DOE-FIU Cooperative Agreement Annual Research Review – FIU Year 2

Tuesday, September 27, 2022		
9:30 - 9:35 am EDT	Kick-Off /Welcoming Remarks (DOE-EM)	Kurt Gerdes (Director, Technology Development) – DOE EM-3.2
9:35 - 9:40 am EDT	Welcoming Remarks (DOE-LM)	Leonel Lagos on behalf of DOE Office of Legacy Management
9:40 - 10:00 am EDT	Projects 4 & 5: STEM Workforce Development and Training	FIU, DOE HQ (EM & LM), SRNL, PNNL, WIPP, SRS, ORP, LBNL, WRPS, INL, Grand Junction
BREAK		
11:00 - 12:00 pm EDT	Projects 4 & 5 (cont'd): STEM Workforce Development and Training	FIU, DOE HQ (EM & LM), SRNL, PNNL, WIPP, SRS, ORP, LBNL, WRPS, INL, Grand Junction
BREAK		
1:00 - 2:30 pm EDT	Project 1: Chemical Process Alternatives for Radioactive Waste	FIU, DOE HQ, PNNL, WRPS, SRNL, SRS
2:30 - 4:00 pm EDT	Project 3: Waste and D&D Engineering & Technology Development	FIU, DOE HQ, SRNL, PNNL, LBNL, INL, ANL
Wednesday, September 28, 2022		
10:00 - 11:30 am EDT	Project 2: Environmental Remediation Science & Technology	FIU, DOE HQ, SRNL, PNNL, ORNL, LANL, CBFO
11:30 - 1:00 pm EDT	Wrap Up (FIU Projects 1, 2, 3, 4 & 5)	FIU, DOE HQ (EM & LM)

PROJECT 2

Environmental Remediation Science & Technology

FIU Personnel and Collaborators

Principal Investigator: Leonel Lagos

Project Manager: Yelena Katsenovich

Faculty/Staff: Ravi Gudavalli, John Dickson, Vadym Drozd, Angelique Lawrence, Pieter Hazenberg

Postdoctoral Fellows: *Hamid Bazgirkhoob

DOE Fellows/Students: *Juan Morales, Gisselle Gutierrez, Mariah Doughman, Phuong Pham, Stevens Charles, Angel Almaguer, Caridad Estrada, Aubrey Litzinzger.

DOE-EM: Genia McKinley, Kurt Gerdes, *Paul Beam, Skip Chamberlain, Nick Machara, John Mocknick, Karen Skubal

DOE-SRS: Jeff Crenshaw, Nixon Peralta

SRNL: Brian Looney, Hansell Gonzalez-Raymat, Carol Eddy-Dilek, Mark Amidon, Bruce Wiersma, Connie Herman, Brady Lee

SREL: *John Seaman, Daniel Kaplan

LBNL: Haruko Wainwright, Zexuan Xu

PNNL: *Vicky Freedman, Rob Mackley, Nik Qafoku, Jim Szecsody, Hilary Emerson, Matthew Asmussen

LANL: Paul Dixon, Don Reed, Juliet Swanson, David Moulton

DOE-CBFO: Anderson Ward

ORNL: Eric Pierce, Alexander Johs

*Former staff/student contributors

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Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE	
Subtask 1.2	Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants
Subtask 1.3	Eval. of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments
Subtask 1.4	Experimental Support of Lysimeter Testing
TASK 2: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE SAVANNAH RIVER SITE	
Subtask 2.1	Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site
Subtask 2.2	Investigating the Effect of KW-30 (Humate Material) on the Removal of Uranium
TASK 3: CONTAMINANT FATE AND TRANSPORT MODELING FOR THE SAVANNAH RIVER SITE	
Subtask 3.1	Modeling of Surface Water Flow and Contaminant Transport in the Tims Branch Ecosystem
Subtask 3.2	Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands
TASK 5: RESEARCH AND TECHNICAL SUPPORT FOR WIPP	
Subtask 5.2	Fate of Actinides in the Presence of Ligands in High Ionic Strength Systems
TASK 6: HYDROLOGY MODELING OF BASIN 6 OF THE NASH DRAW NEAR THE WIPP	
Subtask 6.1	Basin 6 DEM Development and Delineation of Surface Hydrological Features
Subtask 6.2	Model Development
TASK 7: ENGINEERED MULTI-LAYER AMENDMENT TECHNOLOGY FOR HG REMEDIATION ON OAK RIDGE RESERVATION	

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Task 1

Remediation Research and Technical Support for the Hanford Site

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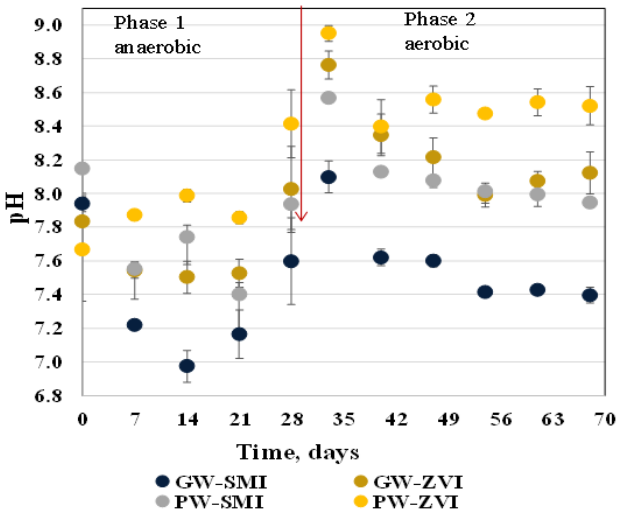
Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 2 Research Highlights & Accomplishments:

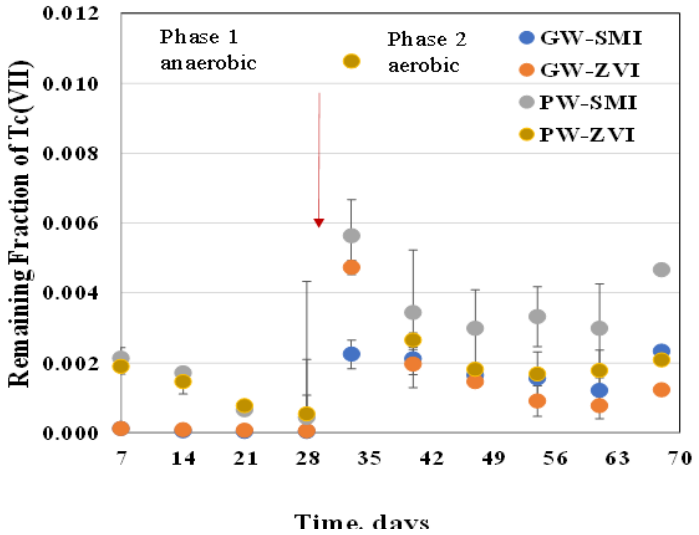
- Batch expts. to study re-oxidation behavior of ^{99}Tc, U(VI), and NO_3^- after treatment with strong reductants:
  - 1% zero valent iron (ZVI) and
  - 1% sulfur modified iron (SMI)

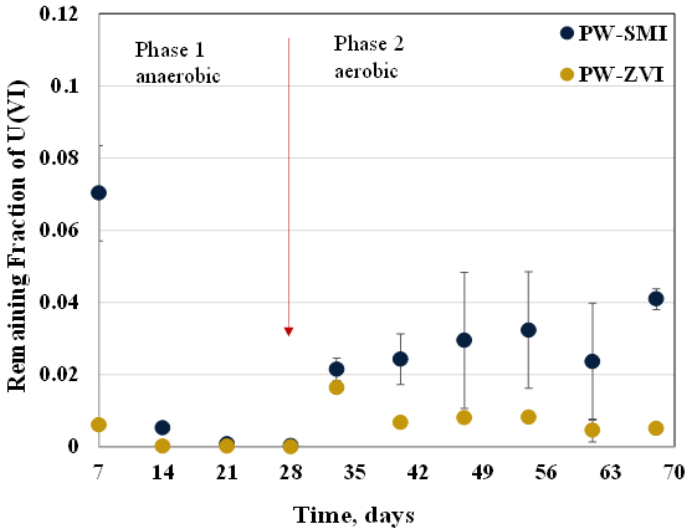
  (per mass of GW or PW)
- Two phases of experiments for reduction of ^{99}Tc, U(VI), and NO_3^-:
  - In presence of strong reductants and anaerobic conditions for up to **28 days**
  - In aerobic conditions for up to **40 days with aeration 2x/week for 30 s**.

  Total testing = 68 days.
- Hepure ZVI was a more effective reductant than SMI
  - ZVI-treated triplicates contained smaller remaining fraction of U(VI) & Tc(VII) in solution throughout both phases.



SMI-amended samples exhibited lower pH compared to ZVI.





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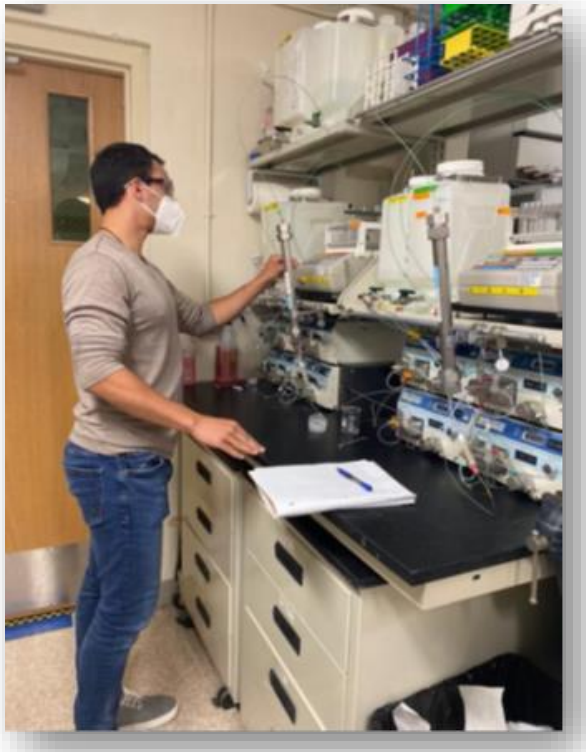
Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 3 Projected Scope

- Finalize analyses for nitrate/nitrite via IC.
- Study the re-oxidation behavior of perched and groundwater contaminants, Tc(VII), U(VI), and NO_3^-, that have been initially reduced by 0.5% and 5% calcium polysulfide (CPS) under anaerobic initial conditions followed by aerobic conditions.
- Conduct solid characterization studies via XRD and SEM-EDS to investigate for changes in sediment mineralogy, surface morphology and elemental composition.
- Initiate preliminary experiments on coupling zero valent iron approach with ammonium hydroxide and investigate their effect on the re-oxidation behavior of comingled Tc, U and nitrate.
    - Research will follow experimental matrix outlined as part of DV-1 Operable Unit treatability study ongoing at Hanford Site.



DOE Fellow Angel Almaguer at PNNL during summer internship working on column studies.

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Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 2 Research Highlights & Accomplishments:

Dominant U(VI) species:

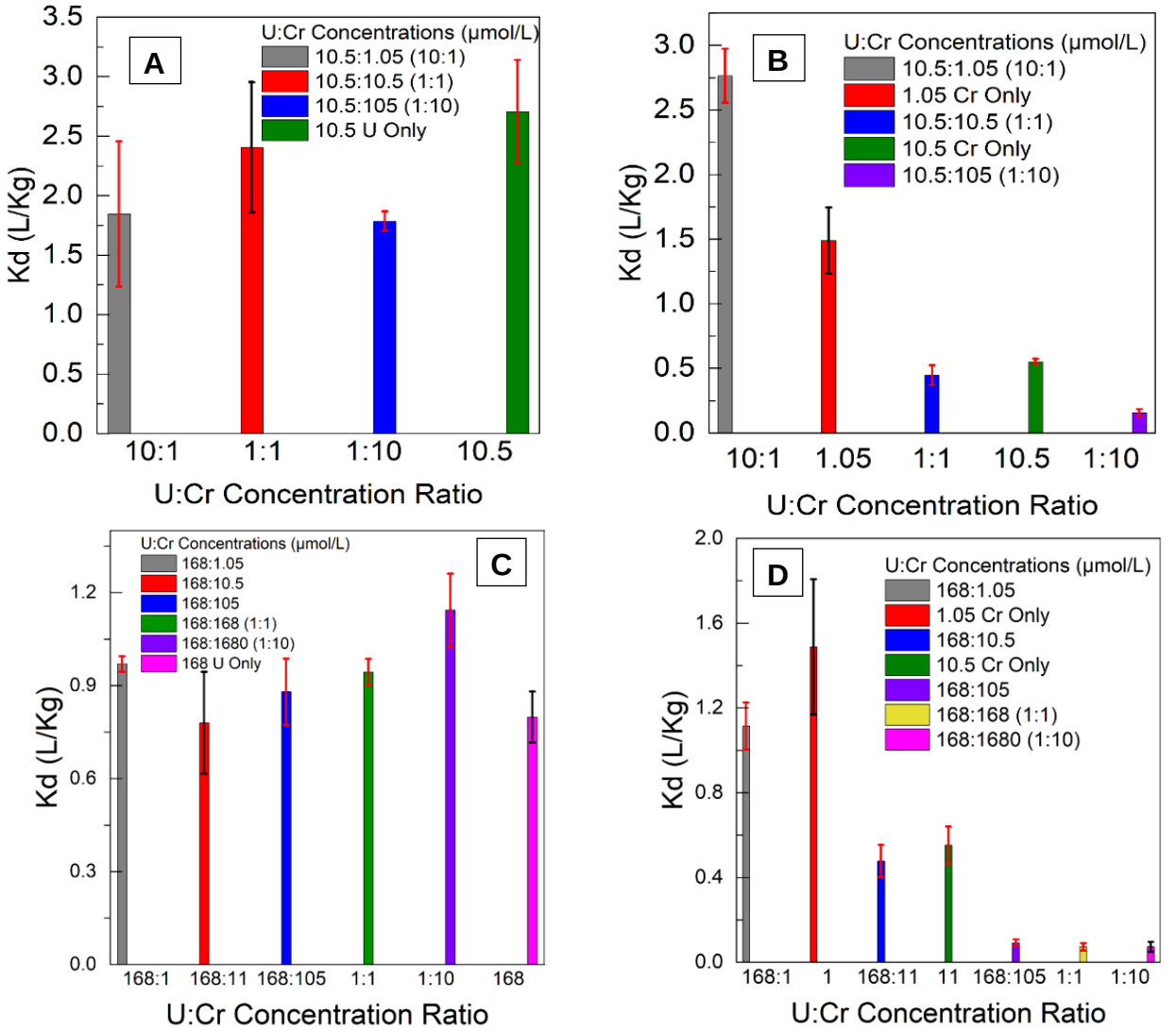
- **$Ca_2UO_2(CO_3)_3^0$(aq) and $CaUO_2(CO_3)_3^{2-}$**

Dominant Cr(VI) species:

- **$CaCrO_4$(aq)**

$$K_d = \frac{[contaminant_{sediment}]}{[contaminant_{solution}]}$$

A&C: Change in U(VI) Kd B&D: Change in Cr(VI) Kd



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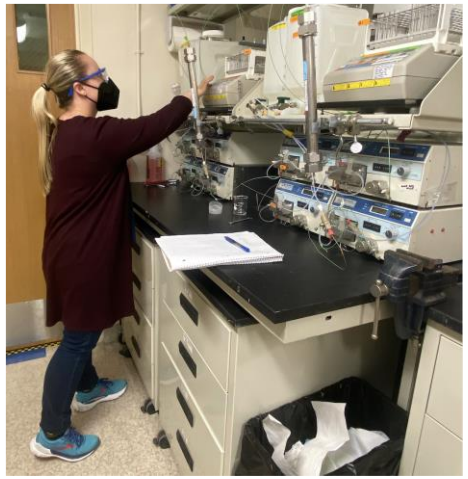
Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 3 Projected Scope

- Conduct column studies: U, Cr, and competitive U and Cr
- Develop competitive batch studies including U, Cr, and I-127
- Characterize post treated sediment via x-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM) analysis



DOE Fellow PhD student Mariah Doughman presented at WM 2022 Symposia, was a Roy G. Post scholarship recipient and did Summer Internship at PNNL with Drs. Qafoku, Szecsody, and Emerson.

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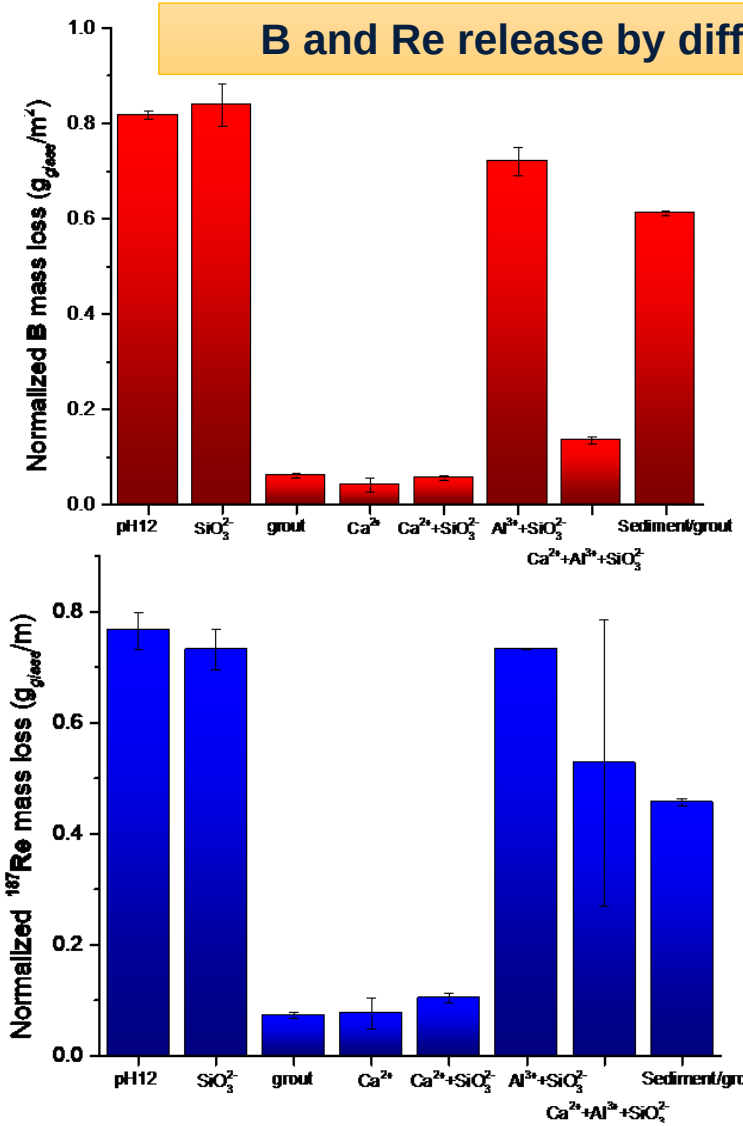
Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 2 Research Highlights & Accomplishments:

- Investigated impact of major elements on dissolution behavior of borosilicate ORLEC28 glass
  - Test matrix in SPFT: duplicated reactors with grout, grout/sediment soln., Ca-amended, pH 12 buffered soln., flow rate 40 mL/day at 25°C, 40°C, and 70°C
  - Test matrix in PCT: triplicated reactors, pH 12 buffer, grout soln, grout/sediment soln., Si (5 ppm), Ca (130 ppm) and Al (7 ppm) amended buffers at 90°C
- SEM/EDS in cross-sections of glass coupons to study glass erosion

B and Re release by different solutions at 90°C via PCT



BET surface area and volume of pores of glass in the PCT at 90°C

Sample	BET surface area, m^2/g	BJH adsorption cumulative volume of pores (17.000 Å to 3000.000 Å width) cm^3/g
Pristine glass	0.004(6)	0.0090 (9)
pH12	0.788(4)	0.891(8)
grout-contacted solution	0.075(5)	0.0003(4)
Si-amended solution	0.354(8)	0.417(8)
Ca^{2+}-amended solution	0.121(7)	0.0004(6)

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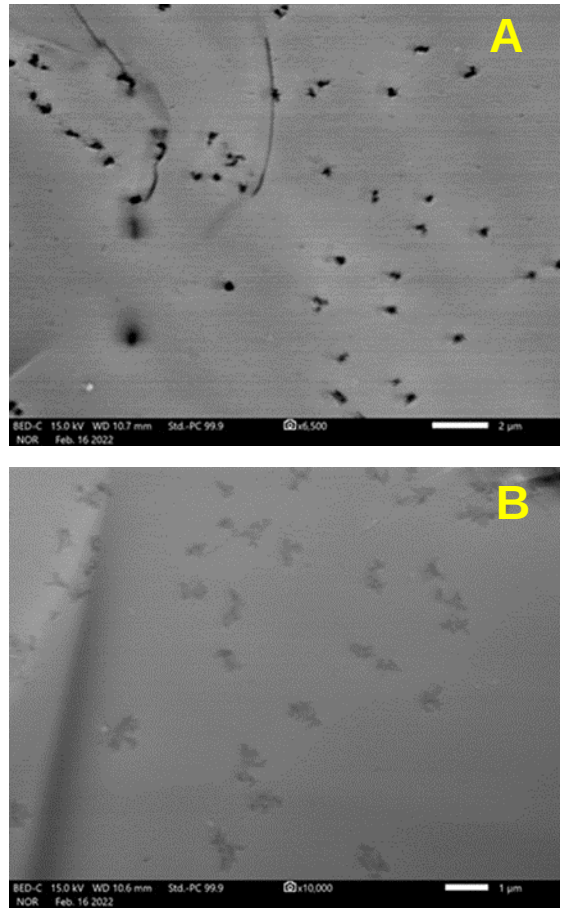
Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 3 Projected Scope

- Investigate glass dissolution in contact with Al- and grout/sediment-contacted groundwater to investigate any common ion effect.
  - Varying Ca across a few order of magnitude; pH 8, 12
  - Al concentrations in the leachate will range from 0.3 ppm to 30 ppm at different pHs (7, 9, 10, 11).
- Complete a grout-sediment static experiment at variable temperature of 25^{o} C, 40^{o} C, 70^{o}C
- Continue the long-term static PCT experiment with three solutions: pH 12 buffer, Ca^{2+} (130 ppm) in pH 12 buffer, and grout-contacted solutions.
  - Collect samples after 2 weeks and 1 month in epoxy for SEM/EDS
- Support glass characterization studies via microscopy, spectroscopy, and X-ray diffraction techniques.

SEM images of glass particles after PCT test



A) pH 12 buffer; B) glass surface defects after grout-contacted soln.

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Task 2

Remediation Research and Technical Support for the Savannah River Site

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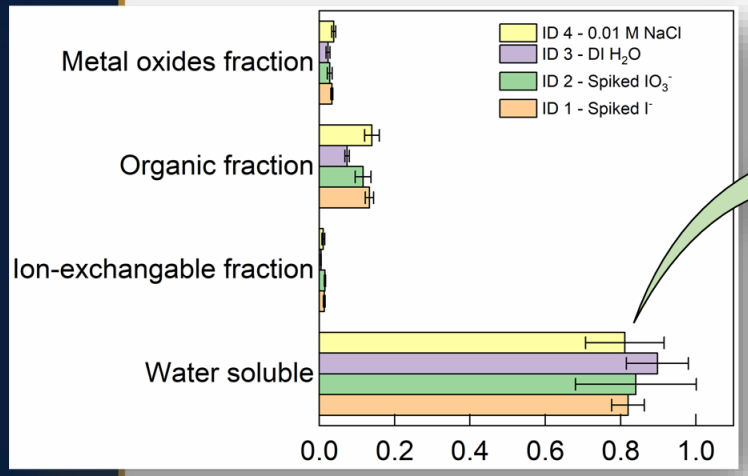
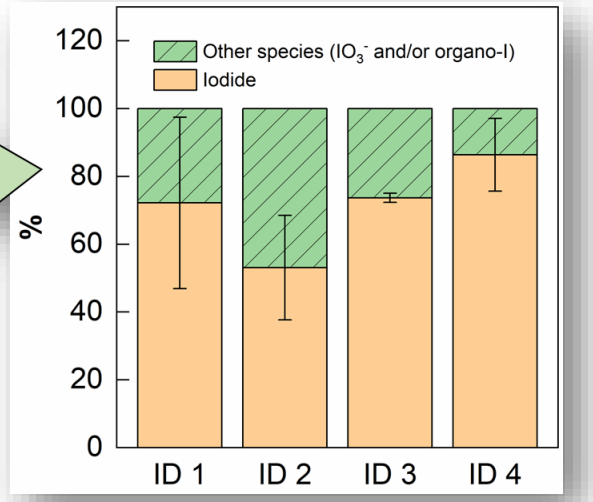
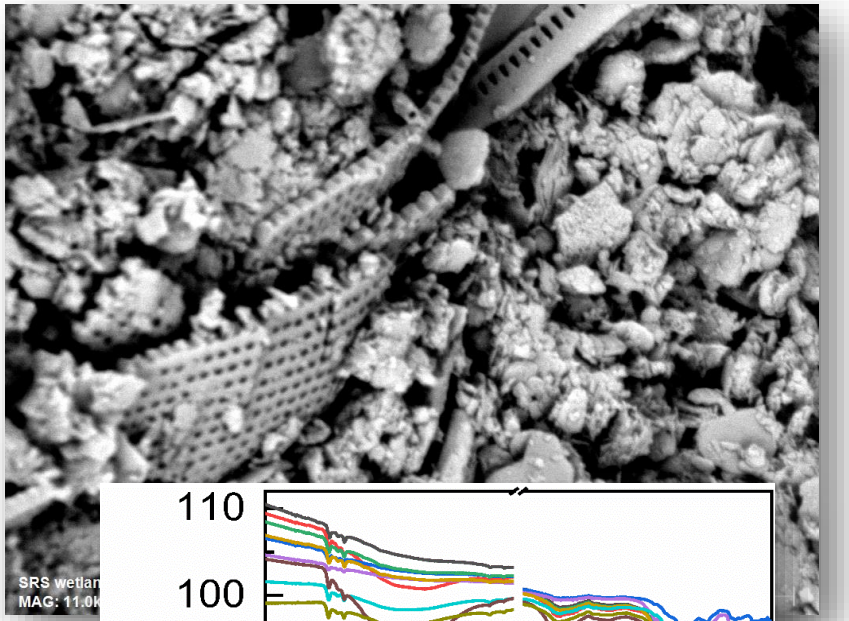
Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

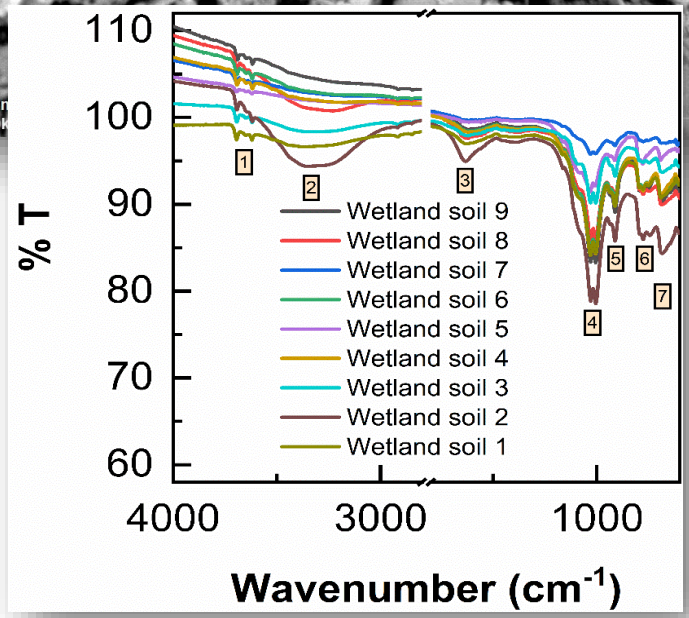
FIU Year 2 Research Highlights & Accomplishments:

- Characterized top soil obtained from SRNL prior to use in the experiments
- Performed sequential extraction of wetland sediment









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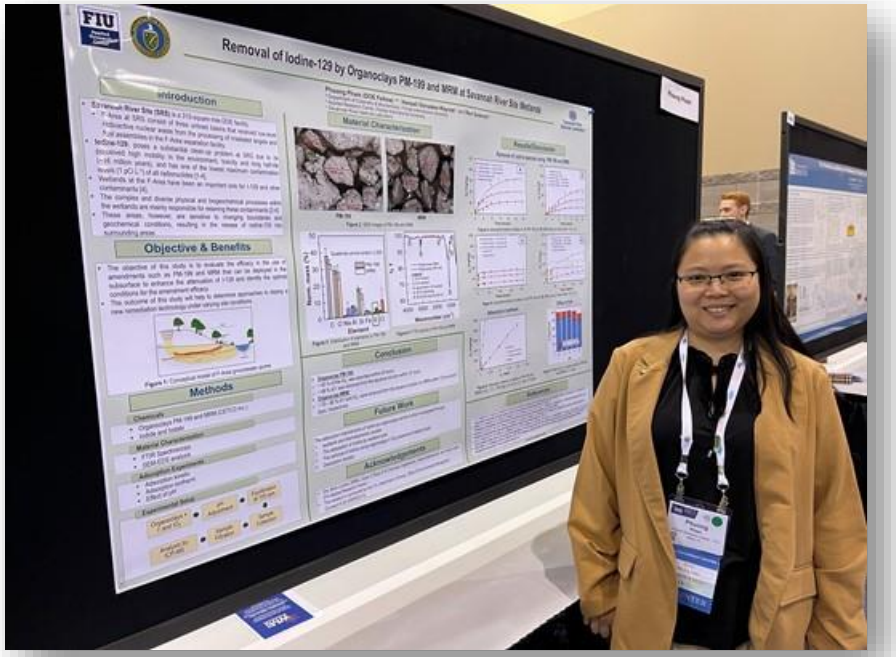
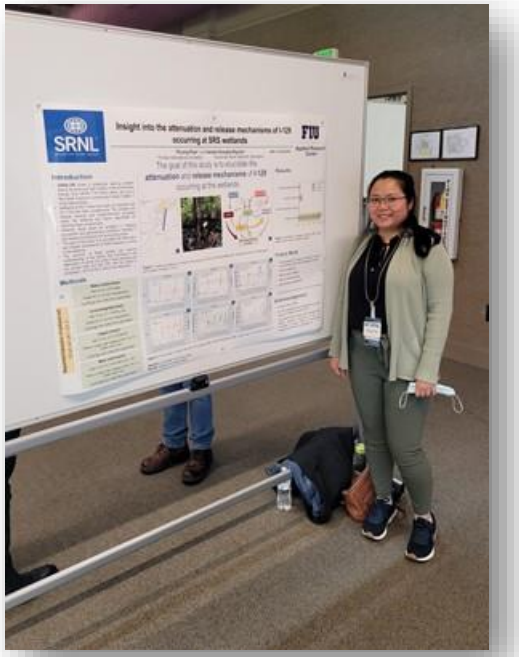
Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

FIU Year 3 Projected Scope:

- Investigation of iodine speciation batch adsorption studies using organoclays in the presence of wetland soils
- Sorption and release of iodine species on soils collected at different depth intervals





DOE Fellow, PhD student Phuong Pham at WM 2022 Symposia and Summer internship at SRNL working under the mentorship of Dr. Hansell Gonzalez-Raymat on the attenuation/release of I-129 by wetland soils.

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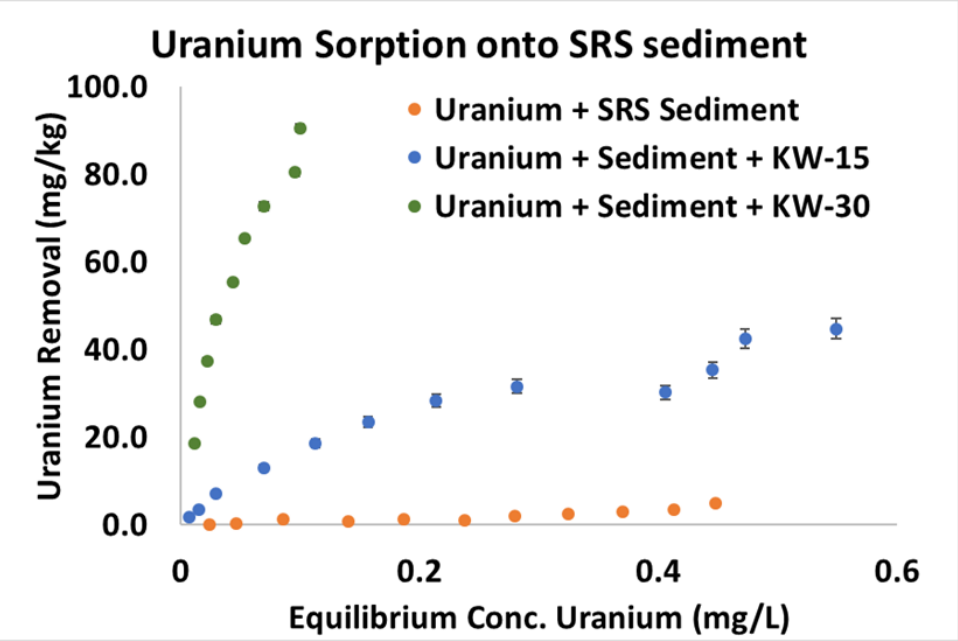
Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Removal of Uranium

FIU Year 2 Research Highlights & Accomplishments:

- Studied the sorption of uranium at pH 4 onto KW-30 coated sediment and compared data with KW-15 and plain sediment data.
- While 6X more KW-30 was sorbed onto SRS sediment compared to KW-15, uranium removal increased ~30X compared to KW-15 and 300X compared to plain sediment.



	Average Humate Sorption (mg/kg)	Average U Removal (mg/kg)	Max U Removal (mg/kg)
Sediment	NA	1.9	5.00
Sediment + KW-15	393	24	44.82
Sediment + KW-30	2435	474	1478

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Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Removal of Uranium

FIU Year 3 Projected Scope

- Investigation of the effect of pH on sorption and desorption of uranium with humate (KW-30) coated sediment
- Study the influence of KW-30 on other contaminants of concern such as Iodine and Strontium

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Task 3

Contaminant Fate and Transport Modeling for the Savannah River Site

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Task 3: Contaminant Fate and Transport Modeling for the SRS

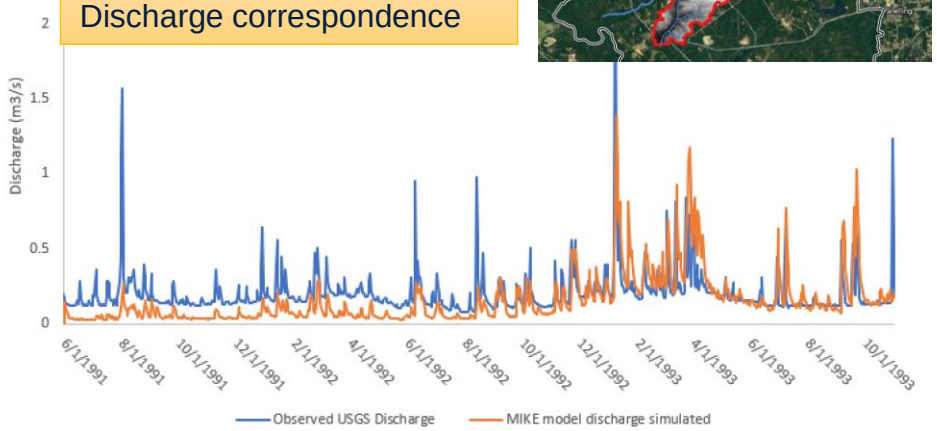
Tims Branch (Subtask 3.1):

- Identified sediment and heavy metal transport parameters for uranium, tin and nickel.
- Calibrated of MIKE 11 sediment & contaminant transport modules (AD & ECO Lab) for simulation of uranium transport.
- Automated and accelerated hydrological model development, to enable the transformation of event-based MIKE SHE/MIKE 11 hydrological model into a continuous model.

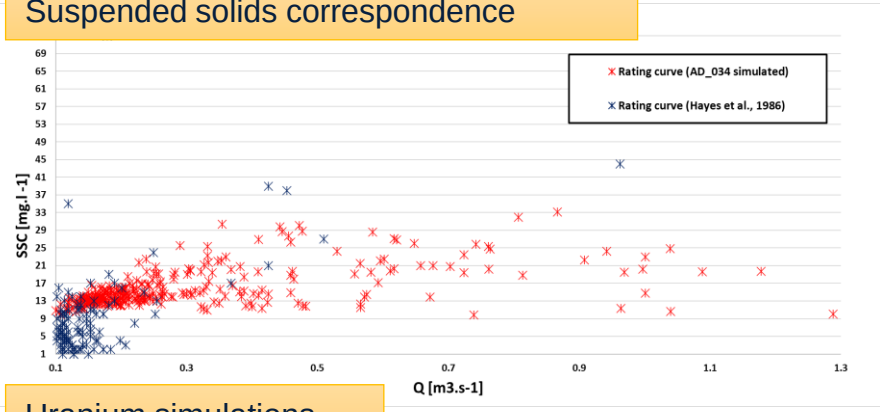
Fourmile Branch (Subtask 3.2) – FIU has developed:

- A conceptual model of hydrological flow processes within seepline over time via detailed assessment of in situ observations.
- Initial version of MIKE SHE / MIKE 11 model to enable simulations of groundwater-river network interaction and flow variability.

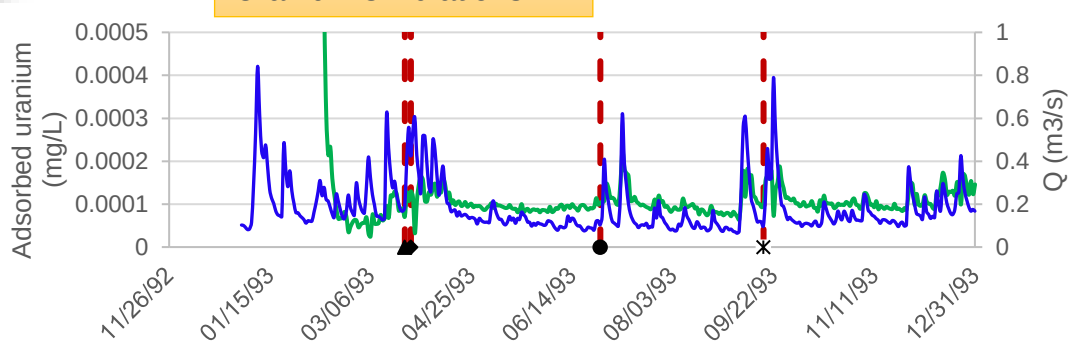
Discharge correspondence

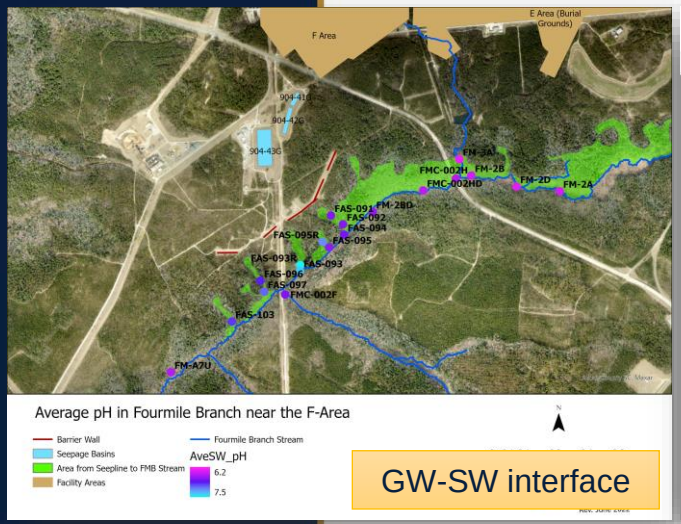


Suspended solids correspondence

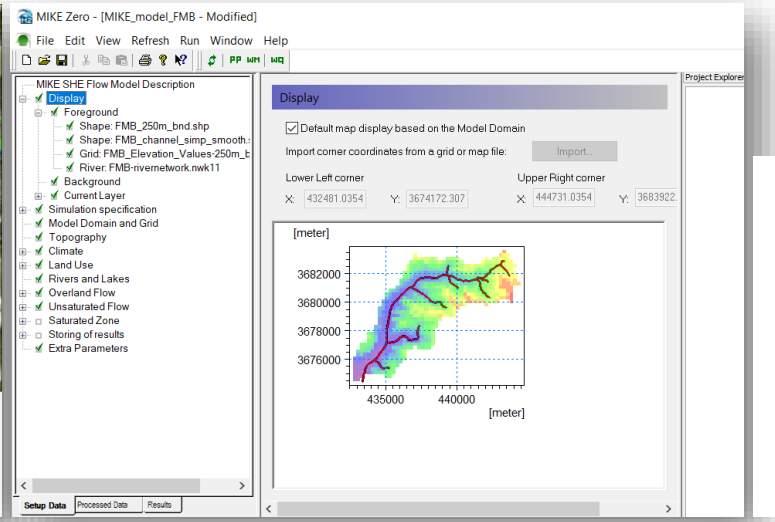


Uranium simulations





GW-SW interface



Task 3: FIU Year 3 Projected Scope

- Complete FIU Year 3 Project Technical Plan.

Subtask 3.1 (Tims Branch):

- Complete calibration MIKE SHE/MIKE 11 hydrological model for Tims Branch long-term simulations.
- Deliver calibrated/validated MIKE 11 sediment & contaminant transport for Tims Branch for uranium to DOE.
- Perform scenario modeling analyses for extreme events and long-term climate-scale simulations.

Subtask 3.2 (Fourmile Branch):

- Calibrate hydrological model of Fourmile Branch riparian stream system using MIKE SHE/MIKE 11.
- Examine impact of seasonal changes as well as long-term changes in hydrological variability due to climate change.
- Extend MIKE model by adding contaminant fate and transport simulations.

- Train FIU graduate and/or undergraduate students on GIS data processing, model development. using MIKE, and data generation and model evaluation using Python.

- Complete FIU Year 3 Year End Report.

Task 5

Research and Technical Support for WIPP

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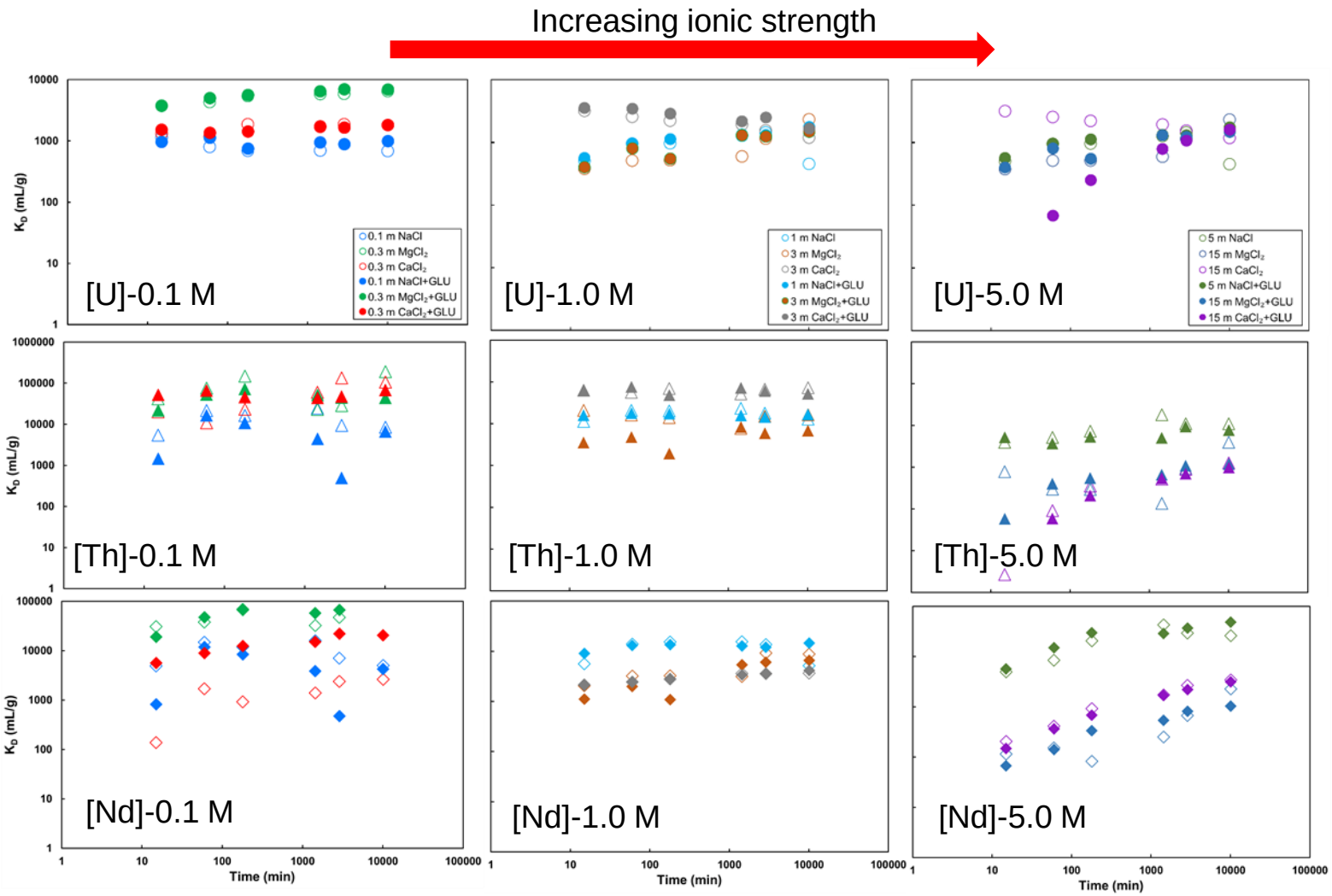
Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

FIU Year 2 Research Highlights & Accomplishments:

- Completed batch sorption experiments investigating the impact of GLU on actinide sorption onto magnetite in WIPP−relevant brines.
- GLU addition have little impact on adsorption of contaminants onto magnetite.
- Sorption trends for the GLU-free brines were similar to that for GLU-amended brines.
- Brine types had a significant influence on actinide solubility in the following order: $CaCl_2 \approx MgCl_2 > NaCl$ with increasing ionic strength.



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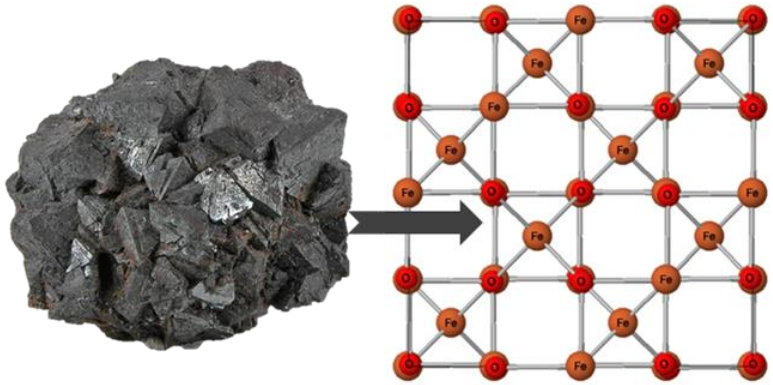
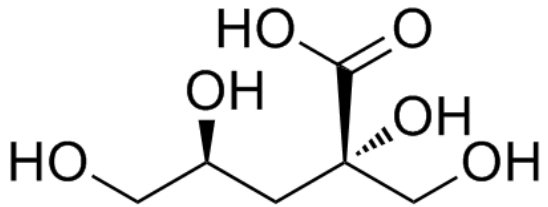
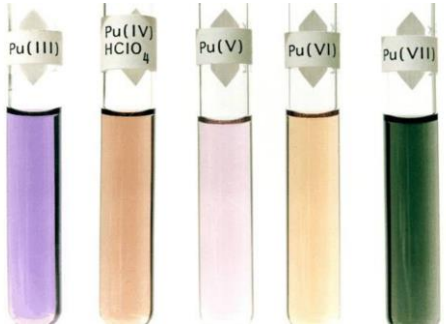
Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

FIU Year 3 Projected Scope

- Complete modeling of collected sorption data to obtain pertinent interaction parameters (virial coefficients) required for high salt systems.
  - TOUGHREACT
- Study the impact of citrate or isosaccharinate (ISA), an important byproduct of alkaline degradation of cellulose on sorption of actinide onto iron (II) hydroxide in WIPP-relevant brines and conditions.
- Characterization of treated solid phases employing microscopy, spectroscopy and x-ray diffraction techniques.







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Task 6

Hydrology Modeling of Basin 6 of the Nash Draw Near the WIPP

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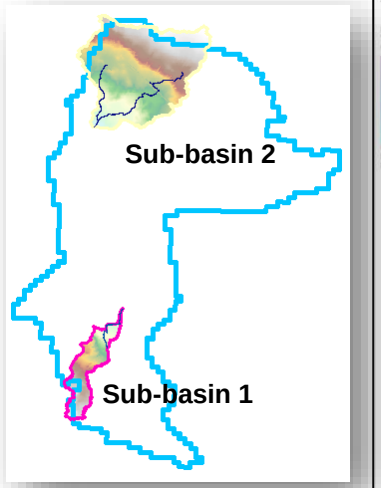
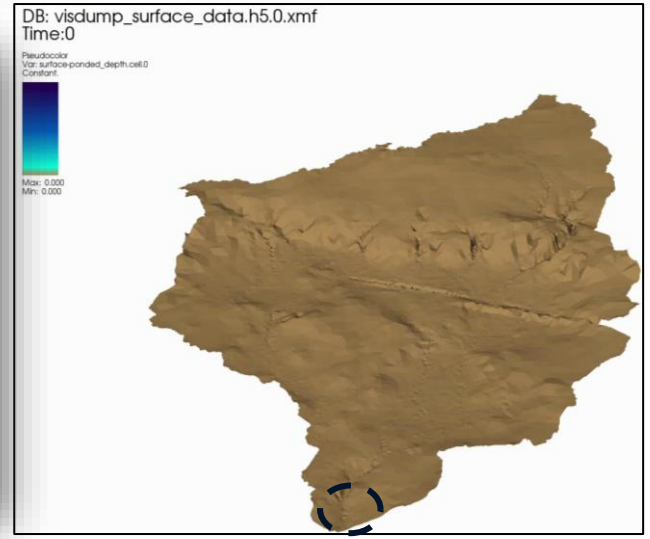
Task 6: Hydrology Modeling of Basin 6 of the Nash Draw Near the WIPP

To develop GW-basin model for Basin 6/Nash Draw west of WIPP FIU has:

1. Developed and handed over a 1-meter DEM for Basin 6 (**Subtask 6.1**):
   - Sampled part of Basin 6 in December 2021.
   - Finalized approach to correct observations for influence of vegetation.
   - Handed over the 1-meter DEM to DOE collaborators.
2. Performed hydrological simulations using the Advanced Terrestrial Simulator (ATS) (**Subtask 6.2**):
   - Simulations for 2 smaller sub-basins using input from the 1-meter DEM.
   - Basin wide simulations using a coarser-scale model set up.





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Task 6: FIU Year 3 Projected Scope

- Complete FIU Year 3 Project Technical Plan.

Subtask 6.1:

- FIU anticipates completing this sub-task in FIU Year 2 and no new scope will be incorporated in FIU Year 3.

Subtask 6.2:

- Finalize workflow for ATS model development for Basin 6 to enable seasonal-scale simulations
- Perform field work:
  - Collect soil samples in Basin 6 to evaluate soil physical properties for ATS model input.
  - Identify location of local depressions (e.g., sinkholes) that impact groundwater-surface seeps.
- Finalize ATS model development of Basin 6 by including information from publicly available datasets as well as locally collected observations.

- Train FIU graduate and/or undergraduate students on GIS data processing, model development using MIKE, and data generation and model evaluation using Python.

- Complete FIU Year 3 Year End Report

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Task 7

Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

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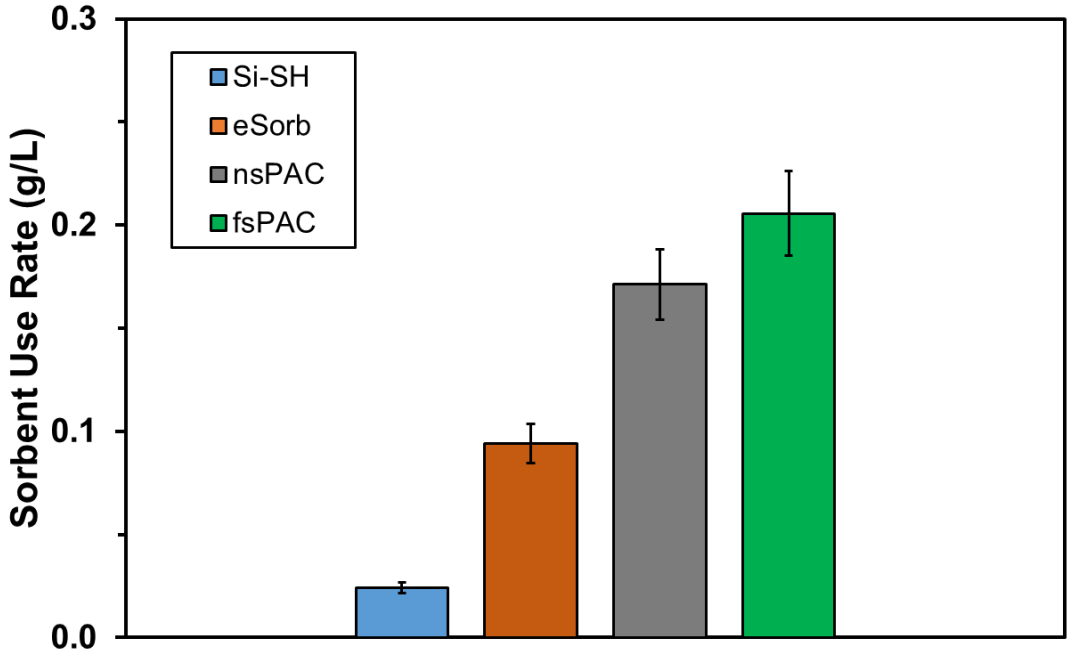
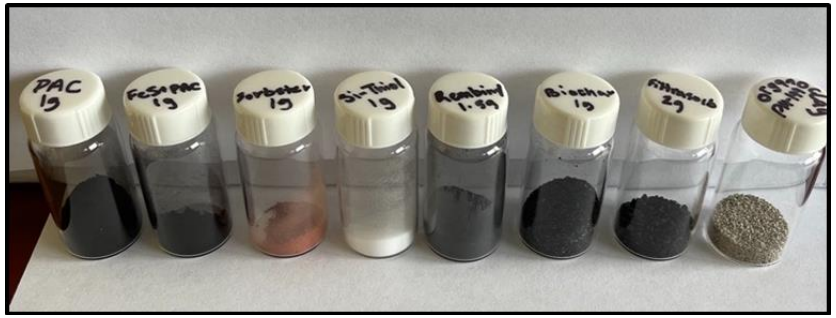
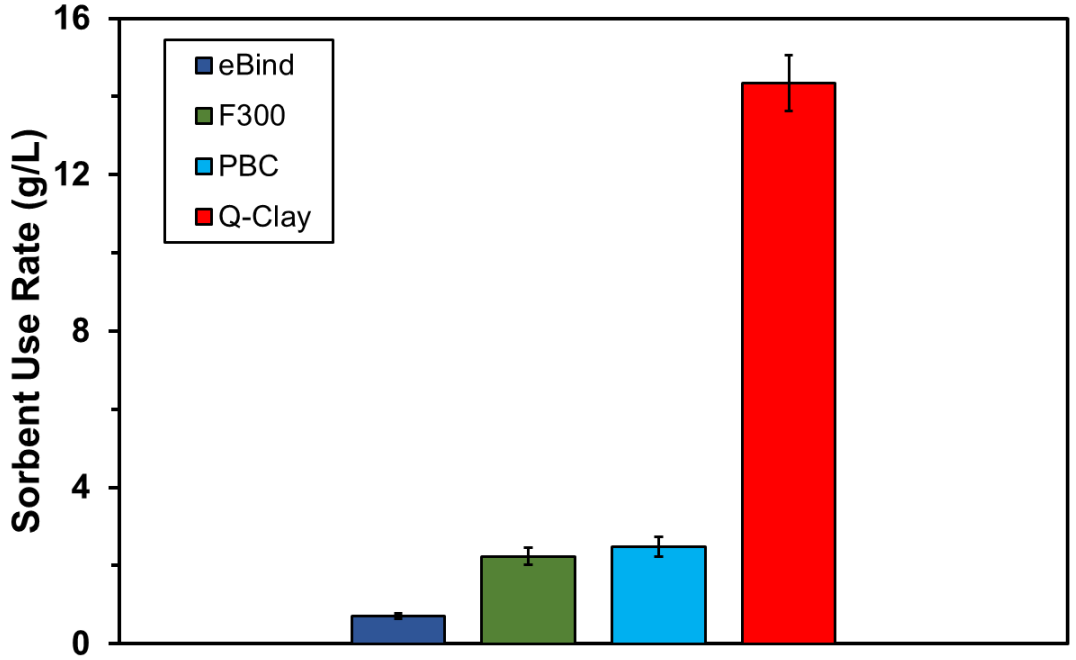
Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 2 Research Highlights & Accomplishments:

- Completed evaluation of eight low-cost, sustainable sorbents for in-situ remediation of mercury species in EFPC ecosystem:







Hg–DOM adsorption capacity decreased as follows: **Si-thiol > Sorbster > FeS+PAC > PAC > RemBind > Filtrasorb > Biochar > Organoclay.**

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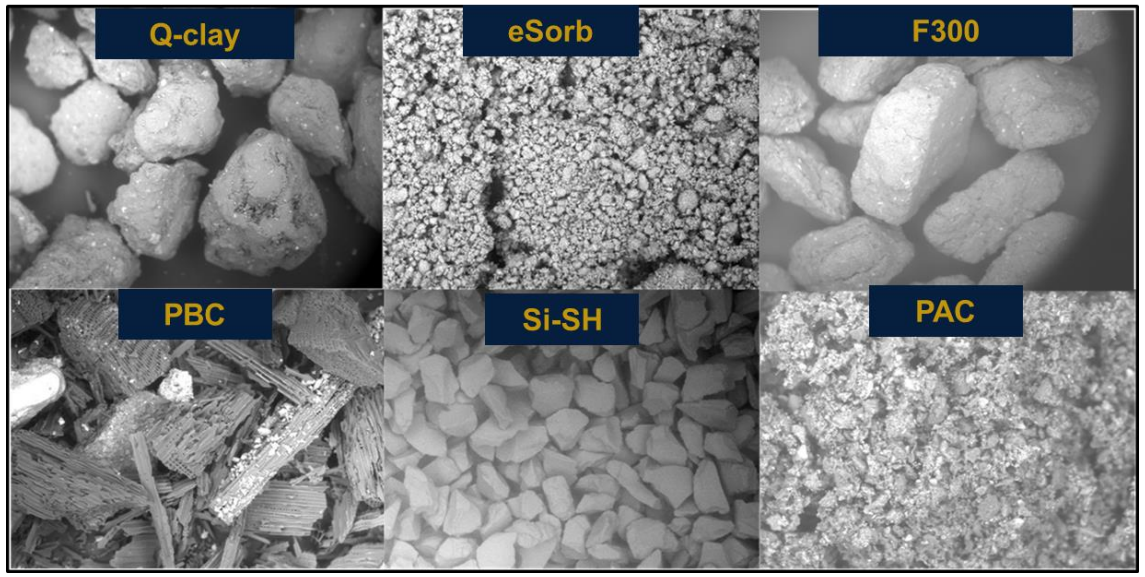
Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 2 Research Highlights & Accomplishments:

- Perform speciation modeling to assess mercury species dynamic within EFPC site.
- Conduct stability evaluation of sorbents via EPA's Toxicity Characteristic Leaching procedure (TCLP).
- Conduct column studies to better understand mercury sorption under representative conditions of EFPC.



DOE Fellow Caridad Estrada during summer internship at ORNL working on column studies under the mentorship of Drs. Alexander Johs and Eric Pierce.

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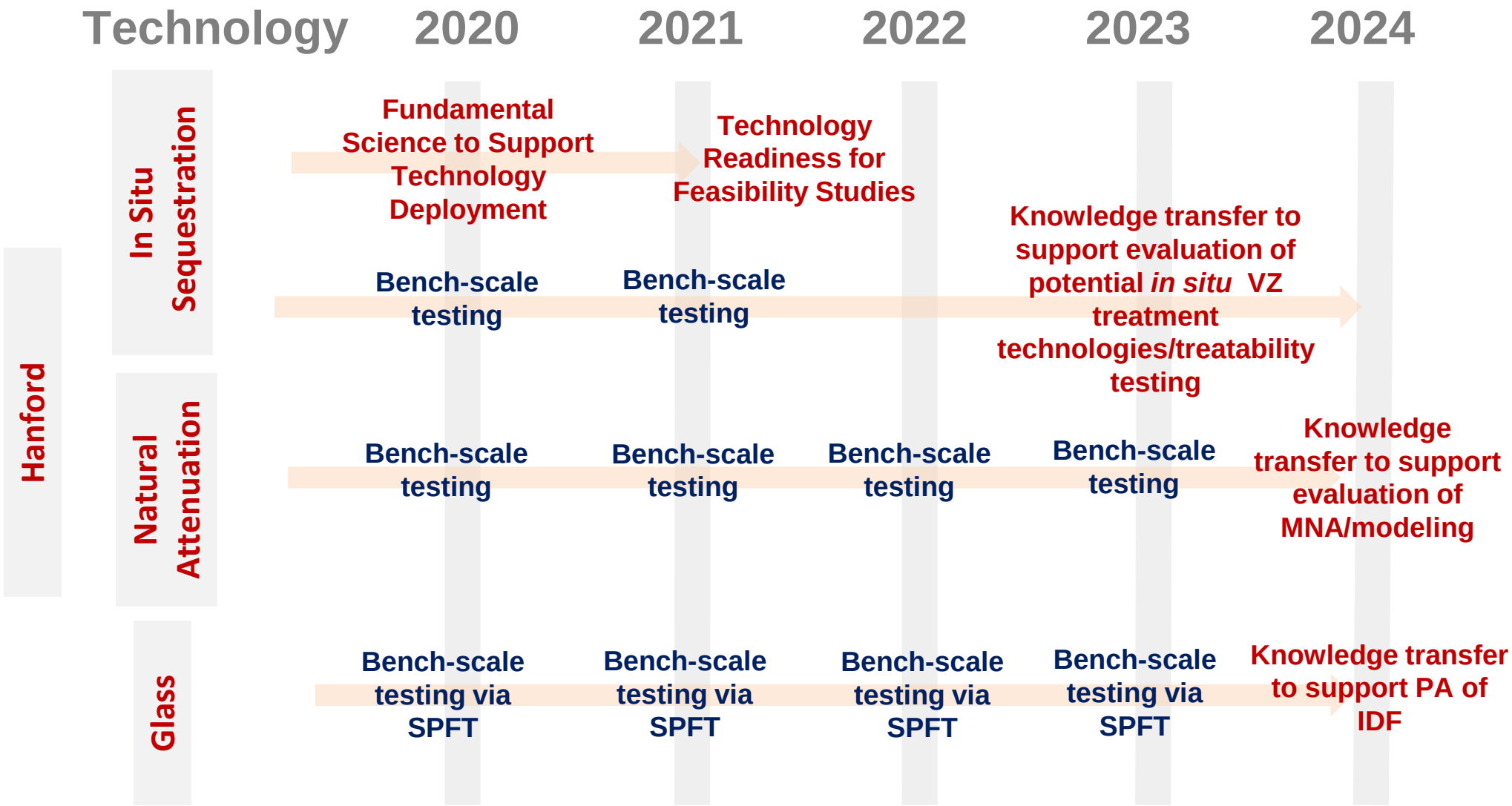
Technology Development and Deployment Road Map



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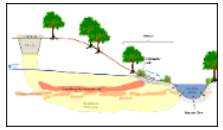
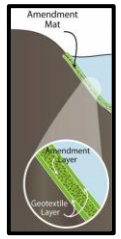
Technology Development and Deployment Road Map

Technology	2020	2021	2022	2023	2024
SRS	Environmental factors controlling contaminants at SRS 	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Knowledge transfer for long term monitoring	
SRS	Evaluation of Humic Acid for uranium sequestration 	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Knowledge transfer for long term monitoring	
Mercury ORNL		Conceptual Design of Technology	Sorbents Development	In-house Testing	Site Testing	Site Deployment of Technology
WIPP		Knowledge Development	Development /Testing	Development /Testing	Development /Testing	Knowledge Transfer

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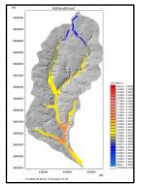
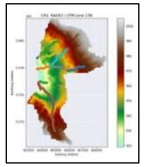
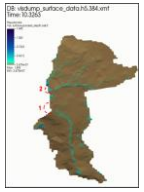
Technology Development and Deployment Road Map

Technology		2020	2021	2022	2023	2024
SRS		Tims Branch Model: Integrated SW/GW Model Calibration	Sed. Transport Model Calibration/ Validation	Contaminant Transport Model Calib./Validation	Contaminant Transport Model Calib./Validation	Model Implementation/ Hand-over
		Fourmile Branch Model: Conceptual Model Development	Conceptual Model Development	Integrated SW/GW Model Dev. & Calib.	Sed./Contam. Transport Model Calib./Validation	Model Implementation/ Hand-over
WIPP (Basin 6)		Basin 6 DEM: Aerial Survey & DEM Dev. Methods Assessment	Basin 6 Aerial Survey & DEM Development	Basin 6 DEM Hand-over & Implementation in ATS Model		
		WIPP (Basin 6) Model: Numerical Model Assessment	ATS Basin 6 SW/GW Model Training & Development	ATS Basin 6 SW/GW Model Training & Development	ATS Model Calib./Validation	Model Implementation/ Hand-over

*DEM: Digital Elevation Model, SW: Surface water, GW: Groundwater

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Thank You. Questions?