FIU PROJECT 2:
YELENA KATSENOVICH

ENVIRONMENTAL REMEDIATION SCIENCE & TECHNOLOGY

FLORIDA INTERNATIONAL UNIVERSITY

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Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE	
Subtask 1.1	Remediation Research of Ammonia Gas for Uranium Treatment
Subtask 1.2	Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants **(NEW)**
Subtask 1.3	Eval. of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments **(NEW)**
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 Sediments **(NEW)**
Subtask 2.2	Humic Acid Batch Sorption Experiments with SRS Soil
TASK 3: CONTAMINANT FATE AND TRANSPORT MODELING IN THE TIMS BRANCH WATERSHED	
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 FOR WIPP	
Subtask 6.1	Digital Elevation Model and Hydrologic Network
Subtask 6.2	Model Development

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

Task 1.1 - Remediation Research with Ammonia Gas for Uranium

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Site Needs:

DOE-EM has a critical need to understand the geochemical reactions that may occur with pH manipulations via alkaline treatment for uranium sequestration in the vadose zone following release of >200,000 kg of U during WWII and the Cold War. Alkaline pH manipulation is a potential remediation technology that can lead to incorporation of U(VI) into the sediments. These studies will provide information that can potentially aid in the interpretation of long-term monitoring of the disposal sites.

Objectives for FIU Year 10:

Identify the physicochemical mechanisms controlling immobilization of U via NH_3(g) injection in the Hanford vadose zone.

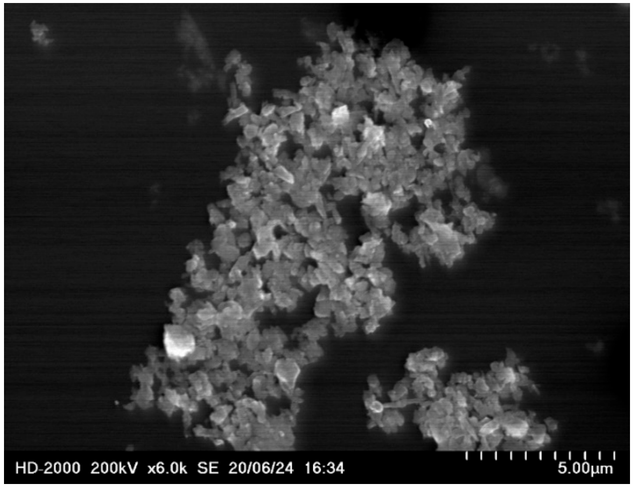
- Measure removal of U from the aqueous phase following NH_3(g) injection.
- Characterize physicochemical changes in minerals.
- Determine the long-term stability of U-solid phases after NH_3(g) injection.

Task 1.1 - Remediation Research with Ammonia Gas for Uranium

FIU Year 10 Research Highlights

- **Completed**:
  - Finalized high loading experiments containing higher U loading in phyllosilicate minerals
  - Clemson collaboration to analyze high loading expt. samples for U-bearing minerals. Unfortunately none found; however, EDS (elemental composition) data allows corroboration of EDS-FIU data
- **On-going**:
  - SEM-EDS analysis to prove secondary precipitation and incongruent dissolution phenomena
  - TEM analysis suggesting ammonium intercalation in phyllosilicates
  - Wring a draft manuscript on illite mineral solid phase characterization under alkaline conditions

Illite high loading experiment while being ammonia-treated



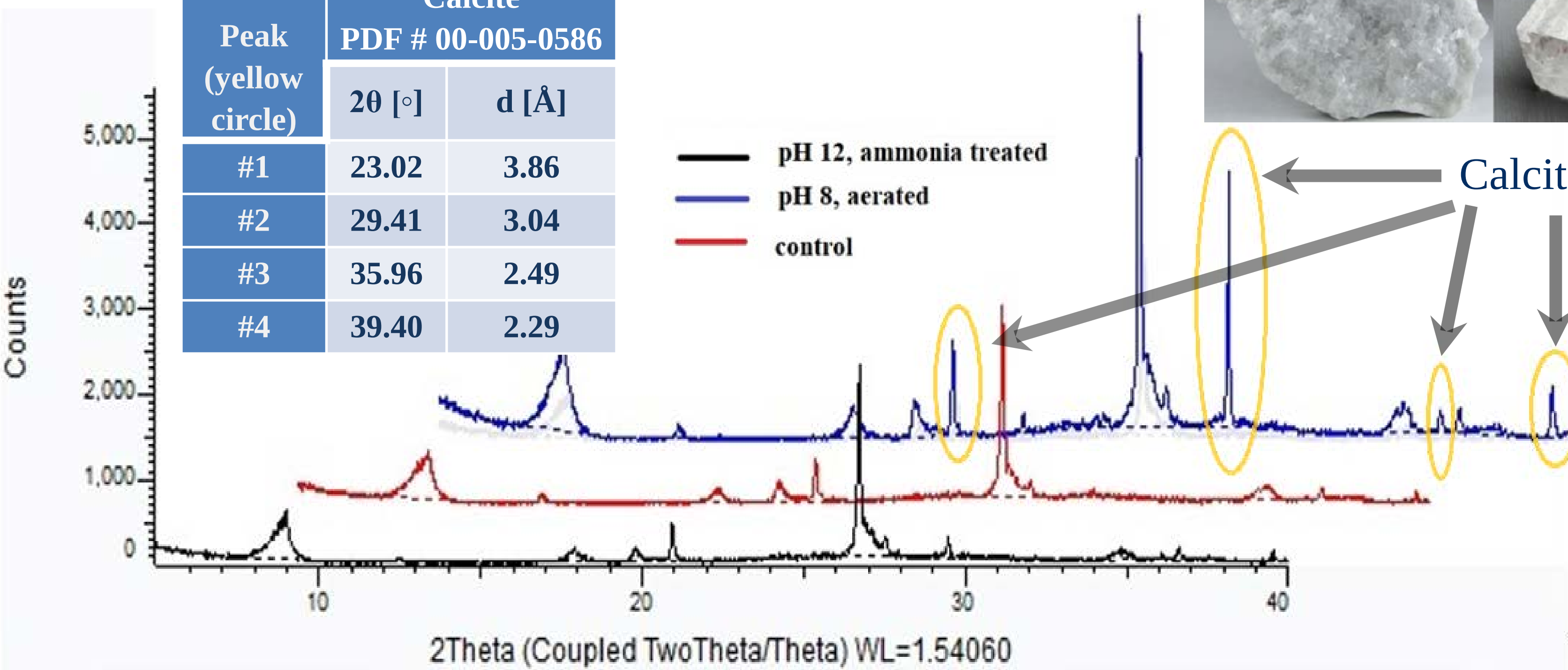
Illite high loading experiment TEM-EDS image in collaboration with Clemson University

Task 1.1 - Remediation Research with Ammonia Gas for Uranium

FIU Year 10 Research Highlights

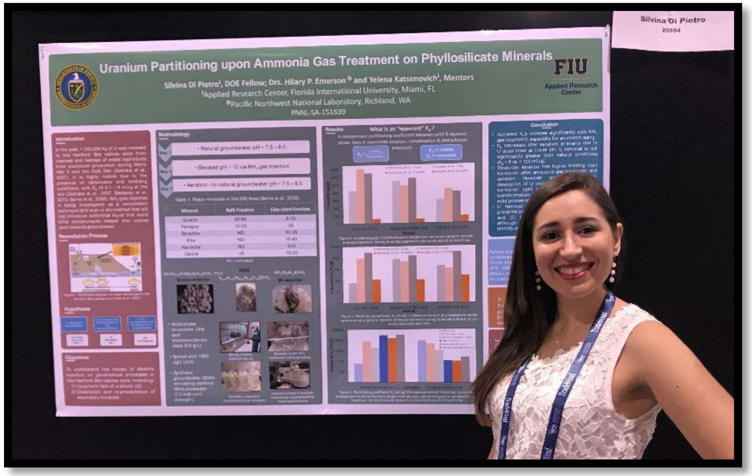
- Illite underwent ammonia & aeration treatment and XRD found calcite as a solid phase for aeration treatment. Same for other minerals (not shown).
- Thermodynamic speciation simulations based on our SGW solution predicted calcite formation (Szecsody et al., 2012; Emerson et al., 2018)

Peak (yellow circle)	Calcite PDF # 00-005-0586	
	2θ [◦]	d [Å]
#1	23.02	3.86
#2	29.41	3.04
#3	35.96	2.49
#4	39.40	2.29



Task 1.1 - Remediation Research with Ammonia Gas for Uranium

FIU Year 10 Accomplishments

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ELSEVIER

Research paper

Phyllosilicate mineral dissolution upon alkaline treatment under aerobic and anaerobic conditions

Silvina A. Di Pietro[a], Hilary P. Emerson[b,*], Yelena Katsenovich[a], Nikolla P. Qafoku[b], Jim E. Szecsody[b]

- First-author publication in the *Applied Clay Science* journal*,* "Phyllosilicate Mineral Dissolution upon Alkaline Treatment and Anaerobic Conditions", March 2020
- Manuscript in preparation to be submitted to *Applied Clay Science* or *Geochimica and Cosmochimica Acta,* "Solid phase characterization and transformation of illite mineral under alkaline conditions"
- Awards
  - *Clay Mineral Society Annual Meeting Student Travel Award - Clay Mineral Society*
  - *Student Best Poster, 2nd place* - Waste Management Symposia 2020
  - Acceptance into Neutron and X-ray scattering Summer School - Oak Ridge and Argonne National Laboratories
- Poster at Waste Management Symposia (March 2020), and upcoming at the Clay Mineral Society (virtually) in Richland, WA

Task 1.1 - Remediation Research with Ammonia Gas for Uranium

FIU Year 01* Objectives

Experimental work for this task has been completed

Future Work

- Finalize data analyses to complete manuscripts and Silvina DiPietro dissertation thesis
- Silvina's dissertation defense

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

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

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 of the fate of Tc in conditions related to the Hanford Site and re-oxidation of prior immobilized Tc-99 under aerobic conditions to facilitate identification of promising Tc-99 remediation technologies using strong reductants.

Objectives for FIU Year 10:

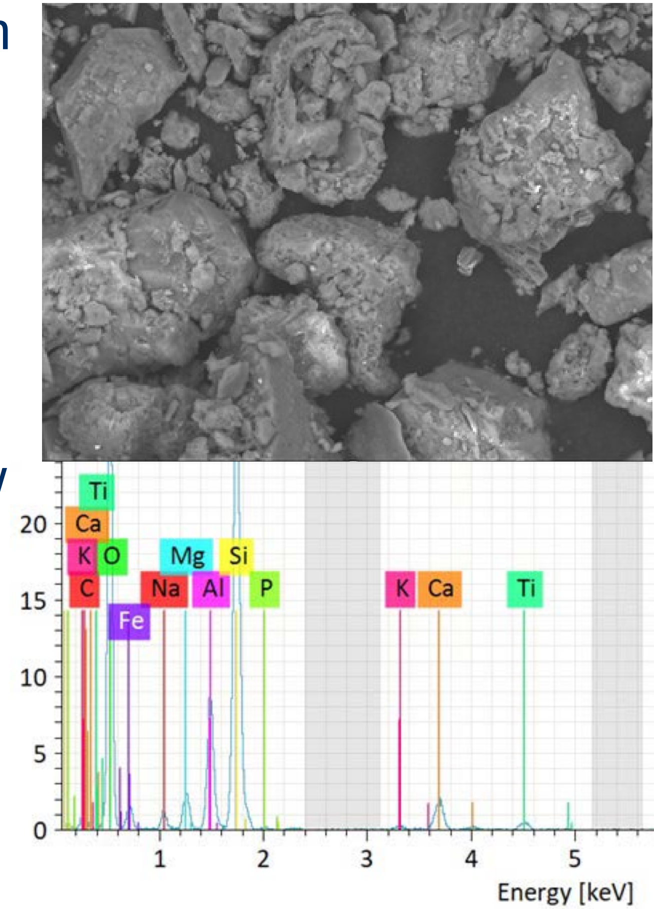
Provide insights on the stability of immobilized Tc-99 after sequestration with strong reductants.

- Study re-oxidation kinetics of Tc-99 in perched and groundwater that has been initially reduced by strong reductants such as ZVI, SMI and CPS in batch-scale experiments under anaerobic initial conditions followed by aerobic conditions.
- Monitor ferrous iron concentrations released into the aqueous phase.

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

FIU Year 10 Research Highlights

- Conducted batch experiments to study re-oxidation kinetics of reduced ^{99}Tc after treatment with strong reductants
  - **Zero valent iron** (ZVI), 0.1% and 1% mass of GW or perched water (PW) used in experiments
  - **Sulfur modified iron** (SMI), 0.1% and 1% mass of GW or PW
  - **Polysulfide** (CPS), 0.5% and 5% mass of GW or PW
- Obtained sediment samples from the Hanford Site Ringold Formation
  - Sieved sediment < 2mm
  - Performed sediment characterization using BET method, X-ray diffraction (XRD) and surface morphology and elemental composition via SEM-EDS.



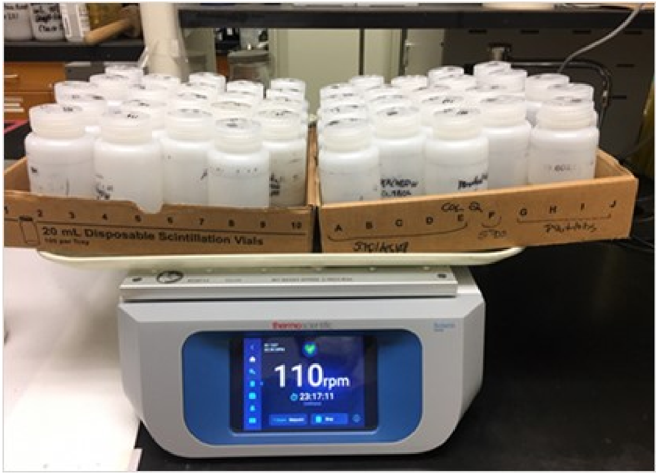
SEM/EDS of Ringold sediment <2 mm

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

FIU Year 10 Research Highlights

FIU Applied Research Center

- Prepared synthetic solutions of groundwater and perch water
  Purged with N_2, pH adjusted, and spiked with ^{99}Tc
  - **Perch water**: pH 8.2 & 10µg/L ^{99}Tc
  - **Ground water**: pH 7.8 and 420µg/L ^{99}Tc
- Conducted experiments in two phases:
  - **1. Reduction** of ^{99}Tc in the presence of strong reductants under anaerobic conditions for up to 5 days
  - **2. Re-oxidation** of ^{99}Tc under aerobic conditions for up to 30 days
  - Measured pH, oxidation reduction potential (ORP) at each sampling time point



42 experimental bottles in total

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

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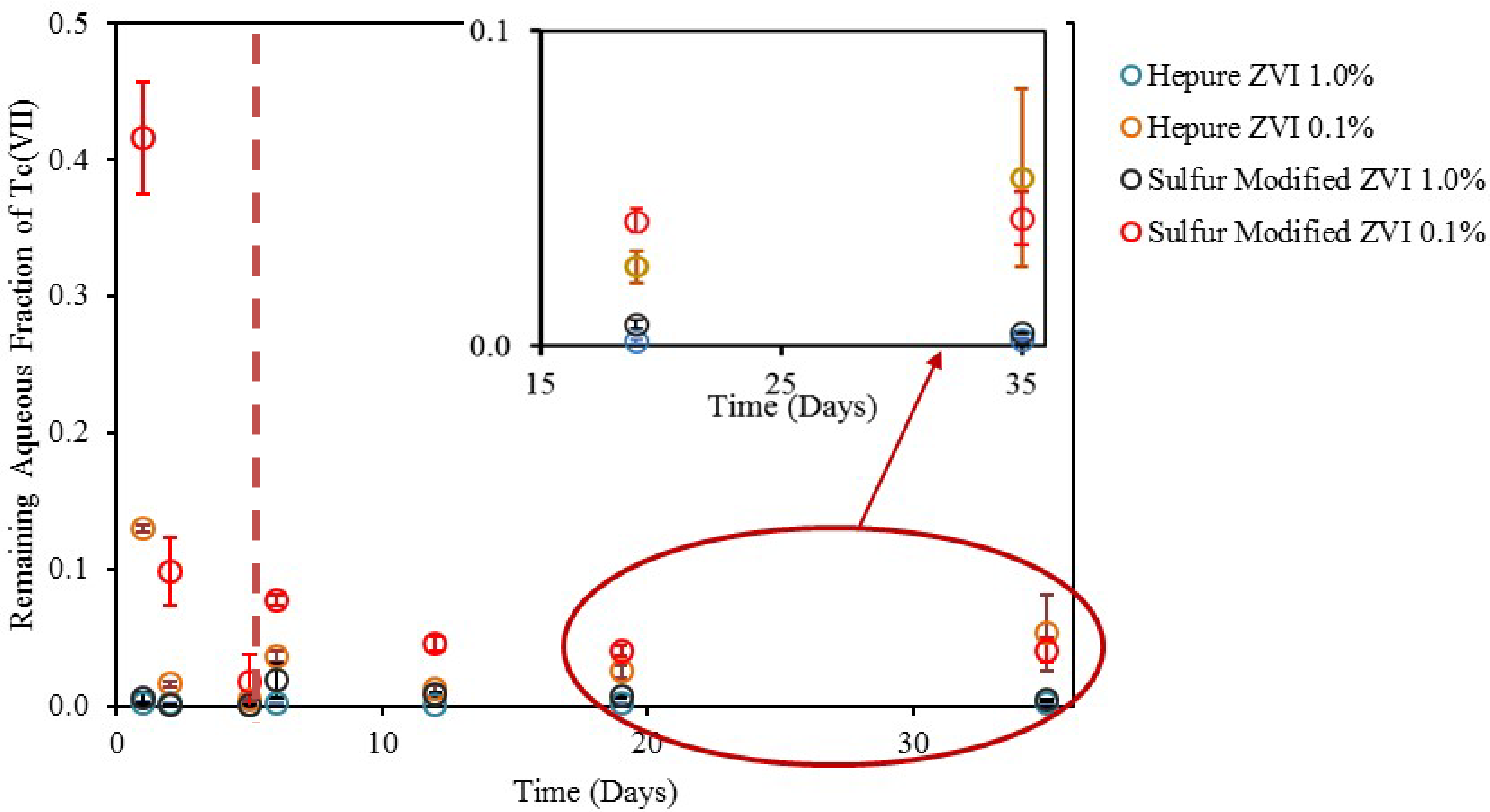
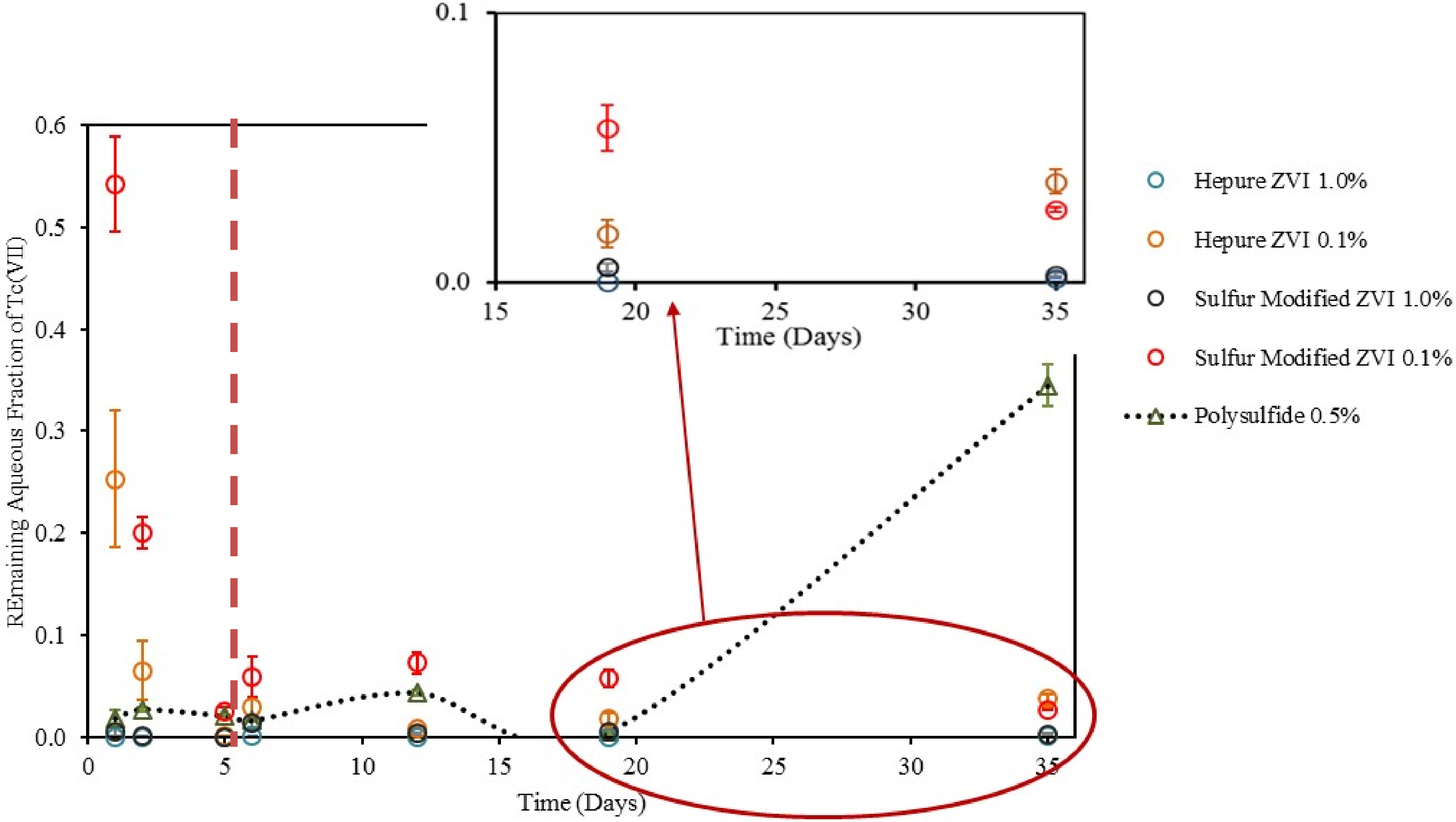
Perched Water, Remaining Aqueous Fraction of Tc(VII) (C_i = 10ppb)



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

Remaining aqueous fraction of Tc in GW samples (Ci = 420 ppb)



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

Reoxidation Kinetics

Batch Name	Perched Water (10ppb ^{99}Tc)		Ground Water (420ppb ^{99}Tc)	
	Tc-99 Reoxidation Kinetics $Ln[C_t/C_o]$, k (hr^{-1})	R- Squared	Tc-99 Reoxidation Kinetics $Ln[C_t/C_o]$, k (hr^{-1})	R- Squared
Hepure ZVI 0.1%	0.0035±0.0008	0.91	0.0042±0.0015	0.80
Hepure ZVI 1.0%	0.0016±0.0007	0.73	0.0039±0.0018	0.71
Sulfur modified ZVI 0.1%	-0.0007±0.0005	0.49	-0.0014±0.0005	0.81
Sulfur modified ZVI 1.0%	-0.0018±0.0006	0.83	-0.0018±0.0009	0.66

Task 1: Remediation Research and Technical Support for Hanford
Task 1.2 - Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

Ongoing work

- Data analyses of LSC results for CPS amended perched and GW samples.
  - Compare LSC results with ICP-MS data for GW samples amended with 0.5% CPS.
- Correlate dissolved iron results with Tc re-oxidation behavior
- Perform kinetic calculations and regression statistics for CPS reductants

Objectives for FIU Year 01 of Renewal

- Complete investigation of re-oxidation kinetics of perched and GW contaminants, such as $^{99}Tc(VII)$ comingled with ^{238}U and NO_3, that have been initially reduced by strong reductants, ZVI, SMI and CPS, under anaerobic conditions followed by aerobic conditions.

Task 1: Remediation Research and Technical Support for Hanford
Task 1.3 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Applied Research Center

Site Needs:

Contaminants (U (VI), I-129, Tc-99, Cr(VI) and NO_3^-) that were released to the environment can potentially impact groundwater. Once active remediation is completed, a transition to monitored natural attenuation (MNA), is needed. Effective MNA requires a thorough understanding of the contaminant immobilization processes that keep the contaminants stable and resistant to remobilization due to changes in environmental conditions or GW chemistry.

Objectives for FIU Year 10:

Evaluate attenuation processes that affect fate and transport mechanisms of contaminants of concern present in VZ sediment collected from the Hanford Site.

- Conduct physical, chemical and mineralogical characterization of sieved sediment fractions.
- Initiate competitive adsorption experiments on selected sediment fractions with key contaminants of concern at the max concentrations found at Hanford 200 Area GW and porewater when all contaminants are commingled together to compare adsorption results when each contaminant is present separately.

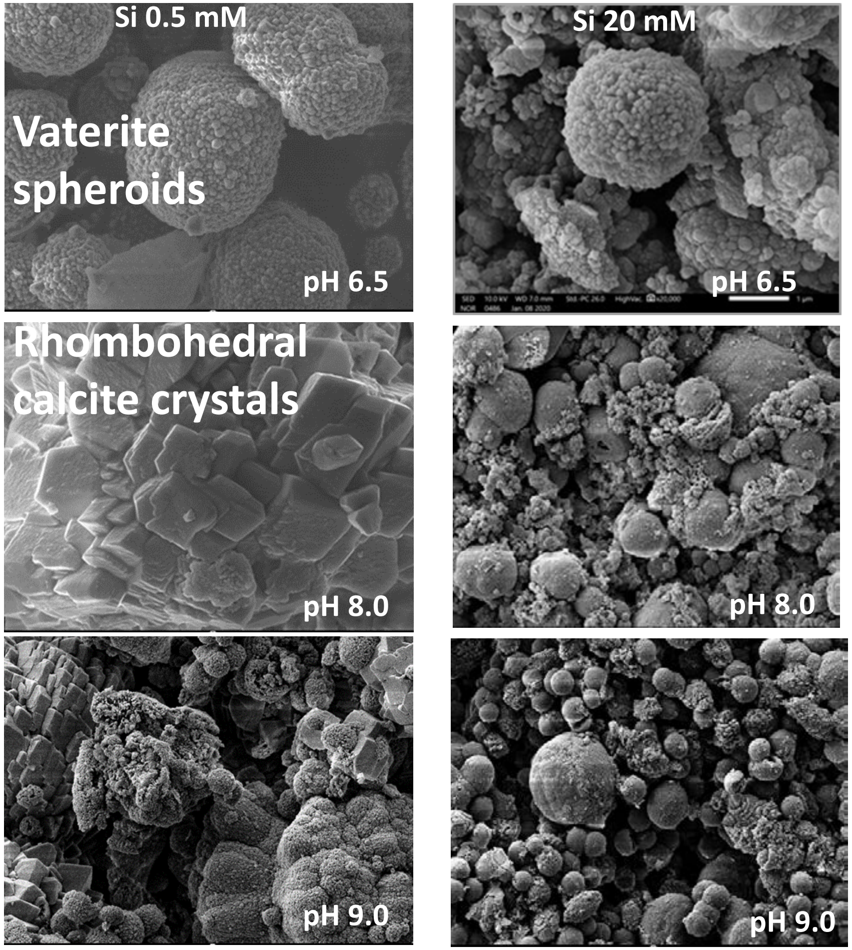
Task 1.3 - Remediation Research on Iodine Incorporation into Calcite (carryover scope- study completed)

FIU Year 10 Research Highlights

- The presence of CrO_4^{2-} has little effect on IO_3^- removal
- Removal of IO_3^- is pH and Si concentration dependent
  - Enhanced IO_3^- incorporation at the lowest pH 6.5
  - Increase in Si contributed to higher iodate uptake
- Si controls or slows down $CaCO_3$ phase transformation
- More CrO_4^{2-} than IO_3^- is released during $CaCO_3$ dissolution

Achievements:

- Manuscript "*Silicon concentration and pH controls over competitive or simultaneous incorporation of iodate and chromate into calcium carbonate phases*" is under review in Applied Geochemistry
- Oral presentation and poster at WM20 "*Iodine Co-Precipitation with Calcium Carbonate in the Presence of Silica Ions*".



Si slows down calcite crystallization.

Task 1.3 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 10 Research Highlights

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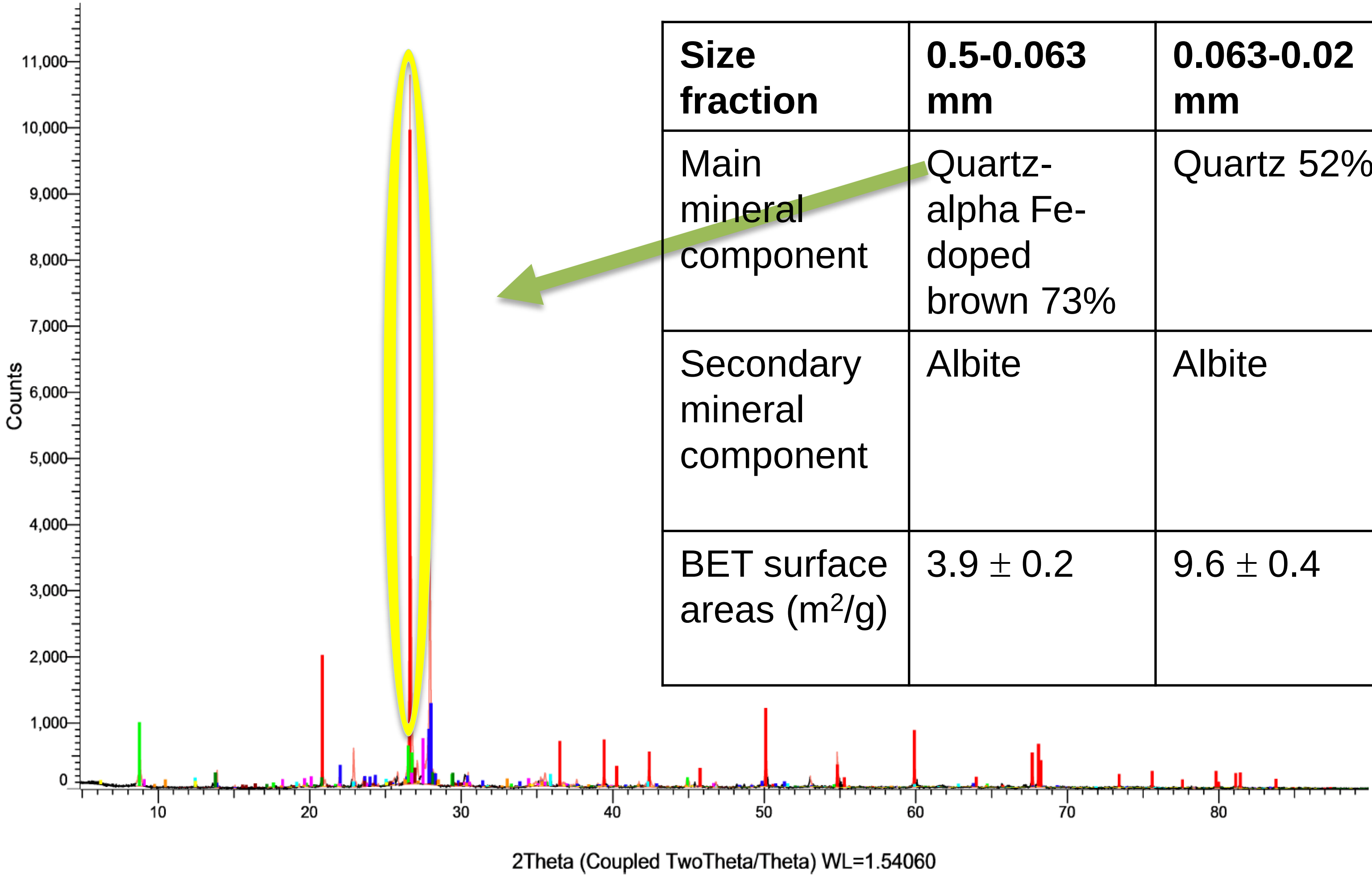
Results for XRD and BET measurements on Hanford Formation sediments



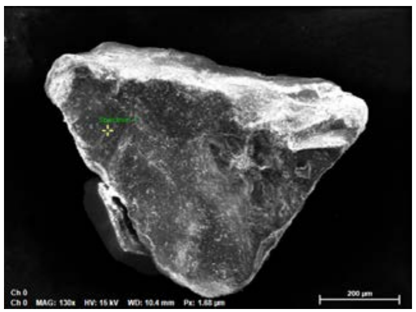
Size fraction	**0.5-0.063 mm**	**0.063-0.02 mm**	**>0.02 mm**
Main mineral component	Quartz-alpha Fe-doped brown 73%	Quartz 52%	Albite 40%
Secondary mineral component	Albite	Albite	Cobalt Aluminum Silicate and Lindackerite
BET surface areas (m^2/g)	3.9 ± 0.2	9.6 ± 0.4	14.7 ± 0.6

Task 1.3 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

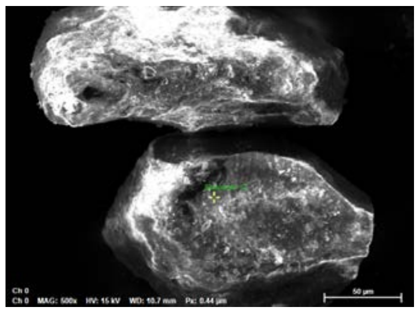
FIU Year 10 Research Highlights

SEM-EDS analysis of Hanford sediment

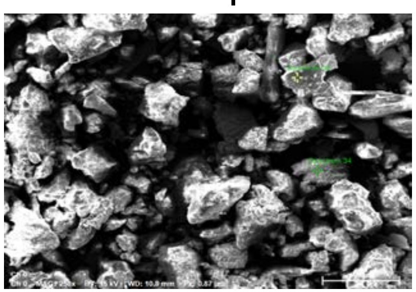
2-0.5mm



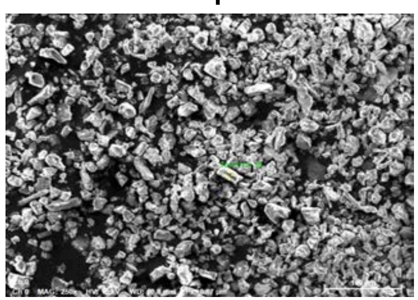
0.5-0.063mm



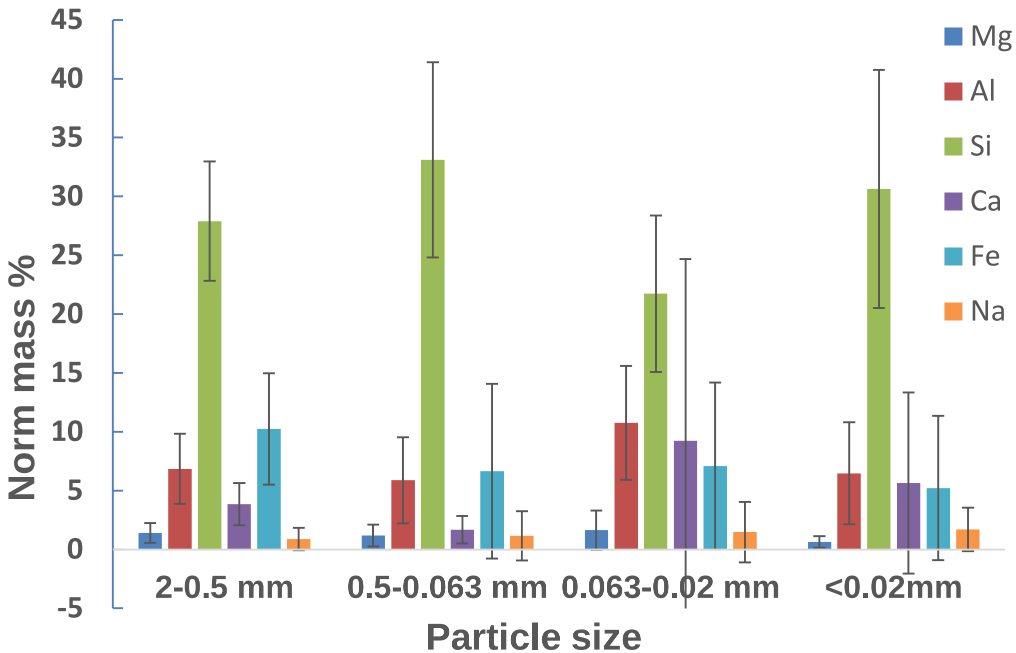
63-20µm



<20µm



EDS elemental distribution for Hanford sediment



Task 1.3 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 10 Research Highlights

Contaminant (1,147 data points)	I-129 (µg/L)	Tc-99 (µg/L)	Cr (VI) (µg/L)	NO_3^- (mg/L)	U(VI) (µg/L)
Maximum concentration	**(299-W21-3): 0.13**	**299-E33-350: 2.62**	**299-W14-16:** 531.0	**299-E33-351** 1990	**200-BP: 99,000**
Minimum concentration	**699-40-62: 0.002**	**299-W23-236: 0.0004**	**200 West P&T Extraction Well:** 1.5	**basalt confined aquifer:** 0.29	**699-31-31: 0.073**
Maximum concentrations in GW Central Plateau	**0.07**	**1.06**	151.69	588	1591.48
Average concentration from 2018 groundwater report	**0.05**	**0.54**	122.0	272.28	4116.67
Average concentration from 2018 pump and treat report	**0.013**	**0.27**	37.32	163.16	5923.63
Average concentration from both reports	**0.03**	**0.33**	57.06	193.36	5386.24

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

Task 1.3 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

Preliminary concentrations for competitive sorption experiments

Contaminant	I-129, µg/L	Tc-99, µg/L	Cr(VI) µg/L	NO_3^- µg/L	U(VI) mg/L	U(VI) µg/L
1	TBD	2.6	532	1990	99	9000
2	TBD	2.6	400	1600	80	6500
3	TBD	2.6	300	1200	60	4000
4	TBD	2.6	200	800	40	1500
5	TBD	2.6	100	400	20	100

Ongoing:

- Competitive sorption: batch experiments with contaminant concentrations from left table
- Solid phase characterization post treatment

Objectives for FY1 of Renewal

Determine the mechanisms affecting the behavior and fate of contaminants and provide the technical basis needed to assess the long-term effectiveness of MNA at Hanford, thereby supporting Hanford site cleanup.

- Continue competitive sorption batch experiments with key contaminants of concern, U(VI), Tc-99, iodine (as IO_3^-), Cr(VI), and NO_3^-

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

Task 1.4 - Experimental Support of Lysimeter Testing

Site Needs:

- This work supports the safe disposal of immobilized low-level waste at the Integrated Disposal Facility (IDF) at the Hanford Site.
- The near-surface location will allow for eventual contact between the immobilized waste forms (e.g. glass, grout) and groundwater or cement contacted GW.
- Long-term field-scale lysimeter testing coupled with laboratory experiments will assist with validating modeling efforts to predict contaminant mobility at larger field environment scales.
- Single-pass flow-through laboratory experiments have been conducted to investigate the effects of grout-contacted groundwater on glass dissolution behavior in support of a recently initiated long-term field-scale lysimeter test and a proposed test configuration containing both grout and glass samples (Bacon et al. , 2018).

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

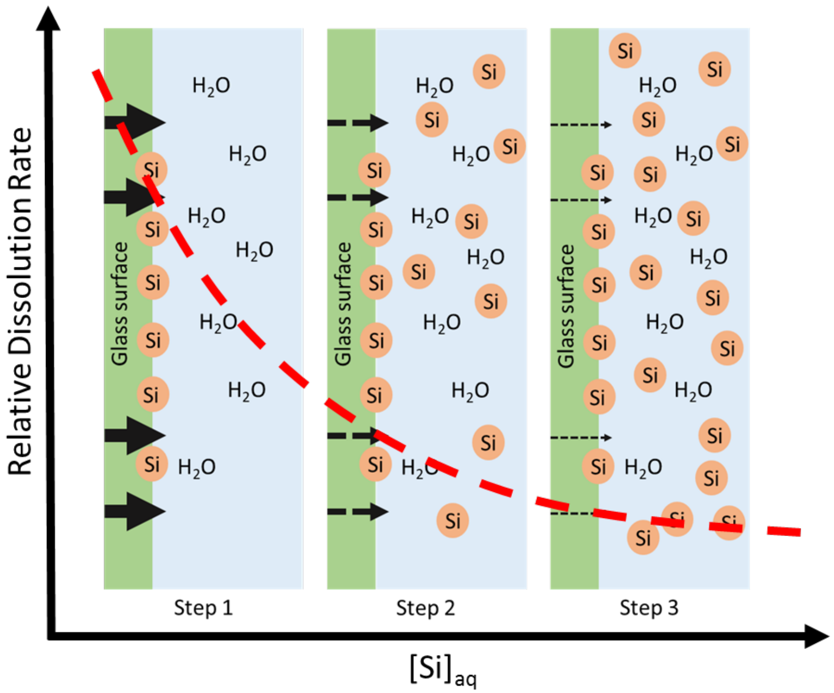
Task 1.4 - Experimental Support of Lysimeter Testing

FIU Year 10 Objectives:

To investigate the effect of grout-contacted groundwater on glass dissolution behavior at varying pH (9-12) and temperature (25°C, 40°C, 70°C) using single-pass flow-through (SPFT).

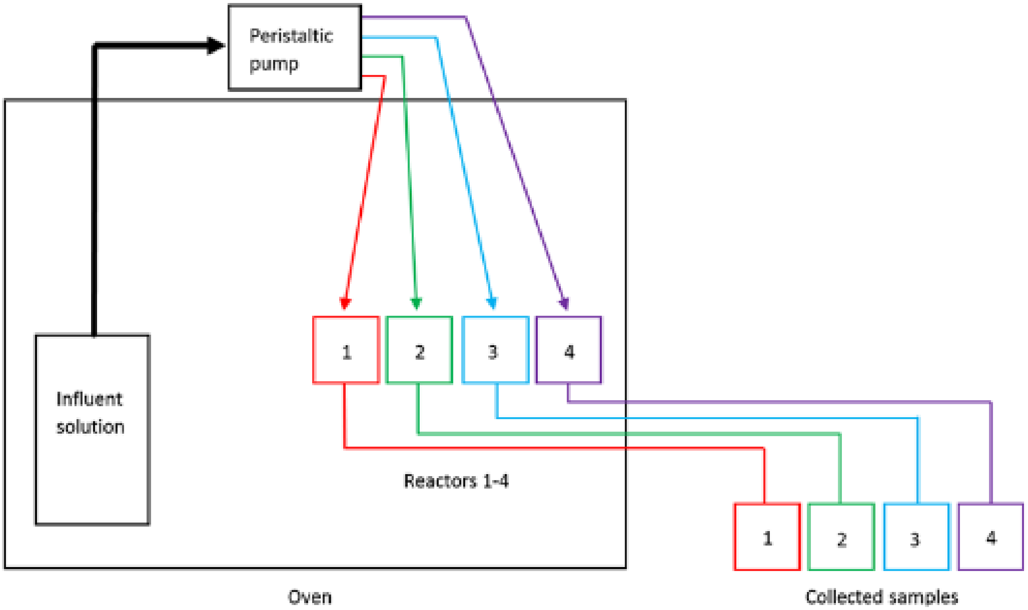
Experiments determine if the glass dissolution behavior is controlled by a pH-mediated effect by the sediment or by the chemical compositions of grout-contacted GW at 25°C, 40°C, and 70°C.

- Determine baseline glass dissolution behavior using buffered pH solutions.
- Investigate the effect of grout-contacted GW on dissolution behavior of ORLEC28 glass.
  - Test matrix: duplicate reactors with grout – contacted sol, a reactor with pH 12 buffered sol, flow rate 40mL/day.



Task 1.4 - Experimental Support of Lysimeter Testing

SPFT Experimental Set Up



(Left) Spectrum IS-95 interval collector for SPFT experiments;

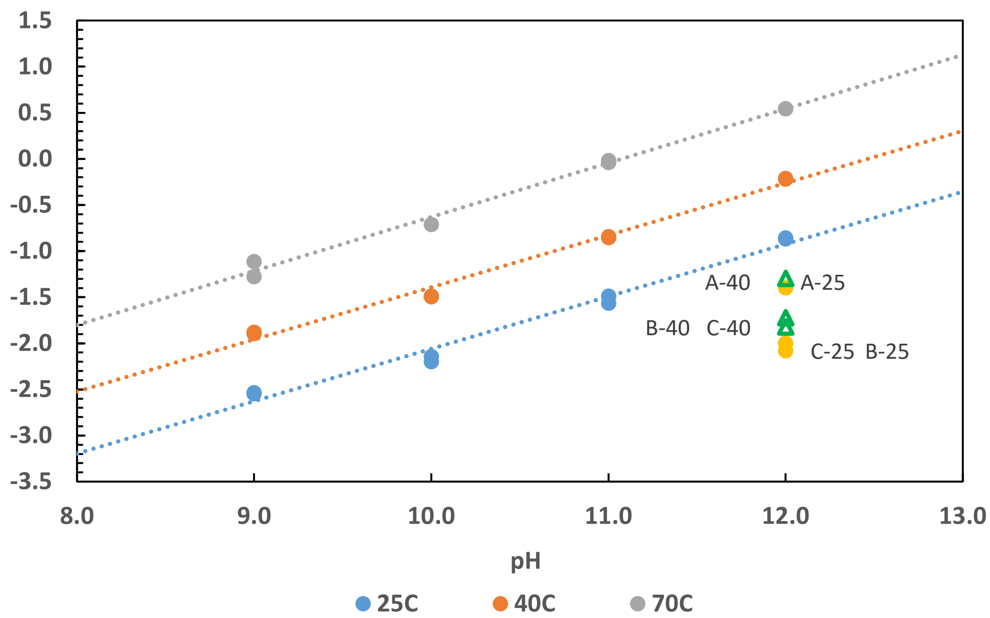
(Right) Experimental setup of SPFT experiments in a temperature-controlled environment.

Task 1.4 - Experimental Support of Lysimeter Testing

FIU Year 10 Research Highlights

Continued with SPFT experiments utilizing grout-contacted groundwater as the leachate

- The dissolution rates for B from PNNL-27098 (Blue, Orange, Gray)
- A, B, C- dissolution rates for B from FIU experiments at 25°C and 40°C with grout-contacted groundwater at pH 12.
- Higher temperature corresponds to higher dissolution rate of glass
- Preliminary data suggests grout contacted solution reduces the dissolution rate. May result from a common ion effect from species in the grout solution.



Baseline B dissolution of ORLEC28 glass in varying pH PNNL-27098 (Neeway, et al. 2018) in gray, orange, and blue. Experiments at 25°C and 40°C utilizing grout-contacted water at pH 12 in yellow and green

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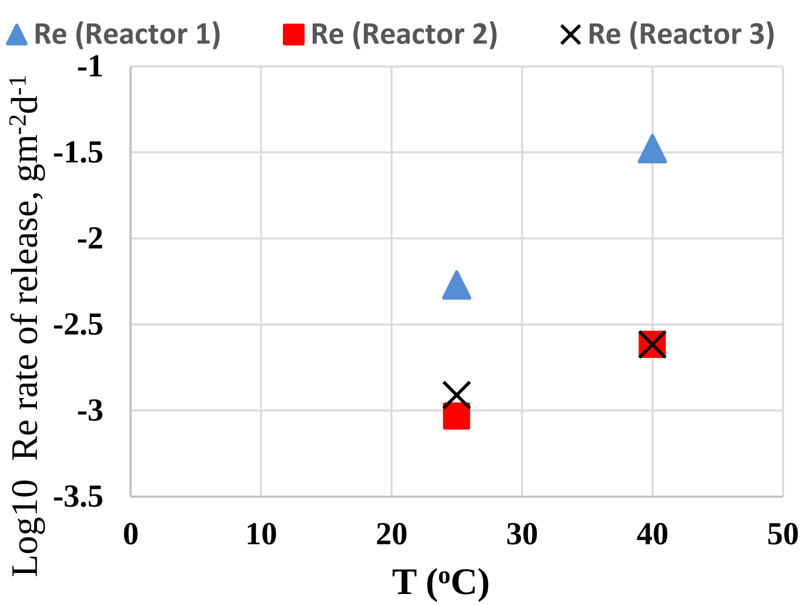
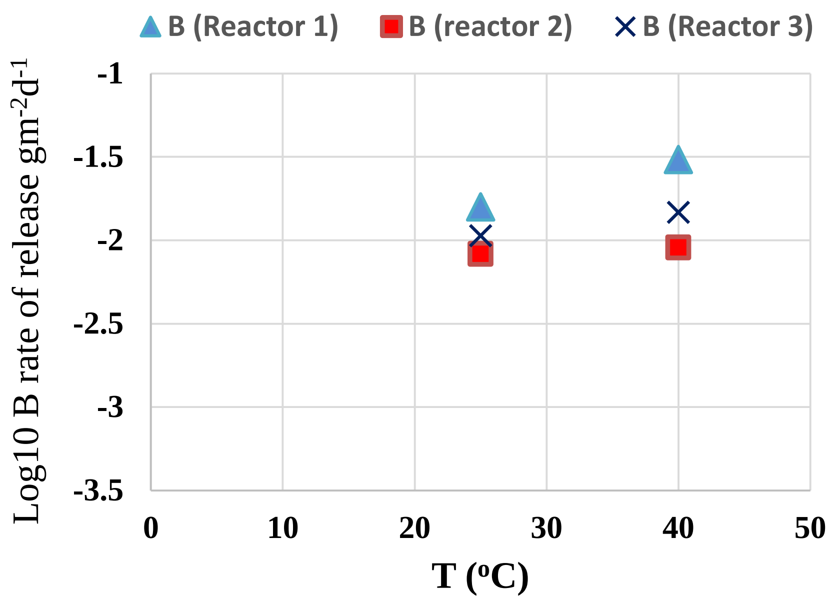
Task 1.4 - Experimental Support of Lysimeter Testing

FIU Year 10 Research Highlights

Reactor 1 = buffer (pH 12), Reactors 2 and 3 = grout contacted solutions



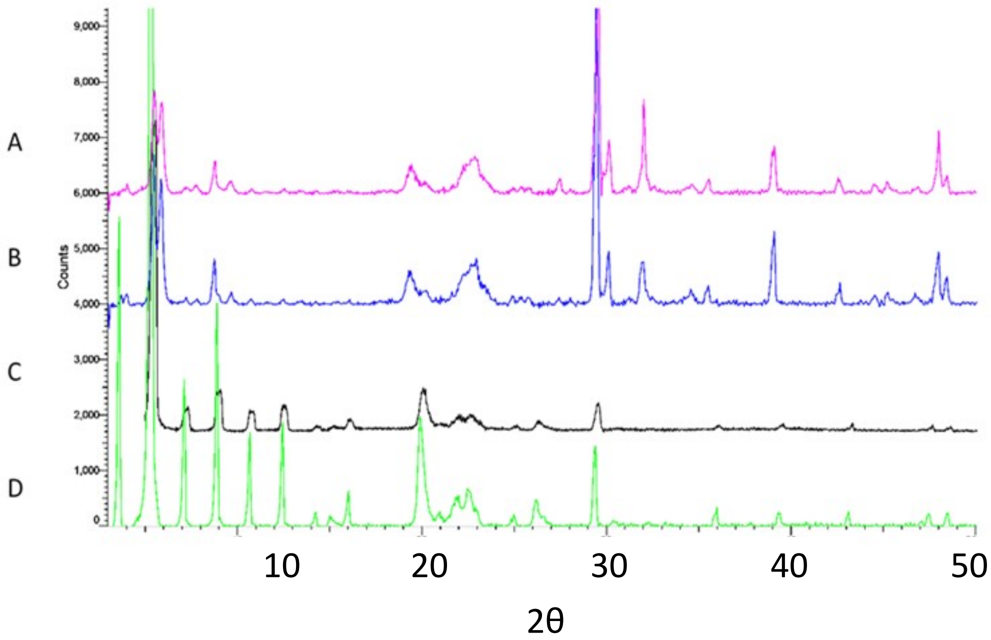


Release rates for Re (left) and B (right) at 25°C and 40°C. The x-axis represents temperature (^{o}C) and the y-axis represents the release rate (g m^{-2} d^{-1}). Both can be used as tracers for glass dissolution.

Task 1.4 - Experimental Support of Lysimeter Testing

FIU Year 10 Research Highlights

Reactor 1 = buffer (pH 12), Reactors 2 and 3 = grout contacted solutions



X-ray spectra

A and B: ppt clogged at reactors
C and D: ppt from a stock bottle

Solid	Formula
Grout Solution	$AlPO_4$
	$CCaO_3$
	$C_4H_{12}SiO_4$
	SiO_2
	$Al_{12}Ca_4Na_4Si_{12}O_{48}$
	SO_3
Reactor Solid	$NNaO_3$
	$AlPO_4$
	$Al_2CaSi_4O_{12}$
	$H_2NNa_3SO_8$
	AlO_2
	$CCaN_2$

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

Task 1.4 - Experimental Support of Lysimeter Testing

Ongoing:

- Grout-contacted leachate at 70°C
- SEM/EDS on glass impacted by grout solution
- Initiate experiments on possible buffering of glass dissolution in sediment-contacted grout solutions.

FIU Year 01* Objectives:

- Determine the effect of sediment on the grout solution buffering effect on the glass dissolution behavior
- Evaluate possible common ion effect in alkaline conditions
- Continue evaluating baseline glass dissolution behavior

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

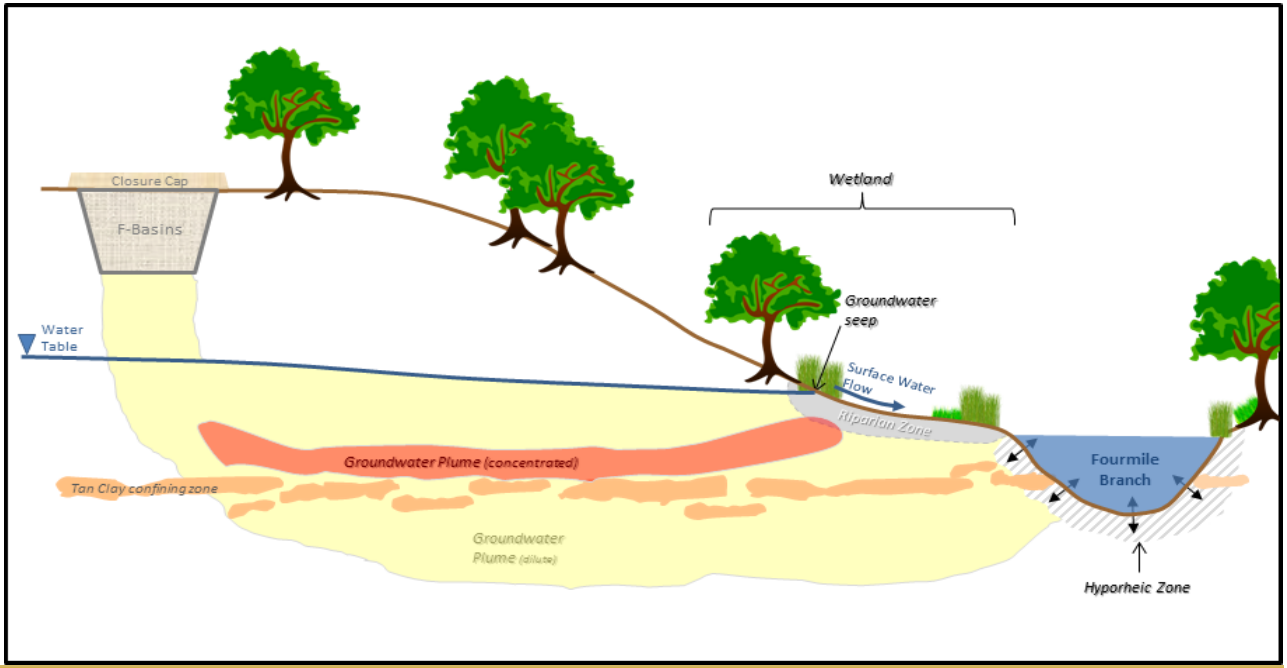
Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments at the Savannah River Site

Site Needs:

Wetlands at the F-area have been receiving the acidic plume from the basins for many years. Once these contaminants reach the wetlands, complex and diverse physical and biogeochemical processes are mainly responsible for retaining these contaminants. However, changes in the geochemical conditions could cause the remobilization of 129I.

Objective:

Understand the dominant mechanisms of attenuation and release of 129I in wetland soils; so, the progress toward remedial goals can be assessed and monitoring data can be properly interpreted.



Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

Methods

- **Particle Size Fractions**
- **XRD**
  - Mineralogy
- **BET Surface Analysis**
  - Surface Area
- **SEM-XRF**
  - Elemental Analysis
- **Soil pH**
- **Natural Iodine Content**

Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

FIU Year 10 Accomplishments

- SRS wetland soil was dried at 30°C

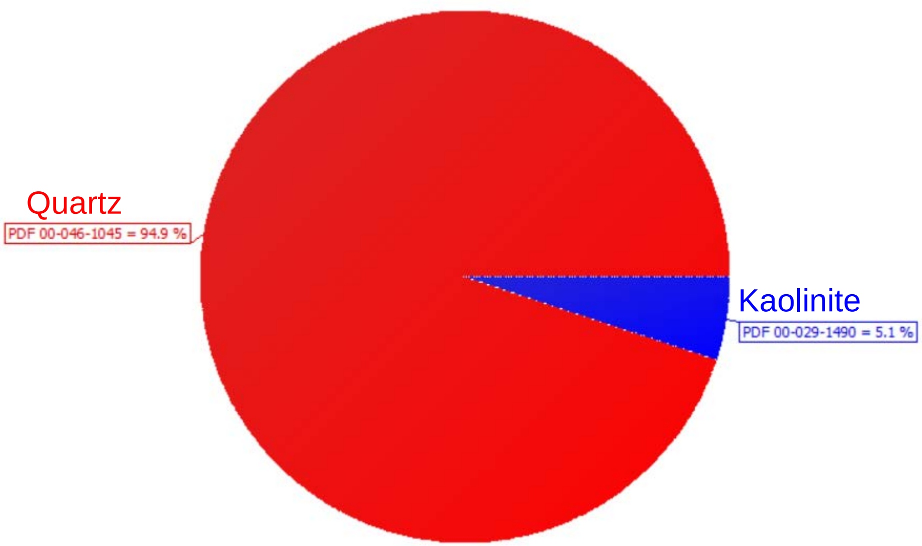
- 50 g of soil was passed through 2mm, 63µm, and 2µm sieve
  - Weighed fraction passed through
  - Repeated in triplicated

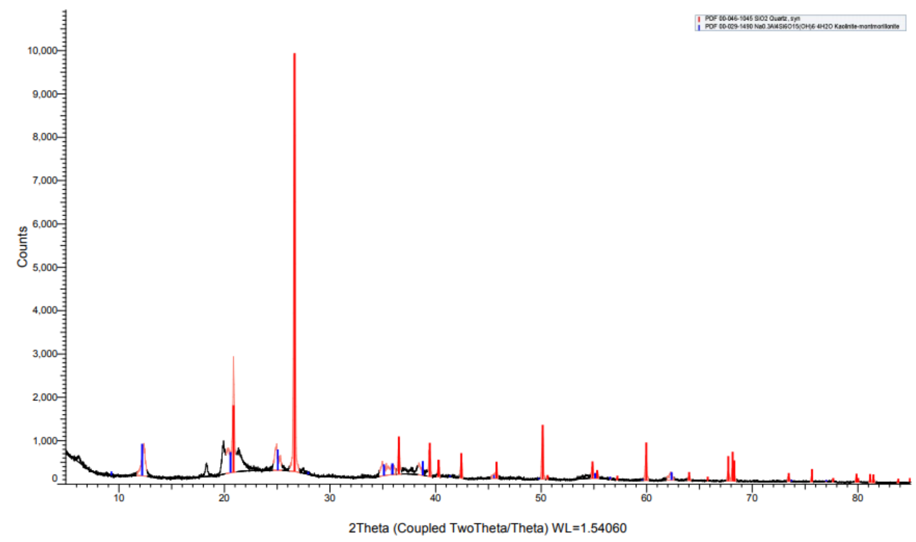
Soil Fraction	Average (%)
Sand (2mm - 63µm)	98.55 ±0.008
Silt (63µm - 2µm)	0.97 ±0.006
Clay (< 2µm)	0.05 ±0.0002

Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

FIU Year 10 Accomplishments

XRD (Sand Fraction)

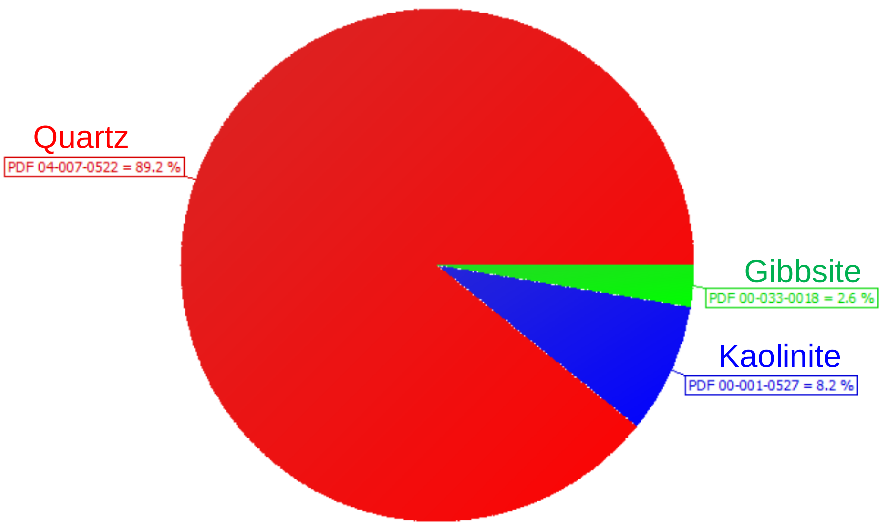


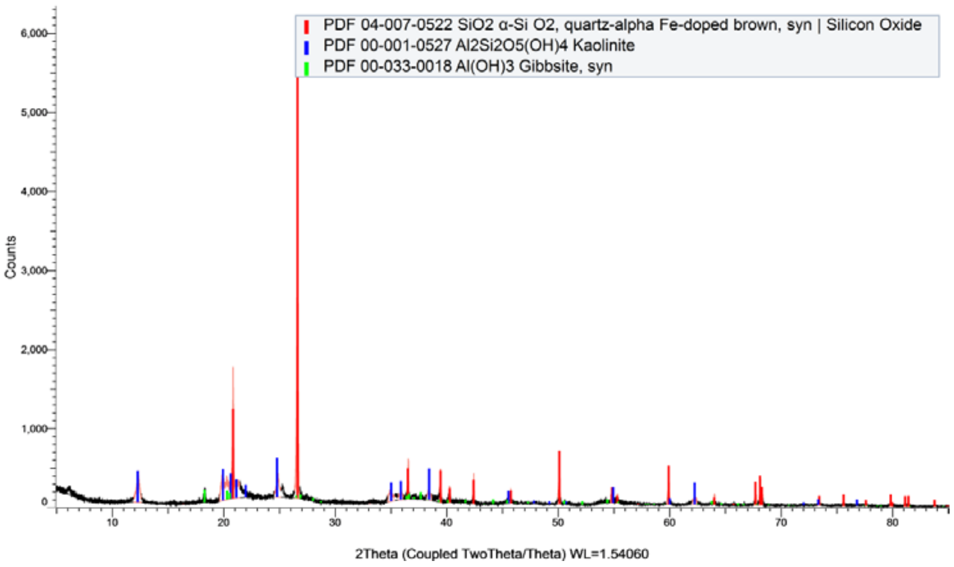


Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

FIU Year 10 Accomplishments

Results- XRD (Silt + Clay Fraction)

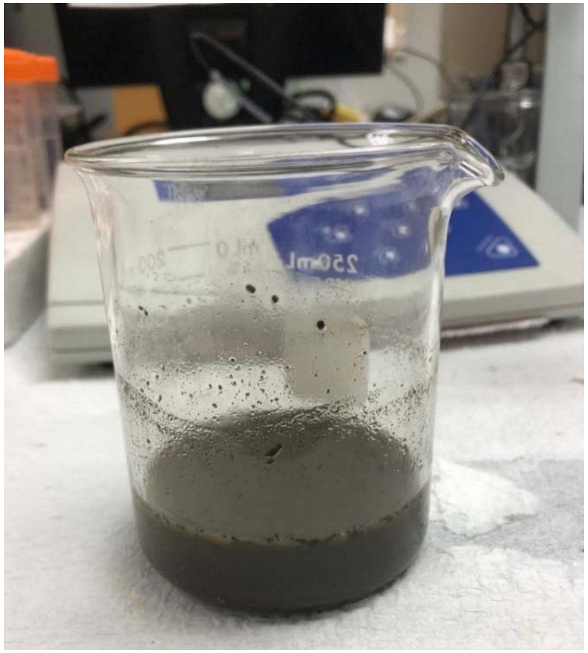




Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

FIU Year 10 Accomplishments

	#1	#2	#3	Average
Sample Mass (g)	1.38	2.03	2.08	1.83 ± 0.38
Surface Area (m^3/g)	7.11	7.86	7.50	7.49 ± 0.37
Pore Volume (cm^3/g)	0.025	0.028	0.027	0.027 ± 0.001
Pore Size (Å)	144.50	144.63	145.46	144.86 ± 0.52



- Followed USDA method for soil pH analysis
- Soil paste created - 1:2 Ratio of soil to 0.01M $CaCl_2$
- SRS wetland sediment pH - 5.67

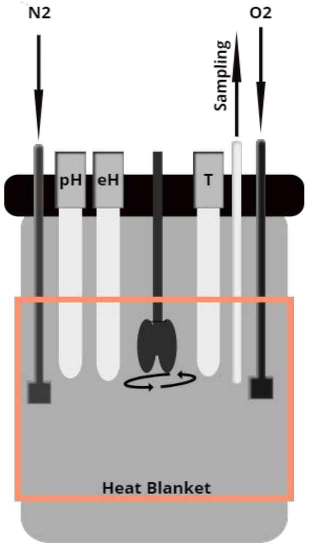
Task 2.1 - Environmental Factors Controlling the Attenuation and Release of Iodine-129 in the Wetland Sediments

FIU Year 01* Scope

- Conduct experiments to understand effects of pH, successive aerobic/anaerobic conditions, and temperature on iodine mobility.

- Batch Experiments
  - Kinetics: Determine reaction rates of iodine adsorption/desorption to sediment
  - Isotherms: Evaluate sorption capacity of sediments
  - Effect of pH on Iodine Desorption

- Microcosm Experiment
  - Effect of successive aerobic and anaerobic conditions on iodine mobility
    - This will be done for sterilized and non-sterilized soil
  - Effect of temperature on iodine mobility
    - Summer temperatures (80 - 90 F)
    - Winter temperatures (40 - 50 F)



Microcosm experimental set up

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

Task 2.2 - Humic acid batch sorption with SRS soil

Site Needs:

Low cost unrefined humic substances are potential amendments for treatment of uranium in groundwater associated with F-Area Seepage Basins plume.

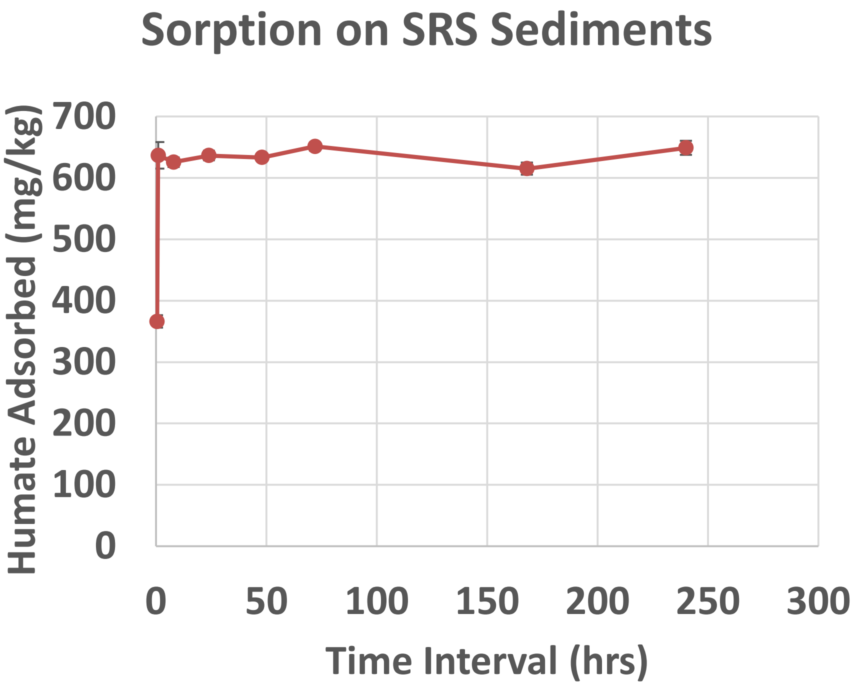
Objectives:

- Determine if the modified humic acid (KW15 modified Humics) can be used to control the mobility of uranium in groundwater and study the sorption/desorption of modified HA on SRS sediment at various pH via batch experiments.
  - Perform batch sorption experiments with humic acid to simulate the creation of a sorbed humate treatment zone in acidic groundwater contaminated with U.
  - Evaluate humic acid sorption/desorption onto SRS sediment and the effect of humic acid on U(VI) removal.

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

Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments

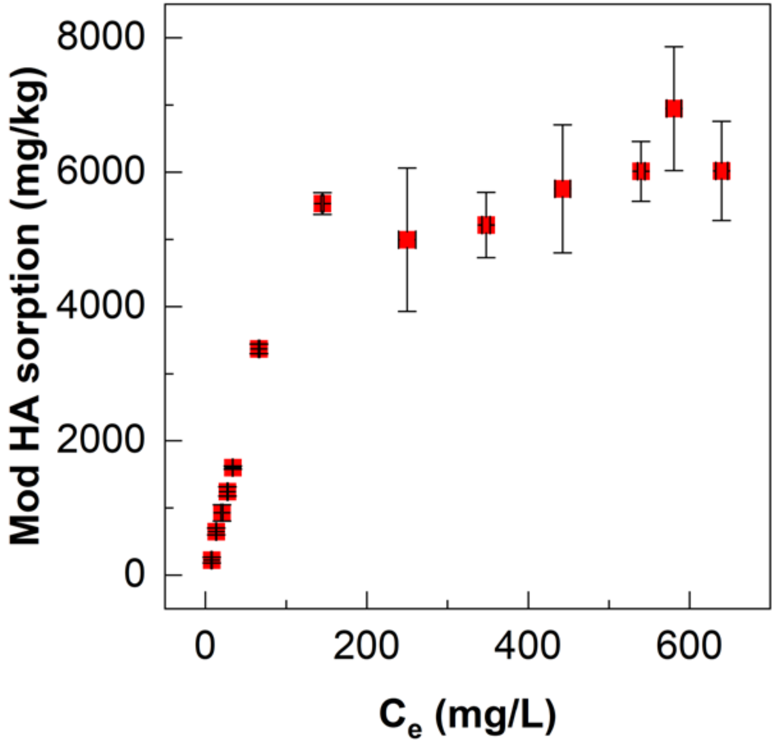
- Kinetic study performed by contacting 20 mL of 50 mg/L mod-HA with 200 mg of SRS sediment at pH 4.
- The sorption of humate on to SRS sediment was relatively fast, reaching equilibrium within 60 minutes.
- Experiments were conducted for 5 days to be able to compare mod-HA data with Huma-K.



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

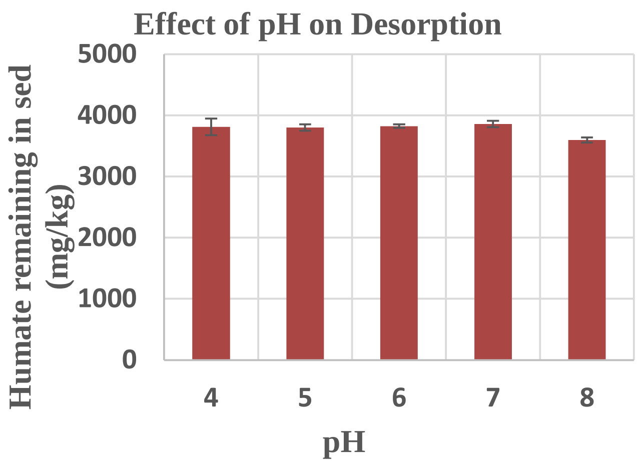
Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments

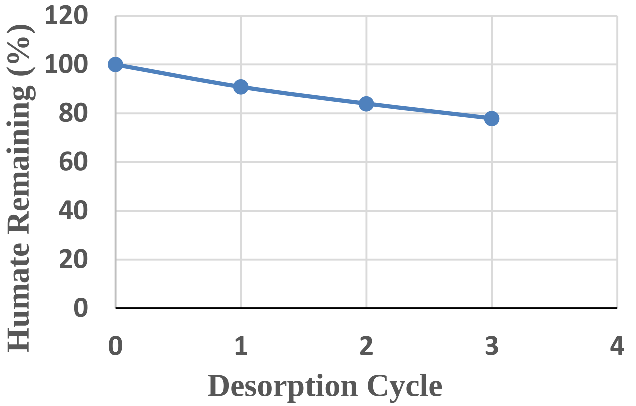
- Conducted isotherm experiments with 200 mg SRS sediment (particle size: < 2mm)
- Used HA concentrations in the range of 10 -750 mg/L at pH 4.
- The sorption of mod-HA increased linearly up to concentration of 200 mg/L then slowed down reaching an equilibrium around 500 mg/L.



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

Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments



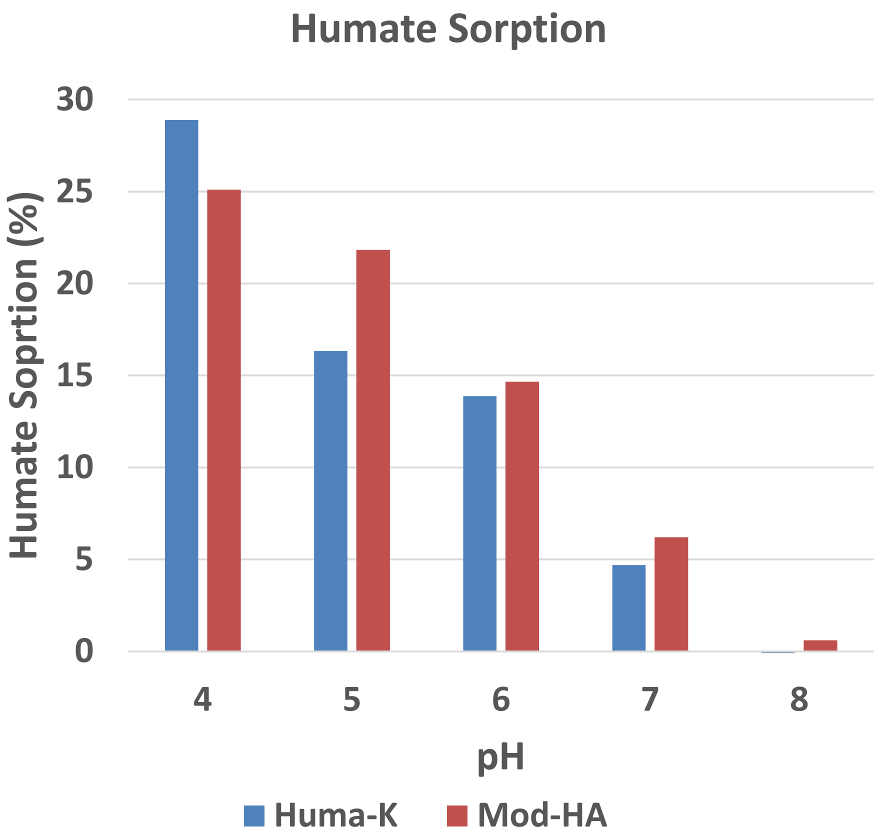


Desorption:

- Initial Mod-HA sorption was around - 4000 mg/kg
- After 1st desorption: 3500-3800 mg/kg
- Effect of desorption was studied by repeating desorption 3 times with DIW adjusted to pH 4
- Desorption increased with each desorption cycle; however, the amount of desorbed Mod-HA was decreased

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

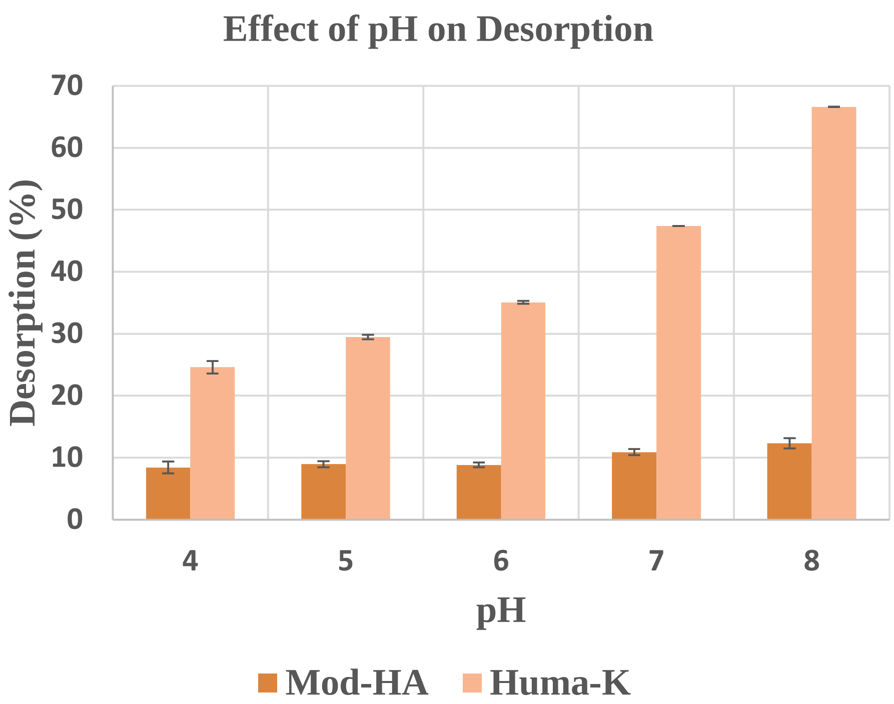
Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments

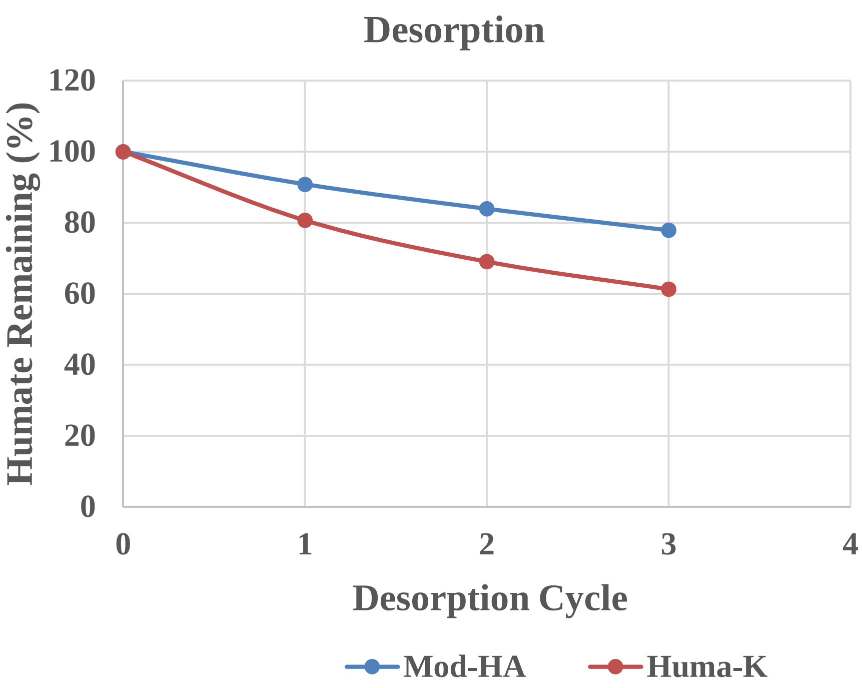


- Both humic acids have similar sorption behavior
- Mod-HA have slightly higher sorption at pH >5 suggesting it could be applied at sites with higher pH

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

Task 2.2 - Humic acid batch sorption with SRS soil FIU Year 10 Accomplishments



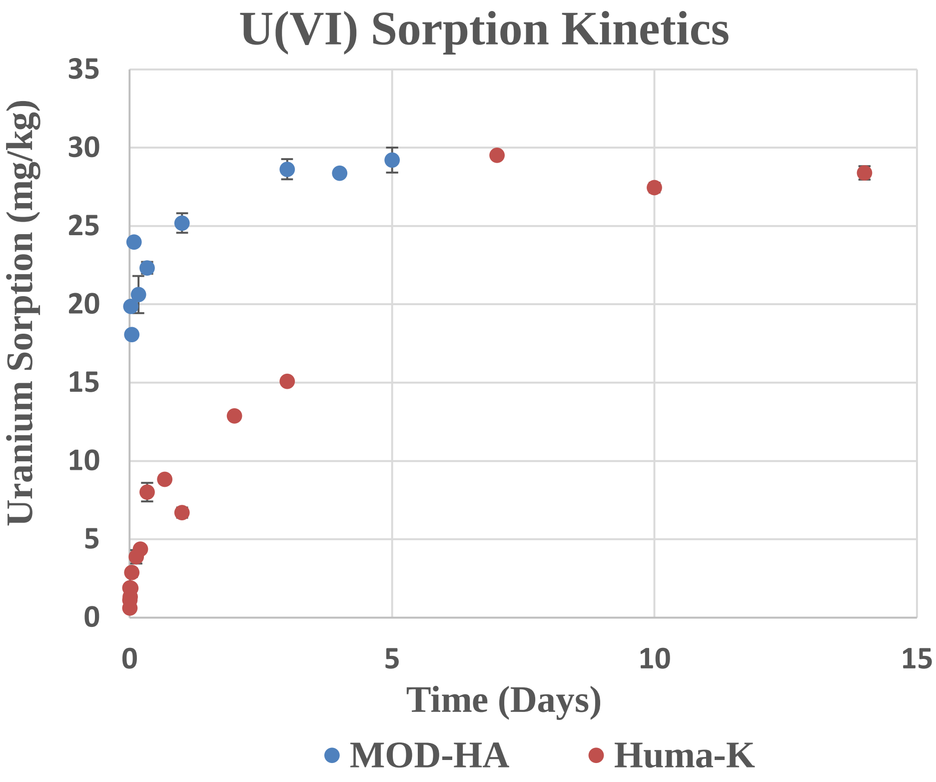


- Desorption of Huma-K was increased with pH (25% - 65%), while mod-HA desorption was only about 10-12%
- Similarly, more Huma-K was desorbed with each desorption cycle

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

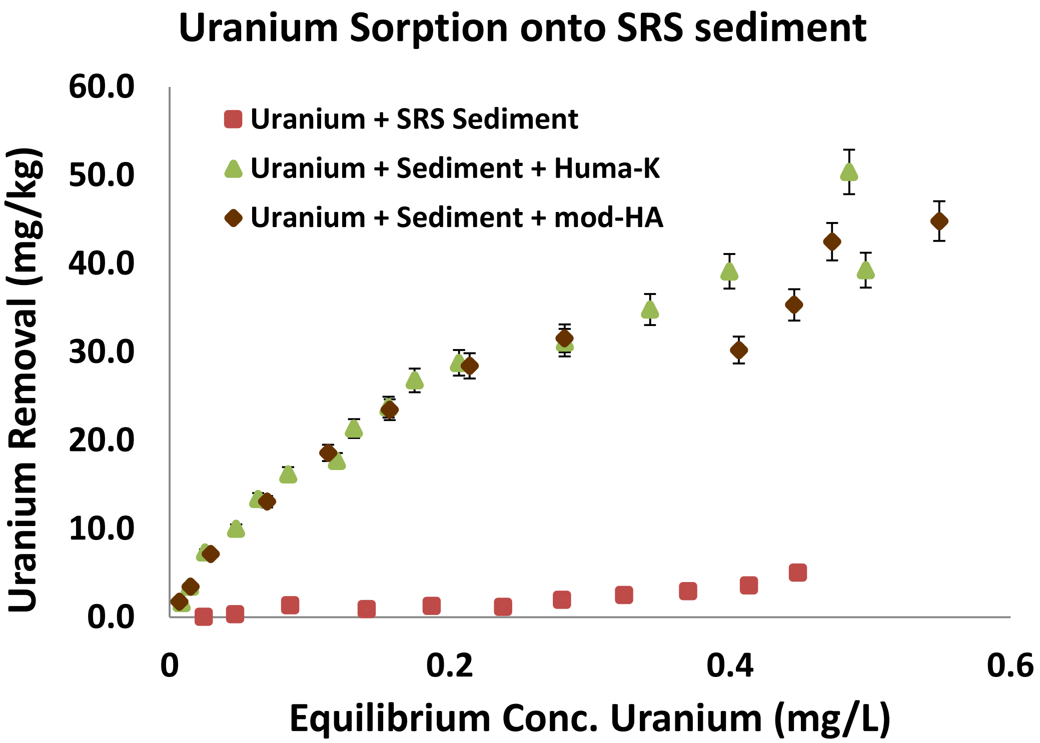
Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments

- Mod-HA amended sediment has fast uptake of uranium and reached equilibrium in 5 days
- Uranium uptake onto Huma-K coated sediment was slower and reached equilibrium within 7 days



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

Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments



- Both Huma-K and Mod-HA removed significantly higher uranium compared to plain sediment

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

Task 2.2 - Humic acid batch sorption with SRS soil
FIU Year 10 Accomplishments

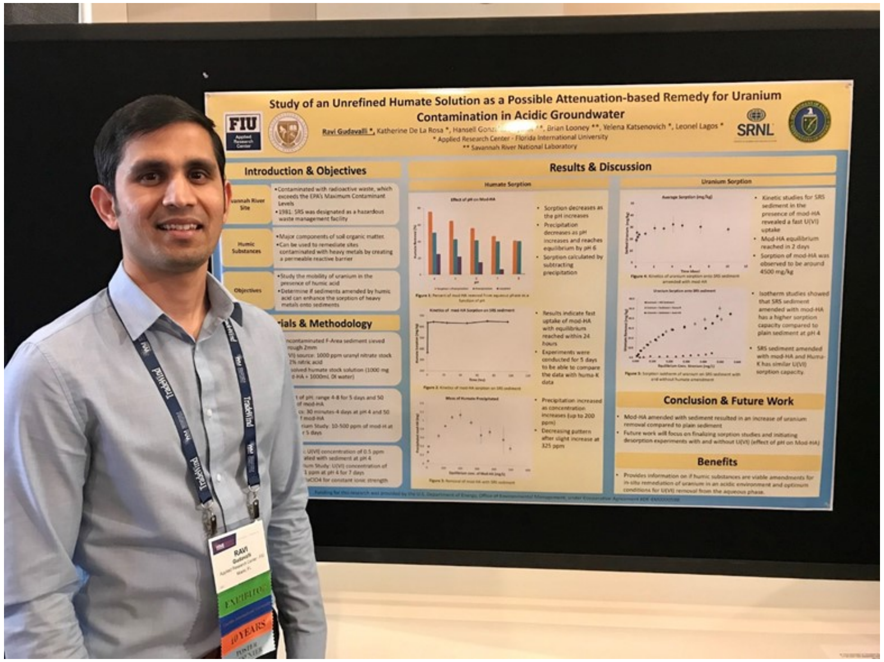
Applied Research Center

Accomplishments for FIU Year 10:

- Presented a poster at WM2020.

Objectives for FIU Year 1:

- Finalize uranium sorption studies and initiate desorption experiments.
- Study new humic acid material specially formulated for heavy metal remediation.

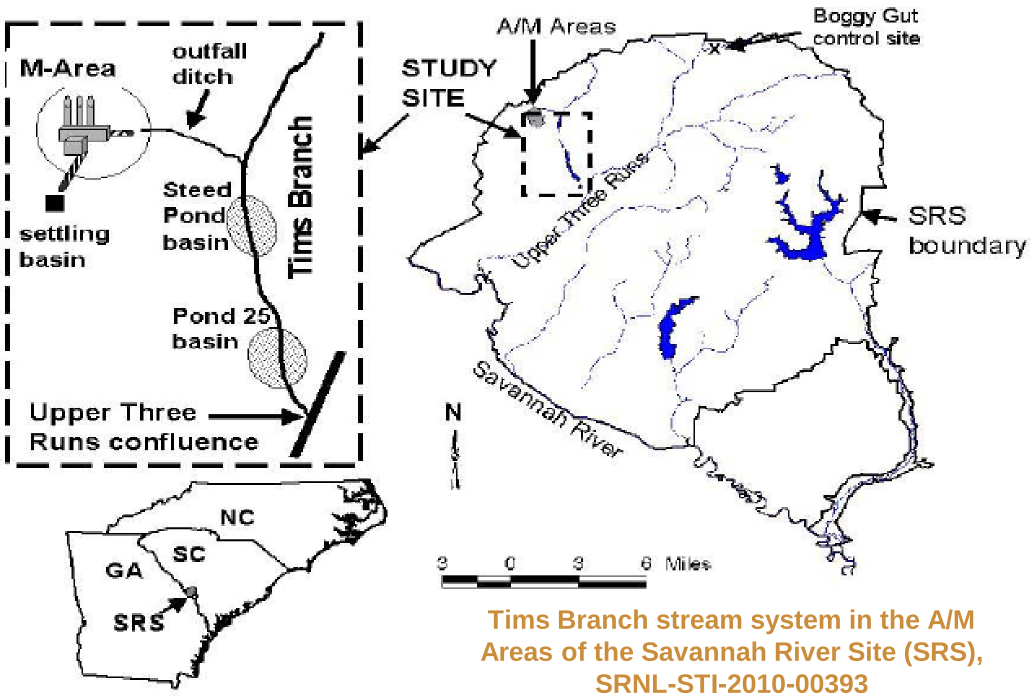


Task 3: Contaminant Fate And Transport Modeling in the Tims Branch Watershed

FIU Applied Research Center

Background:

- FIU has developed a contaminant fate and transport model of Tims Branch watershed - a small-scale watershed that received contaminant discharge from nuclear research in SRS A/M Area.
- Historical data has shown contaminant migration in surface water/sediment and deposition downstream in ponded areas during heavy rainfall/storm events.
- Data on the concentration and timing of the release of a Sn-based mercury treatment (2007) has provided a unique opportunity to use Tims Branch as a test bed to develop a numerical modeling tool.
- Residual Sn by-products can be treated as conservative tracer to evaluate impacts of extreme hydrological events on sediment movement and the fate and transport of major sediment-bound contaminants of concern (e.g., Hg, U, Ni) in Tims Branch.



Tims Branch stream system in the A/M Areas of the Savannah River Site (SRS), SRNL-STI-2010-00393

Task 3: Contaminant Fate And Transport Modeling in the Tims Branch Watershed

FIU Applied Research Center

Site Needs:

- Heavy metal and radionuclide contamination (e.g. Hg, Ni, U) at SRS and other DOE sites still exists*. Prediction of their fate and transport during severe rainfall/storm events is required, as well as long-term monitoring to evaluate the effectiveness of implemented remediation technologies.

Objectives:

- Develop numerical modeling tool to evaluate impact of extreme hydrological events on fate and transport of major contaminants of concern in Tims Branch.
- Develop a technology potentially applicable in other contaminated stream systems at SRS/other DOE EM sites.
- Collect field data (e.g., flow depth & velocity, suspended particle conc. and other water quality parameters) to support model calibration and validation via in-situ sampling and data collection as well as deployment of remote monitoring devices.
- Train FIU graduate and undergraduate students (DOE Fellows) on field data collection techniques, model development as well as data interpretation, reporting and visualization.

**DOE EM's Technology Plan to Address EM Mercury Challenge & DOE EM's Innovation & Technology Program*

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

Research Highlights

FIU Applied Research Center

Drs. Brian Looney, Mike Paller and Hansell Gonzalez Raymat from SRNL assisting the FIU team with the reinstallation of the Lower Tims Branch HOBO unit.

FIU Year 9 Carry-Over

– **Subtask 3.1:** FIU continued calibration and performance optimization of Tims Branch hydrology model.

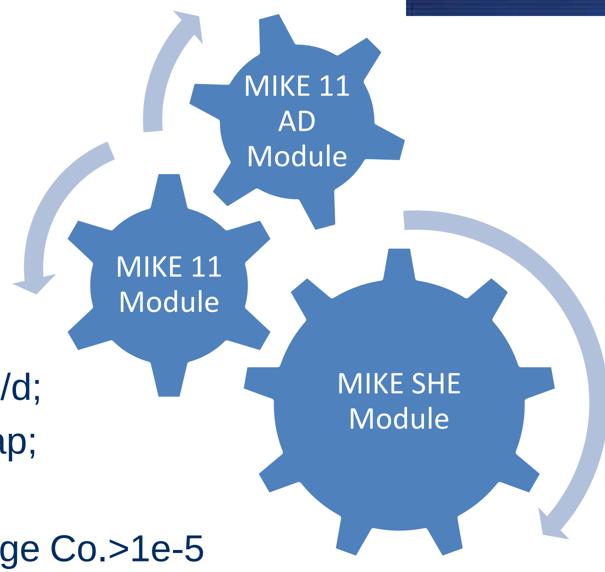
– **Subtask 3.3:** Dr. Yan Zhou and DOE Fellows Amanda Yancoskie and Juan Morales visited SRS in Dec. 2019 to perform routine maintenance on remote water level monitoring devices (HOBO units) in Tims Branch and successfully reinstalled and calibrated as the culvert repairs were completed.

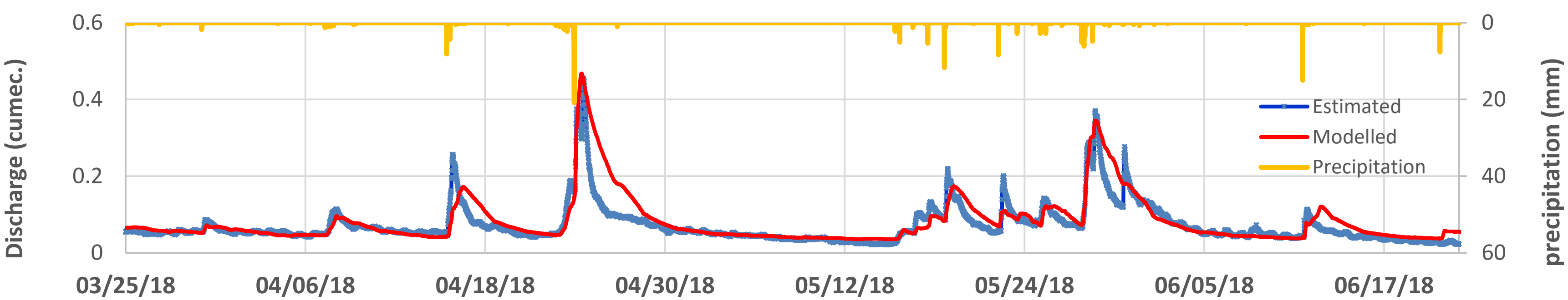
Task 3: Contaminant Fate And Transport Modeling in Tims Branch
FIU Year 10 Research Highlights

FIU Applied Research Center

Tims Branch MIKE SHE Hydrology Model Calibration and Validation

- MIKE SHE hydrology model calibration completed
  - Calibration process reviewed
  - Model parameters assigned based on lit. review and hydrology modeling standards
  - Updated model parameters: OL>Detention storage>2 mm; SZ>Drainage>Time constant>9.5e-07 [/s]; SZ>Hawthorn>HHC>1 m/d; SZ>Initial potential head map>based on monitored GWL contour map; SZ>Open GW boundary condition in the vicinity of the outlet MIKE11> Manning's M>20; MIKE11>River-aquifer exchange>Leakage Co.>1e-5

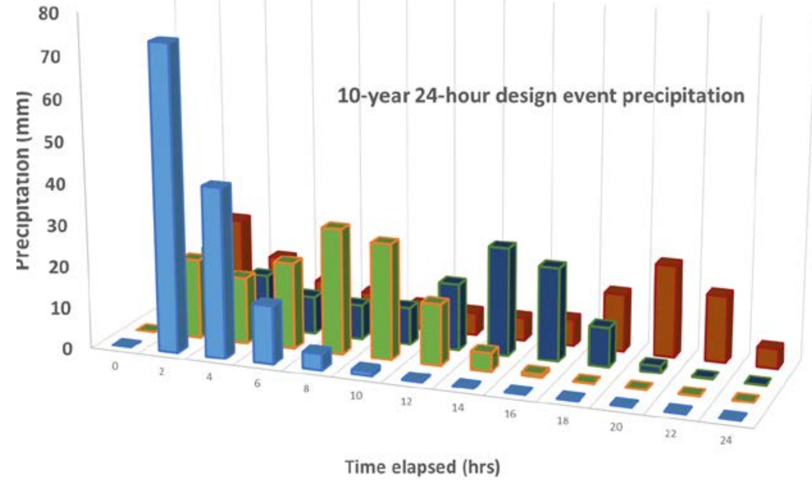


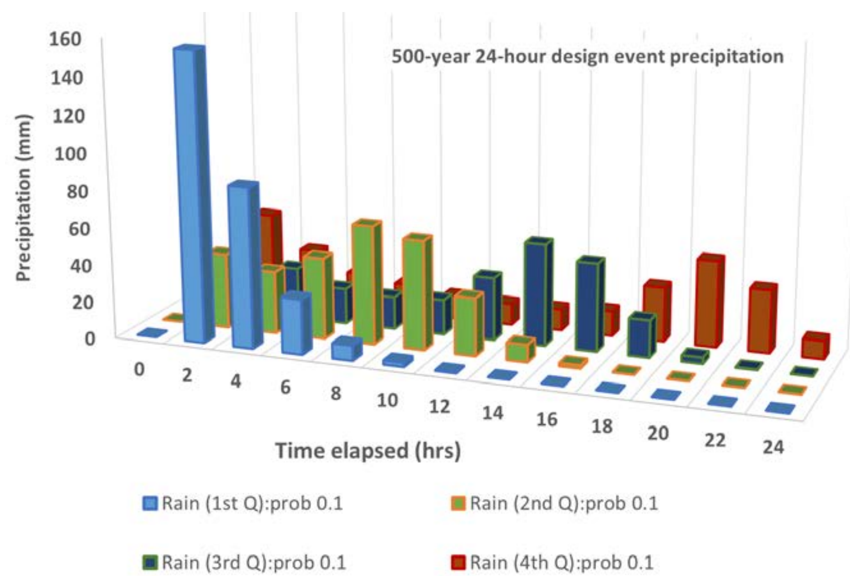


Task 3: Contaminant Fate And Transport Modeling in Tims Branch
Research Highlights

Design Precipitation Estimates

- Precipitation depth estimation
  - Depths extracted from NOAA's Precipitation Frequency Data Server
  - ARIs considered: 5yr, 10yr, 25yr, 100yr and 500yr
  - Durations considered: 6hr, 12hr, 24hr and 96hr
  - Depths are point datasets for the catchment centroid
- Temporal distribution of precipitation for all ARIs and durations
  - NOAA Atlas 14 Vol. 2 Ver. 2.1 considered
- Restructured temporal distribution
  - Development of MIKE SHE .dfs0 formatted precipitation time series



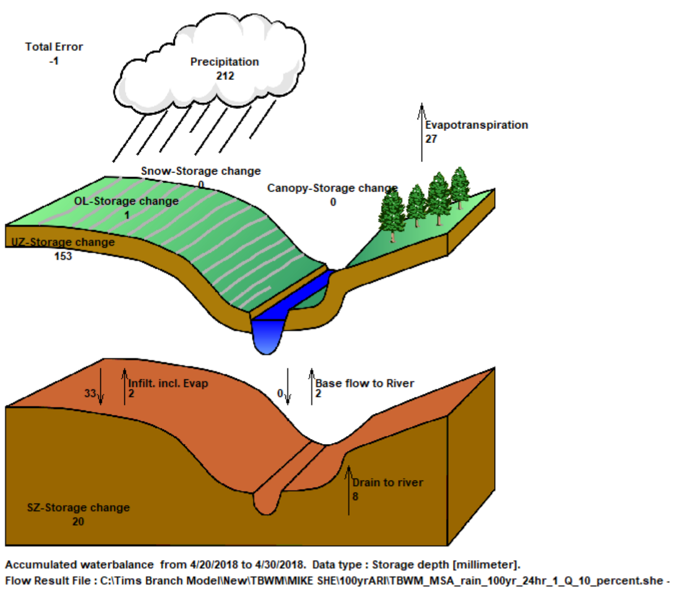


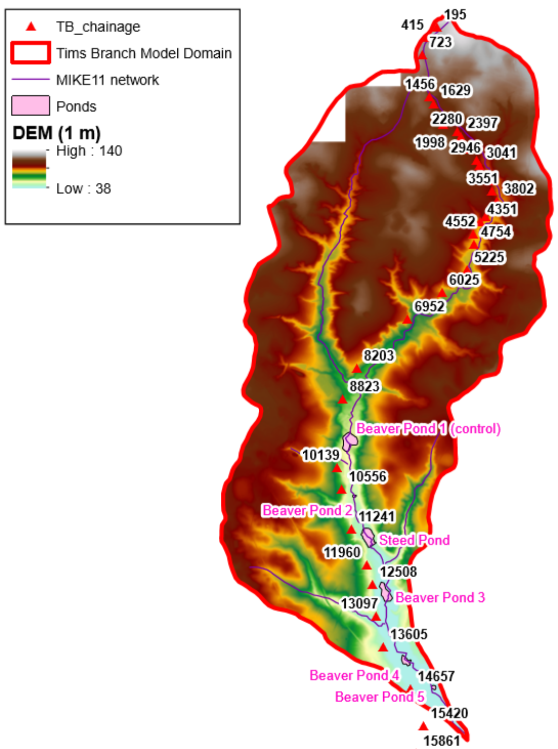
Task 3: Contaminant Fate And Transport Modeling in Tims Branch

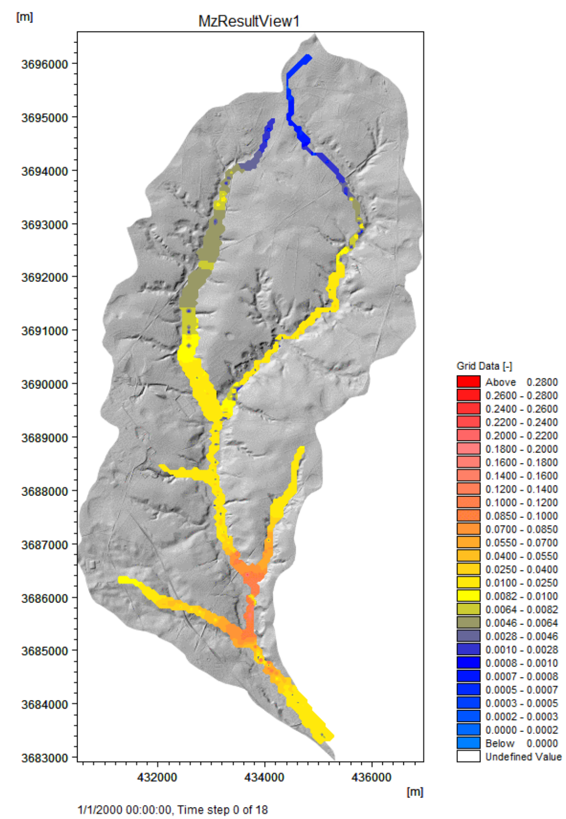
Research Highlights

Post-processing of Extreme Event Scenario Modeling Results

FIU Applied Research Center







Water balance estimation for a 100-year 24-hour design storm event.

Animation: Temporal distribution of Velocity*Flow Depth (U*D) for a 100-year 24-hour design storm event.

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

Research Highlights

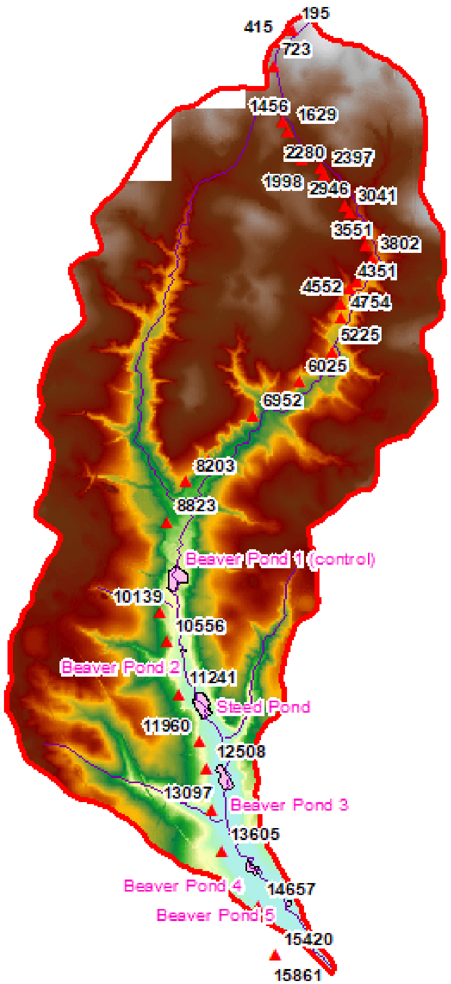
Post-processing of Extreme Event Scenario Modeling Results

Animation: Time dependent shear stress, discharge and velocity profiles for a 100-year 24-hour design storm event.

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

Research Highlights

Modeling Results of Sediment Transport Model

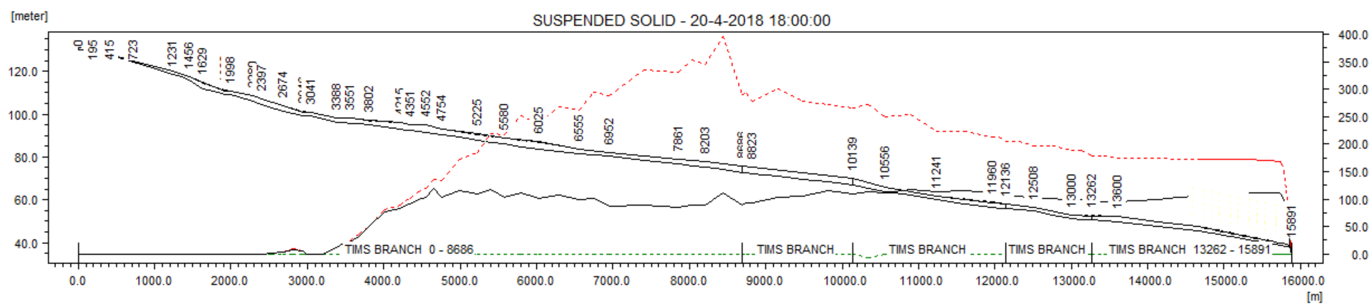


Scenario 1:

D50=6.25e-5

Cr. shear stress, ero.=0.165 N/m^2

Cr. Shear stress, depo.=0.10 N/m^2

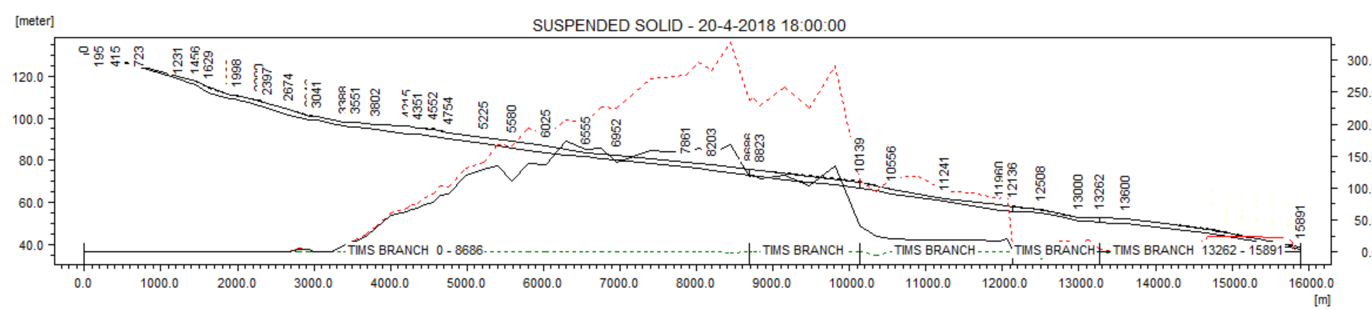


Scenario 2:

D50=3.53e-4

Cr. shear stress, ero.=0.2115 N/m^2

Cr. Shear stress, depo.=0.10 N/m^2



Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 10 Research Highlights

Extreme Event Scenario Modeling: Sediment Transport Process

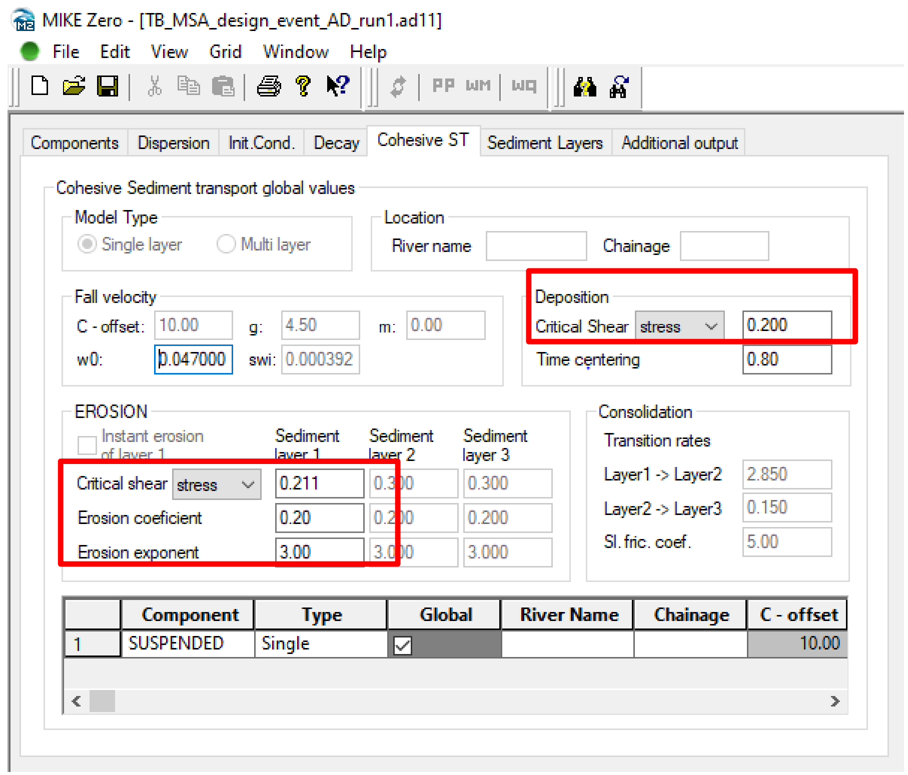
FIU Applied Research Center

Model parameterizations

- Qualitative particle size
- Critical shear stress for deposition is assumed
- Critical shear stress for erosion is dependent on the particle size

Recommendations/future research

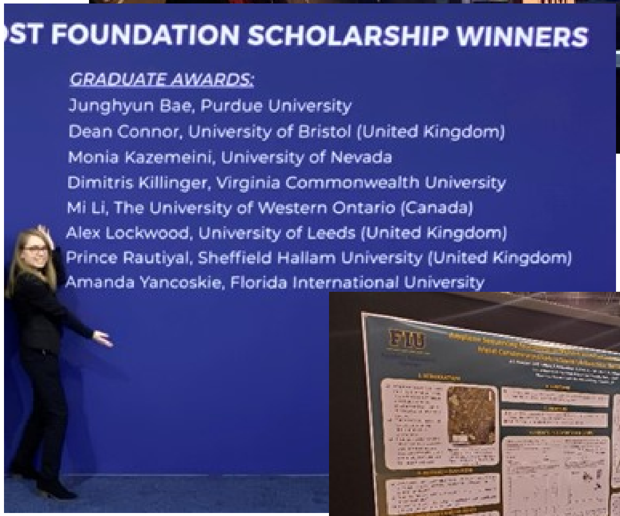
- *"Data! Data!"……."I can't make bricks without clay." Arthur Conan Doyle, Adventures of Sherlock Holmes*. Availability of data and data quality is imperative for the model calibration.
- The sediment transport process needs to be gauged to provide more confidence in the model performance.

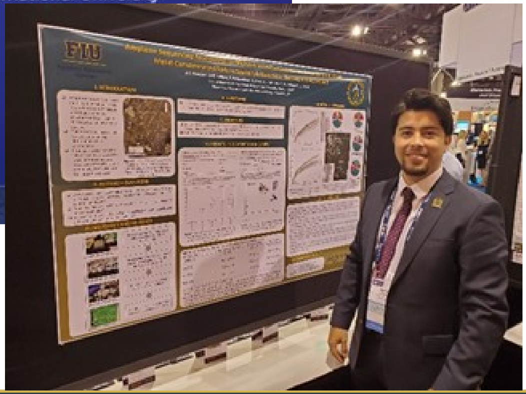


MIKE11 AD module interface for providing key model parameters for sediment transport process.

Task 3: Contaminant Fate And Transport Modeling in Tims Branch
Accomplishments

- WM20 paper & oral presentation by Dr. Yan Zhou:
  - Zhou, Y., M. Mahmoudi, A. Lawrence, R. Hariprashad, A. Yancoskie, J. Morales, M. Valencia, B. B. Looney, J. C. Seaman*. “Contaminant Transport Modeling for Technology Evaluation and Long-Term Monitoring in the Tims Branch Testbed, SC”*, Proceedings of the Waste Management Symposia 2020, Phoenix, AZ, March 2020.
- DOE Fellow Amanda Yancoskie awarded Roy G. Post Foundation Graduate Scholarship at the WM20 Symposia.
- Amanda also presented poster at WM20 based on her Summer 2019 internship *“2D Dam-Break Analysis of Lake and Par Pond Dams Using HEC-RAS”.*
- DOE Fellow Juan Morales presented poster at WM20 based on his Summer 2019 internship *“Amplicon Sequencing Assessment to Measure Microbial Community Response from Heavy Metal Contaminated Soils in Savannah River Site, Tims Branch Watershed”*.
- Juan also completed a10-wk **remote** Summer 2020 internship with PNNL mentored by Dr. Katrina Waters.





Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FIU Year 01 (Sept 2020 - Sept 2021)* Objectives

* Assuming new contract number is issued

Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

- Model optimization to improve and verify Tims Branch model performance
  - Sensitivity analysis, calibration and validation
- Scenario analysis under extreme hydrological conditions to determine stormflow impacts and downstream transport of priority contaminants of concern.
- Download water level data from remote devices in Tims Branch for calibration and validation.
- Travel to SRS to perform routine maintenance and calibration of remote monitoring devices.
- Explore the potential for migration of the data inputs from the Tims Branch model to an open source environment for easier integration with other DOE-EM modeling efforts.

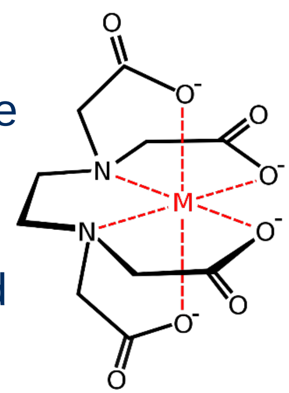
Subtask 3.2: Model Development for the Fourmile Branch (FMB) and/or Lower Three Runs (LTR) Watersheds (NEW)

- **Aim:** To develop surface water and sediment transport models of the FMB and/or LTR stream systems to evaluate potential fate and transport of ^{137}Cs in these contaminated watersheds during extreme meteorological events.
- Initiate data collection and pre-processing activities and develop conceptual models.

Task 5 - Research and Technical Support for WIPP

Site Needs:

This research effort is aimed to assist the LANL ACRSP (Actinide chemistry & repository science) team to better understand the long-term fate and transport of the actinides in the Waste Isolation Pilot Plant (WIPP). Specifically, the effects of ligands in the waste stream (e.g. EDTA) 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 fully understood in high ionic strength systems. EDTA presents a major risk factor due to its significant occurrence in waste, reaching up to 0.3 mM in the repository (*Roach et al., 2008*).



Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

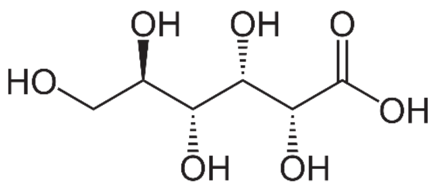
Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

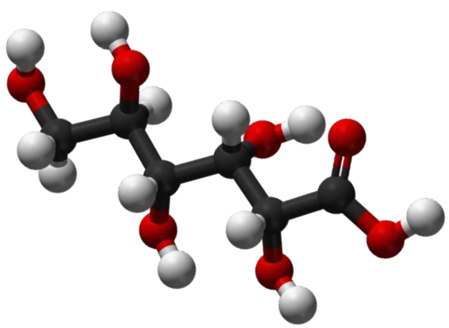
Task 5 - Research and Technical Support for WIPP

FIU Year 10 Objectives:

To understand the ternary interactions between actinides and WIPP-relevant ligands and minerals and their potential fate in the subsurface. This research indirectly supports future performance assessment models

- Measure dissolution of dolomite in variable ionic strength matrices with and without EDTA (FY 9 Carryover scope)



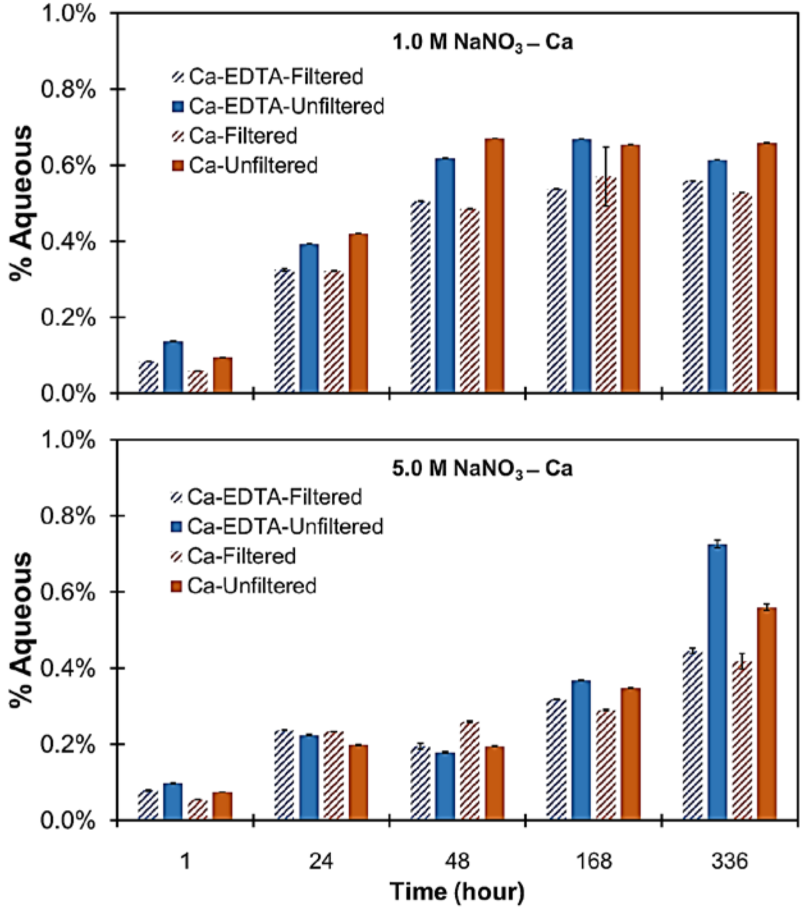


Contaminants	Brine	Magnetite	Gluconate	Concentration
(ppb)		(g/L)	(mg/L)	(M)
10 Nd, Th, U	NaCl	1	1	0.1
		1	1	0.5
		1	1	1.0
		1	1	5.0
	ERDA-6	1	1	Borkowski et al. (2009)
	GWB	1	1	Borkowski et al. (2009)
1000 Nd, Th, U	NaCl	1	1	0.1
		1	1	0.5
		1	1	1.0
		1	1	5.0
	ERDA-6	1	1	Borkowski et al. (2009)
	GWB	1	1	Borkowski et al. (2009)

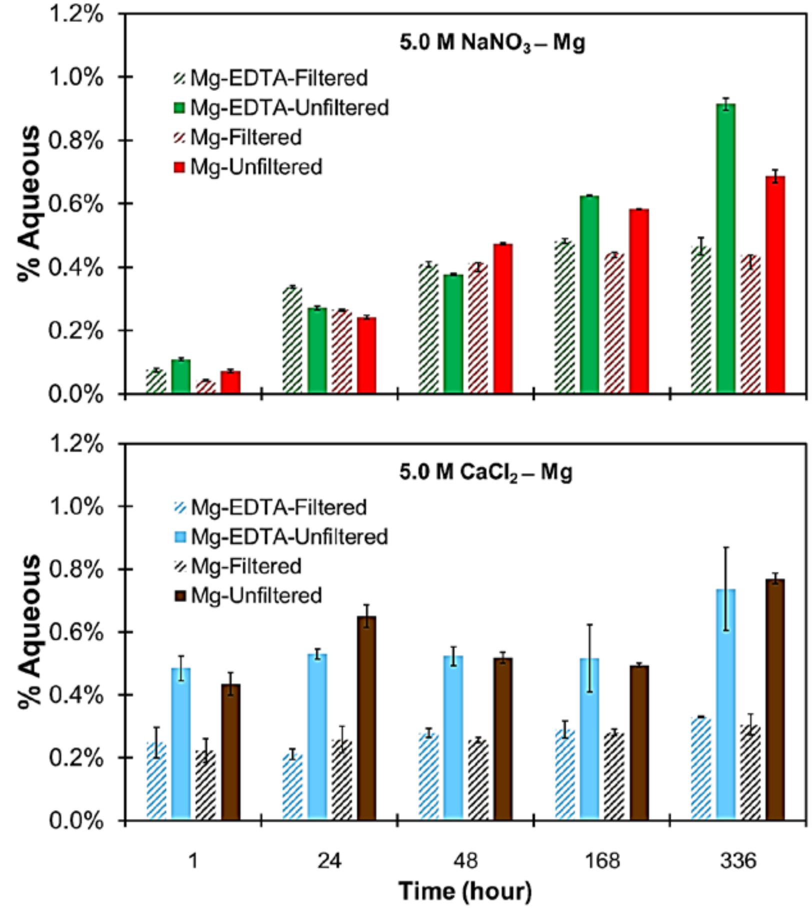
Task 5 - Research and Technical Support for WIPP

Research Highlights

Aqueous Ca over time in 1.0 and 5.0 M $NaNO_3$ with and without EDTA



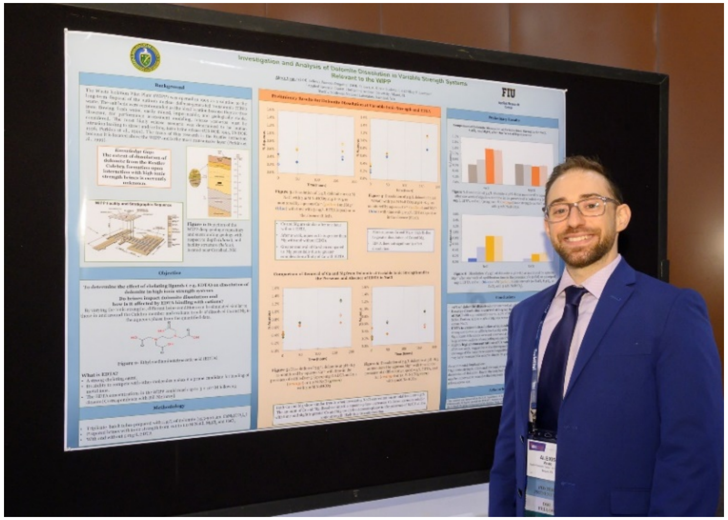
Aqueous Mg over time in 5.0 M $NaNO_3$ and $CaCl_2$ with and without EDTA



Task 5 - Research and Technical Support for WIPP
FIU Year 10 Accomplishments

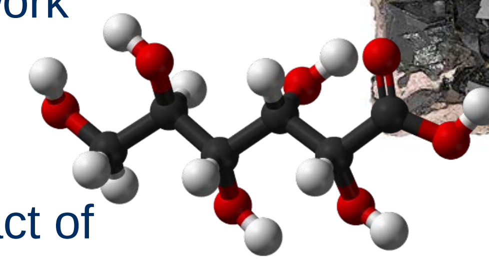
FIU Applied Research Center

- Finalized batch experiments on the effect of ionic strength on sorption of Nd(III), Th(IV), and U(VI) to dolomite in NaCl (0.1, 0.5, 1.0, and 5.0 M), ERDA-6 and GWB (Borkowski et al., 2009)
- Completed batch experiments evaluating the impact of EDTA, ionic strength and ions on dissolution of dolomite in 0.1- 5.0 M NaCl, $MgCl_2$, $CaCl_2$, $NaNO_3$, Na_2SO_4, CsCl, and $Na_2B_4O_7$
- A poster on *“the impact of EDTA on sorption of Nd(III), Th(IV) and U(VI) onto dolomite in WIPP-relevant brines, GWB and ERDA-6”* was presented at WM2020 conference, Phoenix AZ.
- DOE Fellow Alexis Vento presented a poster “*dolomite dissolution in variable ionic strength systems relevant to the WIPP*” Waste Management Symposia in Phoenix, Arizona (March 2020).



DOE Fellow Alexis Vento presenting a poster at WM2020.

Task 5 - Research and Technical Support for WIPP



Upcoming for FIU Year 10:

- Complete collections/analyses of data on the impact of EDTA/ionic strengths on dissolution of dolomite in WIPP-relevant matrices
- Visit LANL collaborators to discuss updates for work supporting the WIPP

Objectives for FIU Year 01*:

- Conduct batch experiment investigating the impact of gluconate on the sorption of Nd(III), Th(IV), and U(VI) onto various iron oxide minerals in high ionic strength systems relevant to WIPP brines, GWB and ERDA-6 under anoxic conditions
- Continue experimental support through identification of minerals and ligands of interest to the WIPP (iron oxides, key contaminants with co-located lead) for risk assessment models for the WIPP re-certification.

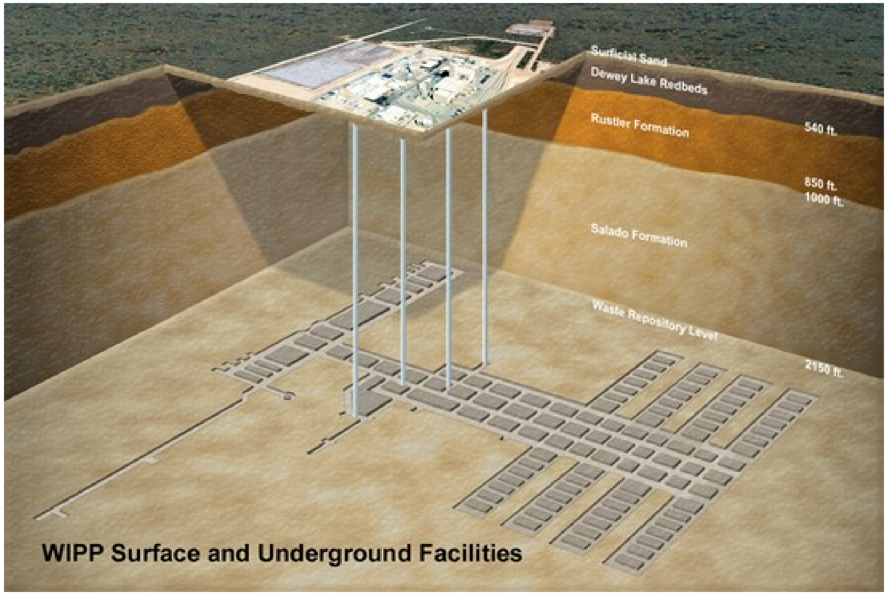
Task 6: Hydrology Modeling for WIPP

Background:

- Federal regulations require predictions of WIPP performance to be based on extrapolating current land-use practices in its vicinity to 10,000 years.
- Administrative controls are to be implemented to deter incompatible activities within the Land Withdrawal Act (LWA) boundary.
- Significant changes in recent years, including increased water withdrawals outside the LWA boundary have impacted water levels and chemistry in compliance monitoring wells on site.
- Questions about recharge to the Rustler Formation overlaying the Salado Formation that hosts the repository remain unanswered.

Site Needs:

- Improved understanding of regional water balance, particularly the relationship between Culebra recharge and intense, episodic precipitation events typical of the monsoon.
- Improved understanding of rate of propagation of shallow dissolution front, and the impact of land-use changes around the WIPP facility on water levels in compliance-monitoring wells.
- These analyses require revision of current site conceptual model to couple surface water and groundwater processes, which both require a high resolution DEM including channels and sink holes to account for surface water routing and return flow.



WIPP Surface and Underground Facilities

Task 6: Hydrology Modeling for WIPP

FIU Applied Research Center

Objectives:

- Development of a GWM for the WIPP site using the DOE-developed Advanced Simulation Capability for Environmental Management (ASCEM) modeling toolset to improve the current understanding of regional and local groundwater flow at the WIPP site.

- An open source LSM will also be used to provide surface process parameters for input into the ASCEM model (e.g. infiltration rate) to compute the surface water balance, across multiple scales and reduce uncertainties in recharge estimates and propagation of the shallow dissolution front.

Subtasks:

6.1 Digital Elevation Model (DEM) and Hydrologic Network

- High-res DEM needed to accurately delineate significant topographical/hydrological features such as drainage basins, brine lakes, channels, sink holes, discharge points, etc. used for LSM model development to simulate terrestrial overland flow, channel routing, and subsurface flow processes.

6.2 Model Development

- FIU personnel/student training on development of LSM using open-source code/software, high-res DEM, delineated features and other relevant parameters that will provide surface process parameters for input into the ASCEM model (e.g. infiltration rate).

- FIU personnel/student training on ASCEM modeling toolset using existing case studies of ASCEM implementation at DOE sites to determine best practices/lessons learned for similar implementation at WIPP.

Task 6: Hydrology Modeling for WIPP

Workflow Diagram

Student Mentoring & Training

DEM
- High-res DEM (1 m) development using photogrammetric techniques
- Detailed delineation of hydrologic and topographic features from high-res DEM

GWM
- Training & development of GWM using ASCEM

LSM
- Development of basin-scale LSM using open-source code/software, delineated features and other relevant input parameters

LSM-GWM
- Incorporate LSM outputs (e.g., infiltration rate) into GWM

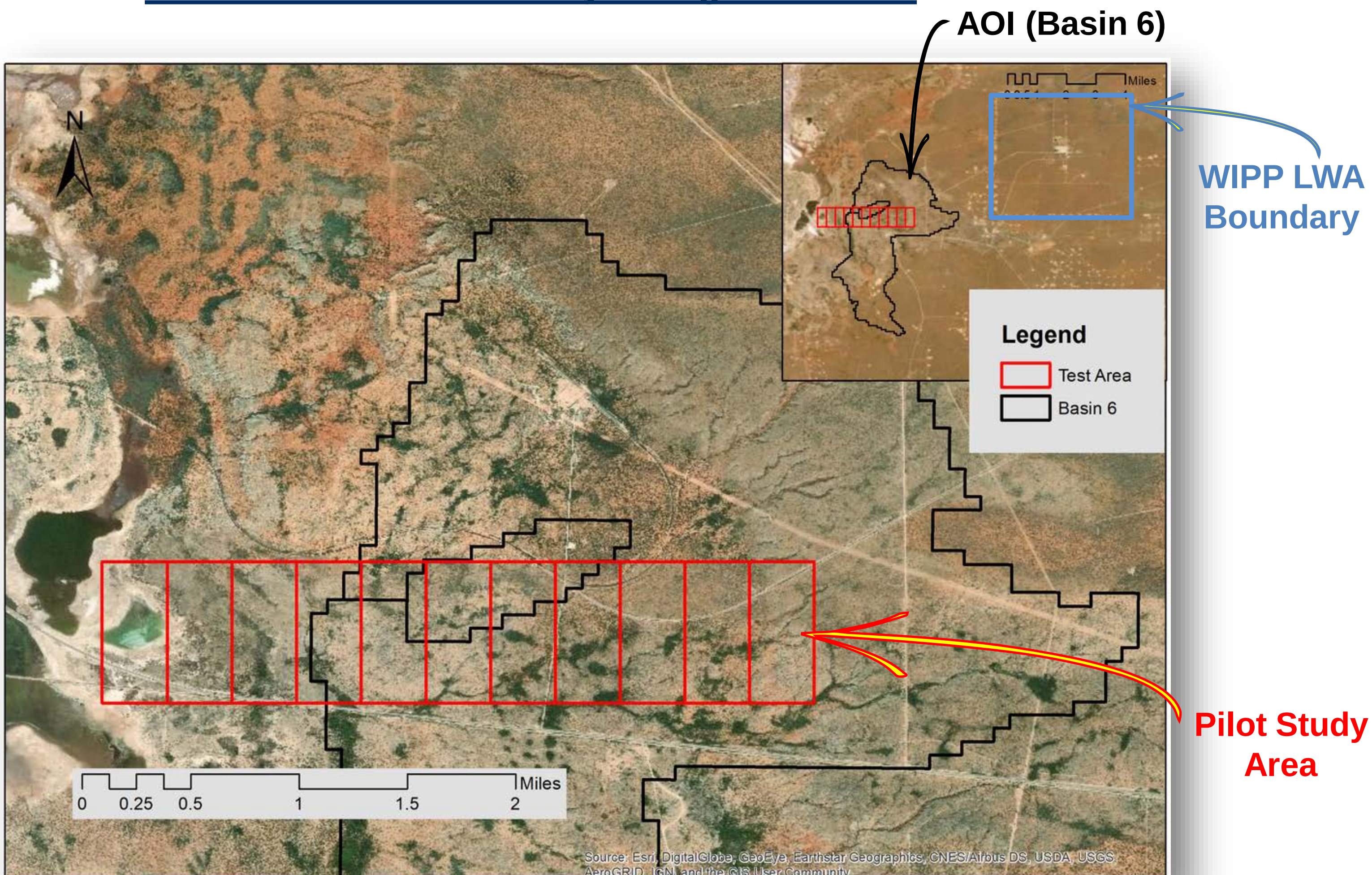
Task 6: Hydrology Modeling for WIPP

Research Highlights

Subtask 6.1: DEM and Hydrologic Network

Area of Interest (AOI)
Basin 6

Pilot Study Area
Small representative area within Basin 6, west of the WIPP Land Withdrawal Act (LWA) Boundary

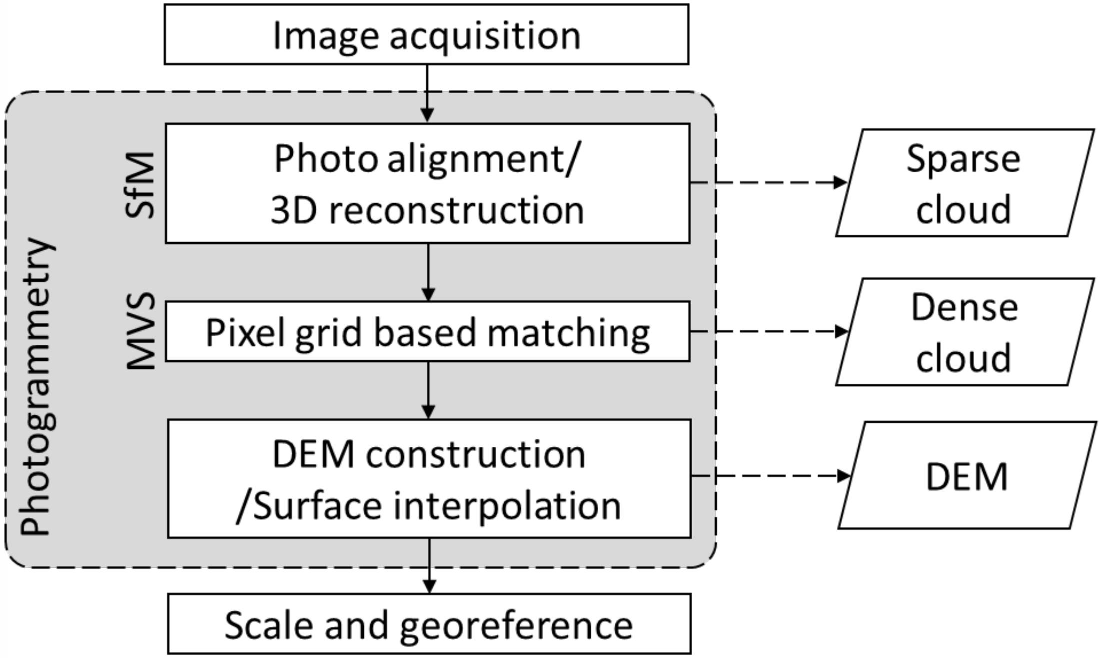


Task 6: Hydrology Modeling for WIPP

Research Highlights

Subtask 6.1: DEM and Hydrologic Network

Survey Equipment: UAV GNSS



Photogrammetry Workflow

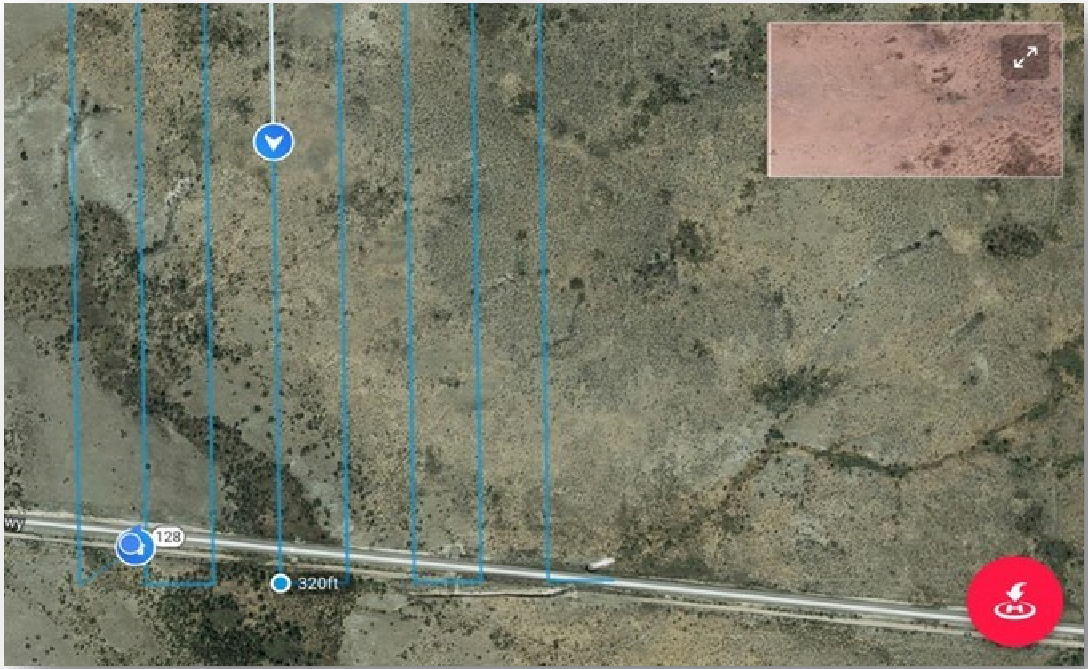
Task 6: Hydrology Modeling for WIPP

Research Highlights

Subtask 6.1: DEM and Hydrologic Network

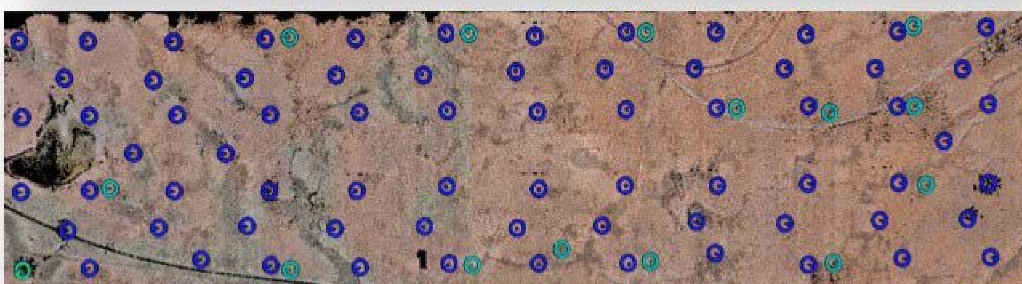
Procedure:

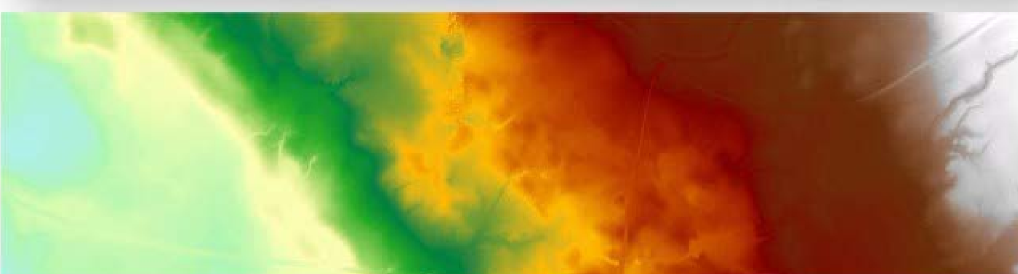
- Ground control points (GCPs) surveying
- Automated aerial image collection



Task 6: Hydrology Modeling for WIPP
Research Highlights

Subtask 6.1: DEM and Hydrologic Network





Procedure:

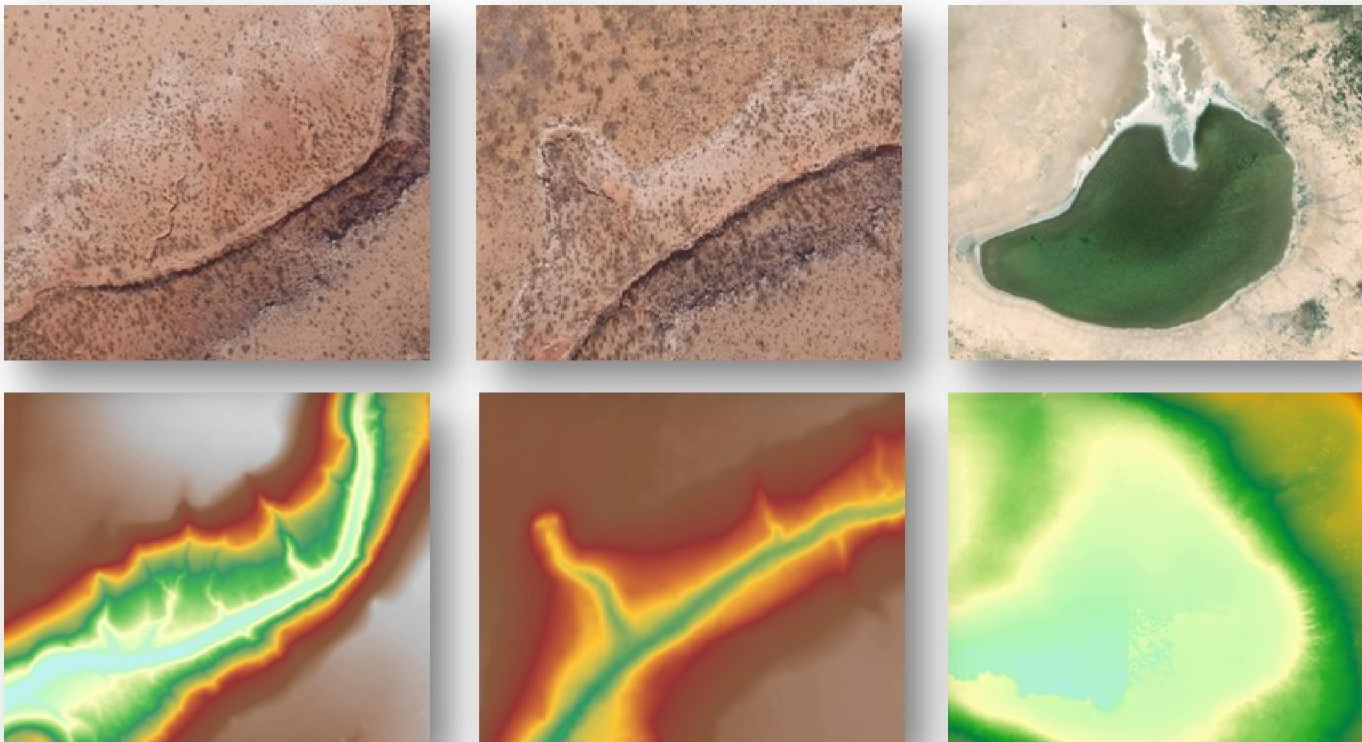
- Image processing using Pix4D
- Geo-referencing using GCPs

Result:

- 5 km^2 DEM, up to 0.05 m resolution

Task 6: Hydrology Modeling for WIPP
Research Highlights

Subtask 6.1: DEM and Hydrologic Network

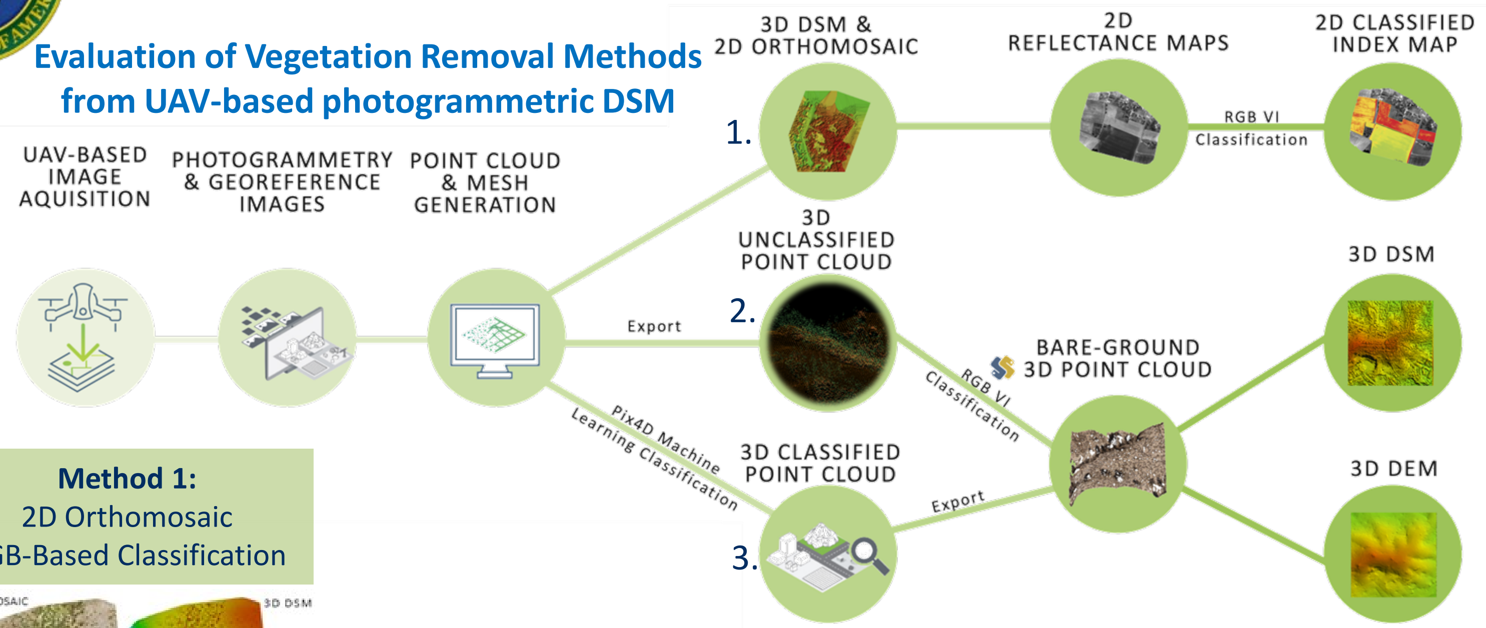


Gully | Land Sink | Brine Lake

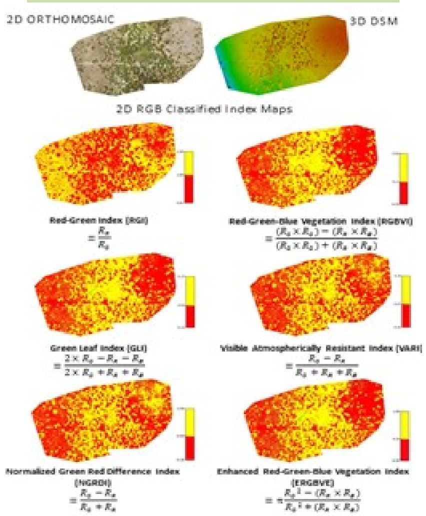
Significant topographical/hydrological features are easily identifiable.

Task 6: Hydrology Modeling for WIPP
Research Highlights

Evaluation of Vegetation Removal Methods from UAV-based photogrammetric DSM



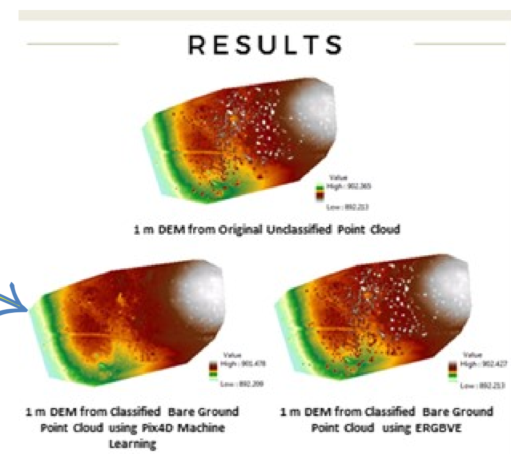
Method 1:
2D Orthomosaic
RGB-Based Classification



Method 2:
3D Point Cloud
RGB-Based Classification using Liblas in Python

Method 3:
Pix4D 3D Point Cloud Classification
using Machine Learning (ML)

Pix4D ML method (Method 3) produces DEM with mostly bare ground as opposed to Methods 1 & 2 where a large amount of vegetation is still visible.

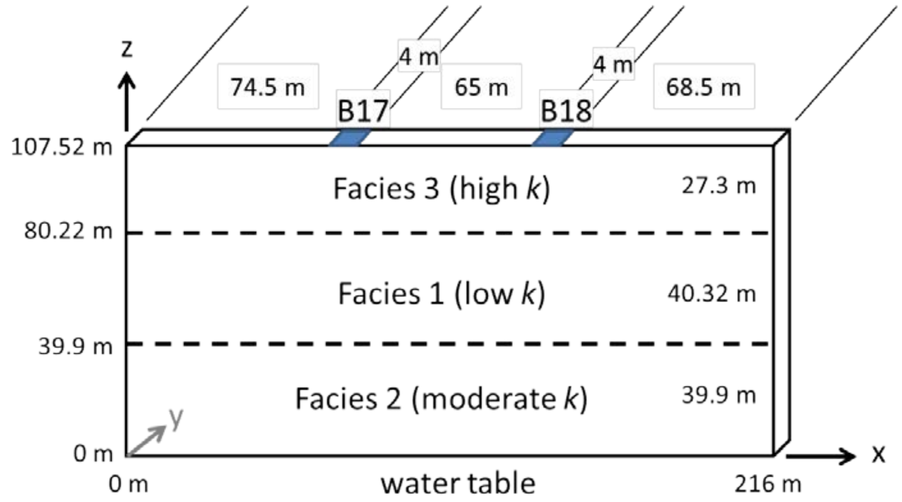


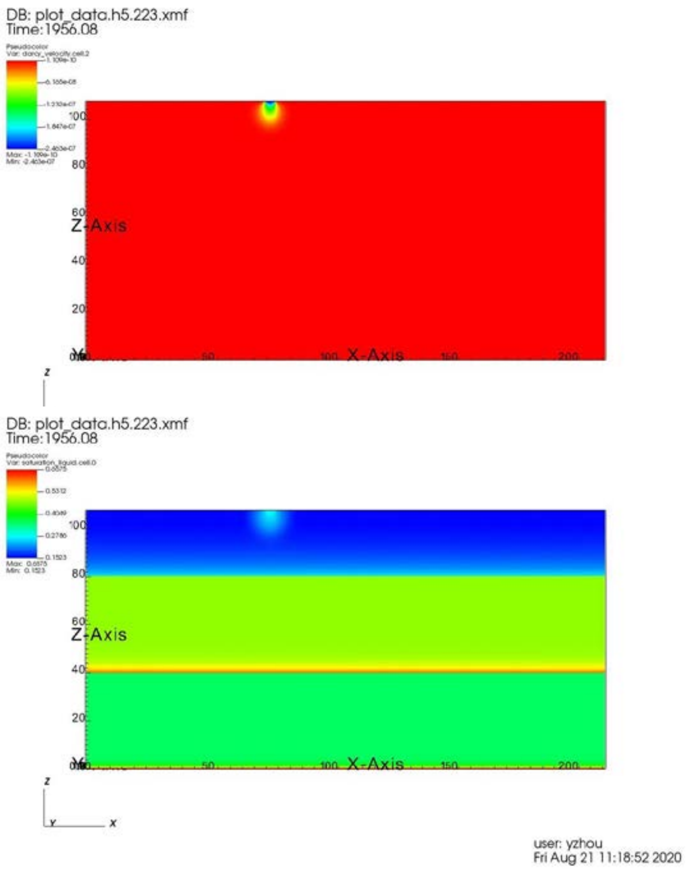
Task 6: Hydrology Modeling for WIPP
Research Highlights

Subtask 6.2: Model Development

Land Surface Model
- WRF-Hydro (Weather Research and Forecasting)

ASCEM Groundwater Model (GWM)
- Water/solute movement
- On-going training





Task 6: Hydrology Modeling for WIPP
Research Highlights

FIU Year 10 Ongoing:

- ASCEM GWM training
- Analysis and optimization of DEM

FIU Applied Research Center

Task 6: Hydrology Modeling for WIPP
Accomplishments

DOE Fellow Gisselle Gutierrez:

- Presented poster at WM20 Symposia *"Evaluation of Techniques for Vegetation Removal from UAV-based Photogrammetric DSM Near WIPP Land Withdrawal Act Boundary, NM" based on this project work.*
- Awarded Roy G. Post Foundation Undergraduate Scholarship at WM20 Symposia.
- Graduated with BS in Env. Eng. Summer 2020. Pursuing MS in Civil Eng. with focus in Water Resources and continuing as DOE Fellow assigned to WIPP Hydrology Modeling task.
- Completed 10-wk **remote** Summer 2020 internship with CBFO mentored by Dr. Anderson Ward.

Task 6: Hydrology Modeling for WIPP

FIU Year 01 (Sept 2020 - Sept 2021)* Objectives

* Assuming new contract number is issued

Subtask 6.1: Digital Elevation Model (DEM) and Hydrologic Network

- Capture high-res imagery of entire Basin 6 west of the WIPP in Nash Draw area using UAV.
- Process imagery using state-of-the-art photogrammetric techniques to build high-res DEM.
- Delineate stream channel and other relevant hydrologic features to support model development.

Subtask 6.2: Model Development

- Initiate development of LSM of Basin 6 that provide parameters that account for variations in surface processes, i.e., land use and climatic changes.
- Initiate development of ASCEM GWM using parameters acquired from LSM (i.e., spatial distributed recharge) to simulate water table fluctuation and estimate the rate of halite dissolution and propagation of the shallow dissolution front, which both have potential to affect post-closure repository performance.
- Train FIU's research personnel/students on selected LSM & ASCEM to execute scope.
- Train undergraduate/graduate students (DOE Fellows) on UAV photogrammetry methods and provide mentorship and field experience through student summer internships in collaboration with CBFO and PNNL scientists.