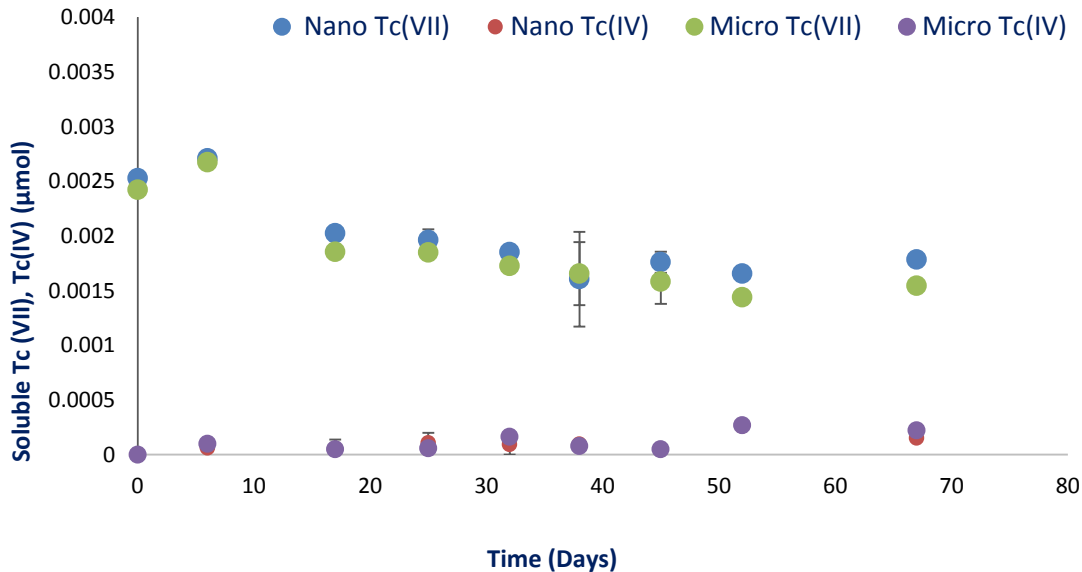
Dissolution levels in the presence of 0mM, 5mM and 50 mM of bicarbonates at pH 8

Bicarbonate Concentration (mM)	0	5	50
Dissolution Concentration (M)	$4.1 \cdot 10^{-7} \pm 0.1 \cdot 10^{-7}$	$3.8 \cdot 10^{-7} \pm 0.3 \cdot 10^{-7}$	$3.9 \cdot 10^{-7} \pm 0.3 \cdot 10^{-7}$



Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

FY8 Research Highlights



Tc(VII)_{aq} and Tc(IV)_{aq} as a function of time in the presence of 50 mM bicarbonates at pH 8 for nano- and micro-magnetite.

- Preliminary results reveal that reduction of pertechnetate by both nano- and micro-magnetite at pH 8 is rather similar and there is negligible amount of Tc(IV)_{aq}.
- A decrease in reduction rate was observed, when compared to the bicarbonate free counter parts.
 - This decrease was attributed to a spike in pH from 8 to 9
 - The pH was readjusted and samples is being monitored for further reduction



Task 1.4 – Investigation of the Fate of Tc Under Conditions
Relevant to the Hanford Site



Investigate the effect of bicarbonate on the reduction of Tc

Ongoing experiments

- Study pertechnetate reduction in the presence of HCO_3^- at pH 8 to compare the reduction rate by Hanford sediment and magnetite, as well as to investigate the formation of soluble Tc(IV)-carbonate complexes
- Measure the concentration of leachates from the sediments to investigate their possible effects on the reduction of Tc(VII)
- Conduct characterization of magnetite-ferric oxide samples to identify factors responsible for mineral transformation and faster pertechnetate reduction by means of FTIR, XRD and possibly XPS
- Investigate critical mass of Fe(II) needed for Tc-99 reduction to occur



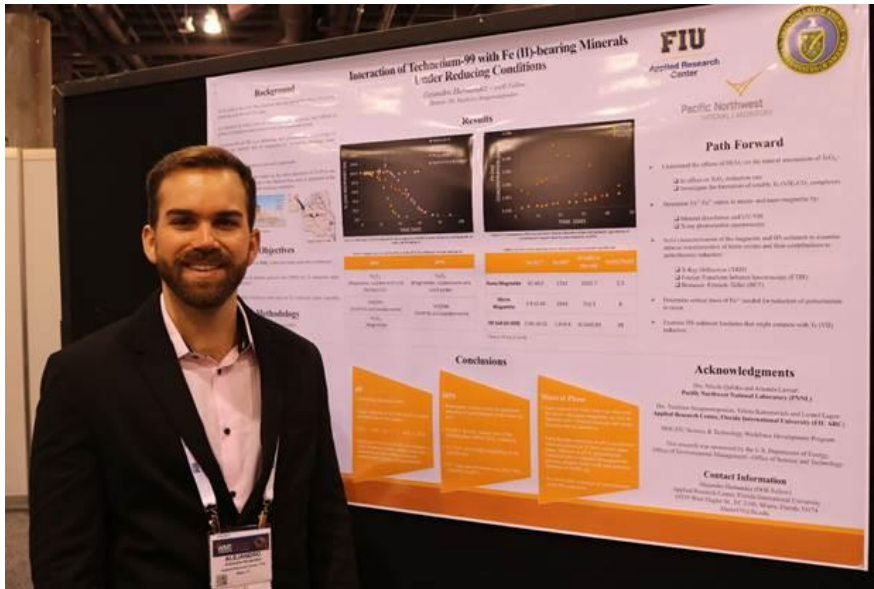
Task 1.4 – Investigation of the Fate of Tc Under Conditions Relevant to the Hanford Site

FY8 Accomplishments & FY9 Scope



Accomplishments for Year 8

Research was presented at WM 2018 by the DOE Fellow Alejandro Hernandez.



Objectives for FIU FY9

- Study the reduction of pertechnetate in the presence of Hanford relevant Fe(II)-bearing minerals such as ilmenite, siderite and biotite.
- Investigate for Tc re-oxidation rate.



Task 1: Remediation Research and Technical Support for the Hanford Site

Task 1.5. – Stability of Contaminants in Carbonate Precipitates



Site Needs:

Currently, the DOE has no approved treatment technologies to control iodine mobility in the vadose zone (VZ) and groundwater. The largest ^{129}I plume is associated with the 200 West Area in the 200-UP-1 operable unit (OU) and dilute plumes in the subsurface of the Central Plateau at the Hanford Site covering an area greater than 50km^2 . Studies conducted previously confirmed that iodine removal from the aqueous phase can occur through incorporation into calcite, which is a common mineral at the Hanford subsurface. This incorporation is assumed to be mainly as the IO_3^- group substituting for CO_3^{2-} .

Objectives for FIU FY8

Investigate co-precipitation of iodine with calcium carbonate and study the effect of silica content in the synthetic pore water composition on the co-precipitation process

- Study the effect of pH and different silica concentrations (0-20mM) in 0.1M calcium carbonate forming solutions (CaCl_2 and NaHCO_3) on iodate co-precipitation with calcium carbonate (iodate is the predominant aqueous species of iodine in GW samples at 200-UP-1);
- Conduct iodine “late spike” experiments after calcium carbonate precipitation at different pH and Si concentrations.
- Initiate characterization of produced solids.



Task 1.5 – Remediation Research on Iodine Incorporation into Calcite

FY8 Research Highlights



- Evaluated samples preparation procedures using calcium carbonate forming solutions and metasilicate
 - Mixing sodium bicarbonate and sodium metasilicate targeting 0.1M NaHCO_3 and Si-free, 0.5mM, 2mM, 5mM, and 20mM Si concentrations in the solution mixtures.
 - Iodate spike at concentrations 500ppb and 250ppb
 - pH adjustment with 1M NaOH solutions (studied pH range 7-11);
 - Mixing with 0.1M CaCl_2
 - Readjustment of pH
 - Addition of remaining DIW to the required sample volume
- Completed sampling of solutions after iodate-carbonate precipitation at each pH and silica concentration

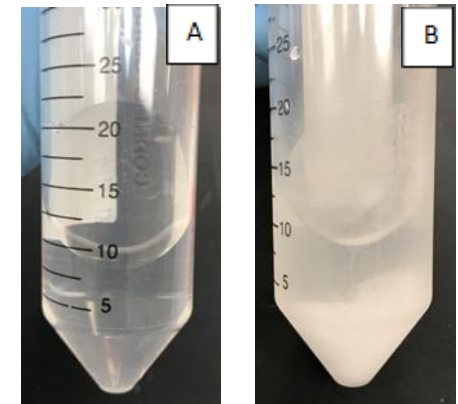


Task 1.5 – Remediation Research on Iodine Incorporation into Calcite

FY8 Research Highlights



- Completed sampling of iodate control samples in DIW and Ca-free solutions at tested pH and Si concentrations.
- Samples were taking for 1,3,7 days via 0.2um syringe filters; kept in the fridge until analysis.
- *Ongoing*-IC-ICP-MS (IC Dionex Integrion, ThermoFisher iCAP RQ ICP-MS) installation for speciation analysis of iodine and other constituencies.
- *Ongoing*- Characterization of dried solid phases via SEM/EDS.
 - Samples prepared at Si 20mM and pH 7-10.



Control Ca-free solution (A) and Ca-amended solution showing formation of CaCO₃ precipitate (B).

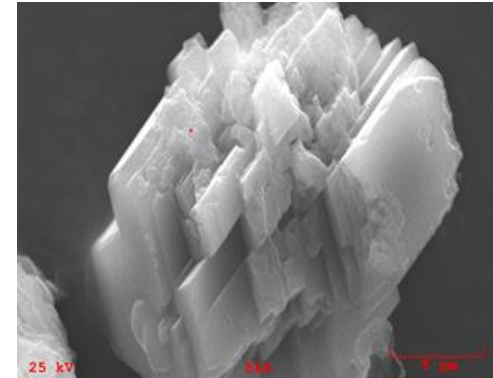
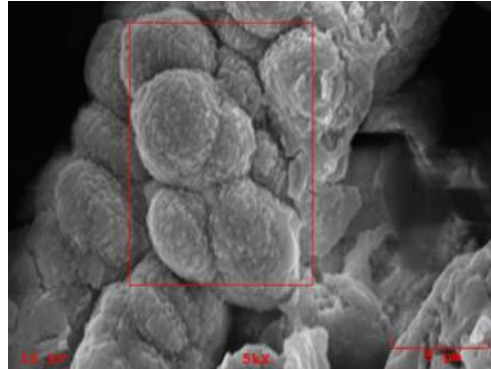
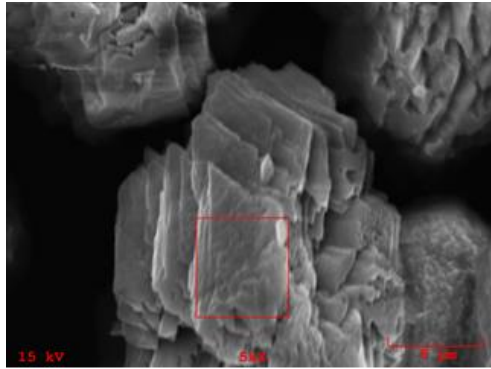


Task 1.5 – Remediation Research on Iodine Incorporation into Calcite

FY8 Research Highlights



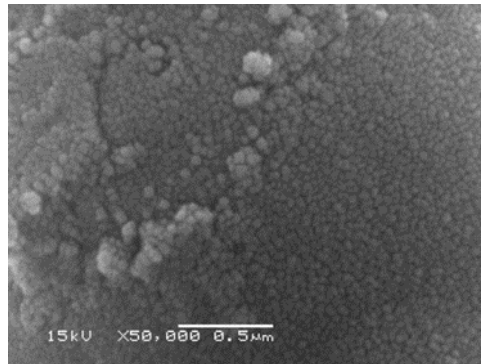
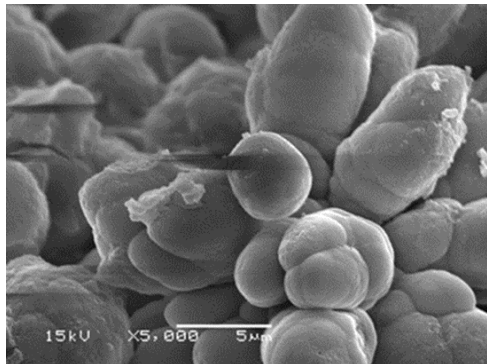
SEM identified different morphologies at each pH conditions.



Sample with 500ppm of iodine, 20mM Si, pH 7. Iodine found between 2.9%-4.5%. The lowest iodine content of 0.6-0.7% is in the “sponge-looking” areas.

Sample with 500ppm of iodine, 20mM Si, pH 8.

Ongoing - Sample preparation for microprobe and XRD analysis.



Sample 20mM Si, pH 10. Surface Si coating is visible at x50K magnification.

Accomplishments
2018 Waste Management Conference student poster “Iodine precipitation with calcium carbonate”.

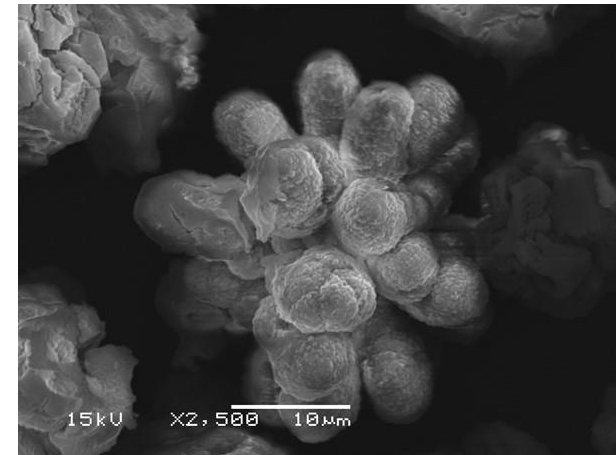


Task 1.5 – Remediation Research on Iodine Incorporation into Calcite

FY9 Objectives



- Continue studies on the iodate incorporation into by calcium carbonate in the presence of silica in a wide range of pH (7 to 11).
- Study the effect of Si on sequestration of iodine by calcite in the presence of co-mingled contaminants (chromate).
- Conduct characterization of the produced solids.
- Investigate the stability of contaminant-substituted calcite in the presence of silica.
 - Batch experiments on iodate co-precipitation at lower concentrations.
 - Solids characterization via XRD, surface area BET, FTIR, EMPA and SEM-EDS.
 - Sequential extractions for stability studies at different pH.



SEM image of “Sponge-looking” solid phases in a sample prepared with 500ppm of iodine, 20mM Si, pH 7



Task 2: Remediation Research and Technical Support for Savannah River Site

Task 2.1 – Impact of reactive oxygen species on the fate of Tc, I, and U in Wetlands at Savannah River Site



New Task! Savannah River Site

Site Needs:

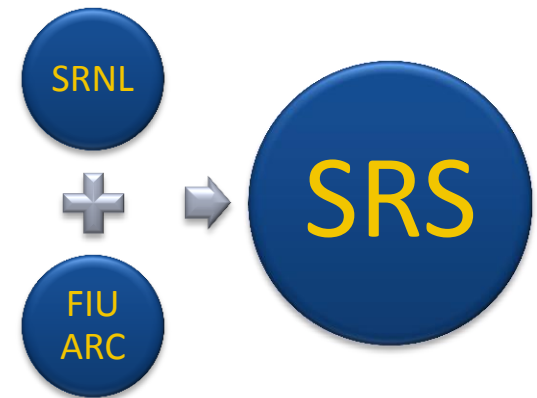
DOE-EM is interested in quantifying the effect of co-mingled contaminant plumes (McCabe et al 2017). This research will supplement ongoing activities at SRS pertaining to the Area Completion Project and associated permitting strategies to evaluate and meet standards for contaminants in the Four Mile Branch Wetland. It will also impact conceptual model development for Tim's Branch Wetland.

Objective in FIU FY8-9:

To understand I, Tc, and U fate in a wetland environment including the impacts of reactive oxygen species (ROS) formation due to co-mingled nitrate contamination interacting with natural organic matter and light.

Research Questions:

1. *How do ROS impact organic matter in the presence of nitrate?*
2. *Do ROS or altered organic matter impact the fate of I, Tc, and U?*
3. *Is there a synergetic effect between ROS and organic matter degradation on radionuclide fate?*





Task 2.1 – Impact of reactive oxygen species on the fate of Tc, I, and U in Wetlands at Savannah River Site

FY8 Accomplishments & FY 9 Scope



New Task!

Accomplishments in FIU FY8: (March 2018 – present)

- Trained DOE Fellow Silvia Garcia.
- Initiated experiments characterizing humic acid at pH 3, 5, and 7, 0 and 100 mM NO_3^- , and in the presence and absence of full sunlight (natural and in environmental chamber).

Ongoing:

- Characterize humic acid via UV-vis, TOC, ATR-FTIR, FT-ICR-MS, and NMR.
- Compare changes in functional groups and total organic carbon content in humic acid.

Objectives for FIU FY9:

1. Investigate variable nitrate and light exposure on humic acid and consider chemicals that quench ROS to identify dominant degradation pathways.
2. Evaluate the behavior of I, Tc, and U both during and following interaction of humic acid with light and nitrate.





Task 2: Remediation Research and Technical Support for Savannah River Site

Task 2.2 – The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)



Site Needs:

Low cost unrefined humic substances are potential amendments for treatment of uranium in groundwater associated with F-Area Seepage Basins plume. In addition, it is thought that elevated silica concentrations in the acidic plume may enhance uranium removal when pH is increased by base injection. Understanding the synergy between humate and silica is important to developing an optimized pH adjustment to treat uranium in groundwater.

Objectives:

- Investigate for synergistic interactions between U(VI) ions, HA and colloidal silica in the presence of pure minerals relevant to SRS sediment.
- Determine if the low cost unrefined humic acid (Huma-K) and modified humic acid (KW15 modified Humics) can be used to control the mobility of uranium in groundwater and study the sorption/desorption of humic acid (Huma-K) and modified HA on SRS sediment at various pH via batch and column experiments.
 - Perform batch and column sorption experiments with humic acid to simulate the creation of a sorbed humate treatment zone in acidic groundwater contaminated with U.



Task 2.2 – The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)

FY8 Research Highlights



Completed batch samples with combinations of HA, Si, U and pure minerals at pH 3,5 and 8.

Set #1	<ul style="list-style-type: none"> ▪ Batch 1: Quartz (400mg) + U(VI) (0.5 ppm) ▪ Batch 2: Quartz (400mg) + U(VI) (0.5 ppm) + HA (30 ppm) ▪ Batch 3: Quartz (400mg) + Si (3.5 mM) + U(VI) (0.5 ppm) + HA (30 ppm)
Set #2	<ul style="list-style-type: none"> ▪ Batch 1: Kaolinite (400mg) + U(VI) (0.5 ppm) ▪ Batch 2: Kaolinite (400mg) + U(VI) (0.5 ppm) +HA (30 ppm) ▪ Batch 3: Kaolinite (400 mg) + Si (3.5 mM) +U(VI) (0.5 ppm) + HA (30 ppm)
Set #3	<ul style="list-style-type: none"> ▪ Batch 1: Quartz (380 mg) + Kaolinite (20 mg) + U(VI) (0.5 ppm) ▪ Batch 2: Quartz (380 mg) + Kaolinite (20 mg) + U(VI) (0.5 ppm) +HA (30 ppm) ▪ Batch 3: Quartz (380 mg) + Kaolinite (20 mg) + Si (3.5 mM) + U(VI) (0.5 ppm) + HA (30 ppm)



Task 2.2 – The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)

FY8 Research Highlights



- Prepared triplicate samples for each batch and adjusted pH of the mixture to the desired value of 3, 5, and 8 using 0.01 M HCl and 0.01 M NaOH.
- Kept samples on a shaker platform at 100 rpm for 7 days at room temperature.
- Centrifuged at 2700 rpm at 22°C for 30 minutes.
- Filtered via 0.45 μm PTFE syringe filter and unfiltered aliquots were diluted for U(VI), Si and Fe analysis via KPA and ICP-OES.

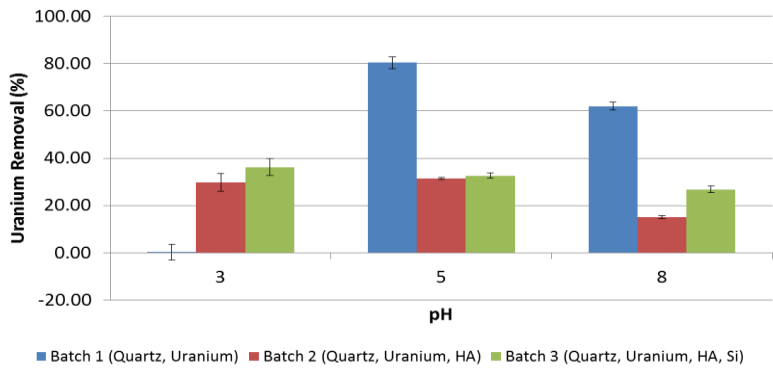


Task 2.2 – The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI) FY8 Research Highlights

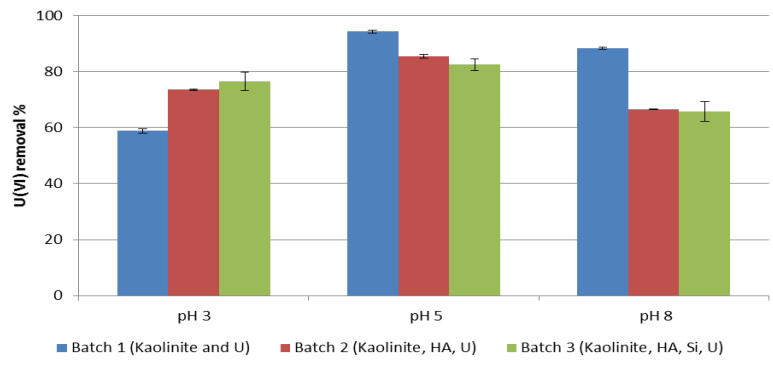


- Studied the removal of uranium and found that humic acid is effective in removing uranium at acidic pH
- Colloidal silica is shown to have little effect on the removal of U(VI) when in composition with HA;
- Filtration removed particles larger than 0.45 μm and any U(VI) that may have bonded to them and resulted in similar trends of uranium removal.

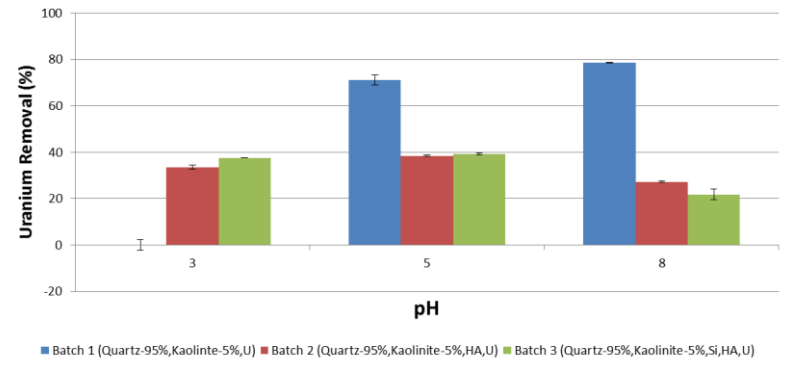
Uranium (VI) Removal for Unfiltered Samples - Quartz



Uranium Removal Filtered samples - Kaolinite



Uranium Removal - Unfiltered Samples - Quartz/Kaolinite

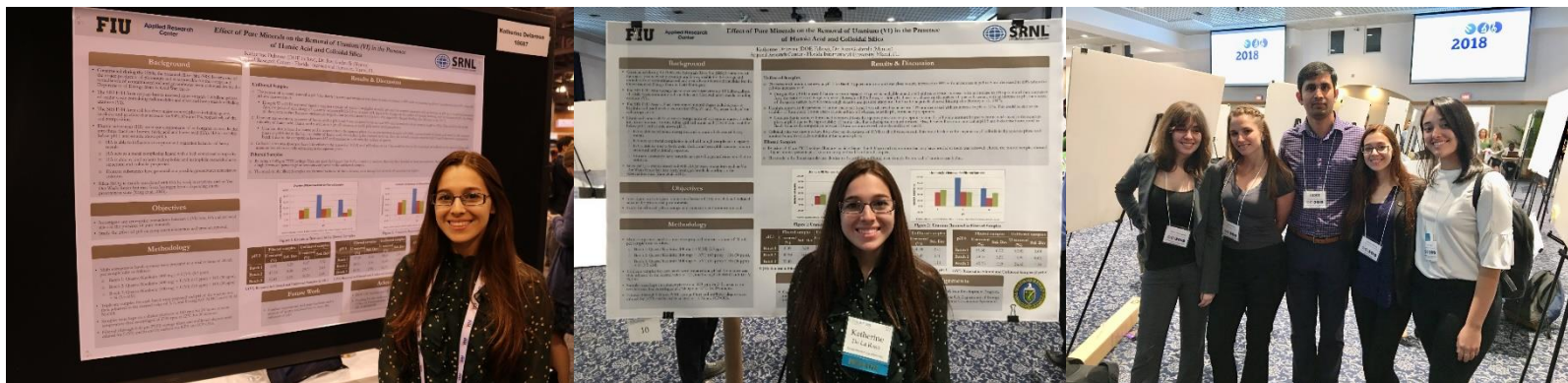




Task 2.2 – The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI) FY8 Accomplishments & Future Work



- **Accomplishments for Year 8**
 - Presented a poster at WM2018.
 - Katherine presented a student poster at WM 2018, LSSF, CURFIU.
- **Future Work Until End of Year 8**
 - Perform batch experiments with Quartz, Kaolinite and Goethite.
 - Perform surface area analysis on pure minerals.
 - This task will be completed in FIU Year 8.





Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Column Studies)

FY8 Research Highlights



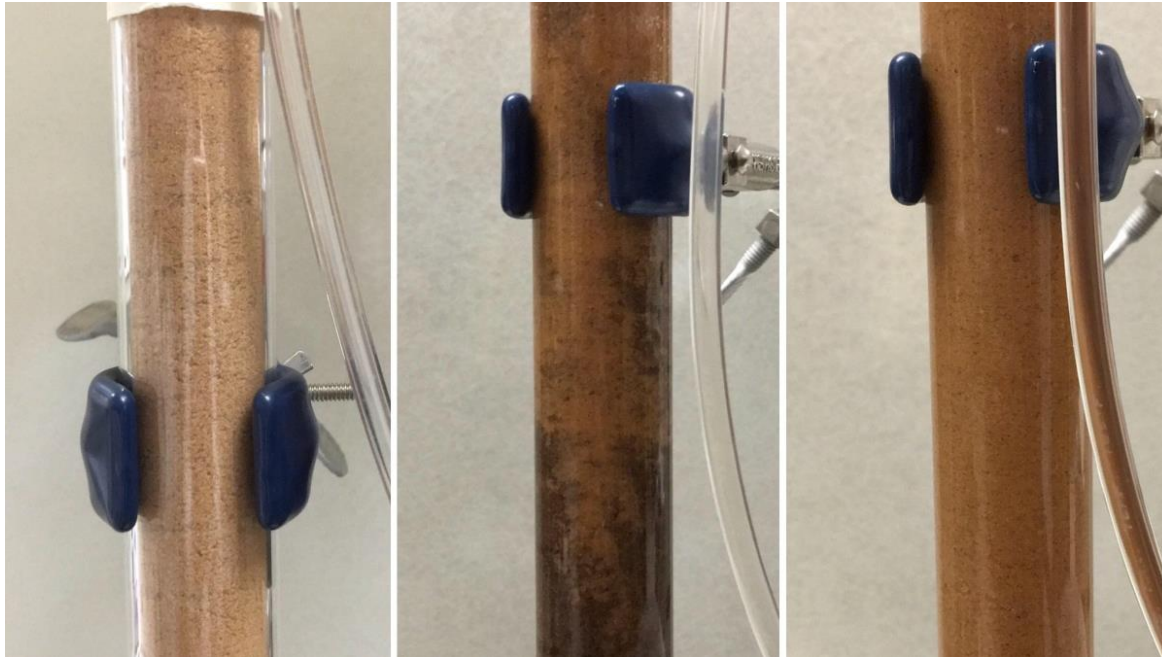
Conducted column experiments to study the sorption of uranium on to SRS sediment and influence of sorbed humate on uranium sorption:

- Filled column with a known amount of SRS FAW-1 sediment.
- Performed tracer test to determine column parameters.
- Conditioned the column with AGW with a pH of 3.5.
- Injected column with humate solution followed by uranium solution (for humate column).
- Injected column with uranium solution (for control column).



Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Column Studies)

FY8 Research Highlights



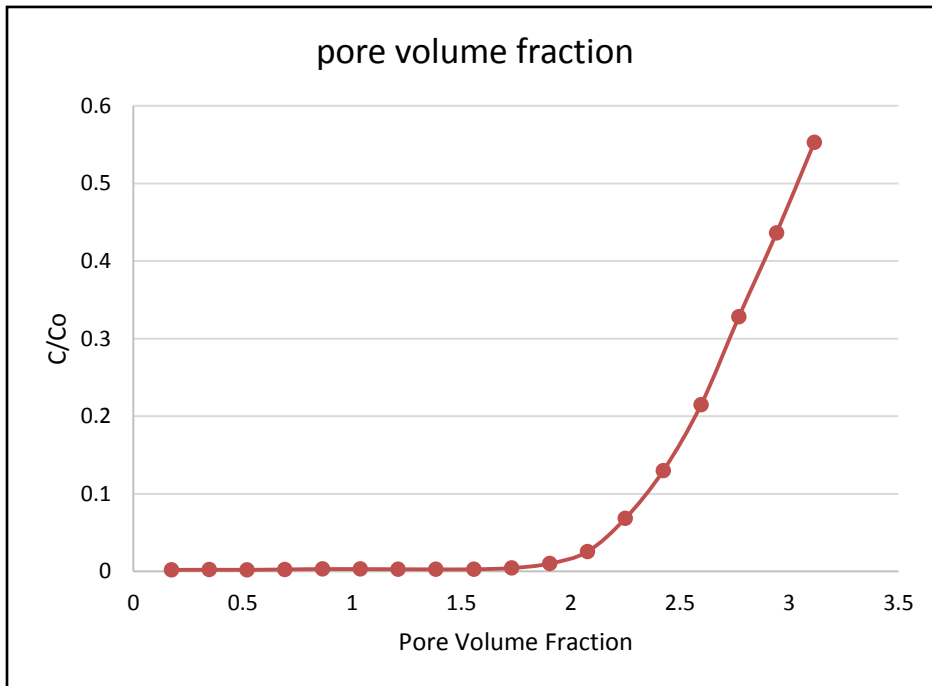
	Sediment weight (g)	Sorption/Desorption of Humic Acid					Sorption/Desorption of Uranium					
		pH		Injected (mg)	Recovered (mg)	Retained (mg/kg)	pH		Injected (ug)	Recovered (ug)	Retained (ug/kg)	% Recovered
		Initial	Final				Initial	Final				
Mod. HA	266.42	3.42	6.92	862.22	633.75	857.57	6.92	5.42	20.05	0.59	73.04	97.06
Uranium Ctl.	260	-	-	-	-	-	3.80	4.02	20.12	0.68	74.78	96.62



Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Column Studies) FY8 Research Highlights



- Repeated experiments by reducing the column size (4”) and increasing uranium concentration.



Uranium Control Measurements		
Initial Con. (C ₀)	500.00	ppb
Pore Volume	79.99	mL
Mass of Soil	0.11	kg
Uranium injected	263.00	ml
	131.50	µg
Uranium Recovered	16.75	µg
Uranium Retained	114.75	µg
	1073.76	µg/kg
Percent Retained	87.27	%

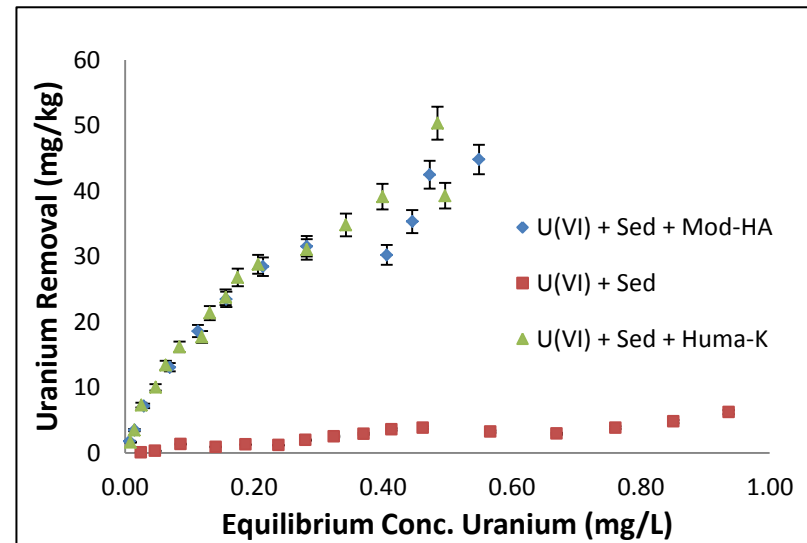


Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Batch Studies with Humate)

FY8 Research Highlights



- Completed isotherm experiments of uranium sorption onto SRS sediments with and without Huma-K/Mod-HA coating at pH 4.
 - The removal of uranium is significantly higher in the presence of Huma-K or Mod-HA compared to just plain sediments for the range of uranium concentrations studied. This indicates that Huma-K/Mod-HA enhances the removal of uranium in acidic conditions (pH 4).
 - Data suggested that uranium removal for Huma-K and Mod-Ha are relatively the same.



Isotherm of U(VI) sorption on sediments with and without Huma-K/Mod-HA (initial 0.025-1 mg/L U, 10 gr/L of sediment, pH 4, seven days, and $I = 0.01 \text{ M NaClO}_4^-$).

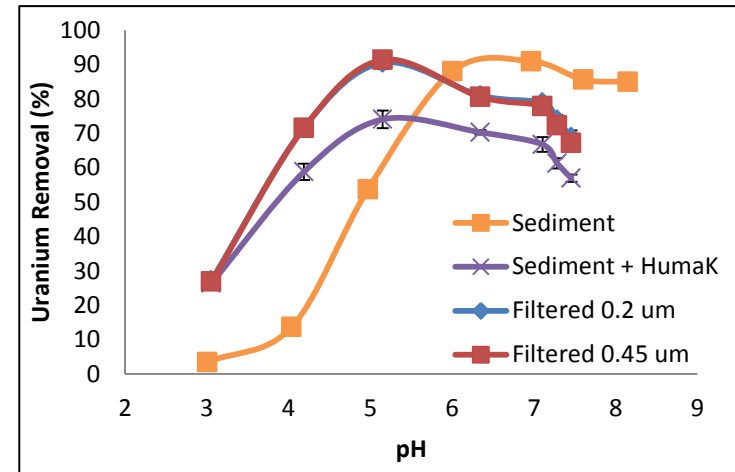


Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Batch Studies with Humate)



FY8 Research Highlights

- Studied the effect of pH on U(VI) removal by SRS sediments with and without Huma-K coating.
 - Huma-K increased the extent of U(VI) removal within the region of $\text{pH} \leq 6$ probably due to the carboxylic moieties of Huma-K where U(VI) can bind.
 - Huma-K decreased the extent of U(VI) removal in neutral and basic conditions. This decreased could be explained by the desorption of Huma-K from the sediment with the increase of pH and forming aqueous uranium-humic complexes.
- A manuscript titled “Unrefined humic substances as a potential low-cost amendment for the management of acidic groundwater contamination” was published in the Journal of Environmental Management.



Effect of pH on U(VI) removal onto SRS sediment under conditions of solid concentration 10 g/L, initial 0.5 mg/L U, seven days, and 0.01 NaClO_4^- M.



Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Batch Studies with Humate) FY8 Research Highlights



Ongoing:

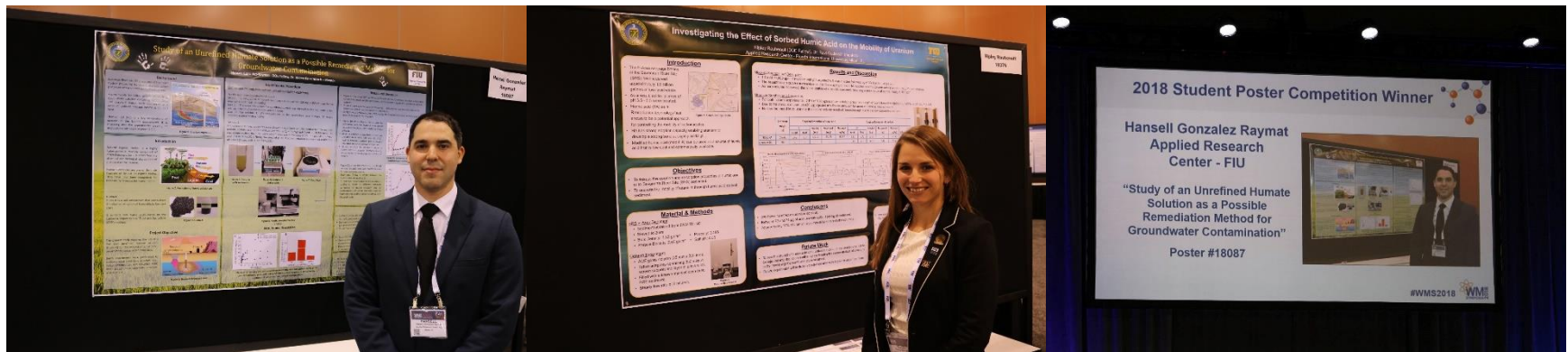
- Perform experiments with Huma-K and modified humic acid.
- Compare the data with control column.
- Evaluate the effect of pH on U(VI) desorption behavior using experimental matrix that includes SRS sediment, U(VI), Huma-K.
- Perform batch experiments using mix minerals (quartz + kaolinite and goethite) to compare the removal of U(VI) with those of SRS sediment at different pH.



Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Batch Studies with Humate) Accomplishments



- This research was presented at WM 2018 Symposia, LSSF, CURFIU.
- Hansell Gonzalez was a WM2018 Student Poster Winner.
- Published a manuscript in the *Journal of Environmental Management*, “Unrefined humic substances as a potential low-cost amendment for the management of acidic groundwater contamination”.





Task 2.3 – Application of Humic Acid for Uranium Remediation at SRS (Batch Studies with Humate) FY9 Objectives



- Evaluate the effect of time, pH, and initial uranium concentrations on U(VI) sorption/ desorption behavior using experimental matrix that includes SRS sediment, U(VI) and modified humic substances.



Task 3 - Surface Water Modeling of Tims Branch

Site Needs:

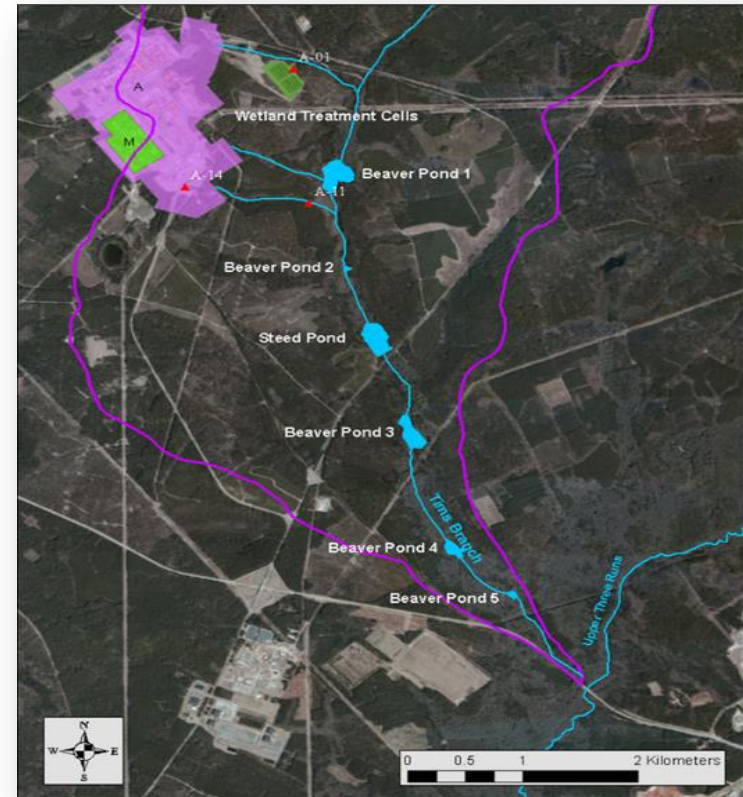
- DOE EM's Technology Plan to Address EM Mercury Challenge & DOE EM's Innovation & Technology Program indicate mercury & other heavy metal and radionuclide contamination at SRS and other DOE sites still exist.
- Long-term monitoring of heavy metals and radionuclides (e.g. Hg, U, Ni, Tc, etc.) required to evaluate effectiveness of implemented remediation technologies.

Objectives:

- Utilize Tims Branch as a test bed to develop a numerical modeling tool to evaluate the effect of extreme hydrological impacts on the fate and transport of major contaminants of concern (e.g. Hg, U, Ni, radionuclides).
- Develop a transferable technology that is potentially applicable in other contaminated stream systems at SRS and other DOE EM sites.
- Collect *in-situ* field data such as flow depth and velocity, suspended particle concentration and other water quality parameters to support model calibration and verification. This will be supported by in-person sampling and data collection as well as deployment of remote monitoring devices.

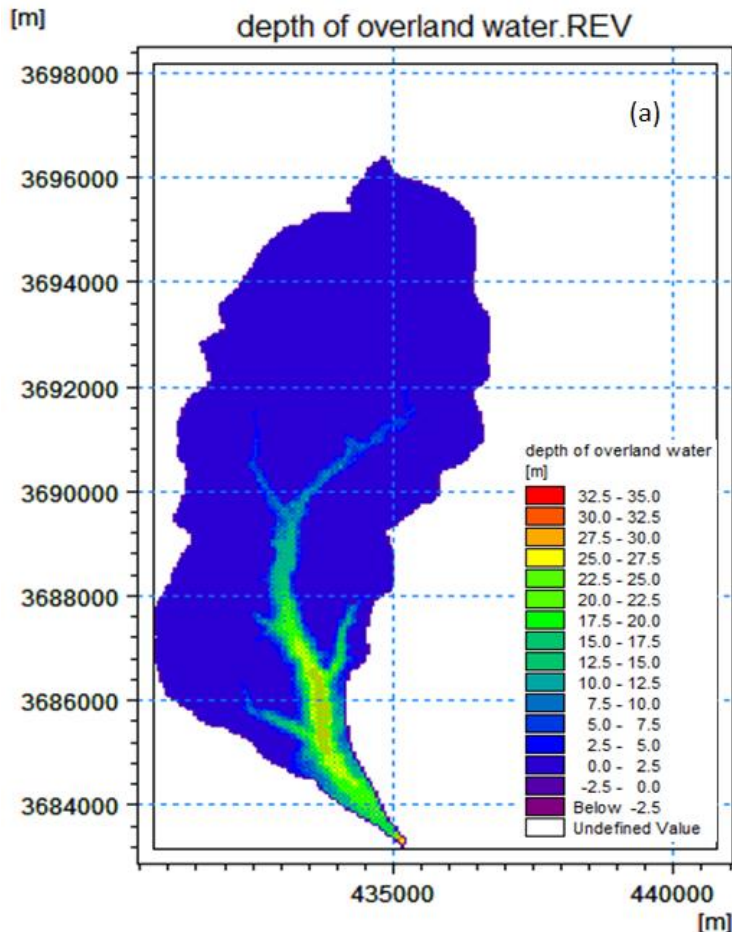
Present (Year 8) Subtasks:

- Modeling of Surface Water Flow and Contaminant Transport in the Tims Branch Ecosystem
- Application of GIS Technologies for Hydrological Modeling Support
- Data Collection, Sampling and Analysis in Tims Branch Watershed





Task 3.1: Modeling of Surface Water and Sediment Transport in the Tims Branch Ecosystem FY 8 Research Highlights



MIKE SHE Overland Flow Model:

Calibration and sensitivity analysis of MIKE SHE 2D Overland Flow (OL) Model completed.

- In FIU Yr 7, simulations for Detention Storage, Initial Water Depth and Separated Flow Area performed and analysis for Surface-Subsurface Leakage (SSLC) initiated.
- In FIU Yr 8, sensitivity analysis of model to changes in SSLC completed.
- 16 simulations performed with $\pm 5\%$ changes in SSLC under varying initial water depth conditions for time period 2010 - 2012.
- Results showed that the model was sensitive to both SSLC and initial water depth, so these parameters were used for model calibration.

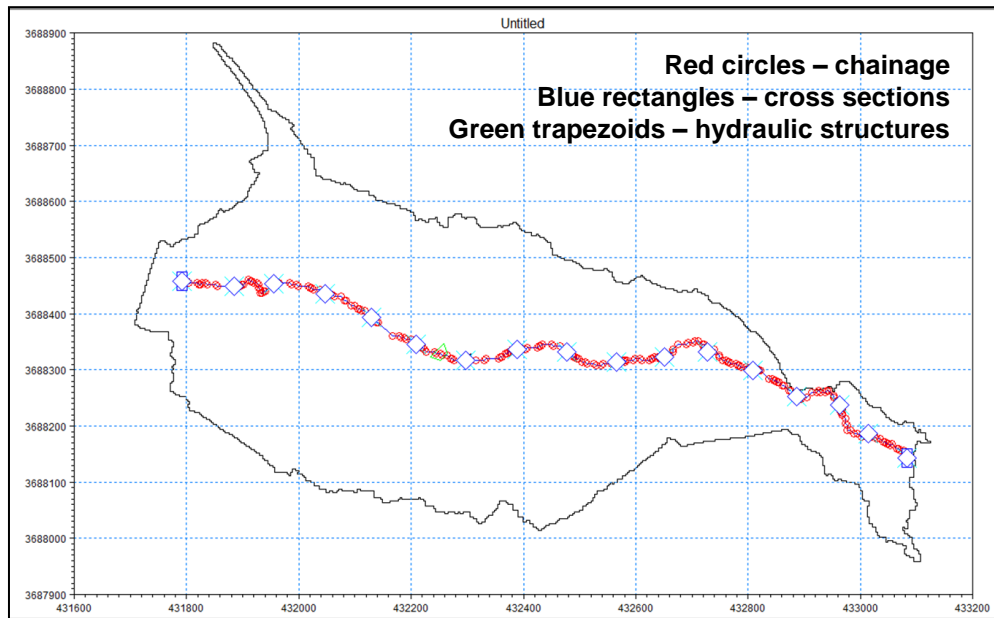


Task 3.1: Modeling of Surface Water and Sediment Transport in the Tims Branch Ecosystem

FY 8 Research Highlights



A-014 Stream Network, Chainage & Cross Sections Generated by MIKE Hydro



MIKE 11 Stream Flow Model (A-014):

Modification of model input parameters to achieve steady state flow in stream:

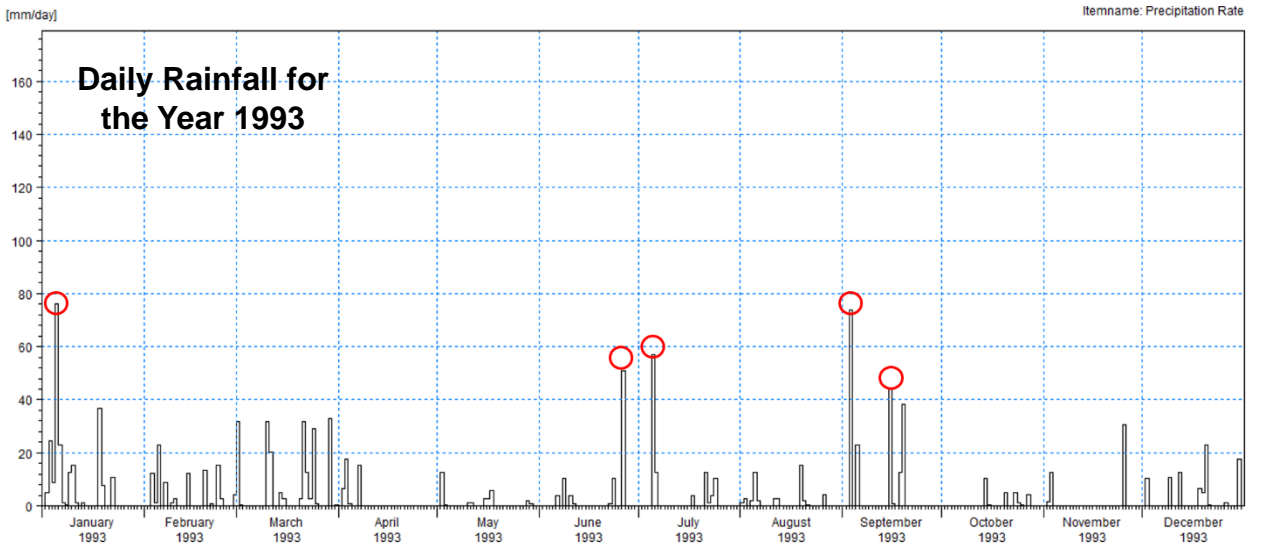
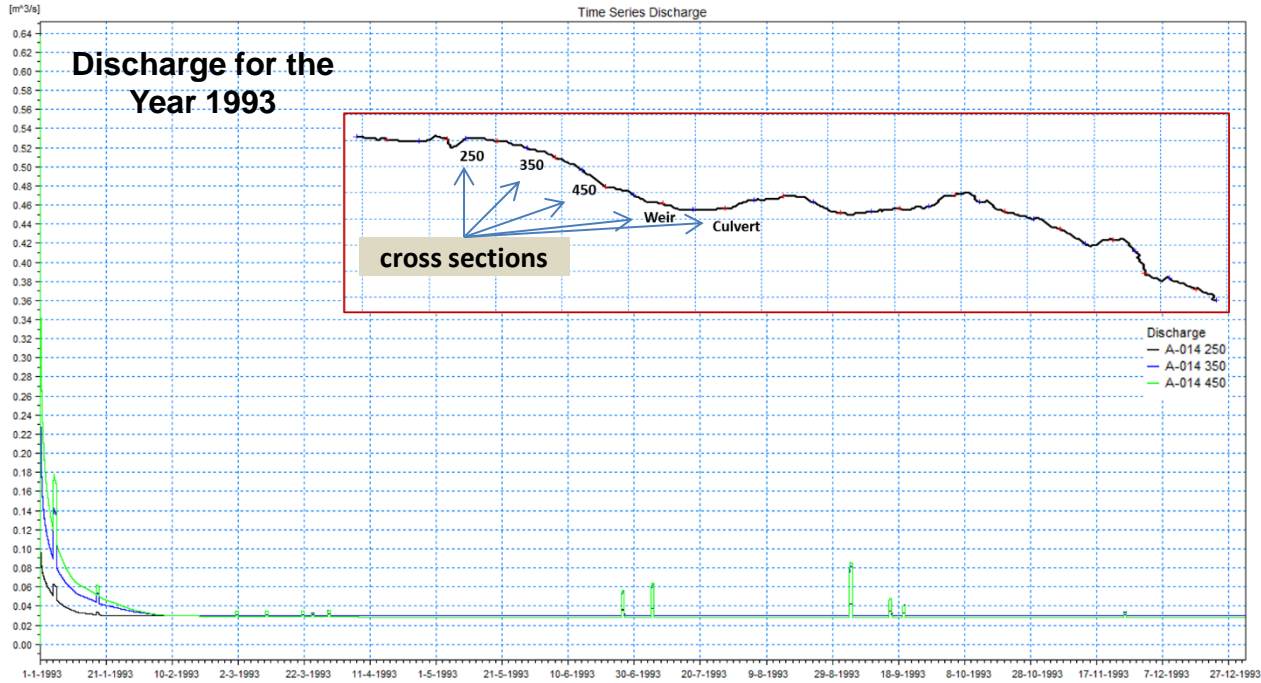
1. River network simplified.
2. Cross sections modified to reflect natural trapezoidal shape characteristic of stream.
3. Boundary conditions:
 - Constant flow rate ($0.03 \text{ m}^3/\text{s}$) assumed.
 - Open boundary condition assumed downstream.
4. Constant channel roughness coefficient (Manning's value) assumed – used as calibration parameter.
5. Man-made structures (weir and culvert) incorporated.
6. MIKE 11 stream flow model coupled with MIKE SHE overland flow model to incorporate rainfall.
7. Horizontal and vertical hydraulic conductivities in unsaturated and saturated zones adjusted.
8. Vegetation file modified based on simulation period.

Accomplishments Year 8:

- GIS shapefile of the stream network imported into MIKE 11.
- Cross sections generated using ArcGIS/MIKE Hydro tools.
- MIKE 11 1-D stream flow model of A-014 OF tributary completed.
- Simulations completed for a period of 9 months then 3 yrs.



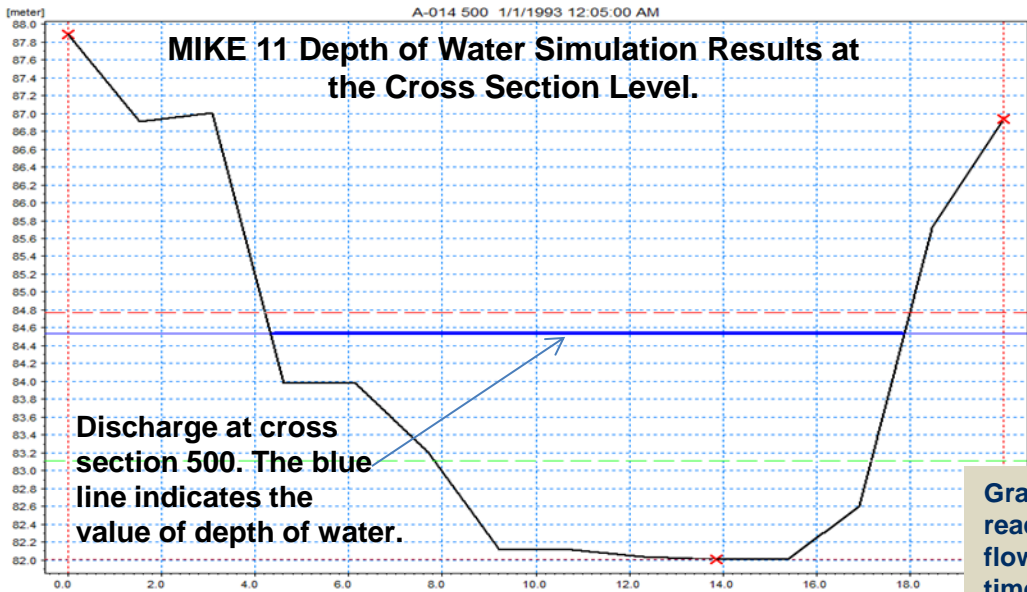
Simulated discharge for 1993 at various cross section locations along A-014 outfall tributary. Each color refers to a cross section location.



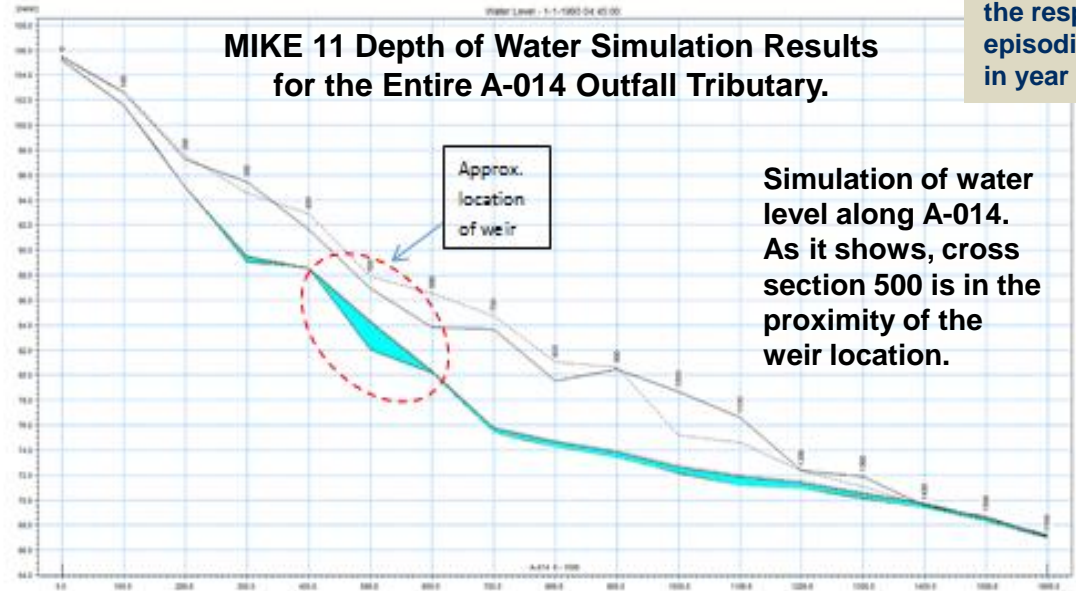
Daily rainfall data for 1993. The red circles correlate with the peaks seen in the discharge graph above.



- Simulation results indicate model capable of replicating steady state base flow within A-014 outfall tributary.
- Model can be used as a platform to develop flow simulations in Tims Branch and other streams in SRS.
- Model to be constantly updated and calibrated as data from stage gauges implemented.



Graphs show model reaches steady state flow depth after a few time steps of the simulation and shows the response to episodic rainfall events in year 1993.



Simulation of water level along A-014. As it shows, cross section 500 is in the proximity of the weir location.



Task 3.2 – Application of GIS Technologies for Hydrological Modeling Support FY 8 Research Highlights



Process flow models developed: ArcGIS ModelBuilder

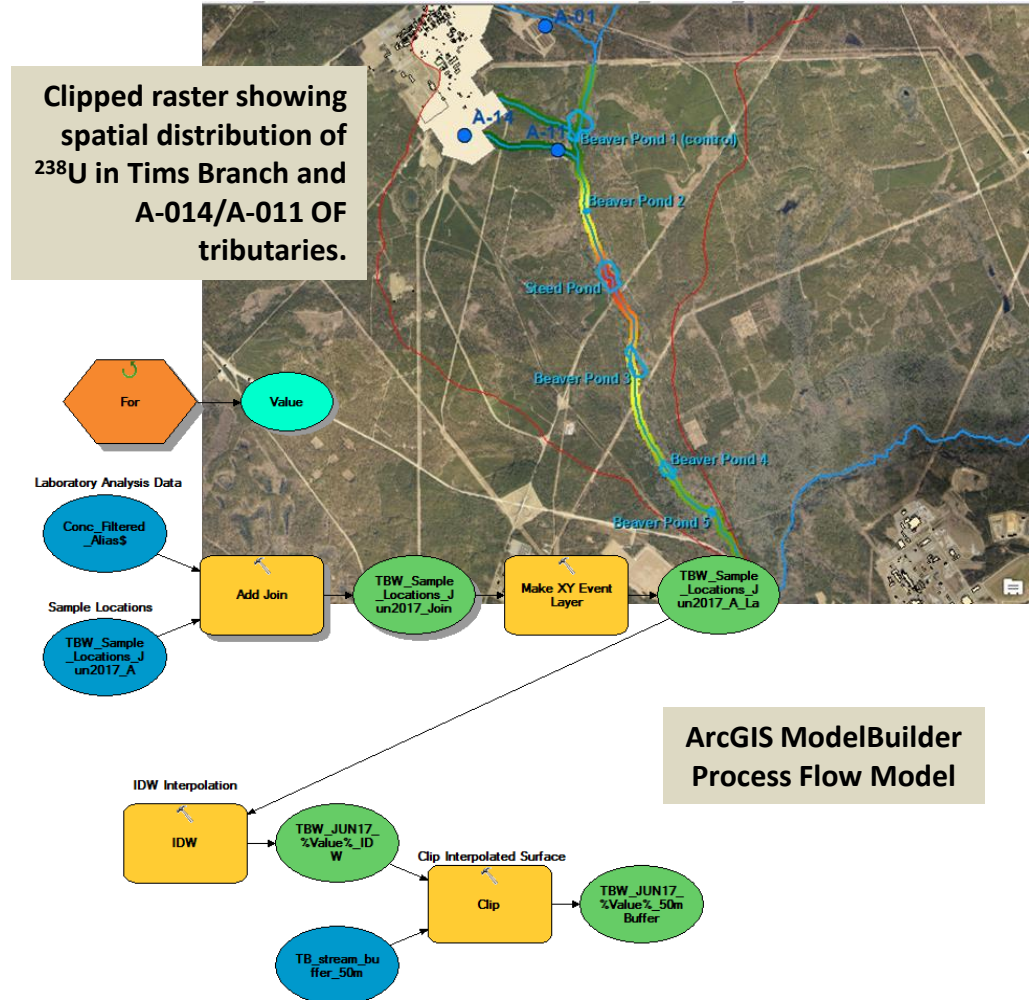
- Automates repetitive geoprocessing tasks.
- Shortens processing time.

Processes field data & generates maps.

- Interpolates heavy metal/radionuclide conc. or water quality data measured at sampling pts. along Tims Branch & A-014 OF tributary.
- Creates gridded surfaces showing spatial distribution.
- Clips grids to 50 m/100 m buffers along length of A-014 OF tributary & Tims Branch study areas.
- Several parameters processed simultaneously to create spatial distribution maps of contaminant conc./water quality parameters in the stream.

Delineates study domain.

- Delineated A-014 OF tributary study area from 3 m resolution DEM of Tims Branch watershed.
- Utilizes Archydro tools to delineate drainage lines and catchments.
- Files generated used in MIKE 11 stream flow model.



ArcGIS ModelBuilder Process Flow Model



Task 3.3 – Data Collection, Sampling and Analysis in Tims Branch Watershed FY 8 Research Highlights

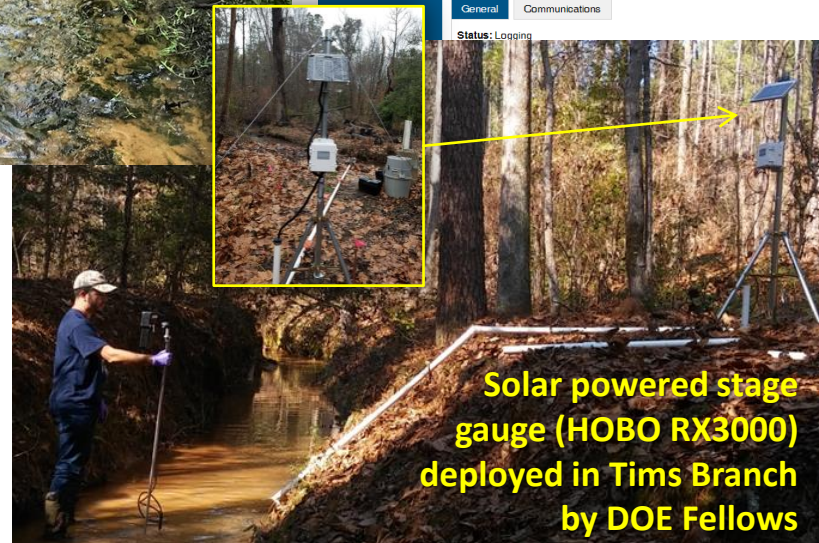
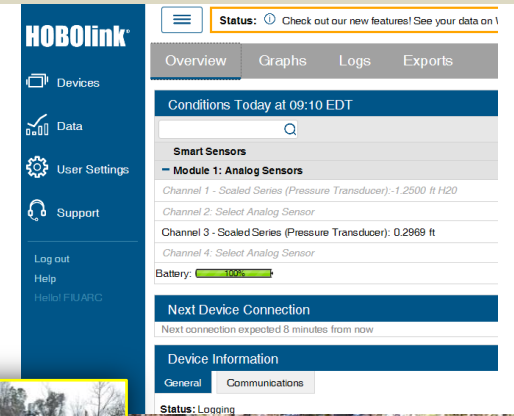


Field sampling, in-situ & remote data collection (February 2018).

- Collaboration between SRNL & SREL researchers, assisted by SRS RADCON.
- Data collected: water level & water quality.
- Water sample analysis: heavy metals & radionuclides (e.g., U, Sn, Ni, Fe, As, Pb).
- 2 solar-powered remote monitoring stations installed along A-014 OF tributary & Tims Branch.
 - Measures water level.
 - Data stored in cloud in 15-min intervals.
 - Can be downloaded every 4 hrs.
- Supports model development & calibration.



HOBOLink GUI to access recorded data



Solar powered stage gauge (HOBO RX3000) deployed in Tims Branch by DOE Fellows



Task 3 - Surface Water Modeling of Tims Branch Future Work



To be Completed in Year 8

- Develop MIKE 11 1-D stream flow model of main Tims Branch stream.
- Couple MIKE SHE & MIKE 11 models for Tims Branch (Milestone 2017-P2-M9).
- Perform simulations for time period October 1993 - September 1996 when USGS gauge station downstream Tims Branch was active and flow data from that station was available. This data will be used as a downstream calibration point.
- Conduct sensitivity analysis & calibration of coupled model.

Proposed Scope for Year 9

- Develop geochemical component of the model using ECO Lab.
- Develop advection-dispersion model for contaminant transport using MIKE 11.
- Couple geochemical, advection-dispersion & hydrology components and conduct sensitivity analysis.
- Examine groundwater/surface water interaction in TBW using historical time series of GW table. Assists in quantifying discharge/recharge as part of TBW water balance.
- Create raster hydrographs using GIS tools for visualization of hydrologic timeseries data so large temporal datasets (rainfall, discharge) can be more easily reviewed and interpreted.
- Conduct literature review to identify best remote sensing application for determining spatial and temporal variability in evapotranspiration across SRS; serves as indicator of environmental response to landscape disturbances and the effect these changes can have on the energy and water budget; Compliments and optimizes SRS resource managers' current long-term post remediation environmental monitoring activities.



Task 5 – Waste Isolation Pilot Plant Collaboration

Site Needs:

This research strives to help the LANL ACRSP team to better understand the long-term fate of the actinide elements in the Waste Isolation Pilot Plant (WIPP). Specifically, the effects of ligands in the waste stream (e.g. EDTA and oxalate) on near field mobility of actinides is still unknown (Dunagan, 2007; Brush, 1990). Complexation constants have been measured for most actinides and lanthanides (Thakur *et al.*, 2014; 2015; Borkowski *et al.*, 2001). However, their long-term stability and sorption are not yet understood in high ionic strength systems. EDTA is a significant risk factor as it is present in significant amounts in waste and could reach up to 0.3 mM in the repository (Roach *et al.*, 2008).

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment					
Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium



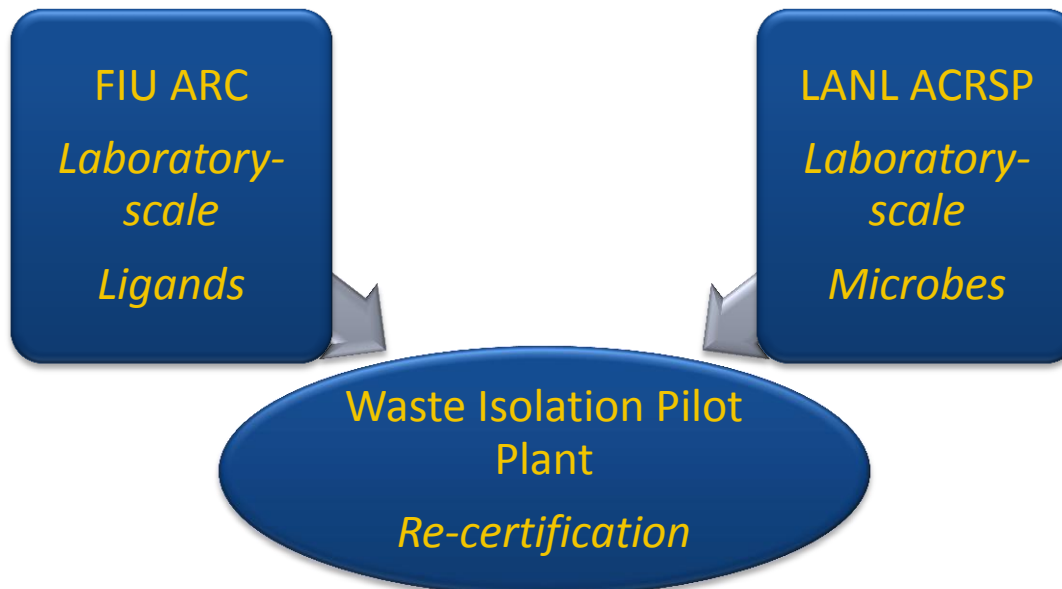
Task 5 – Waste Isolation Pilot Plant Collaboration



Objectives in FIU FY8:

To understand the ternary interactions between actinides and WIPP-relevant ligands and minerals and their potential fate in the subsurface.

1. Measure sorption parameters for Nd/Am(III), Th(IV), and U(VI) complexed with EDTA at variable ionic strength.
2. Measure Nd(III), Th(IV), and U(VI) sorption to dolomite without EDTA.
3. Compare mobility of Nd (Year 7 results) versus Nd-EDTA complexes.





Task 5 – Waste Isolation Pilot Plant Collaboration FY8 Research Highlights

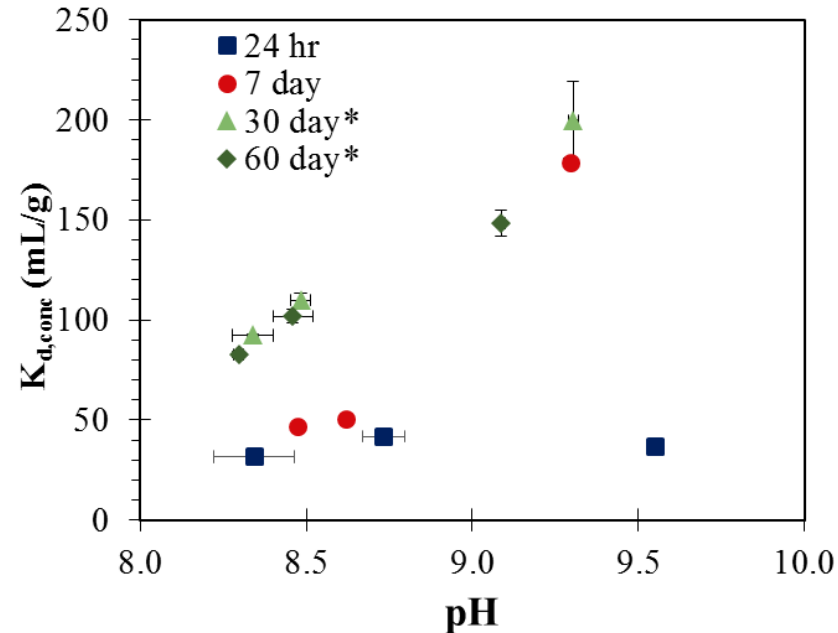


Results highlight conservatism in WIPP PA sorption assumptions:

- Finalized batch and mini-column experiments to investigate Nd(III) sorption as an analog to Am/Pu(III) in variable ionic strength 0.01 – 5.0 M NaCl.
- Showed that the fundamental mechanisms controlling removal of Nd change depending on flow (i.e. sorption versus incorporation processes).
- Conducted batch experiments with Nd(III), Th(IV), and U(VI) in 0.1 and 1.0 M NaCl, CaCl₂, and MgCl₂.
- Showed that EDTA decreases removal kinetics and sorption to dolomite (equilibrium in > 7 days).

Continued research with LANL-CEMRC

- Deploy DOE Fellow Zengotita for summer 2018.



1000 ppb Nd partitioning in the presence of 5 mg/L EDTA and 5 g/L dolomite

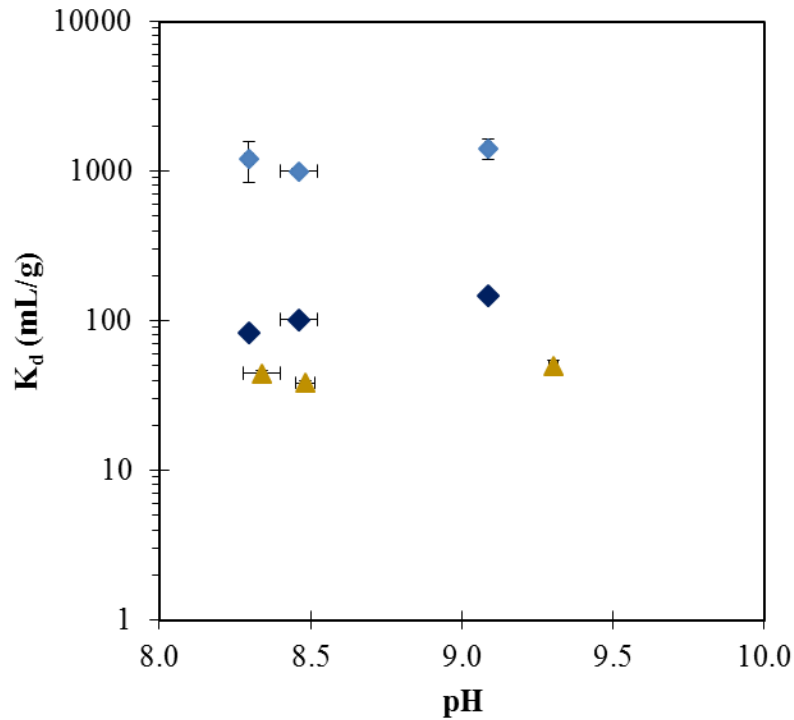
WIPP PA assumes K_d of
20-400 mL/g



Task 5 – Waste Isolation Pilot Plant Collaboration FY8 Research Highlights

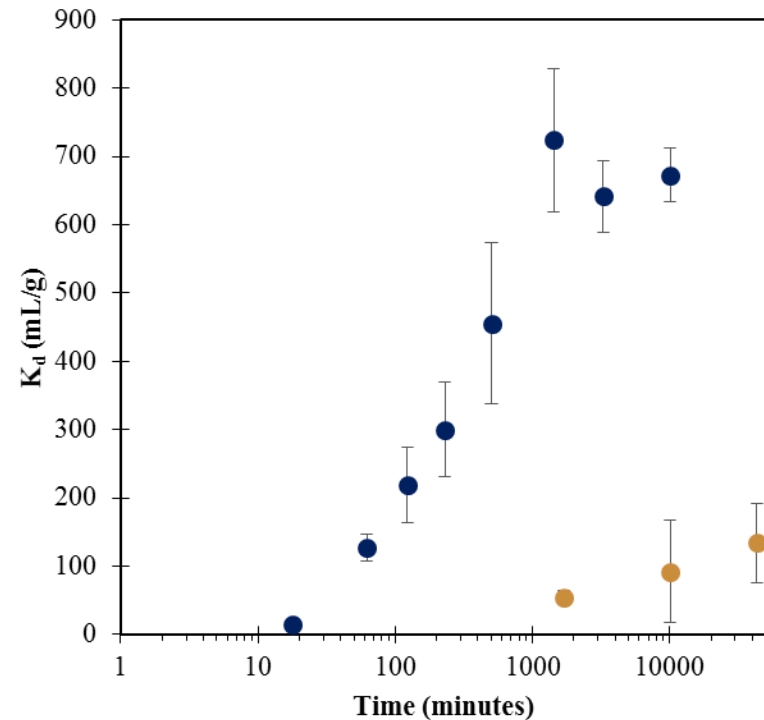


Equilibrium Partitioning of Nd, Th, and U with EDTA in 0.1 M NaCl



◆ Th-60 day ▲ U-30 day ◆ Nd-60 day

Comparison of Nd Partitioning with and without EDTA in 0.1 M NaCl



● Nd ● Nd-EDTA



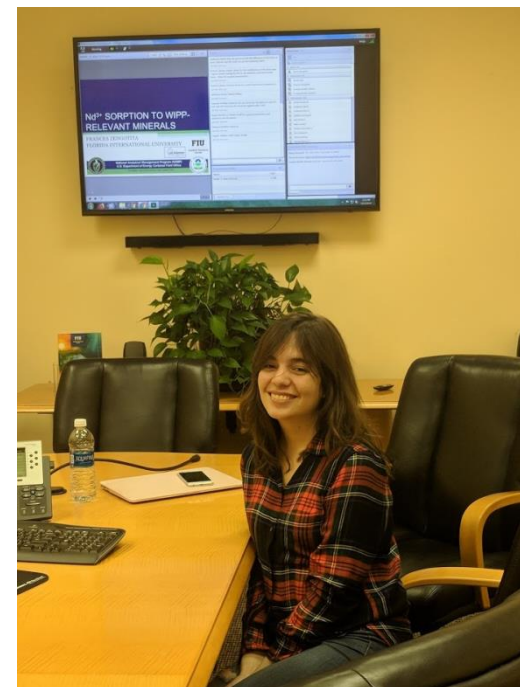
Task 5 – Waste Isolation Pilot Plant Collaboration FY8 Accomplishments



- DOE Fellow Zengotita presented during the inaugural webinar for NAMP's Young Investigators in Radiochemistry series.
- Publication titled "Retention of neodymium by dolomite at variable ionic strength as probed by batch and column experiments" accepted to *Journal of Environmental Radioactivity* (April 2018).
- DOE Fellow Zengotita's internship report indexed on OSTI "The role of *Chromohalobacter* on transport of lanthanides and cesium in the dolomite mineral system," LA-UR-17-30894 – report awarded in the undergraduate competition of DOE-NE's Innovations in Nuclear R&D program (Zengotita, \$1000).
- Presented work at Waste Management 2018, FIU McNair Scholars 2018 Research Conference, and Life Sciences South Florida 2018.

Upcoming:

- Deploy DOE Fellow Frances Zengotita to LANL ACRSP as summer intern, June 2018.
- Present results on microbial and ligand effects with two presentations at the Fall ACS national meeting, August 2018.



**Frances Zengotita
presenting her NAMP
webinar**



Task 5 – Waste Isolation Pilot Plant Collaboration FY9 Objectives

Proposed Scope FIU FY9:

During Year 9, research will expand to include additional ligands: citrate (common plant and microbial exudate) and gluconate (plasticizer in cement). There is significant synergy with the LANL ACRSP focus on understanding microbial impacts to actinide fate at the WIPP as these ligands and EDTA may interact with local microbial populations. In addition, both Am and Pu will be included in the scope as these are the major risk drivers.

Objectives for FIU FY9:

To understand the impact of EDTA, citrate, and gluconate on the sorption of actinides in the +3, +4, and +6 oxidation states to dolomite and iron oxides in simplified systems via batch and column experiments.

Crosscutting research bridges the basic and applied sciences

